A Course of Thermodynamics

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Yoshi Oono oono@me.com

This book gives an outline of the basic thermodynamics as a part of natural science rather than mathematical physics. Thus, the exposition will be based on the elementary knowledges of physics and chemistry of macroscopic phenomena.

Each 'lecture' (chapter) is built up from relatively short 'units'[2] that focus on single concepts or propositions. These units reference each other as hypertexts.[3]

This 'source' version contains numerous comments, some of which are excessively long and pertain to cultural criticisms or corrections of conventional views and approaches found in existing textbooks. The final textbook version will slim these comments down.

This version aims to seamlessly integrate classical thermodynamics and chemical thermodynamics, but note that the logical organization of chemical thermodynamics has not yet been published.

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[1] Shoki Koyanagi's critical comments on the Japanese version 0.81 is gratefully acknowledged which removed some mathematical incorrect statements. Barry Friedman's corrections and comments are gratefully acknowledged.

[2] just as *Perspectives on Statistical Thermodynamics* (Cambridge University Press, 2017) by the same author.

[3] There are likely readers, especially serious ones, who are bothered by an abundance of links. The purposes of these links are:
(1) Even readers who do not actively construct their own comprehension scaffold could benefit from the notes by gaining new knowledge.
(2) Individuals familiar with relevant prior knowledge can understand the units even without systematically reviewing the preceding portion.
Therefore, readers who engage with the book seriously and systematically can generally ignore most links and can use them as points to recall relevant concepts.

List of symbols

Symbols and notations often used in the book are collected here.

A: Helmholtz energy **18.1**
a: activity **25.15**

$\boldsymbol{B}$: magnetic field **B.2**

C: heat capacity **14.6**

$\boldsymbol{D}$: electric flux density **B.4**
d: differential, external differentiation **9.10**
Δ: denoting general changes
δ: small change or variation
∂: partial differentiation, Jacobian or boundary of a set

E: internal energy **3.7**, electrode potential **26.24**
$\boldsymbol{E}$: electric field
$\mathcal{E}$: the totality of equilibrium states of a system **5.6**
e: elementary electric charge

F: Faraday constant **26.9**
$\boldsymbol{F}$: force
f: thermodynamic degree of freedom **23.9**, fugacity **25.15**
ϕ: number of phases **23.9**, Galvani potential **26.11**

G: Gibbs energy **19.1**

ζ: chemical work form **4.12**

H: enthalpy **19.3**
$\boldsymbol{H}$: magnetic field strength **B.4**
η: efficiency **15.1**

K: kelvin

κ: compressibility **22.12**

L: latent heat **17.17**

μ: chemical potential **4.12**, **17.7**

$\boldsymbol{N}$: materials coordinate (collective notation for N_i) **4.8**
$\tilde{\boldsymbol{N}}$: chemical composition coordinate (collective notation for $\tilde{N}_i$) **4.8**
ν: (generalized) stoichiometric coefficient **25.7**

ξ: extent of chemical reaction **25.8**

o: higher order infinitesimal **9.3**

P: pressure
π: osmotic pressure **19.15**

Q: heat **7.10**, quantity in general **2.14**, **3.3**

R: gas constant, reaction map **4.11**

S: entropy **11.7**

T: (absolute) temperature **11.7**
θ: (empirical) temperature

V: volume

W, w: (mechanical work = electromagnetic and mechanical work)
ω: work form **3.10**

$\boldsymbol{X}$: (mechanical) work coordinate (collective notation for X_i) **3.9**
$\boldsymbol{x}$: conjugate intensive quantities for $\boldsymbol{X}$ (collective notation for x_i)**3.10**
χ: surface potential **26.14**

$\boldsymbol{Y}$: operational coordinates (collective notation for Y_i) **4.13**

$\boldsymbol{y}$: conjugate intensive quantities for $\boldsymbol{Y}$ (collective notation for y_i)**10.1**

Z: mass action **17.1**
z: charge measured in elementary charge unit e **26.10**

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1 Introduction

1.1 What is thermodynamics?

'Thermodynamics' originated as a scientific field[4] to comprehend phenomena related to 'temperature' and 'heat' ("thermal phenomena") within our experiences at our scale (→**1.4**). Eventually, the understanding of the nature of 'heat' shaped thermodynamics into a general science for quantitatively describing various macroscopic phenomena involving the transformation among various forms of energy.

The key observations that established our understanding of the nature of 'heat' were the following two: The first was the recognition by Mayer and Joule (→**A.9**, **7.14**) that 'heat' is a mode of energy transfer. The second was the recognition by Carnot (→**A.8**, **8.13** or **15.2**) and later by Clausius (→**8.1**) that energy transferred as 'heat' cannot be converted to mechanical work, if no trace is allowed to remain.

1.2 What are thermal phenomena?

We mentioned 'thermal phenomena' in **1.1**, but it may not be clear what 'thermal' or 'heat-related' implies.

We intuitively understand what 'warm' or 'cold' means; we know heating water can make it boil, and rubbing wood together can generate fire. Phenomena related to these typical examples are thermal phenomena.

We may roughly define 'thermal phenomena' as follows: "Macroscopic physical phenomena in which the fundamental laws of macroscopic electromagnetism and mechanics do not hold" are thermal phenomena. For example, when there is friction, the fundamental laws of analytical mechanics cease to hold. In particular, the conservation of mechanical energy fails in such cases.

1.3 What foundation should thermodynamics be based on

What is the clear meaning of the word we use daily such as 'temperature' or 'heat?

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[4] ⟪**What is science?**⟫ Many books that discuss or promote science are widely available, but most tend to overlook the idea that science is a particular way of engaging with the world, characterized by a specific stance. At its core is the principle: 'Recognize what you know as what you know, and acknowledge what you don't know as what you don't know.' For instance, part of the scientific attitude involves continuously reflecting on whether our worldview, our Weltanschauung, is appropriate. Science must be fundamentally grounded in this reflection on 'knowing.'

According to a dictionary, "'temperature' is the degree or intensity of heat present in a substance or object." Then, 'heat' is explained as "the quality of being hot; high temperature." To avoid circularity in our understanding, we must define "thermal phenomena" in terms of concepts that are clearly understood.

As discussed in **1.1**, our goal is to achieve a clear understanding of thermal phenomena at our scale or at the scales we can directly feel (→**1.4**). Therefore, the empirical facts upon which thermodynamics is based must also be empirical facts observable at our scale. Thermodynamics, as an empirical science, also tries to be free from any particular metaphysical beliefs,[5] such as a mechanical Weltanschauung.[6,7]

Consequently, to comprehend the nonthermal physics required for the development of thermodynamics, we rely entirely on the principles of macrophysics (classical mechanics and electromagnetism). We will employ the logic and mathematics traditionally employed in macrophysics, as the foundations of macrophysics were established before thermodynamics was fully developed. Rudimentary chemistry (or common sense chemistry) is also needed and its terse summary will be stated later (→**4.3**).

Therefore, the readers seeking to understand thermodynamics should have a grasp of elementary mechanics and electromagnetism and common-sense chemistry.[8] As logic/mathematical tools, we will freely use rudimentary linear algebra and (multivariable) calculus.

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[5] ⟪**Metaphysics**⟫ The term 'metaphysics' is understood as an attempt to comprehend the world rationally based on *a priori* principles: "our world must be such and such without any prior proof."

More succinctly, Metaphysics is an endeavor "to expand one's cognition without synthetic judgement" [See, K. Karatani, *Transcritique: on Kant and Marx* (MIT Press 2005)]. Here, 'synthetic judgement' implies judgement referring to/relying upon empirical facts.

[6] ⟪**Mechanical Weltanschauung**⟫ The picture of the world assuming that it can be totally understood if we understand the behaviors of particles governed by mechanics. A typical example can be seen in Helmholtz' famous exposition advocating the conservation of energy: **A.17**.

[7] However, isnt the concept of experiential science described in **1.5** also based on a certain kind of metaphysical motivation? In the authors view, accepting the reality that "if you go against it, you'll have a terrible time (you won't be able to stay in this world)" is not a metaphysical issue. You are free to argue against this, but you must not ignore the consequences of actions consistent with your arguments (if you and your descendants wish to remain in this world a little longer). While there is freedom of thought and speech, there is far less freedom of action.

[8] Relativity and quantum mechanics, although not usually mentioned, are not excluded so far as non-thermal macrophysics is concerned.

1.4 What is 'our scale'

'Our scale' implies 'macroscopic scale.' 'Macroscopic' usually means 'observable directly by our five senses.'

The macroscopic space scale ranges roughly over our size times $10^{\pm 6} \approx 2^{\pm 20}$ (1 μm $\sim$ 1,000 km), and the macroscopic time scale ranges roughly over one hour times $10^{\pm 6}$ (1 ms $\sim$ our life scale ($\sim 10^9$ s)), generously speaking. Thermodynamics aims to precisely describe and systematize thermal phenomena observable within this macroscopic space-time.[9]

1.5 Why must we take our existence as human beings seriously

As seen in **1.4**, this exposition emphasizes 'our scale.' Why are we, human beings, in the foreground? Isn't science objective and independent of human beings?

It is often said that the so-called empirical science is a logical summary of the world observed objectively, detached from the human beings.[10] However, we cannot

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[9] Compared to the scale of atoms and molecules, we are quite enormous, but why must this be so? The reader is recommended to ponder on the question. Refer to footnote 17 on page 10 of my book *The Nonlinear World* (Springer Japan, 2013) under ⟪Our scale⟫.

[10] **⟪Planck on the relevance (or, rather, irrelevance) of human beings⟫** According to *Eight lectures on theoretical physics delivered at Columbia University in 1909* by Planck (translated by A. P. Willis) (Columbia University Press, New York, 1915; a PDF version was kindly provided by Barry Friedmann), Planck outlined the progress of theoretical physics as follows. He begins with the explanation of 'positivistic attitude': "Through sense perceptions only do we experience anything of nature; they are the highest court of appeal in questions under dispute." However, "this view has never contributed to any advance in physics." He eventually concludes: "In short, we may say that the characteristic feature of the entire previous development of theoretical physics is a definite elimination from all physical ideas of the anthropomorphic elements, particularly those of specific sense perceptions." [T. Tanaka, *Development of Physical World Picture* (Iwanami, 1988) summarized the whole lectures as follows: "Science starts with empirical observations that depend on human beings, but, once established, they turn into objective reality apart from the presence of human beings. That is, the progress of science is a step-by-step approach toward objective understanding that does not depend on the human framework."]

While Planck's perspective may sound reasonable, it still remains that the facts supporting science must be verified or verifiable empirically; empirical verification is impossible apart from the human being.

Contrary to Planck's assertion, what must definitely be removed from all physics (science) is the illusion that we can entirely eliminate anthropic elements. From this point of view, upon reflection, the approach of trying to deduce everything in various fields of physics based on the premise that "the world has such and such properties" seems to quite miss the essence of science.

Incidentally, the statement that "once established, they turn into objective reality apart from the presence of human beings" gives the impression that facts are not objectively real unless they are established by humans. This is amusing and reminiscent of postmodernism. (For example, see experience the world apart from being human beings. Whatever our experiences may be, they are events in which we, as human beings, participate through our bodily sense organs (and nervous systems). Therefore, it is evident that we cannot directly recognize phenomena occurring beyond our scale (→**1.4**). Consequently, empirical sciences inevitably take into account our scale seriously.[11]

Against such a 'primitive' assertion, there may be an objection that we have various devices such as microscopes, telescopes, etc.

We cannot claim that what we see through a telescope is an image of an object that truly exists in the world simply by observing it through the telescope. We trust telescopes, because many people can confirm the correspondence between the actual object and its telescopic image. Then, we extrapolate this correspondence to the objects we cannot directly confirm. One might add that the explanation of the principle by geometrical optics also reinforces our trust in the telescope. Needless to say, to this end we trust our logic and mathematics. Besides, what is demonstrated by geometrical optics is that there is a direct correspondence between the actual object and the image we observe. That is, however sophisticated the observation is, its basis is our direct sensory recognition. Therefore, to construct the physics for the understanding of the phenomena at our scale is the very foundation of the totality of physics as an empirical science.

Empirical science is an intellectual activity based on the *principle of immediacy of experience* which dictates that we must be skeptical about what we cannot directly

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Alan Sokal and Jean Bricmont, *Fashionable Nonsense* (Picador USA, New York, 1998).

[11] ⟪**Remark on Aristotle and Descartes**⟫ "We trust our senses. It is worth noting that this (so-to speak the Aristotelian epistemology) is diametrically different from the 'modern epistemology' since Descartes (1596-1650). Descartes, sharply distinguishing our internal and external worlds and renouncing the bridge across the gap between mental and material world, secured the certainty of the realm of human thoughts.* In contrast, for Aristotle our perceptual activity is the very reflection of external events, so there is no gap between them where skepticism sneaks in." See M. Nakahata, *The philosophy of Aristotle* (Iwanami, 2023) p152.

∗ However, according to D. Kanbouchner, *Descartes n'a pas dit* (Société d'Édition Les Belles Lettres, 2015) 2 Descartes' opinion was not this extreme; he, too, wished to rehabilitate the functions of senses as such that are imparted by God who joined our souls and our bodies.

experience.[12,13] However, we must not forget that "to believe only what one sees," and "to think with one's own brain" are also fertile grounds for 'anti-scientism,' 'conspiracy theories,' etc.[14]

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[12] ⟪**Healthy example of this immediacy**⟫ The last chapter of D. L. Everett, *Don't Sleep, There Are Snakes, Life and language in the Amazonian jungle* (Pantheon 2008) [a linguistic ethnography of the tribe called Pirahã] eloquently describes the principle of immediacy of experience:

"Hey Dan, what does Jesus look like? Is he dark like us or light like you?"

I said, "Well, I have never actually seen him. He lived a long time ago. But I do have his words."

"Well, Dan, how do you have his words if you have never heard him or seen him?"

They then made it clear that if I had not actually seen this guy (and not in any metaphorical sense, but literally), they weren't interested in any stories I had to tell about him. Period. (p266)

Then from p270 onward:

I began to seriously question the nature of faith, the act of believing in something unseen. Religious books like the Bible and the Koran glorified this kind of faith in the nonobjective and counterintuitive—life after death, virgin birth, angels, miracles, and so on. The Pirahãs' values of immediacy of experience and demand for evidence made all this seem deeply dubious.

[13] However, incidentally, there might be a historical fact related to Jesus. It is certain that Mary was pregnant before her marriage to Joseph; "Usually, when such potentially damaging stories appear in the Gospels, it indicates that the underlying oral or written tradition was simply too persistent or well-known for the writer to ignore." (Jean-Pierre Isbout, *Search for the Historical Jesus* (The Teaching Company, 2022)). The name of the true father of Jesus, a Roman soldier named Tiberius Julius Abdes Pantera (22 BCE-40 CE), was mentioned in Celsus' work, *The True Discourse* (ca. 178 CE). Very interestingly, in 1859, his tomb was discovered in Germany, revealing that this soldier was indeed stationed in Palestine until 9 CE (Jean-Pierre Isbout, ibid.). However, most historians do not consider Celsus' account to be credible.

[14] See C. D. Ruiz and T. Nilsson, "Disinformation and echo chambers: How disinformation circulates on social media through identity-driven controversies," J. Public Policy & Marketing **42**, 18 (2022).

⟪**Genuine vs. vulgar empiricism**⟫ These can be classified under the term "vulgar empiricism." Its chief characteristic or flaw is its disregard for or minimal consideration of phylogenetic experiences (→**1.6**) and confusing empirical wisdom with mere experience.

We must recognize clearly that Aristotle was the first thinker/scientist to stress the supreme importance of experiences. M. Nakahata (on p11 of *The Philosophy of Aristotle* (Iwanami, 2023); this is the best introduction to Aristotle the author has ever read in Japanese and in English) "The world we experience has diverse aspects, yet they can be perceived in an appropriate way for each. Human beings possess the cognitive ability to respond to such a world. Furthermore, this world has an intellectual depth that reveals itself in response to human intellectual advancement. Therefore, through exploration, we can come to intellectually understand the world. Its entire exploration is the philosophy of Aristotle." Nakahata also points out: It should be emphasized that when Aristotle uses the word "*έμπερία*" (= experience; the word 'empirical' came from this) in the context of inquiry or the formation of knowledge, what it signifies is not just a mere event or a single experience, but something that can only be acquired by repeatedly observing or practicing the same or similar cases oneself. In particular, it refers to the activity or ability of recognition obtained in this way.

1.6 Two categories of our experiences

Empirical sciences are based on our experiences through our bodily senses (and nervous systems), but these experiences are not simply based solely on our experiences since birth. For example, the mechanism from the photoreceptor cells to our brains supporting vision is constructed in such a way that all our sensory inputs as to our surrounding world are consistent.[15] We are not born in the state of *tabula rasa*, but in the state resulting from the evolution process of the past three gigayears (3 Ga); we were born in the state in which the totality of our ancestors' experiences since life was born are built in, so to speak. For example, the three-dimensionality of the world at our scale is ingrained (or hard-wired) in the semicircular canals.[16] There are at least two categories of experiences, experiences during our lifetime and those during our phylogenetic history.

Even if we gather all the empirical facts, science is not possible. Especially in physics we wish to find the logic unifying the collection of empirical facts. This is the task in which our central nervous system is directly involved. The observation that the shapes of fishes reflect the fluid dynamic properties of water in which they have evolved strongly suggests that our possession of logical capability mirrors the logical and lawful nature of the world in which we have evolved. Needless to say, our nervous system is not *tabula rasa* when formed ontogenetically.[17]

It may not always be the case that our direct experiences align with the logic we consider natural. In such instances, mathematical logic takes precedence, as phylogenetically accumulated empirical facts are deemed the most reliable.[18] Vigilance

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Thus, Aristotle's, or scientific, empiricism is diametrically different from 'vulgar empiricism' (lack of scrutiny of experiences).

[15] For example, the law of inertia is incorporated in the neurons connecting the retina and the visual cortex (yes, before reaching the brain). See Johnson et al., Position representations of moving objects align with real-time position in the early visual response eLife **12**, e82424 (2023).

[16] Even the shapes of semicircular canals can be used to infer behaviors/activities of reptiles (including birds). See M. Bronzati, et al., Deep evolutionary diversification of semicircular canals in archosaurs, Curr. Biol. **31**, 2520 (2021). The following paper is compelling in demonstrating how quickly the structure of the mammalian inner ear evolved and adapted to their lifestyle: N. D. S. Grunstra, F. Hollinetz & A. Le Matre, Convergent evolution in Afrotheria and non-Afrotherians demonstrates high evolvability of the mammalian inner ear, Nature Commun., **15**, 7869 (2024).

[17] See K. Lorenz, *Behind The Mirror: A Search for a Natural History of Human Knowledge* (Harcourt Brace Jovanovich, 1977).

[18] Even what is commonly termed a tautology reflects a stable property of our world. Perhaps there is nothing trivial that is analytic (in Kant's sense) in the world. Incidentally, the reader might expect discussions on phylogenetic effects in mathematics, given that G. Lakoff and R. E. Nez's *Where Mathematics Comes From* (Basic Books, 2000) delves into "embodied mathematics."

against vulgar empiricism is warranted (see footnote 13).

1.7 What is the characteristic of thermodynamics?

Thermodynamics is a mathematically consistent system aimed at understanding macroscopic thermal phenomena based on facts that are as empirically immediate (→**1.5**) as possible.

Thermodynamics is fundamentally different from the kind of physics that tries to answer questions such as 'What is the world made of?' or 'How did the world begin?', even entertaining mythical fictions.[19] The most important cultural value of thermodynamics may lie in this distinction. Thus, the author believes that there must be textbooks respecting this nature of thermodynamics.

Therefore, in this book, in line with what was written above, we will not overlook reflecting on the premises of thermodynamics. Hence, we do not adopt the 'postulational approach' since Callen.[20,21] According to this style, classical mechanics begins with the Hamiltonian or Lagrangian forms, classical electromagnetism starts with Maxwell's equations, and thermodynamics begins by defining entropy. For thermo-

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However, they may be thoroughly disappointed to find no mention of Darwin, evolution, or Kant. The authors seemingly overlook that 'embodied' must imply 'evolutionarily constructed.'

[19] See, for example, S. Hossenfelder, *Existential Physics*—a scientist's guide to life's biggest questions (Viking, 2022).

[20] This approach is strongly advocated in the preface of H. B. Callen's own textbook on thermodynamics: H. B. Callen, *Thermodynamics*: an introduction to the physical theories of equilibrium thermostatics and irreversible thermodynamics (John Wiley & Sons, Inc., New York, 1959) p. vii. The advantages of this approach are: (1) it more explicitly exhibits the 'internal' logical consistency of the logical structure; (2) (after sufficient experience with the abstract postulates) it allows to develop a deeper insight and intuition; (3) it frequently suggests important extensions of the theory. The reason why thermodynamics was the last of the major classical theories to adopt this approach is because, at the turn of the 20th century, molecular theory was still highly suspect, and for safety, the foundations of thermodynamics were built as much as possible on macroscopic experimental observations. Now, those concerns are no longer relevant, and quantum mechanics and quantum statistical mechanics are considered more reliable than macroscopic science.

This view contradicts the spirit of empirical science.

It may take decades for the author's opinion to dominate. Then, after another 100 or 200 years, there may be a swing back (at a higher level). That is what science is.

[21] Many physicits might believe the first 'top-down' textbook was by Callen, but Guggenheim already adopted this style in his book: E. A. Guggenheim, Thermodynamics an advanced treatment for chemists and physicists (North-Holland Publishing Co, 1949), although the title contains 'advanced treatment' (→**14.1** footnote).

dynamics, the arguments justifying this approach are not persuasive.[22,23]

1.8 What does thermodynamics assume as known?

The fundamental strategy of constructing thermodynamics is to expand the already established framework of physics for macroscopic phenomena, other than thermal phenomena, so that the empirical facts of macroscopic thermal phenomena can also be understood as a scientific discipline. Here, the macroscopic physics with an already established framework refers to mechanics and electromagnetism, but as long as they relate to macroscopic phenomena, relativity and quantum mechanics are not excluded. The term "framework" refers to the foundational basic parts, and "already established" pertains to the "framework," not implying that these fields are

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[22] The common justification for this approach in textbooks available today is that entropy, like the Lagrangian, provides a variational principle, making it just as natural to start from the Lagrangian in classical mechanics. There is some merit to this argument, but the relationship between Newton's equations of motion and the Lagrangian formulation is such that the Lagrangian can be directly derived from the inverse problem of the variational principle by functionally integrating the equations of motion. In other words, it is a functional analog to the relationship between potential and force (see Vainberg's theorem), and is almost trivial. In contrast, it seems highly unlikely that entropy could be directly derived from a practical thermodynamic system without entropy (assuming such a theoretical framework is even possible) as a solution to an inverse problem. Thus, the advocated correspondence is not adequate.

A more detailed perspective is found in A. Arai's *Mathematics of Thermodynamics* (Nippon Hyoronsha, Tokyo, 2020) (p. 154). In classical mechanics, space-time is taken as a fundamental framework for describing motion, and the construction of rulers and clocks as physical objects is not discussed. Similarly, in thermodynamics, there is no need to refer to the empirical operational definitions of temperature and entropy; it is better to regard these as fundamental principles related to energy transfer and develop the theory accordingly for a clearer structural understanding. Central to Arai's thinking is the (probably KMS-inspired) correspondence between time and temperature, and motion and heat flow: the former determines the direction of the latter. Of course, as Y. Yamamoto points out, entropy involves not only heat but also matter, making this analogy dubious; since Arai completely disregards chemistry, that might not be his concern.

[23] ⟪**An approach that begins with entropy is not commendable**⟫ It is unlikely that you would find an introductory physics course anywhere in the world that starts classical mechanics with the Lagrangian formalism or electromagnetism with Maxwell's equations. The idea of the Hamiltonian or energy was intuitive, as Mayer reached it through 'divine revelation' and, as Yamamoto discusses, aligning quite naturally with the concept of conservation laws, especially in a world where a monetary economy is widespread. In contrast, Clausius's approach to entropy, as one feels upon reviewing it, seems to stem from a completely different level of thinking. It is noteworthy that Thomson could neither reach nor understand it. The "just get used to it, learn to use it" approach, akin to a policy of national prosperity and military strength, goes against the spirit of science.

fully completed as academic disciplines. Even classical mechanics, for example, is far from being fully developed, as can be exemplified by non-integrable systems; electromagnetism of complex material systems is far from complete.

Besides, physics alone is insufficient. To specify an actually existing system, obviously, it is essential to describe its material composition. Therefore, the basics of chemical phenomena, such as the concept of the mole, must be assumed as known. Furthermore, it must be accepted as a chemical empirical fact that the equilibrium composition of a materially closed system is uniquely determined when equilibrium is reached (the uniqueness of chemical equilibrium). These concepts can be formulated and described in terms of quantities that can be measured and observed without presupposing thermodynamics.

Thus, in constructing thermodynamics, the foundation of non-thermal macroscopic physics and non-thermal basic chemistry is assumed to be already established and known.[24]

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[24] Traditionally, explanations and formulations of thermodynamics have rarely made these basic assumptions explicit. This is not surprising, as the teaching of thermodynamics, as a branch of theoretical physics, relies heavily on "common sense," unlike mathematics. This approach is common in physics education. Many have long believed (and some still do) that thermodynamics can be framed in an axiomatic way. However, thermodynamics cannot be formulated without incorporating the physics and chemistry discussed above.

However, some might argue that a complete theoretical system could be established by introducing physical and chemical concepts as undefined terms. Yet, since thermodynamics deals with real-world phenomena, we cannot overlook the operational definitions of these concepts. Without such definitions, it is often possible to construct non-equivalent (non-standard) models that are consistent with an axiomatic system (see the latter part of this footnote). For this reason, this book avoids an axiomatic approach. We also steer clear of pseudo-mathematical descriptions, such as labeling certain propositions as "theorems." Of course, when discussing mathematics, theorems will be presented, but only when the context requires a meaningful level of mathematical rigor. We should avoid mimicking mathematical formalism when explaining arguments that are not inherently mathematical.

As a side note, for those interested in exploring an axiomatic approach, it is advisable to first read the foundational work in this area, David Hilbert's *Foundations of Geometry* (revised and updated 2021, independently published, E. J. Townsend, Translator). Poincaré was most impressed by the book, and in the aftermath, he considered the "automation of mathematics," as noted in C. McLarty, "Poincaré on the Value of Reasoning Machines," Bull. Am. Math. Soc., **61**, 411 (2024). As this paper points out, formalizing a theory allows for various interpretations: "A formal theory T admits arbitrarily many different informal interpretations, giving T as many different meanings. A computer with T encoded on it, and able to derive formal conclusions from T, does not also know the informal interpretation(s) of T." In other words, operational definitions and formalization are entirely incompatible. Hilbert also wrote a note titled "Axiomatic Thinking," where he outlined the axiomatization of various fields of physics, a project he was advocating at the time. It is well known

1.9 A strategy to construct/elucidate thermodynamics

As stated at the beginning of **1.8**, when attempting to build the framework of thermodynamics, only physics related to empirical facts that do not involve thermal phenomena can be used as a foundation. Consequently, concepts and measurable quantities related to thermal phenomena cannot initially be considered as understood within the domain of physics. Therefore, when constructing thermodynamics, it is only permissible to use concepts and measurable quantities that are entirely unrelated to heat in order to introduce thermal concepts and the measurement of heat-related quantities. In other words, thermodynamics must be constructed based solely on knowledge of macroscopic physics (and basic chemistry) that does not involve thermal phenomena.

Consequently, apparatuses preventing any involvement of 'heat,' and processes that do not produce any 'heat' (that is, processes for which nonthermal macrophysics holds) emerge as crucial conceptual and experimental tools. The former is the 'adiabatic wall' (→**7.7**) and the latter is the 'quasistatic reversible process' (→**6.6**).

1.10 Two restrictions imposed on thermodynamics

Even if thermodynamics is completed, we will not be able to realize a general and ambitious theoretical framework that allows us to understand all the thermal phenomena of every macroscopic system. There are two fundamental limitations.

(1) Not all the states of a given system can be comprehended. States in which no observable change occurs in the system and its surrounding environment[25] for macroscopic observers like us can be discussed (referred to as *equilibrium states*).[26]

(2) Equilibrium states of not all the macroscopic systems can be understood. Only

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that Einstein strongly opposed this, criticizing it as a mathematician's bad habit of neglecting the empirical approach to nature.

In most thermodynamics textbooks it is true that "mathematical concepts and ideas are not clearly separated from empirical and operational concepts, and are ambiguously mixed together", but if full formalization is completed, the resulting formal theory would no longer be a theory about the phenomena of this world. As a branch of physics, the discussion should remain as closely aligned as possible with the operational side.

[25] This is to exclude nonequilibrium steady states.

[26] There is no theoretical framework that allows us to understand all 'nonequilibrium states.' There is a framework called 'nonequilibrium thermodynamics' that can discuss states slightly deviated from 'equilibrium states,' but it is not a big deal.

the systems can be discussed such that, when divided into isolated halves,[27] each half must have exactly half the energy of the original system (the system must be 'additive' →**2.14**).[28]

Additive systems are not uncommon, but the restriction (1) may look extremely stringent. However, in reality, the states we encounter are (i) not rarely close to equilibrium, and (ii) it is possible to calculate various useful things, such as how much work is needed to realize the transition from one equilibrium state to another, making thermodynamics quite practical (→**6.8**: Why is thermodynamics useful?).

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[27] We assume the original system is macroscopically spatially uniform.

[28] assuming the same energy origin is adopted for all the energy measurements.

A Appendix: From the theory of heat to thermodynamics

This Appendix provides an overview of the prehistory of thermodynamics.[29] The actual exposition of thermodynamics will begin in Section 2, so readers can skip this Appendix. By following through this detour, however, readers will realize how meager empirical facts originally supported the so-called chemical thermodynamics. This historical contingency still appears to impede the exposition of thermodynamics today.

A.1 Before 'modern' heat theory

Although temperature has been of interest for a long time due to its relevance to medicine, interests in devices that could convert 'heat' into mechanical work did not gain much attention. Despite the fascination with firearms, this did not lead to the concept of a relationship between the 'ordinary' slow motions and 'heat'.

Particles or the element of fire were once conceived as fundamental, making 'heat' and chemistry (or its precursor, alchemy) inseparable. Chemistry aimed to understand the diversity of the material world, but its strategy vacillated between two extremes: monism and pluralism. Monism assumed that the fundamental substance was singular, with the diversity of its motions and interactions producing the material diversity of the world. In contrast, pluralism assumed that various particles existed from the beginning. The success of Newtonian mechanics encouraged monistic approaches to explain the diversity of materials in terms of the diversity of forces acting among particles.[30]

However, the limitation in the monistic approach that attributes all material complexity to force complexity was gradually recognized, and chemistry was systematized by Boerhaave's[31] *Elementa Chemiae* (1732) in terms of pluralistic materials theory and the element of fire: ⟨fire⟩. Contemporaneously, it was recognized from the publication of Newton's then unpublished manuscripts that he had conceived 'ether' long before. This, with the increasing interests in electromagnetic phenomena, made ⟨fire⟩ acceptable as related to Newton's ether. It was also during 1730-40 when Linnaeus' *Systema naturae*[32] was published, and when reductionism was critically reassessed (e.g.,

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[29] The author heavily relies on an excellent book: Y. Yamamoto, *Historical development of thermodynamic thoughts* 1-3 (Chikuma 2008-2009) to construct the narrative outline, although the units on Carnot **A.6** and **A.7** considerably deviate from this book.

[30] **⟪From the preface to *Principia*⟫** Newton wrote in author's preface to *Principia* (the following English translation is taken from the first US version published by D. Adee in 1846), "I wish we could derive the rest of the phenomena of nature by the same kind of reasoning from mechanical principles; for I am induced by many reasons to suspect that they may all depend upon certain forces by which the particles of bodies, by some causes hitherto unknown, are either mutually impelled towards each other, and cohere in regular figures, or are repelled and recede from each other; which forces being unknown, philosophers have hitherto attempted the search of nature in vain; but I hope the principles here laid down will afford some light either to this or some truer method of philosophy."(*Principia*, author's preface (May 8, 1686).)

[31] Herman Boerhaave (1668-1738) `https://en.wikipedia.org/wiki/Herman_Boerhaave`.

[32] *Systema naturae, sive regna tria naturae systematice proposita per classes, ordines, genera, &*

the reevaluation of the empiricism of Bacon).[33]

A.2 Beginning of the modern heat theory

The modernization of chemistry and heat theory was initiated by Black[34] of Glasgow.

His teacher Cullen[35] criticized Boerhaave for ascribing most qualities to corresponding particular elements and adopted repulsive forces due to thermal ether and affinities (selective attractive forces meaning intrinsic tendency for various substances to bind in multifaceted fashion) as the conceptual framework to unify understanding of chemical phenomena. As a result, affinity and repulsive force became the central issues of chemistry.

Black adopted the fact that two objects in contact reaching states without any further change indicate the same temperatures as the foundational universal law of heat theory. As can be seen from this, the invention of thermometers was the key to the development of modern heat theory.[36]

Black demonstrated that he could introduce the concept of heat capacity operationally which was consistent with the idea that 'heat' was conserved: when two objects at different temperatures are brought to equilibrium through thermal contact, the ratio of the temperature changes of these two objects is the inverse ratio of their heat capacities.[37] Black viewed the heat capacity as the strength of a certain chemical attractive force between 'heat substance' and the ordinary substance. That is, his heat theory was along the extension of Cullen's chemistry, which attempted to systematize chemical reactions in terms of selective attractive forces and repulsive forces, and was a source of the later 'caloric theory' of Cleghorn[38] and Lavoisier.[39]

The heat theory starting from Black was a source of thermodynamics, but no heat engines appeared, which were the other source, also deeply ingrained with the concept of caloric.

A.3 Steam engines before Watt

The idea to produce work through converting heat did not appear to exist till the modern era since

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species (Leiden: Haak 1735). https://en.wikipedia.org/wiki/Systema_Naturae.

[33] Francis Bacon (1561-1626) https://en.wikipedia.org/wiki/Francis_Bacon.

[34] Joseph Black (1728-1799) https://en.wikipedia.org/wiki/Joseph_Black.

[35] William Cullen (1710 -1790) https://en.wikipedia.org/wiki/William_Cullen.

[36] The modern thermometer was invented by Galileo, but the mercury thermometer was invented by Fahrenheit (1686-1736) https://www.youtube.com/watch?v=vPmZohDmgwo. For Celsius' contribution, see https://www.youtube.com/watch?v=rjht4oAByCI.

⟪**Remark on temperature**⟫ Here, what we can observe directly are the temperature changes and whether thermal equilibrium is achieved or not. We cannot directly observe 'heat.' Therefore, 'temperature' is the fundamental quantity for heat theory. However, notice that this is a historic view when heat theory was not a part of physics but an independent discipline (or perhaps a part of chemistry). In thermodynamics, heat theory must be a part of macrophysics. Concepts and quantities directly concerning 'heat' are not operationally fundamental, and must be derived as subordinate concepts from the concepts and quantities more fundamental in physics (→**1.8**).

[37] Let C_1 and C_2 be the heat capacities of the individual objects. From $C_1\Delta T_1 + C_2\Delta T_2 = 0$, we get $C_1/C_2 = |\Delta T_2/\Delta T_1|$.

[38] William Cleghorn (1751-1783) https://www.uh.edu/engines/epi1956.htm.

[39] Antoine Lavoisier (1743-1794) https://en.wikipedia.org/wiki/Antoine_Lavoisier.

Hero's 'aeolipile'[40]. For the modern idea of heat engines the discovery of vacuums was crucial.[41] As the *Magdeburg hemisphere* demonstrated, the power of atmospheric pressure was overwhelming. Papin[42] invented a device that utilizes atmospheric pressure to push a piston into a cylinder in which a vacuum was created by cooling the vapor in it (1690).

At about the same time Savery[43] obtained a patent for a practical lifting pump.[44] There was a strong incentive in England to solve the flooding problem of coal mines. Newcomen[45] who was born in Devon, the birthplace of Savery, perfected an atmospheric engine by 1710, based on a similar principle as Papin's atmospheric engine.[46,47]

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[40] Hero of Alexandria (ca. 10-70 CE) https://en.wikipedia.org/wiki/Hero_of_Alexandria. Also, see Lecture 4 "Ctesibius and Hero: Alexandrian Inventors," of G. Aldrete, *Unsung Heroes of the Ancient World* (The Great Courses).

[41] **⟪Significance of the discovery of vacuums⟫** As stressed by Yamamoto the greatest discoveries in modern physics regarding gases were the discoveries of atmospheric pressure and vacuum by Torricelli (1608-1647), Pascal (1623-1662), and von Guericke (1602-1686). This was a groundbreaking revelation that distinguished the medieval from the modern era, and its significance is second only to the heliocentric theory. Even Galileo explained the inability of water to be lifted more than 10 meters by the competition between the aversion of air to vacuum and the force of gravity.

The dramatic demonstration of atmospheric pressure is best exemplified by von Guericke's public experiment in Regensburg in 1654, known as the Magdeburg hemispheres. An actual reenactment of the experiment, where horses are used to pull apart the hemispheres, can be seen in the following video: https://www.youtube.com/watch?v=IIQC8iEnCIY.

[42] Denis Papin (1647-1713), https://en.wikipedia.org/wiki/Denis_Papin.

[43] Thomas Savery (ca. 1650-1715) https://en.wikipedia.org/wiki/Thomas_Savery, https://www.gracesguide.co.uk/Thomas_Savery.

[44] For an explanation of the principle of his pump, see https://www.youtube.com/watch?v=0vK80s2WEno. As can be seen from this video, vapor pushes water up, so the work is not solely due to atmospheric pressure. How an actual device installed at a mine works is illustrated in https://www.youtube.com/watch?v=Dt5VvrEIj8w (after around 1min 10 sec). In principle, the pump could lift water from any depth. However, the contemporary precision of metal work caused leaks and high pressure boilers were prone to explosion, so, in practice, the engine was operated around atmospheric pressure.

[45] Thomas Newcomen (1664-1729), https://en.wikipedia.org/wiki/Thomas_Newcomen, https://www.gracesguide.co.uk/Thomas_Newcomen.

[46] Newcomen and his engine (with Watt's engine as well) are depicted in https://www.youtube.com/watch?v=QltRwiu4U2Q. To understand the mechanism alone https://www.youtube.com/watch?v=9GqVQPMCtY4 is recommended. An actually restored engine can be seen in https://www.youtube.com/watch?v=4DZxwGoNI5Q; https://www.youtube.com/watch?v=HC6LUWSBXjk is more faithful to the original.

[47] Noteworthy event from the same period: The last legal execution of a witch on the island of Britain took place in Scotland in 1727 (see https://en.wikipedia.org/wiki/Janet_Horne). "Our period is a period of transition. The Middle Ages did not end in the fifteenth century, and the modern era did not begin immediately afterward. End and beginning imply a process which has lasted over four hundred years—a very short time indeed if we measure it in historical terms and not in terms of our life span." (E. Fromm, *Man for himself* (Reinhart & Company Inc. New

A.4 Watt and his engines

Watt[48] was an instrument maker with his shop in University of Glasgow, who had good personal relationships with distinguished professors such as Black (→**A.2**). He came from an intellectual family, and his assets were his intelligence and good personality.[49]

In the winter of 1763-4, he was asked to repair a model of Newcomen's engine (Fig. A.1 Left). The model consumed a lot of fuel. When steam is introduced to the cylinder, it must be hot, but to make a vacuum, it must be cool. In short, the same cylinder must be alternately hot and cool, wasting a lot of heat. He realized that the cylinder could be maintained hot, if the steam could be cooled in a separate cooler (condenser; Fig. A.1 Right).

The epoch-making development after the separate condenser was the '*expansion principle*,' which Watt patented in 1782. Watt observed that the steam, after pushing the piston, gushed into the condenser, wasting its ability to do work. Thus, he stopped supplying steam before the piston moves all the way to the end of the cylinder and let the steam cool while expanding and doing work (the expansion principle). This resulted in 2.5 times more work produced from the same amount of fuel. Later, Carnot held Watt's expansion principle in high regard, saying that Watt was the first to use steam under gradually decreasing pressure.

Thanks to this principle, it was discovered that the higher the steam temperatures, the more powerful the engines became. Woolf[50] made high pressure engines practical (1814), which was not only powerful, but also fuel-efficient.

A.5 Applications of steam engines outstripped science[51]

Remarkable historical facts before the development of thermodynamics were the extensive applica-

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York 1947) p290.

[48] James Watt (1736-1819), `https://en.wikipedia.org/wiki/James_Watt`, `https://www.gracesguide.co.uk/James_Watt`. The place where he was born is where his father's workshop was located, and now a statue of Watt stands there. It is at the corner of Williams Street and Delrymple Street (A8) in Greenock (on the left side towards Delrymple). The coordinates are [55.947926, −4.7548874].

[49] His personal relationships with his friends and business partners were always congenial and long-lasting [`https://en.wikipedia.org/wiki/James_Watt`].

[50] Arthur Woolf (1766-1837) `https://www.gracesguide.co.uk/Arthur_Woolf`. He was born in Cornwall, which is bounded to the east by Devon.

[51] We must not forget that the economical foundation of the Industrial Revolution was colonialism and slavery [see Eric Williams, *Capitalism and Slavery* (The University of North Carolina,1944; 3rd Edition 2021)]. HP of University of Glasgow had the following statement (which is removed now):

Watt's great scientific and engineering achievements are rightly celebrated. But it is also true that his family profited through the trade in slave-produced goods (such as sugar, rum and cotton from Antigua and other Caribbean islands) and on occasion they were actively involved in the purchase and sale of enslaved people. In March 1762, for example, Watt's brother John arranged for the shipment of a young boy, who was quite likely enslaved, from the Caribbean to Glasgow.

In later years, Watt undoubtedly made money by producing machinery for businesses in the Caribbean which owned enslaved people. On the other hand, during the Haitian revolution in 1791, Watt is on record cancelling an order placed by a French farm for a steam engine intended for

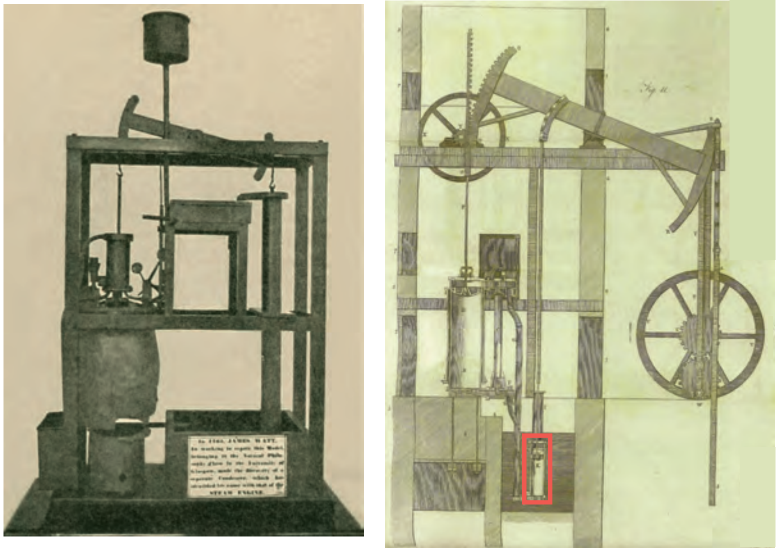

Figure A.1: The actual Newcomen engine model Watt repaired. The plate says: ‘In 1764, James Watt. In working to repair this Model, belonging to the Natural Philosophy Class in the University of Glasgow, made the discovery of a separate Condenser, which has identified his name with that of the STEAM ENGINE.’. Right: An atmospheric engine improved by Watt. The red box highlights the separate condenser. [Fig. of https://en.wikipedia.org/wiki/Watt_steam_engine]

tions of steam engines to transportation.

Trevithick’s[52] steam locomotive ‘Puffing Devil’ was made in 1804, and the opening of Stephenson’s[53] Stockton-Darlington railway was 1825.[54] On the opening day of the Manchester-Liverpool railway, September 15th, 1830, eleven-year-old Joule (→**A.9**) went to see the trains to the suburbs of Manchester with his elder brother; there was obviously no thermodynamics whatsoever.[55]

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the colony of Saint Domingo (now Haiti). Watt writes: “We sincerely condole with the unhappy sufferers, though we heartily pray that the system of slavery so disgraceful to humanity were abolished by prudent though progressive measures.”

We cannot celebrate the achievements of James Watt and other great men and women of the Enlightenment without remembering their society’s complicity in race slavery and imperialism, and without acknowledging that our present-day experience and understanding of race developed out of the attempts of Enlightenment thinkers to address the basic contradiction between professing liberty and upholding slavery.

[52] Richard Trevithick (1771-1833), https://en.wikipedia.org/wiki/Richard_Trevithick, https://www.gracesguide.co.uk/Francis_Trevithick.

[53] George Stephenson (1781-1848), https://en.wikipedia.org/wiki/George_Stephenson, https://www.gracesguide.co.uk/George_Stephenson.

[54] Stephenson’s locomotive model made of glass is seen in https://www.youtube.com/watch?v=73txXT21aZU. A replica of his ‘Rocket’ is given in https://www.youtube.com/watch?v=yNn0LC_9imY; why it lacked brakes is explained in https://www.youtube.com/watch?v=3woUopc1ZS4. The history up to Rocket can be seen in https://www.youtube.com/watch?v=wOGYZC-IJPQ.

[55] Also noteworthy is that Clapeyron (1799-1864 →**15.3**, **19.11**), https://en.wikipedia.org/wiki/Emile_Clapeyron, supervised the construction of the first railway line between Paris and

Applications to ships were even older, as smaller engines were not necessary. In 1807, Fulton[56] connected New York and Albany (240 km) in 32 hours with a ship powered by Watt's engine.

Turner's painting of 1839: "The fighting Temeraire tugged to her last berth to be broken up, 1838" symbolizes the era.[57]

A.6 Father and son Carnot

In England steam engines were greatly improved during the Napoleonic Wars, so the information did not spread to France. After the wars ended in 1815, France was shocked by the progress in England, particularly by the practical high pressure engines (→**A.4**). In France, not so abundant in coal resources, saving fuel was emphasized and Woolf engines (→**A.4**) were built already in 1815. However, it was not understood why high pressure engines had good fuel efficiency. The answer was given by Carnot later on. His work was heavily influenced by his father Lazare Carnot,[58] and the caloric theory (→**A.2**) played a crucial role.

On the Continent, taking advantage of its non-flat terrain, utilization of water power was highly developed. L. Carnot was one of the engineers who completed the study of maximizing the efficiency of water powered machines.

L. Carnot generalized the principle of the loss of 'energy' due to inelastic collisions to the machine

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Saint-Germain; In 1835, upon authorization of a line from Paris to St. Germain, Clapeyron and Lamé (who left shortly thereafter to accept the chair of physics at the École Polytechnique) were charged with direction of the work [based on Milton Kerker, "Sadi Carnot and the Steam Engine Engineers," Isis **51**, 257 (1960) footnote 15]. According to Kerker, "(Clapeyron was) specializing in the design and construction of steam locomotives. In 1836, he traveled to England to order some locomotives that would negotiate a particularly long continuous grade along the Saint-Germain line. When the illustrious Robert Stephenson declined to undertake the commission because of its difficulty, the machines were built in the shops of Sharp and Roberts, according to the designs of Clapeyron. He extended his activities to include the design of metallic bridges, making notable contributions in this area."

[56] Robert Fulton (1765-1815), `https://en.wikipedia.org/wiki/Robert_Fulton`; Robert Fulton's biography: `https://www.youtube.com/watch?v=2w6x5QdswYE`.

[57] The painting is explained in `https://www.youtube.com/watch?v=8O-fna8HrWw&list=WL&index=3`. C. Scallen, *Museum Masterpieces: The National Gallery, London* (Great Courses) "Lecture 22 British and French Masters c. 1785-1860" contains a nice introduction to this masterpiece.

By the way the impressionist style of paintings by Turner, Monet, and others depict trends in 19th century air pollution partly due to rampant use of steam engines. See A. L. Albright and P. Huybers, Paintings by Turner and Monet depict trends in 19th century air pollution, Proc. Nat. Acad. Sci. **120**, e2219118120 (2023). There is a followup exchange for this article: M. F. Marmor, Most paintings by Turner and Monet show stylistic evolution, not changes in pollution, Proc. Nat. Acad. Sci. **120**, e2302177120 (2023) and a reply to it by the authors: Reply to Marmor: Multiple perspectives for appreciating the meaning and beauty of Turner and Monet paintings, Proc. Nat. Acad. Sci. **120**, e2303372120 (2023).

[58] Lazare Nicolas Marguerite, Count Carnot (1753-1823) `https://en.wikipedia.org/wiki/Lazare_Carnot`.

actions in general.[59] In his *On machines in general* (1782)[60] he mentioned two conditions to obtain the maximum efficiency of hydraulic machines: (1) losing all the fluid movement by its action on the machine, and (2) by insensible degrees without any percussion. (1) means all the energy is transferred to the machine, and (2) implies that the transfer must be quasistatic. A universality statement can also be found, claiming that if (1) and (2) are satisfied, independent of the actual mechanism of the hydraulic machines, maximum efficiency can be realized. When Carnot wrote that there was a complete theory for machines that do not obtain motion from heat, he must have had his father's theory in his mind.

Carnot[61] visited his father in 1821, who had exiled himself to Magdeburg. It is almost certain that they discussed the problems of steam engines, since L. Carnot had been interested in the engine built in Magdeburg in 1818. After returning to Paris, Carnot wrote up his later famous paper.[62] in 1822-3.

A.7 Basic consideration by Carnot

Carnot observed: According to established principles at the present time, we can compare the motive power of heat to that of a waterfall with sufficient accuracy. Then, using the caloric theory, he considered the heat engine under the following two premises:[63]
(1) Wherever there exists a temperature[64] difference, we can produce power.[65]

The work is produced by a steam engine not because caloric is consumed, but because caloric moves (falls) from a hot body to a cold body.
(2) A practical condition for a working substance to produce power is that it can overcome certain resistances in their changes of volume. [This is Watt's expansion principle →**A.4**.]

Notice that (1) is the analogy between the flow of water with a height difference and the flow of caloric with a temperature difference, and (2) is the analogy between the water pushing the blade and the expanding working substance pushing the piston.

Carnot then translated L. Carnot's quasistatic condition for the maximum efficiency machine

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[59] See, for example, the Borda-Carnot equation `https://en.wikipedia.org/wiki/Borda-Carnot_equation`.

[60] Its English translation is published in Phil. Mag. in several parts: `https://babel.hathitrust.org/cgi/pt?id=mdp.39015035394322&view=plaintext&seq=314` (LIX).

[61] Nicolas Léonard Sadi Carnot (1796-1832),
`https://en.wikipedia.org/wiki/Nicolas_Leonard_Sadi_Carnot`

[62] Sadi Carnot, *Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance* [Reflections on the Motive Power of Fire and on Machines Fitted to Develop that Power] (Bachelier 1824, Paris)

[63] Although everybody knows that Carnot relied on the caloric theory, it should be noted that this theory of heat was a key element of Carnot's idea. T. Hiroshige's footnote (2) in his translation of Carnot's original paper (T. Hiroshige, Carnot's study of heat engine (Misuzu, 1973)) is the only statement the author noticed that could be interpreted as asserting the indispensability of the caloric theory to Carnot's theory.

[64] Needless to say, here 'temperature' is an empirical temperature in the heat theory since Black.

[65] "Wherever there exists a difference of temperature, wherever it has been possible for the equilibrium of the caloric to be re-established, it is possible to have also the production of impelling power."

(→**A.6**) as follows: the maximum efficiency is realized through operating the machine quasistatically; the exchange of heat must be between the systems at the same temperatures and the pressure difference must be infinitesimal.[66] The ideal engine that realizes the maximum efficiency must be reversible in the sense that the process can be reversed by supplying exactly the same amount of work that the engine produced. Carnot must have thought that all the transfer was gentle and infinitesimal, so the process could be reversed only with higher order differences.

A.8 Carnot's theorem

Carnot considered the maximum efficiency engine working between a high temperature heat source (furnace) at temperature T_H and a low temperature heat source (condenser) at temperature T_L as a cycle, following the basic consideration of L. Carnot (as explained in **A.7**). According to the argument in **A.7** a higher efficiency engine than this engine is not conceivable, but the efficiency could still depend on a particular working substance. Carnot demonstrated, using the reversibility of a maximum efficiency engine, that the maximum efficiency is universal as illustrated in Fig. A.2.[67] That is, the maximum efficiency is not dependent on the working-substance.

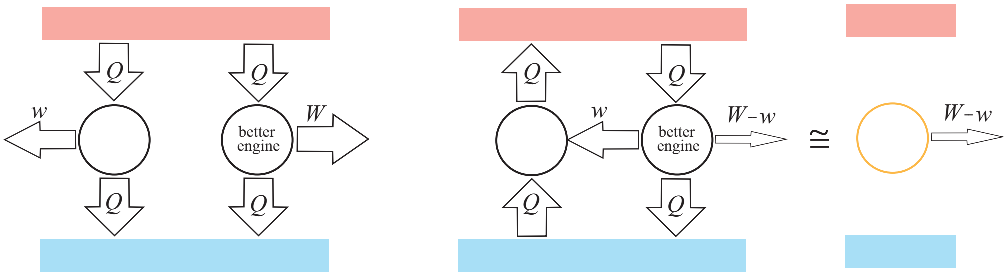

Figure A.2: It is impossible to exceed the efficiency of the Carnot engine.

Fig. A.2 Left: The left engine is the Carnot engine = the maximum efficiency engine, and the right engine is a supposedly more efficient engine that can produce more work $W > w$ from the same heat Q.
Center: Since the left engine is reversible, using a part of the work supplied by the 'better' engine, it can be operated as a caloric pump. Consequently,
Right: The whole device is equivalent to a perpetuum mobile producing work $W - w > 0$ without any supply of caloric (i.e., adiabatically).

A.9 Mayer and Joule: conservation of energy

Mayer,[68] on a voyage to Java as a ship's doctor, became interested in thermal phenomena and

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[66] Use of infinitesimal without any question reflects the wide acceptance of analysis in France.

[67] Notice that, if we use the modern terminology, the proof demonstrates: "Carnot's theorem must be true because energy is conserved." (a wrong reason)

[68] Julius Robert von Mayer (1814-1878), `https://en.wikipedia.org/wiki/Julius_von_Mayer`. Mayer was not recognized for a long time. He suffered from slander by Helmholtz and Joule, as well as from family misfortunes, leading to a deterioration of his mental health. Details about this can be found in the German version of Wikipedia: `https://de.wikipedia.org/wiki/Robert_Mayer`. Mayer's monument can be seen on Google Maps at the coordinates (49.1424067, 9.2189126).

came up with the idea that all the phenomena in the world depend on the changes in materials and their interactions caused by ⟨force⟩ and that the total amount of ⟨force⟩ is conserved, with only its quality changing." From the requirement of conservation of ⟨force⟩ and the fact that 'motion' disappears by the two-body inelastic collision, he concluded that heat and work were both forms of ⟨force⟩, and that they could mutually interconvert under a fixed law (1841). Then, he provided the conversion rate of heat and work for the first time with the aid of the Mayer cycle (→**14.8**).

Independently from this,[69] Joule[70] demonstrated that the constancy of the heat-work conversion rate (the so-called *work equivalent of heat*) using various phenomena.

Thus, it was established that thermal energy is a form of energy, and that the sum of mechanical energy and thermal energy is conserved, if correctly converted, for all the physical phenomena.

However, this observation was not immediately widely accepted. Conceptually, the biggest obstacle was Carnot's theorem (→**A.8**), which was understood to imply the nonequivalence of heat and work. For example, Thomson recognized the significance of Joule's work, but was troubled by the apparent contradiction with Carnot's theorem, and believed further empirical facts were needed.

A.10 How did Clausius proceed?

Clausius's[71] thinking was as follows.[72] As Mayer and Joule had demonstrated (→**A.9**), if consumption of work produces heat, heat is not conserved. Therefore, it is natural and logical to assume that when work is produced, heat is consumed. Therefore, other than the 'first principle' that the sum of heat and work is conserved, he postulated the following principle:[73]

> In all cases work results from heat, an amount of heat proportional to the work produced is consumed, and, conversely, the same amount of heat can be produced by consuming an equal amount of work.

It is important to note that the work-heat equivalence holds only when work results from heat.

As noted in **A.7** in Carnot's original idea caloric = heat was conserved. However, this idea contradicts the above principle. Therefore, the engine converts only a part of heat into work. Clausius found that if there were a more efficient engine than the reversible engine, Carnot's logic (→Fig. A.2 in **A.8**) in the proof of his theorem implies that heat flows from a lower temperature[74] heat source to a higher temperature heat source without any other trace. Since such a process can never occur naturally, Clausius concluded that work is done only if heat flows from a higher to a

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[69] **Important note**: Just before this, Joule had discovered Joule's law, $Q = RI^2$. He was conducting comparative studies on the efficiency of replacing steam engines with electric motors. In this research, electricity was obtained from batteries, and the amount of current was quantified using Faraday's law (→**26.3**) by measuring the amount of zinc consumed. In other words, electrochemistry was used in an essential way. The first determination of the mechanical equivalent of heat was based on measuring the thermal effect of the current generated electromagnetically.

[70] James Prescott Joule (1818-1889), `https://en.wikipedia.org/wiki/James_Prescott_Joule`.

[71] R. Clausius (1822-1888) `https://en.wikipedia.org/wiki/Rudolf_Clausius`.

[72] R. Clausius, Über die bewegende Kraft der Wärme und die Gesetze sich daraus für die Wärmelehre selbst ableiten lassen, Annalen der Physik **155** 368 (1850).

[73] `https://archive.org/details/ueberdiebewegen00claugoog/page/n11/mode/2up` p7

[74] Here, 'temperature' is an empirical temperature in the tradition of heat theory.

lower temperature heat source and that if heat cannot flow from a lower temperature heat source to a higher temperature heat source without any other trace, then Carnot's theorem can be proved (Fig. A.3).

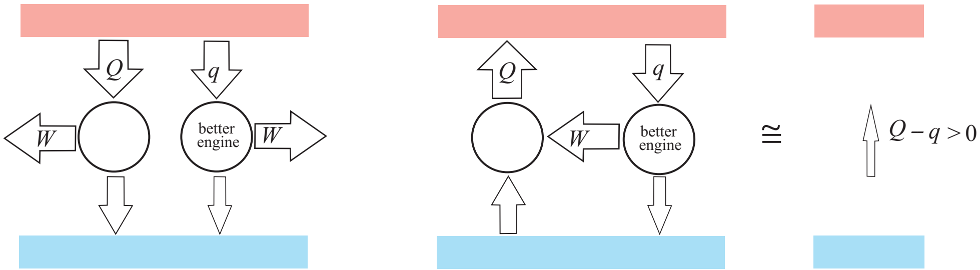

Figure A.3: If heat can flow from a lower to higher temperature heat source, then Carnot's theorem does not hold.

Fig. A.3 Left: The left empty circle denotes a reversible engine, which may be used as a heat pump if work W is supplied. The 'better engine' on the right is a hypothetical engine with a better efficiency, which requires heat q ($< Q$) from the higher heat source to produce the same amount of work W.
Center: If the better engine drives the reversible engine backward as a heat pump, heat $Q - q > 0$ is given to the higher heat source.
Right: According to the 'first principle,' this heat must have come from the lower temperature heat source. Therefore, 'heat flows from a lower temperature heat source to a higher temperature heat source without any other trace.' This is against the general experience that temperature differences naturally diminish and cannot increase without any other trace.

Thus, Clausius' paper of 1850 established the foundation of thermodynamics.[75]

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[75] ⟪**Thomson had no original contribution to the second law**⟫ E. A. Guggenheim, *Thermodynamics* (Fifth, revised edition, North Holland 1967) p17 says, "The second law was foreshadowed by the work of Carnot (1824). The first and the second laws were co-ordinated by Clausius (1850) and by Kelvin (1851).", quoting Clausius Ann Phys Lpz 1850 **79**, 368, 500 and Thomson, Trans Roy Soc Edinb 1853 **20**, 261. Notice that Thomson acknowledged Clausius' priority in his early manuscripts (albeit not straightforwardly) [(according to Yamamoto ibid., p086 of III) quoting p324 of C. Smith and M. N. Wise, *Energy & Empire, a biographical study of Lord Kelvin* (Cambridge UP, 1989): "... in an early draft of his 1851 published paper 'On the dynamical theory of heat':

> The same conclusion has been arrived at by Clausius, to whom the merit of having first enunciated and demonstrated it is due. It is with no wish to claim priority that the author of the present paper states that *more than a year ago* he had gone through all the fundamental investigations depending on it which are at present laid before the Royal Society, at that time considering the conclusion as highly probable even should Carnot's hypothesis be replaced by the contrary axiom of the dynamical theory; and that more recently succeeded in convincing himself demonstrative of its truth, without any knowledge of its having been either enunciated or demonstrated previously, except by Carnot. [footnote 16: William Thomson, Early draft of the 'Dynamical theory of heat', PA132, p. 10. Our emphasis. ...] (here ends quoting

A.11 Interpretation of the second law in terms of 'equivalent'

In a 1854 paper, Clausius interpreted the second law as claiming that any non-spontaneous transformation cannot occur without compensation by a spontaneous transformation.

> The transformation of producing work from heat that cannot occur spontaneously cannot occur without compensation by a spontaneous transformation that transfers heat from a higher temperature object to a lower temperature object.

In other words, there are two kinds of transformation of energy, spontaneously possible and not. Reversible transformations are the changes in which both kinds of transformations balance.

Consider the following two spontaneous processes:
A: Process converting work W into heat at temperature θ;
B: Process converting heat Q at temperature θ into heat Q at temperature θ' $(< \theta)$.
Their reversed processes are denoted as A^{-1} and B^{-1}, respectively.

In a process that actually happens, A^{-1} is compensated by B (an engine), and B^{-1} is compensated by A (heat pump). Transformations that can be substituted for each other are regarded as equivalent transformations. To express this equivalence quantitatively, Clausius introduced a quantity called the 'equivalent of transformation' which is proportional to the relevant energy and additive with respect to the connection of successive transformations so that the total equivalents of a reversible process is zero. The equivalent of a spontaneous transformation is chosen to be positive as follows:

The equivalent of A is $Wf(\theta)$,

The equivalent of B is $QF(\theta, \theta')$ with the sign convention $F(\theta, \theta') > 0$ for $\theta > \theta'$.

The equivalents of the reversed transformations are: $-Wf(\theta)$ for A^{-1}, and $QF(\theta', \theta)$ for B^{-1}. The additivity implies $QF(\theta, \theta') + QF(\theta', \theta)) = 0$, so we require

$$F(\theta, \theta') = -F(\theta', \theta). \tag{A.1}$$

A.12 Carnot engine in terms of Clausius' equivalents

Carnot's reversible engine may be interpreted as follows (Fig. A.4):
Engine direction: Heat $Q_H - Q_L$ at temperature θ_H is transformed into work W and the process is compensated by the natural transformation converting heat Q_L at temperature θ_H into heat Q_L at temperature θ_L.
Heat pump direction: Work W is naturally converted to heat $Q_H - Q_L$ at temperature θ_L, while compensating the transformation of heat Q_H at temperature θ_L into that at temperature θ_H.

For reversible processes the total equivalent must be zero: for the reversible engine

$$-Wf(\theta_H) + Q_L F(\theta_H, \theta_L) = 0, \tag{A.2}$$

Yamamoto)

On p327 of the same book, we find: "In whatever way one judges Thomson's independence from Clausius, his interaction with Rankine during 1850 was crucial." On p325 we read "Rankine's response to Clausius's first paper on the motive power of heat (published earlier that year in Poggendorff's *Annalen*) reinforced Thomson's awareness of the need for new 'proof' of Carnot's criterion...."

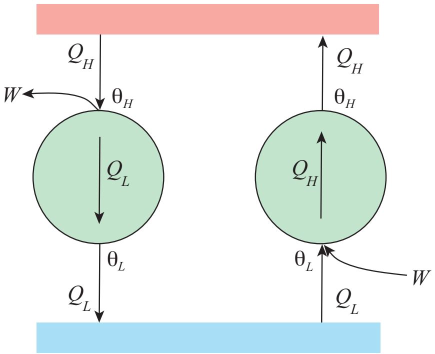

Figure A.4: Carnot's reversible engine interpreted in terms of equivalent compensation; Left: heat engine, Right: heat pump. The conservation of energy implies $W = Q_H - Q_L$.

and for the reversible pump

$$W f(\theta_L) + Q_H F(\theta_L, \theta_H) = 0. \tag{A.3}$$

Adding the above two formulas with the aid of (A.1), we get

$$W[f(\theta_L) - f(\theta_H)] + [Q_L - Q_H]F(\theta_H, \theta_L) = 0. \tag{A.4}$$

The 'first principle' implies $W = Q_H - Q_L$, so the above formula implies

$$f(\theta_L) - f(\theta_H) = F(\theta_H, \theta_L) > 0. \tag{A.5}$$

Hence, $f(\theta)$ is a monotone decreasing function. Therefore, Clausius introduced a monotone increasing function $T(\theta)$ [76] as

$$T(\theta) = 1/f(\theta). \tag{A.6}$$

Thus, we have the following summary:

(1) The equivalent of the process of converting work W ($= Q$) into heat Q at temperature T is Q/T.
(2) The equivalent of the process of heat Q transferred from heat source at temperature T_H to that at T_L is $Q/T_L - Q/T_H$.

(1) agrees with the equivalent of heat Q from temperature $T_H = \infty$ to $T_L = T$ in (2). Thus, Clausius concluded that work is equivalent to an infinite temperature heat.

Furthermore, (2) may be interpreted algebraically as the sum of the equivalent of absorbing heat Q at temperature T written as Q/T; the high temperature heat source absorbs heat $-Q$ whose equivalent is $-Q/T_H$.

Here T is not the temperature of the system but the heat source. Furthermore, the sign convention of Q is 'seen from the heat source.' Thus, the process of heat source releasing $|Q|$ is with $Q < 0$. [Remark: This sign convention is the opposite of the usual thermodynamic convention (→**7.1**) which is system-centered.]

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[76] Here, this is still an empirical temperature, but actually identical to the absolute temperature (→**11.7**).

A.13 Clausius was almost reaching entropy

Suppose there are many heat sources with temperature T_i. For a process in which heat Q_i is absorbed by the ith heat source, the equivalent of the process is

$$N = \sum \frac{Q_i}{T_i}. \tag{A.7}$$

If there are numerous heat sources and if we may use differential expressions, then

$$N = \oint \frac{dQ}{T}. \tag{A.8}$$

Consider a cycle, where the system exchanges heat with the sources and returns to the original state. Suppose $N < 0$ for this cycle. This means that the cycle cannot occur spontaneously. If $N > 0$ and if the cycle is reversible, then $N < 0$, so for a reversible cycle only $N = 0$ is allowed.

(A.8) implies that the integral of dQ/T is conserved in reversible processes.[77] Apart from the sign convention, N is just 'entropy' (→**14.5**). However, it took Clausius ten more years to introduce 'entropy', eventually in 1864.

A.14 Clausius' twists and turns

As we have seen up to **A.13** Clausius almost reached the concept of 'entropy,' which is a thermodynamic quantity of central importance, through the idea of equivalent and compensation (→**A.11**). However, there were processes for which 'equivalents' could not be computed, because the principle of the equivalents of transformations could not be used. For example, take an adiabatic free expansion (→**17.12**). The gas does not do any work nor exchange any heat, but the process is irreversible, so there must be a remaining (i.e., uncompensated) positive 'equivalent.' How much is it? This cannot be obtained by considering transformations such as 'heat ⟺ external work' or 'high temperature heat ⟺ low temperature heat' alone.

Clausius tried to solve this problem as follows: He divided internal energy into real heat corresponding to the translational kinetic energy and the rest. Then, he thought the work to the latter as 'internal work,' and conceived the two transformations, 'heat ⟺ real heat' and 'heat ⟺ internal work.' Then, he wrote $dQ = dH + dQ'$, where dH is the real heat and dQ' is the rest. From this he wrote

$$\frac{dQ}{T} = \frac{dH}{T} + dZ. \tag{A.9}$$

He interpreted the volume increase as internal work, and 'equivalent' Z was assigned to it. He named Z ⟨disgregation⟩ (1862). The naming suggests that Clausius thought of it as measuring the extent of irreversibility due to the spread/diffusion of material. Clausius thought dZ depended only on volume V.[78] Then, dZ is exact. Therefore, Clausius concluded (in the 'modern' saying) that as

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[77] That is, dQ/T is a differential of some function 'S', although to conclude this, we must assume some property for the totality of the thermodynamic states (→**9.12**).

[78] If we use the modern thermodynamics

$$dZ = \frac{1}{T}\left[\left(\frac{\partial E}{\partial V}\right)_T + P\right] dV. \tag{A.10}$$

the sum of two exact differentials $dS = dQ/T + dZ$ is exact; S is named 'entropy.' Thus, entropy change is due to diffusions of heat and of matter.

Although Clausius removed any mention of ⟨disgregation⟩ from his 1876 reprint of his entropy papers, his twists and turns were not useless. 'Thermal chemistry' was grafted to ⟨disgregation⟩ (→**A.15**).

A.15 Horstmann and the beginning of chemical thermodynamics[79]

Horstmann,[80] who attended Clausius' thermodynamics lectures at ETH in 1866, applied the ideal gas law to the ⟨disgregation⟩ part of entropy as $dZ = (P/T)dV$ and calculated the ⟨disgregation⟩ of substance A as

$$Z_{\rm A} = Z^0_{\rm A} - R\log(P_{\rm A}/P_0). \tag{A.11}$$

He considered the reaction A $\longleftrightarrow$ B. When the extent of reaction is ξ for the reaction (→**25.8**),

$$dZ(\xi) = (Z_{\rm B} - Z_{\rm A})d\xi. \tag{A.12}$$

If the reaction heat is Q (per unit reaction), the entropy change can be expressed as

$$dS = \frac{Qd\xi}{T} + dZ(\xi). \tag{A.13}$$

Applying the entropy maximization principle as the equilibrium condition

$$Q/T + \frac{dZ}{d\xi} = Q/T + (Z_{\rm B} - Z_{\rm A}) = Q/T + \Delta Z^0 + R\left(\log(P_{\rm A}/P_0) - \log(P_{\rm B}/P_0)\right) = 0. \tag{A.14}$$

Thus, we have

$$\log(P_{\rm A}/P_{\rm B}) = -Q/T - \Delta Z^0. \tag{A.15}$$

That is, with an appropriate constant C, we have

$$\frac{P_{\rm A}}{P_{\rm B}} = Ce^{-Q/T}. \tag{A.16}$$

This relation was experimentally verified.

Thus, the condition for chemical equilibrium, or the criterion for equilibrium, is given in the form "If the entropy of the system is denoted as S, then at equilibrium, δS must be equal to zero."[81] This provision is considered to be the pioneering theoretical content and this Horstmann's work was regarded as a demonstration of the applicability of the entropy theory to chemistry.

van't Hoff[82] pursued application of thermodynamics to chemistry, influenced by Horstmann's

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[79] T. Inoue, "Formation process of dissociation equilibrium by A. Horstmann—Beginning of chemical thermodynamics in the latter half of the 19th century." Kagakushi Kenkyu II **26**, 1 (1987). The exposition here is simplified.

[80] August Friedrich Horstmann (1842-1929) `https://en.wikipedia.org/wiki/August_Friedrich_Horstmann`.

[81] Now, we must say, "under an adiabatic condition" (→**12.6**).

[82] Jacobus Henricus van't Hoff Jr. (1852-1911). See `https://en.wikipedia.org/wiki/Jacobus_Henricus_van_%27t_Hoff`.

work: "According to Horstmann, the principles of thermodynamics is applicable to chemistry."[83] However, the supporting facts were no more than what is summarized above.

A.16 Faraday, Joule and quantitative applications of electrochemistry

Faraday[84] demonstrated all the electricities (bioelectricity, electricity by magnetic induction, electricity from batteries, etc.) were identical, and the quantity of electricity was measured in terms of the consumption of zinc of the Daniell cell (→**26.34**). That is, electrochemistry was indispensable in measuring charge and current. Faraday established Faraday's law: a chemical equivalent corresponds to a definite amount of electricity (→**26.3**). Joule constructed a galvanometer in 1839 and even proposed a standard method to quantify electricity.[85] Joule's law as to Joule heating was discovered while pursuing the relation between the amount of electricity and heat. The work equivalent of heat was for the first time measured through converting work into electrical energy.

A biographer of Joule summarized[86] his work as follows: through measuring electric action, Joule was able to trace a definitive quantity of physical effect throughout the entire field of physics.

Notice that the foundation of his work was electrochemical in nature.

A.17 What did Helmholtz say about chemical energy?[87]

At the end of his exposition, "On the conservation of force"[88] Helmholtz[89] discussed the combustion of coal.

The carbon and oxygen atoms adhere firmly to form a new compound in combustion: "this attraction between the atoms of carbon and of oxygen performs work just as much as that which the earth in the form of gravity exerts upon a raised weight." "When carbon and oxygen atoms have rushed against each other, the newly-formed particles of carbonic acid must be in the most violent molecular motion—that is, in the motion of heat."

Can we reverse the process? Plants just do that. An easier example is the electrolysis of water. To this end electric current must be supplied from a Galvani cell (→**26.28**), but it is produced by oxidation of metal. That is, to return water, a combustion product, to hydrogen gas another 'combustion reaction' is used; to overcome a chemical force another chemical force[90] is used, but the current may be produced by magnetic induction as well.

Thus, Helmholtz's explanation of chemical reactions using mechanical models was convincing. Of

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[83] M. J. H. van't Hoff, *Etudes de dynamique chimique* (1884), p124. [Its download would take long.]

[84] Michael Faraday (1791-1867), `https://en.wikipedia.org/wiki/Michael_Faraday`.

[85] O. Reynolds, *Memoir of James Prescott Joule* (Manchester Literary and Philosophical Society, 1892) p42.

[86] O. Reynolds, ibid., p66.

[87] "Chemical energy" here means energy in general associated with chemical reactions in an informal fashion.

[88] Hermann von Helmholtz, *On the Conservation of Force*, Introduction to a Series of Lectures Delivered at Carlsruhe in the Winter of 1862-1863 (Translated by Edmund Atkinson). "Force" means energy throughout his exposition just as in Mayer's writings (→**A.9**).

[89] Hermann von Helmholtz (1821-1894). `https://en.wikipedia.org/wiki/Hermann_von_Helmholtz`.

[90] Notice that chemical force = chemical energy in Helmholtz writing.

course, it is clear from the explanation in **A.16** that Faraday and Joule had naturally incorporated the quantitative reversibility of hydrogen-oxygen fuel cells and the electrolysis of water **26.6** into their system as an obvious fact "long before the era of thermodynamics" (since BC = Before Clausius).[91]

A.18 How about the second law for chemistry?

Helmholtz' rhetoric 'established' the conservation of energy as the most general principle of the world. His article quoted in **A.17** was immediately translated into English. This indicates the importance of his exposition.

However, the first law is not truly a thermodynamic principle. The second law is the key. Thus, van't Hoff appreciated Horstmann's demonstration as we have seen in **A.15**. Notice that this was likely the only work on the applicability of entropy to chemical reactions before Gibbs, who introduced chemical potential in his epoch-making work.[92]

Is there any statement justifying that 'chemical coordinates' (or the amounts of chemicals) may be handled in the same manner as the usual work coordinates, in contradistinction to heat? No, there is none, at least before Gibbs. Helmholtz's mechanical model must have hypnotized thermodynamics.

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[91] It is very interesting to recall that a serious doubt about the analogy between atoms and the solar system drove Bohr (and Heisenberg) to quantum mechanics as vividly recalled by Heisenberg in his *Der Teil und das Ganze* (Piper Verlag GmbH, München, 1968) Chapter 3. Bohr told him about his atom model: Perhaps I may first tell you a bit about the history of this theory. The starting point was not the idea that the atom is a miniature solar system and that the laws of astronomy could be applied here. I never took it that literally. For me, the starting point was the stability of matter, which from the perspective of existing physics is a pure miracle.

By stability, I mean the recurrence of the same substances with the same properties, the formation of the same crystals, the same chemical compounds, etc. This must mean that even after many changes that might be brought about by external influences, an iron atom is ultimately still an iron atom with exactly the same properties. This is incomprehensible according to classical mechanics, especially if an atom resembles a solar system.

[92] J. W. Gibbs, "On the equilibrium of heterogeneous substances," Trans. Connecticut Academy, III 108 (1875-6), 343 (1877-8).

2 Equilibrium states: Preliminary I

2.1 What is a macroscopic system?

Throughout this book, a ‘system’ implies an object of our scale (→**1.4**) occupying a definite spatial domain.[93] Its boundary is macroscopically definite due to walls made of a certain material (as in the case of a gas in a canister) or perhaps by the system itself (as in the case of a solid block).

For macroscopic systems if their sizes increase, the amounts of physical quantities (e.g., its mass) carried by (or immediately associate with) the boundary walls become less significant relative to those carried by the system bulk, so we ignore the effects of the physical quantities carried by the walls. Therefore, the effect of a wall is only to impose a boundary condition to the system under consideration, mathematically speaking, so ‘wall’ and ‘boundary condition’ will be used interchangeably. Inserting a new wall in a system is interpreted as imposing a boundary condition between the parts created by insertion of the wall.[94] We assume that inserting a new wall in the system may be realized without any energetic cost. This is a requirement regarding the theory. Even such ‘less important’ requirements must be explicitly stated, just as the so-called principles, in order to engage in proper discussion. The principles and requirements we need for constructing thermodynamics are collected in “The premises for thermodynamics—a summary.”

The world surrounding a given system is called the *environment* of the system.[95] Changing the boundary conditions imposed on the wall between the system and its environment is (as has been already required) assumed to be realized without energetic cost.

2.2 What sort of states of macroscopic systems do we wish to understand?

Even if a system is macroscopic (→**1.4**), its state can be diverse; an explosion may have just occurred inside or is ‘dead’ for a long time so macro-observers like us

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[93] Its boundary is macroscopically two-dimensional (not fractal) just as an ordinary block.

[94] We can say that systems whose walls are allowed to be abstracted as boundary conditions may be studied by thermodynamics. Thus, information thermodynamics that utilizes mesoscale examples with very clear boundary conditions like boxes are often dubious.

[95] Here, the word ‘world’ is used, but, in practice, it is a small portion of the world that surrounds the system and has immediate interactions with the system.

cannot discern any change. If a system is changing in time and is not spatially homogeneous, in order to describe its state even macroscopically, a small number of observables must not be sufficient. Therefore, it is sensible to start with aiming at understanding the simplest states first, and then to use the results to construct a fuller theory to understand more general states.

If a macrosystem is left for a sufficiently long time in a constant environment (that does not cause 'dissipation' →**2.3**), very often the system reaches a state in which 'nothing happens.' Such a state is called an *equilibrium state* (→**2.4**, **2.8**). Thus, 'thermodynamics'—the theory of heat, work and energy transformations—aims, to begin with, at a theoretical system to describe 'equilibrium states' and their quasistatic changes (→**A.6**) precisely.

2.3 Meaning of 'without dissipation'

Dissipation of energy indicates that the conservation of a system's macroscopic energy is not maintained. Therefore, the term 'without dissipation' implies that the macroscopic electromagnetic and mechanical energies remain within the system (are conserved).

If isolated macrophysical systems adhere to the fundamental laws of (macroscopic) mechanics and electromagnetism, their total energy remains conserved. If the total macroscopic mechanical and electromagnetic energies are conserved, then the system complies with the principles of macroscopic mechanics and electromagnetism. Hence, 'a system without dissipation' implies that its time evolution is dictated by macroscopic mechanics and electromagnetism. As a result, the system's time evolution is step-by-step reversible, meaning any change can be retraced.

Dissipation might not arise solely from irreversible processes within the system itself but could also occur due to the generation of sound or (electromagnetic) radiation.[96] While the production of such energy forms may be purely mechanical and/or electromagnetic, very often these radiations do not fully return to the system (even if the system's surrounding space is isolated from the outside world). Consequently, their generation often entails dissipation.[97]

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[96] It might be simpler to consider systems involving radiation as not truly isolated. If we take this point of view, there is no need for a discussion about radiation.

[97] If the system is placed in a box and if the system is in radiation equilibrium with the box walls, then radiation does not cause dissipation. Here 'radiation equilibrium' means that each portion of the system receives net zero energy by radiation. Radiation contradicts equilibrium, only if there is an energy flow generated by radiation.

In summary, a system without dissipation is a system obeying the fundamental laws of macroscopic mechanics and electromagnetism (without radiations).[98]

2.4 What is an equilibrium state?

It was stated at the end of **2.2** roughly as follows: If a macrosystem is left for a sufficiently long time in a constant environment (→**2.1**) (that does not cause 'dissipation' →**2.3**), the system eventually reaches an equilibrium state in which 'nothing happens.' The terms used in this statement may be fairly clear, so the meaning of 'equilibrium state' may be fairly clear. However, still the meaning of the following terms should be better specified: "constant environment," "sufficiently long time," "being left," "eventually," and "nothing happens" (→**2.5**-**2.7**).[99]

2.5 "Nothing happens"

"Nothing happens" in our context means that no time dependence can be observed within our space-time scale (→**1.4**).[100]

If our space-time resolution is much finer than our scale, then we could observe space-time dependent phenomena called 'fluctuations'.[101] However, they are aver-

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[98] In simpler (and more informal) terms, if we were to place the system with dissipation and its environment in a Dewar flask during the process, we would detect increase in temperature. This change is attributable to the irreversibility of the system's time evolution.

[99] Some supposedly mathematically rigorous expositions assume the concept of an "equilibrium state" as a primitive, leaving it undefined. In contrast, the present exposition will avoid a pseudo-mathematical approach and strive to be as operational as possible (hence, for example, atomistic explanations are completely avoided).

The fundamental issue with a formal or mathematical system lies in the failure to specify the relationship between the actual world and the realm of logic or mathematics. Since we are dealing with natural science, any theoretical framework must be firmly rooted in observable phenomena. Therefore, a clear and explicit description of the relationship between the theoretical system and real-world phenomena is essential for natural science.

In this book, we assume that macrophysics and chemistry are sufficiently grounded on the "rough ground," as Wittgenstein remarked in section 107 of *Philosophical Investigations* (Blackwell Publishers, 1953, 50th anniversary commemorative edition).

[100] We may roughly say that the time scale within which we can observe fluctuations is in the range of $2^{\pm 20}$ hours, and the length scale in the range of $2^{\pm 20}$ meters.

[101] However, this scale, where we observe the so-called thermal fluctuations, is still much closer to our everyday scale than to the atomic scale. Thus, the mere observation of the famous 'Brownian motion' does not directly demonstrate the existence of atoms (or the particulate nature of matter); it simply indicates the presence of small-scale pressure imbalances around the Brownian particle. Therefore, those who conclude that atoms exist solely by observing Brownian motion through a

aged out at our scale.

In thermodynamics, “nothing happens” means that there is no time dependence for any macroscopic observables.

2.6 “Sufficiently long time”

In 2.5, the long time scale is set to be $\sim 10^6$ days, but if we wait longer, some change may happen.

If the time scale we are interested in is, for example, a day, then if nothing happens even if we wait for 10 days, we may practically say that there is no change for a sufficiently long time.

Feynman states roughly as follows: if all the fast processes that should happen have happened and if all the slow processes that might happen have not yet started significantly, then the system is in equilibrium (see **21.1** for an example).

“Eventually” implies, ideally, ‘forever after’, but, as implied above, actually or in practice the word implies that our observation time scale is much longer than the time scales of all the fast events in the system (and still no extremely slow processes have started).

2.7 “Constant environment”

A ‘constant environment’ implies an environment (see just below and **2.1**, esp., the last footnote in it) for which “nothing happens” (→**2.5**) for a “sufficiently long time” (→**2.6**). Here, we assume that the system we consider has a definite and stable boundary (→**2.1**). An environment of a system is a part of the world that is enclosing the system and that may affect it. How the environment interacts with the system across its boundary is also specified as a property of the environment (that is, the boundary conditions between the system and its environment are the part of the properties of the environment).

Generally speaking, however, it is not so easy to specify the external environment, so often in thermodynamics, it is assumed that there is nothing outside the system; that is, it is assumed that the system is isolated from the rest of the world: The state is called an equilibrium state, if nothing happens (→**2.5**) in the system after isolating it for a sufficiently long time (→**2.6**).[102]

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microscope are either geniuses or fools.

[102] ⟪**Isolation and equilibrium**⟫ Precisely speaking, according to this definition of equilibrium, it is not simple, for example, to define the equilibrium state in an isothermal (= constant tem-

However, the state of a system may be constant under the effect of constant external influence. For example, the system may be under a constant electric field. Even in such cases after a sufficiently long time the system could reach a constant state in which nothing happens. However, if we take out a portion from the system and isolate it, its state should often be different from the one before isolation. Therefore, relaxing the isolation condition, we allow the imposition of static uniform fields (e.g., electric field, magnetic field, etc.) after isolating the system[103] as a condition for a "constant environment."[104]

"Leaving" implies that we human observers/experimenters do not do anything to the system enclosed in its environment.

2.8 Definition of 'equilibrium state'

Taking account of **2.7**, we would say:

> An equilibrium state of a system is a state without any macroscopic change attained after it is left for a sufficiently long time in a constant environment that does not cause any dissipation.

Needless to say, 'constant environment' (→**2.7**), 'sufficiently long time' (→**2.6**), 'macroscopic change' (→**2.5**) are used as specified above.

However, an equilibrium state is completely determined by its current state of the system irrespective of its history, so it may not be satisfactory to characterize 'equilibrium' by how it is prepared. Therefore, we prefer:

> A state of a system is an equilibrium state, if there is a constant environment in which we can embed the system with an appropriate boundary condition

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perature) environment. Perhaps, we can prepare a system attached to a heat bath at a constant temperature for a sufficiently long time, and then isolate it. However, according to the definition using isolation, the system before isolation may not be in equilibrium, and after isolation it is not isothermal, strictly speaking. Therefore, we need a convention or an assumption of some sort stated explicitly. For example, the state of a system is (thermodynamically) the same even if it is isolated from its original environment. Thus, we assume the partitioning-rejoining invariance **2.13** explicitly.

[103] Generally speaking, imposing a uniform external field could induce a sort of flow in the system causing 'dissipation.' However, if a uniform external field is imposed while the system is isolated, then usually lasting flow would not be induced, so there would be no dissipation (→**2.3**).

[104] However, as Akira Shimizu clearly points out, that there is an effect of external field from outside implies that the system allows long range interactions. Thus, we cannot generally say that the system is energetically additive (→**2.11**). However, still there are situations in which the system energy is additive, so we are allowed to develop an ordinary thermodynamics for such systems.

> (wall) without causing any change of the state of the system and without any dissipation.

It is desirable to guarantee that an equilibrium state does exist, so we may add that the system left alone for a sufficiently long time in a constant environment will reach an equilibrium state. Still it should be emphasized that for the definition of an equilibrium state, how it is reached should be irrelevant.

2.9 Uniqueness of the equilibrium state: a principle of thermodynamics

Prepare a system that is materially closed (i.e., no import/export of any matter allowed) and that is left in a constant environment E until it reaches an equilibrium state (→**2.8**). If we repeat this experiment from the macroscopically identical initial condition in the same environment E, the final state is 'usually' the same.[105,106]

This uniqueness is an empirical fact, so we assume this as the basic premise (principle) of thermodynamics (especially for simple systems →**2.10**) sometimes called the *zeroth law of thermodynamics*:[107]

> If a system is prepared in a macroscopically identical initial state and left in an identical environment for a sufficiently long time, the system will eventually reach the same equilibrium state.

2.10 Simple systems and compound systems

We may prepare unrelated systems in various equilibrium states and then juxtapose them without any interaction between them to declare the resultant collection to be a single equilibrium system. Then, we may introduce various interactions (i.e., walls

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[105] Here, the adverb 'usually' appears. Precisely speaking, for simple systems (→**2.10**) the uniqueness of the final equilibrium state is always the case. Some complications could happen for compound systems (→**2.10** as illustrated in **16.7**), but such cases are very rare, so we may practically assume the reproducibility of the equilibrium state. Therefore, this uniqueness is (unless otherwise stated) assumed as a principle of thermodynamics (called the zeroth law).

[106] Here, 'the same' means that we cannot discern any difference macroscopically. The precise uniqueness of the equilibrium state can only be provided after the equivalence of two equilibrium states is clearly defined. See **5.1**.

[107] In old textbooks, the fact that thermal equilibrium is an equivalence relation is called the zeroth law. However, thermal equilibrium relations cannot be described unless thermal contact **7.12** is clearly defined, so it is impossible to state it at the very beginning. Moreover, it is not a necessary principle. Traditionally, it has been claimed that this old zeroth law leads to the existence of temperature, but it is well known that this cannot be done based on this principle alone. For example, the proof in the Kubo's exercise book makes no sense mathematically or logically.

or boundary conditions →**2.1**) among them and wait for a sufficiently long time for the resultant compound system to reach an equilibrium state. Thus, we can make indefinitely complicated equilibrium systems. Still, to develop a general theory, we should start with the simplest systems.

We define 'simple systems' just below and then we assume all the systems in thermodynamics are simple systems or *compound systems* constructed from simple systems by joining them with appropriate boundary conditions as mentioned just above.

As 'simple systems,' it should be advantageous to pay special attention to the systems that are spatially homogeneous. Unfortunately, however, there is no guarantee that such a system is always spatially homogeneous irrespective of its states (perhaps phase separation could occur, for example). Therefore, we define a system to be a *simple system*, if we can actually observe the system to have a spatially uniform equilibrium state (under some conditions within experimental reach).[108]

In contrast, a *compound system* is defined as a system that is not homogeneous but cannot be thermodynamically distinguished from a system made by connecting various simple systems across appropriate walls.

2.11 What sort of macrosystems do we wish to understand?

For a simple system (→**2.10**), prepare its copy.[109] Both are left in the identical spatially uniform time-independent environment E till no change is observed macroscopically. Thus, the two systems reach an identical equilibrium state (→**2.9**). Then, combine these two systems with an arbitrary boundary condition (i.e., through a certain wall →**2.1**) and leave the combined system in the same environment E as a whole as illustrated in Fig. 2.1.

After a sufficiently long time, we compare the states of an arbitrarily chosen small but macroscopic volume 'B' (illustrated as small ovals in Fig. 2.1) in the system before and after the combination. We only deal with the systems that we cannot discern any macroscopic (→**1.4**) change in the above two states of 'B' for any wall between the system and the copy (Fig. 2.1). Let us call a system satisfying this

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[108] A simple system need not be made of a single chemical. The condition is that we can actually observe it to be in a spatially homogeneous equilibrium state under some condition.

[109] A system in a macroscopically indistinguishable state; for simplicity, let us assume the simple system is in a spatially uniform state. If you wish to be general, then the nonuniform spatial structure must be faithfully copied.

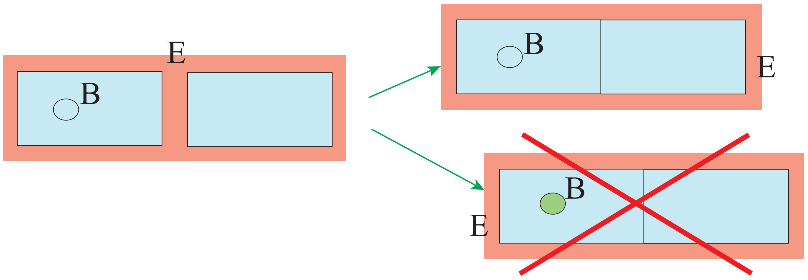

Figure 2.1: Thermodynamics deals with systems in which each small but macroscopic portion (e.g., the oval 'B') exhibits no change in its macroscopic state before and after combining with its copy. The lower right case illustrates a disqualified scenario, where the oval (representing any macroscopic portion) undergoes a change in its state after the combination.

invariance an *(combination) additive system*.[110]

2.12 Nonadditivity due to long-range interactions

If the 'reaching' range of interactions between the parts of the system is not small (i.e., the decay rate of the interaction strength as a function of distance is small), the additivity (in the sense of **2.11**) may be violated. This could cause alteration of energy density as the system volume varies. Gravitational and electrostatic (Coulombic) interactions have such a property.

Gravitational interaction within the system is not significant at our scale, so in the usual thermodynamics, this is ignored.[111] Electrostatic interactions are quite large, so if there are 'naked' charges, we are not allowed to ignore them (see electrochemistry →**26.9**-**26.11**). However, if the system is electroneutral, for example, plus and minus charges could shield each other, and the electrostatic interaction range may be macroscopically infinitesimal. Thus, we may generally assume that electrostatic interactions do not cause nonadditivity.

However, if the distance between the positive and negative charges are fixed as in electric dipoles, electrostatic shielding is not complete, so the electrostatic interaction energy decays as r^{-3}, where r is the spatial distance. Consequently, the additivity mentioned above fails, and, furthermore, even if the system volume is maintained, the total energy can depend on the macroscopic shapes of the system. There are

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[110] The word 'additive' already appeared in **1.10**. If a system is combination additive, then it is also energetically additive as required in **1.10**.

[111] The gravitational interaction between the system and some big external bodies (e.g., the earth) cannot be ignored, but the effect is uniform over the system and appropriately handled within the thermodynamics we can develop (not in this book). In a usual macroscopic system, the gravitational interaction within the system is ignorably small.

many systems such as ferroelectrics containing molecules with permanent electric dipoles. The same difficulty is encountered for ferromagnetic materials for which macroscopic magnetism arises from the collection of permanent magnetic dipoles.

For the systems mentioned above, sufficiently general mathematical theory cannot be constructed. Thus, thermodynamics discusses only (energetically) additive systems for which the total energy[112] of the system is proportional to its volume.

2.13 Partitioning-rejoining invariance of equilibrium states[113]

If a macroscopic system is divided cleanly into two pieces of roughly equal sizes,[114] then the resultant pieces are again macroscopic systems. Here, 'dividing cleanly' refers to a non-fractal dividing surface and the surface areas of the pieces must be proportional to 2/3 power of their volumes, if the linear dimension of the system is scaled, (such partition is called the *van Hove partition*).

Remark. Partitioning and rejoining

In thermodynamics, it is sometimes necessary to divide a system into two systems or combine two systems. Since partitioning can be interpreted as inserting a wall that blocks interactions, as described in **2.1**, it is possible to perform a partitioning without any energetic cost, ensuring that no macroscopic differences are observed in each part after the partitioning.

Regarding rejoining, with respect to the partitioning-rejoining invariance of equilibrium states, we only consider the rejoining of systems that have been obtained by partitioning an equilibrium state to restore the original system before partition. Combining different equilibrium states is not considered in this context.

If a macroscopically non-uniform system in equilibrium may be divided into small and uniform macrosystems, we have only to understand spatially uniform systems. Therefore, the following is explicitly required for convenience:[115]

A macroscopic part of an equilibrium macrosystem is, even if isolated, again

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[112] The origin of energy must be appropriately chosen.

[113] If uniform external fields such as an electric field are imposed, we must perform the partitioning-rejoining procedure under the same external fields.

[114] The illustration Fig. 2.2 might suggest 'brute force breaking of the system into two', but various gentle methods are possible; for example, if you wish to divide an ice block, you can melt it and then freeze it into two half blocks. Thermodynamically, crystal orientation is irrelevant (→**23.7**).

[115] Actually, for the macroscopic part under consideration the rest of the system + the environment is its environment, and the part is in equilibrium with this environment, so the above requirement need not be made particularly according to the second definition in **2.8**.

an equilibrium macrosystem.

If a macroscopic system is in equilibrium, the divided pieces are again in equilibrium.

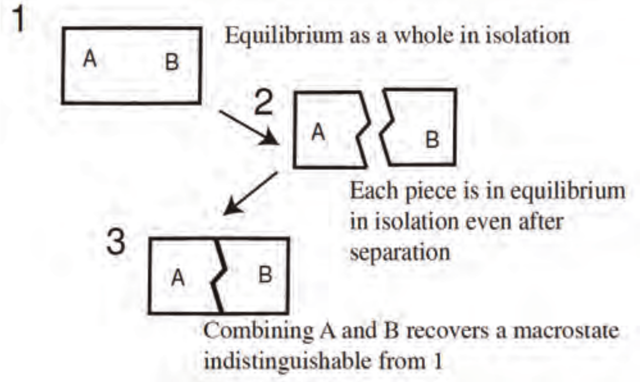

Figure 2.2: The partitioning-rejoining invariance of equilibrium states: A macrosystem is partitioned into two pieces A and B (1→2) and then are rejoined (2 → 3).

If the resultant two pieces are rejoined,[116] we get a macrosystem whose state is (thermodynamically) indistinguishable[117] from the original equilibrium state:

An equilibrium state is partitioning-rejoining invariant.[118]

2.14 Partition additivity and additivity

2.13 tells us that it is natural to consider physical quantities whose total amount is equal to the sum of the amounts in each part of an equilibrium system obtained by partitioning (cf. Remark in **2.13**).

The *partition additivity* of a quantity Q in a system A implies

$$Q(A) = \sum_{i=1}^{n} Q(A_i) \tag{2.1}$$

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[116] This rejoining may not be at the cut ends, since thermodynamic quantities/observables are shape-independent. The reader might worry about the symmetry-broken phases: must not we respect the consistency of order parameters at the connection boundary? Thermodynamics do not respect the order parameter orientations that do not affect the system internal energy, so we may ignore this consistency. The same applies to the flow that can exist in superfluid phases. We need not pay any attention to the flow field if the accompanying kinetic energy is not affected.

[117] Precisely speaking, we must clearly specify when we may say that two states are identical to tell the indistinguishability. As mentioned before, see **5.1**.

[118] Needless to say, for compound systems, the constraints (walls) must not be altered before and after partitioning.

in terms of any finite partition of A into $\{A_i\}$,[119] where $A = \cup_i A_i$ and $A_i \cap A_j = \emptyset$ if $i \neq j$.[120]

Later, a more general additivity will be used: let A and B be arbitrary systems, and let us denote joining the two systems via a certain wall as $A \oplus B$. We will encounter the situation:

$$Q(A \oplus B) = Q(A) + Q(B), \tag{2.2}$$

where $Q(A)$ (resp. $Q(B)$) denotes the amount of Q in A (resp. B) before joining. This is called *additivity*.[121] If there are chemical reactions, even if a quantity is partition additive, it need not be additive.

Additivity implies partition additivity.[122] The distinction between partition additivity (2.1) and (the true) additivity (2.2) becomes important in convex analysis. This is because the additivity in convex analysis is the 'true' additivity. In this case, there are no restrictions on how equilibrium systems A and B carry quantity Q; for example, no matter how equilibrium systems A and B are brought into contact, the resulting system will reach equilibrium **2.9**, so we may discuss additivity.[123]

2.15 Thermodynamic limit

It is said in **2.13** that a macrosystem roughly divided into halves results in two macrosystems, but, needless to say, we cannot indefinitely repeat this procedure to make smaller macrosystems. If we wish to do so, the initial macrosystem must be

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[119] Each A_i is assumed to be measurable (i.e., has a definite volume).

[120] In partition additivity, a whole is partitioned into parts, and the quantity before and after the partitioning is compared; whether the resultant parts can be reassembled back into the original whole is not our concern. In other words, it is distinct from the partitioning-rejoining invariance **2.13**. Even when non-interacting separate systems are placed side by side (i.e., juxtaposed) from the start, confirming that a certain quantity Q is partition additive means that (2.1) has been verified through some experimental means.

[121] **Important note on additivity** As will become clear in the footnotes below, except for internal energy, there may not be physical quantities in thermodynamics that are unconditionally additive. Generally, "additive quantity" should be interpreted as "a physical quantity for which it is possible to arrange the conditions of combination and boundary conditions in such a way that it becomes additive" (→**5.10**).

[122] The converse is generally meaningless, since partition additivity is defined for partitioning equilibrium systems.

[123] A partition additive quantity Q can be mathematically interpreted as an additive measure. Therefore, the range of values for Q can be discrete. In such cases, it can be mathematically interpreted as a discrete measure. Of course, such a quantity Q cannot typically be the subject of standard convex analysis.

‘infinitely’ large. Theoreticians are fond of thinking in this limit, so the limit has a name: the ‘*thermodynamic limit*.’

We have only to recognize that the systems we study macroscopically are very close[124] to this limit.

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[124] ‘Close’: all the densities of extensive quantities are close to the limit densities (→**5.5**).

3 Work coordinates: Preliminary II

3.1 Extensive quantities

Prepare a system that is uniform at our scale (or, more precisely, a simple system →**2.10**).

As we have seen in **2.15**, in thermodynamics it is natural to consider a very large system size limit, so we should first pay attention to the quantities that increases without bound as the system size increases.

We should not, however, forget that we restrict systems we consider to a class of (combination) additive systems (→**1.10**, **2.11**): if the energy of the system depends on a quantity that is not partition additive (→**2.14**), then, generally speaking, the system energy becomes not partition additive, either. Therefore, when we consider a physical quantity Q_V (> 0) that diverges as the system volume V increases without bound, we need not take account of the quantities for which Q_V/V is not bounded from above. If Q_V is asymptotically proportional to V and Q_V/V converges to a density which is not identical to zero, we call such quantities *extensive quantities*. Extensive quantities are partition additive quantities. If a quantity Q is carried by a spatially uniform system and is partition additive, then it is an extensive quantity.[125]

3.2 Fundamental variables are extensive variables

The quantities that increase with the system volume are not restricted to the additive quantities. For example, the surface area of the system or the accompanying surface energy is often proportional to the 2/3 power of the system mass.

Earlier it was said that the theoreticians like the thermodynamic limit (→**2.15**). In this limit all the extensive or partition additive quantities diverge and become meaningless. Consequently, as the corresponding meaningful quantities, densities (extensive quantities/volume) are considered. However, then, the densities of the quantities like surface energy vanish identically in the thermodynamic limit. Accordingly, all the basic quantities describing systems in thermodynamics are extensive quantities. Volume, energy, amount of a chemical, etc., are the examples.

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[125] Recall Cauchy's functional equation, assuming Q_V is continuous or monotone with respect to V.

3.3 Thermodynamic variables are extensive or intensive

An extensive quantity is a first degree homogeneous function (→**3.5**) of the amounts of materials, so a fundamental variable Q of thermodynamics is a first degree homogeneous function of other fundamental (so extensive) quantities Q_i.[126] If we write $Q = Q(Q_1, Q_2, \cdots, Q_n)$, for any λ (> 0) we have[127]

$$\lambda Q = Q(\lambda Q_1, \lambda Q_2, \cdots, \lambda Q_n). \tag{3.1}$$

If Q is partial-differentiable with respect to Q_i, the corresponding partial derivative $q_i = \partial Q/\partial Q_i$ is a homogeneous function of degree zero (→**3.5**(1)). That is, irrespective of λ (> 0),

$$q_i = q_i(\lambda Q_1, \lambda Q_2, \cdots, \lambda Q_n). \tag{3.2}$$

A quantity that is a homogeneous function of degree zero of the amount of materials is called an *intensive quantity*. Although not fundamental quantities (→**3.8**), intensive variables are also important and convenient in thermodynamics. As we will see later, temperature T, pressure P, etc., are the examples of intensive quantities.

3.4 Why do intensive quantities show up in thermodynamics?

As can be seen from **3.3**, the reason why intensive quantities show up in thermodynamics is not because they do not diminish as the system size increases. If that were the reason, we would have to keep, e.g., all the quantities that depend on positive fractional powers of the system volume such as its surface energy. Sometimes, the general observation: "all the variables of thermodynamics are extensive or intensive" is referred to as the fourth law of thermodynamics,[128] but its essence is captured by

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[126] A fundamental quantity may be regarded as a function of non-fundamental quantities as well, but such a functional form is not the basic relations in thermodynamics. For example, as we will see, the internal energy may be written as a function of temperature T. Since T is not a fundamental variable, such a functional relation is *not* a basic thermodynamic relation.

[127] Let $\{M_i\}$ denote the amounts (e.g., moles) of materials/chemicals in the system. Then an extensive quantity Q_j is a first degree homogeneous function of $\{M_i\}$. Since Q is also extensive,

$$\lambda Q(\{M_i\}) = Q(\{\lambda M_i\}).$$

Note that

$$Q(\{\lambda M_i\}) = Q(\{Q_j(\{\lambda M_j\})\}) = Q(\{\lambda Q_j(\{M_i\})),$$

so these two equalities imply that Q is a first degree homogeneous function of $\{Q_i\}$.

[128] ⟪**The Fourth Law**⟫ This was emphasized and named by P. T. Landsberg (1922-2010). According to him, "There is nothing very startling about it since this law is always implicitly adopted,

the fact that all the fundamental variables of thermodynamics are extensive (→**3.2**).

3.5 Homogeneous functions

Let u be a function defined on an n-cone[129] whose apex is at the origin. For any λ (> 0) if there is a real number p such that

$$\lambda^p u(x_1, \cdots, x_n) = u(\lambda x_1, \cdots, \lambda x_n), \tag{3.3}$$

u is called a *homogeneous function of degree* p.
(1) If u is differentiable, partially differentiating (3.3) with x_j ($j \in \{1, \cdots, n\}$) with the aid of the chain rule, we get

$$\lambda^p \frac{\partial u}{\partial x_j} = \lambda u_{x_j}(\lambda x_1, \cdots, \lambda x_n). \tag{3.4}$$

Therefore, $\partial u/\partial x_j = u_{x_j}$ is a homogeneous function of degree $(p-1)$ for any j ($\in \{1, \cdots, n\}$).
(2) Assuming that u is differentiable, we differentiate (3.3) with respect to λ to get

$$p\lambda^{p-1} u(x_1, \cdots, x_n) = \sum_i x_i \frac{\partial u}{\partial \lambda x_i}. \tag{3.5}$$

Setting $\lambda = 1$, we find

$$pu = \sum_i x_i \frac{\partial u}{\partial x_i}. \tag{3.6}$$

(3) [**Euler's theorem for homogeneous functions**] If u is differentiable, (3.6) is a necessary and sufficient condition for u to be a homogeneous function of degree p.

To show this we have only to construct a general solution for (3.6), following the solution method of quasilinear partial differential equations (→**3.6**).

3.6 Euler's theorem for homogeneous functions

Let u be a differentiable function defined on a n-cone whose apex is at the origin.
Theorem [Euler] A necessary and sufficient condition for function u to be a homogeneous function of degree p is that the following quasilinear partial differential equation holds:

$$\sum_{i=1}^{n} x_i \frac{\partial u}{\partial x_i} = pu. \tag{3.7}$$

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and people know about it. It is rarely displayed, however, as a"law"." The real significance, according to him, is that the law seems to be valid for nonequilibrium macrosystems as well (P. T. Landsberg, The fourth law of thermodynamics, Nature, **238**, 229-231 (1972)). However, as the reader should have already realized, the real significance of the fourth law is that, for any macroscopic phenomenology, extensive quantities are the central quantities. Intensive quantities appear merely due to Euler's theorem (→**3.6**).

[129] n-cone (with its apex at the origin) is a subset C of n-vector space such that $x \in C \Rightarrow \alpha x \in C$ for any positive real α.

[Demonstration] If we differentiate (3.3) with respect to λ, as already noted in **3.5**(2), the chain rule gives

$$p\lambda^{p-1}u(x_1,\cdots,x_n)=\sum_{i=1}^{n}x_i\frac{\partial}{\partial\lambda x_i}u(\lambda x_1,\cdots,\lambda x_n). \tag{3.8}$$

If we set $\lambda=1$, we get (3.7).

To demonstrate the converse, we have only to solve the quasilinear partial differential equation (3.7).[130] Writing its characteristic equation with a clever use of the parameter λ as

$$\frac{du}{pu}=\frac{dx_i}{x_i}=-\frac{d\lambda}{\lambda}, \tag{3.9}$$

its general solution can be written as

$$F(\lambda^p u,\lambda x_1,\cdots,\lambda x_n)=0 \tag{3.10}$$

in terms of an arbitrary differentiable function F. That is, if u is a function of $\{x_i\}$, then $\lambda^p u$ must be a function of $\{\lambda x_i\}$, so indeed u is a homogeneous function of degree p.

3.7 Internal energy

Thermodynamics began as a branch of physics that sought to understand how the energy of a system changes due to exchange of heat and work between the system and its environment (→**A.7**-**A.10**). Therefore, the energy E of the system is a necessary variable in constructing thermodynamics.

In macroscopic electromagnetism and mechanics, energy is clearly defined, so thermodynamics adopts the concept of energy and its measurement methods as established in macroscopic physics (→**1.8**). In other words, only those changes that can be understood and measured as the energy (or changes in energy) of a system using macroscopic non-thermal physics are considered as energy in thermodynamics. This is because 'thermodynamics must be constructed based on the knowledge of macroscopic physics (and basic chemistry) that does not involve thermal phenomena' (→**1.9**).

The total energy of the system includes the kinetic and potential energies as a whole. We usually observe a system from the co-moving coordinates, so the energy E relevant to thermodynamics is the total energy minus the mechanical energy as a whole (i.e., the kinetic and potential energies of the center of mass of the system) and is referred to as the *internal energy*.[131,132]

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[130] There is an elementary explanation of the general solution method for quasilinear partial differential equations in Note 3.4 of Y. Oono, *The Nonlinear World* (Springer, 2013) p159-160.

[131] In addition, in this book the system is assumed to be not rotating around its center of mass.

[132] When a fluid is flowing, it can be treated as a thermodynamic system if the dissipation can

It is worth reiterating that thermodynamics discusses only systems whose internal energy is partition additive/extensive (→**2.11**).

3.8 Intensive variables are not fundamental variables

In rudimentary thermodynamics, temperature appears as an important variable. As we can see in **A.2** temperature was historically crucial.[133] However, we know temperature cannot uniquely specify macroscopic states of a system as illustrated by ice-water; even if the temperature is the same, the internal energy of the ice-water system can change according to the ratio of ice and liquid water present. Thus, the internal energy is a better observable to distinguish macroscopic equilibrium states.

It is easy to understand why intensive quantities are not suitable for specifying states, if we see an obvious fact that we can always devise a wall that allows two systems to share the same values of a particular intensive quantity. In contrast, needless to say, we cannot devise a wall that equalizes extensive quantities of the systems in contact through it, whenever these systems equilibrate each other.

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be ignored. Naturally, in that case, the energy of the system is the sum of internal energy + mechanical energy. If this elementary fact is forgotten, one might fall into the illusion that a separate nonequilibrium framework can be created, even though no extension of thermodynamics is necessary. A typical example of this error is the book: P. Glansdorff and I. Prigogine, *Thermodynamic Theory of Structure, Stability, and Fluctuations* (John Wiley & Sons Ltd, 1971).

[133] **⟪How empirical is the 'empirical temperature'?⟫** However, with regard to the concept of empirical temperature, it is necessary to reconsider seriously whether it can truly be given empirically (without thermodynamics):
(1) Any empirical concept must ultimately be based directly on our bodily sensations. Yet, there seems to be no *a priori* reason, nor even a purely empirical one, for temperature to be represented as a single scalar value. This is because sensations such as warmth and cold are detected by different mechanisms. For example, we perceive menthol as cool because the sensory receptors for the sensation of coolness originally evolved to detect menthol-like compounds [D. D. Luu et al., Evidence that the cold- and menthol-sensing functions of the human TRPM8 channel evolved separately, Science Adv., **10**, eadm9228 (2024)]. The equivalence of the concept of 'temperature,' as experienced in various ways or measured by different thermometers, required empirical validation (much like Faraday carefully verified that different types of electricity were the same). Although we now tend to think of hot and warm as differing only in degree, it is entirely possible that this impression is influenced by the already established concept of a unified temperature. Therefore, basing thermodynamic discussions on temperature is logically quite dangerous. Indeed, careful thinkers like Maxwell did not *a priori* assume the unified concept of temperature.
(2) Historically, because the kinetic theory of gases seemed to work well, there may have been a tendency not only to neglect the need to rigorously verify the universality of empirical temperature using gases, but also to believe that the essence of temperature was understood, in conjunction with the mechanical Weltanschauung. This possibility cannot be ignored.

3.9 The material stage and the physical actors for thermodynamics

As we have already discussed, the internal energy E is a key quantity of thermodynamics, so we need it to describe the system under study.

To specify a system, we must first designate its material composition (very often, its chemical composition). To this end we can use the mole numbers $\{\tilde{N}_i\}$ of all the chemical compounds $\{i\}$ actually present in the system (more details →**4.5**). Collectively, we denote the chemical composition of a given system as $\tilde{\boldsymbol{N}} = \{\tilde{N}_i\}$.

In order to describe the macrophysics of the system on this material stage specified by $\tilde{\boldsymbol{N}}$, we choose a set $\{X_i\}$ of extensive observables (as actors) that are required to describe macrophysical events in the system that alter E (more details later →**3.10**). Thus, $\{X_i\}$ are called *work coordinates*, which will be collectively denoted as $\boldsymbol{X}$.

As discussed in **1.8** we may assume the quantities and concepts are unambiguous, if they are understood within nonthermal macrophysics and chemistry. Work coordinates are all understood solely with the aid of nonthermal macrophysics. Also we assume we have knowledge of elementary chemistry (→**4.3**).

Therefore, the set of variables $(E, \boldsymbol{X}, \tilde{\boldsymbol{N}})$ are macroscopically observable variables that may be used to describe the equilibrium states of a system. Unfortunately, however, it is very inconvenient[134] to use this set as the basic thermodynamic coodinates to develop thermodynamics as we will see in Section 4 (e.g., **4.4**). The fundamental variables to develop thermodynamics—thermodynamic coordinates— will be discussed in **4.13**.

3.10 Work coordinates and work

If we consider only the operations without any energy dissipation (→**2.3**), to change the work coordinates $\boldsymbol{X}$ implies that the energy E is changed in a fashion we can quantify with the aid of the fundamental laws of electromagnetism and/or mechanics. There is nothing special; these are the operations on the states of the system observed in the experiments that verify electromagnetic and mechanical fundamental laws and theories. To realize such experiments often we have only to slow down the

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[134] However, as we will later realize (e.g., **4.4**), $\tilde{\boldsymbol{N}}$ is not a convenient way to describe the materialistic aspects of the system, unless we can freely halt chemical reactions in the system at any given moment while modifying other variables, particularly work coordinates $\boldsymbol{X}$. This is actually assumed in standard chemical thermodynamics textbooks. However, this approach is highly artificial and almost impossible to implement in reality. Hence, when we delve into comprehensive chemical thermodynamics, we will make every effort to avoid this *ad hoc* assumption. Also, generally speaking, $\tilde{\boldsymbol{N}}$ is only partition additive and is not additive (→**2.14**).

processes (quasistatic processes →**A.6**).[135] The world solely governed by the fundamental laws of macroscopic electromagnetism and mechanics is the world whose movies do not look strange even if they are played backward.[136] This is often the case, because dissipation[137] is absent. Under the condition in which dissipation can be ignored, the changes of the work coordinates are reversible in the sense that they can be step by step retraced without leaving any trace.

When a work coordinate X_i is changed quasistatically and reversibly, the accompanying internal energy change may be written as a *work form* $x_i dX_i$, where x_i is, as can be seen from **3.3**, an intensive quantity (something like a force) that is a function of E and $\boldsymbol{X}$ given by the nonthermal macrophysics.[138] It is called the *conjugate intensive quantity* of X_i. Thus, generally, the work form reads

$$\omega = \sum_i x_i dX_i. \tag{3.11}$$

If the system is materially closed (→**4.3**), then the conservation law of electromagnetic and mechanical energies implies that ω is exact (→**9.9**): $\omega = dE$. This is why $\{X_i\}$ are called work coordinates.[139] Some examples of work coordinates will be given in Appendix B (→**B.1**-**B.3**).

Needless to say, the procedure or mechanism to alter work coordinates is realizable within nonthermal macrophysics. That is, it is assumed that electromagnetism and mechanics without any dissipation is possible, so we can construct reversible source of work macrophysically.

3.11 Changing work coordinates without thermal phenomena

As long as there is no 'dry friction'[140] we may realize a change in work coordinates without dissipation. The key observation, for example, is that the Joule heat loss

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[135] However, quasistatic processes in electrodynamics can be pretty fast from our 'everyday' standard. The conversion rate between mechanical and electrical energies is said to be up to 95% with the conventional devices. Superconducting devices can significantly improve this number.

[136] if there is no radiation of waves (sound, electromagnetic, etc.) from the system; note, however, that if the system is enclosed in a 'isolated room' of finite size, radiation means ordinary dissipation unless there is a radiation equilibrium between the system and the room. Recall **2.3**.

[137] including production of radiations as discussed in a preceding footnote.

[138] Actually, this also depends on $\tilde{\boldsymbol{N}}$

[139] Thermodynamics does not pay any attention to the quantities that do not change energy, so from the potential list of work coordinates the extensive quantities are excluded whose conjugate intensive quantities are identically (macroscopically) zero.

[140] ⟪**The so-called friction**⟫ As discussed just below, if the 'frictional force' is proportional to

during the transport of charges may be reduced as much as we wish by slowing down the process.

Suppose we wish to move charge q as an electric current I. If the resistance of the wire is R, the heat generation per unit time is given by RI^2 (Joule heating). The needed time is $\Delta t = q/I$, so the total amount Q of heat generated by dissipation is give by

$$Q = \Delta t \times R\left(\frac{q}{\Delta t}\right)^2 = \frac{Rq^2}{\Delta t}. \tag{3.12}$$

Therefore, if Δt is large, that is, if we slow down the process, this can be made as small as we wish.

However, (3.12) tells us that slowing down by increasing R is useless.[141]

3.12 A slightly more general discussion

If there is no 'friction,' and if the general empiriccal formulas for linear transport phenomena apply, we can proceed as follows:

Suppose a small change of a work coordinate X requires energy change $dE = xdX$. Let us assume that connecting system I with $x = x^{\mathrm{I}}$ and system II with $x = x^{\mathrm{II}}$ the flow of X from I to II is driven by the difference in x. If X is conserved, then

$$\frac{d(E^{\mathrm{I}} + E^{\mathrm{II}})}{dt} = (x^{\mathrm{II}} - x^{\mathrm{I}})\frac{dX}{dt} \tag{3.13}$$

and linear transport law with transport coefficient L (like Ohm's law)

$$\frac{dX}{dt} = L(x^{\mathrm{II}} - x^{\mathrm{I}}) \tag{3.14}$$

would hold. If we streamline the above relations as

$$\frac{dE}{dt} = -\delta x\frac{dX}{dt} \tag{3.15}$$

---

the 'changing rate' (as for viscosity in fluids), the dissipated energy is a higher order small quantity. However, for the kinetic friction due to dry friction between solids, the friction force is constant independent of the changing rate (speed), so however slow the relative motion is, the amount of dissipated energy is independent of the changing rate. Thus, quasistatic change cannot be realized however slowly we perform the process.

Precisely speaking, as Granick and his collaborators extensively studied [e.g., S. Granick, Y. Zhu and H. Lee, Slippery questions about complex fluids flowing past solids, Nature Materials **2**, 221 (2003)] what happens at the interface between a fluid phase and a solid surface is very complicated, and 'dry friction' (slip) can happen, although the effect is very small for ordinary fluids.

[141] Since the voltage difference is $V = Rq/\Delta t$, reducing the voltage difference V to transport the charge is the practical way to reduce dissipation when Q is transported.

Notice that increasing R is analogous to choking the passage, analogous to making the size of the gas leak hole smaller. Indeed, the dissipation rate decreases, but the process itself is not reversible as we will discuss later. Also slowing down chemical reactions with the aid of negative catalysts is analogous.

and

$$\frac{dX}{dt} = L\delta x, \tag{3.16}$$

we have

$$\frac{dE}{dt} = -L\delta x^2 = -\frac{1}{L}\left(\frac{dX}{dt}\right)^2. \tag{3.17}$$

The minus sign appears, because we discuss the electromagnetic and mechanical energy E of the system and its decrease due to dissipation.

As can be seen from this, if we change X by ΔX in time Δt, then the total change of X is of course ΔX, but the total change of the energy due to dissipation is

$$\frac{1}{L}\left(\frac{\Delta X}{\Delta t}\right)^2 \Delta t = \frac{(\Delta X)^2}{L\Delta t}. \tag{3.18}$$

That is, even if ΔX is constant, if the needed time Δt is made sufficiently long, the total dissipation can be reduced as much as we wish.[142]

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[142] However, if the driving force is large, increasing Δt by reducing L is useless, since L and Δt appear together, as already noted at the end of **3.11**.

B Appendix B. Examples of work and work form

This is a non-thermal macrophysics topic, so thermodynamics simply adopts the results. Only for convenience, some examples are explained here.

B.1 Work due to volume change

Let us find the work form ω for a quasistatic[143] change of the system volume from V to $V + dV$. Write the surface area element as $d\boldsymbol{S}$ and its small displacement along its outward normal as δl (Fig. B.1).

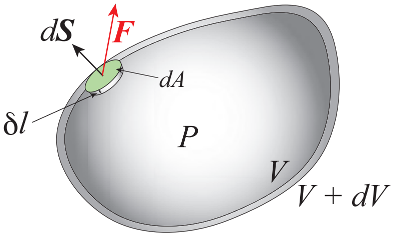

Figure B.1: Volume work

If the outward force per unit area $\boldsymbol{F}$ acts on the surface area element $d\boldsymbol{S}$, displacing it by δl (> 0 outward), the work done to the system is $\boldsymbol{F} \cdot d\boldsymbol{S}\delta l$. If we collect them all over the surface of the volume, we get the volume work:

$$\omega = -\int_{\partial V} \delta l \boldsymbol{F} \cdot d\boldsymbol{S}. \tag{B.1}$$

Here, the minus sign is required because this is the work done by the system. Let us denote the area of the surface element $d\boldsymbol{S}$ by dA. Then, since the force is due to the pressure P which exerts force parallel to $d\boldsymbol{S}$, so

$$\boldsymbol{F} \cdot d\boldsymbol{S} = PdA. \tag{B.2}$$

Thus, (B.1) becomes

$$\omega = -\int_{\partial V} \delta l PdA. \tag{B.3}$$

The volume change is given by

$$\delta V = \int_{\partial V} \delta l dA, \tag{B.4}$$

and the pressure is everywhere the same during quasistatic changes, so (B.3) becomes

$$\omega = -PdV. \tag{B.5}$$

Notice that this P is the mechanical quantity defined in mechanics and is independent of thermodynamics. There is no thermodynamic pressure, but only mechanical pressure. Do not forget that all the work coordinates are defined outside thermodynamics.

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[143] sufficiently slowly; in this case slowing down also implies reversibility, because the dissipation is due to volume viscosity, so the linear irreversible formalism used in **3.12** applies.

B.2 Work done by magnetic field

For the needed Maxwell's equations see **B.4**.

Magnetic field itself does not do any work directly on charged systems. The work done by magnetic field is the work done on the current by the electric field induced by the magnetic field. Thus, the term relevant to work is $\boldsymbol{J}_f \cdot \boldsymbol{E}$ due to the current $\boldsymbol{J}_f$ supplied from outside the system and $\boldsymbol{E}$. Subtracting (B.24)$\cdot\boldsymbol{H}$ from (B.24)$\cdot\boldsymbol{E}$ and ignoring the displacement current, we get

$$\boldsymbol{E} \cdot \operatorname{curl} \boldsymbol{H} - \boldsymbol{H} \cdot \operatorname{curl} \boldsymbol{E} = \boldsymbol{E} \cdot \boldsymbol{J}_f + \boldsymbol{H} \cdot \frac{\partial \boldsymbol{B}}{\partial t} \tag{B.6}$$

If we look at the formulas

$$\nabla \cdot (\boldsymbol{A} \times \boldsymbol{B}) = (\nabla_A + \nabla_B) \cdot (\boldsymbol{A} \times \boldsymbol{B}) = \boldsymbol{B} \cdot (\nabla_A \times \boldsymbol{A}) - \boldsymbol{A} \cdot (\nabla_B \times \boldsymbol{B}) = \boldsymbol{B} \cdot \operatorname{curl} \boldsymbol{A} - \boldsymbol{A} \cdot \operatorname{curl} \boldsymbol{B}, \tag{B.7}$$

the left-hand side of (B.6) reads $\operatorname{div}(\boldsymbol{H} \times \boldsymbol{E})$, so

$$\operatorname{div}(\boldsymbol{H} \times \boldsymbol{E}) = \boldsymbol{E} \cdot \boldsymbol{J}_f + \boldsymbol{H} \cdot \frac{\partial \boldsymbol{B}}{\partial t}. \tag{B.8}$$

If all the systems and relevant apparatuses are contained in a finite space, we may assume the fields decay sufficiently quickly to zero outside this space, so integrating the above formula over the whole space, we obtain

$$0 = \int dV\, \boldsymbol{E} \cdot \boldsymbol{J}_f + \int dV\, \boldsymbol{H} \cdot \frac{\partial \boldsymbol{B}}{\partial t}. \tag{B.9}$$

If we add work quasistatically, the current is constant throughout the experiment, so the strength of the magnetic field is also constant. Integrating the above equation over the whole experimental duration, and writing the total change of $\boldsymbol{B}$ as $\delta\boldsymbol{B}$, we get

$$\boldsymbol{H} \cdot \delta \boldsymbol{B} = -\int dt\, \boldsymbol{E} \cdot \boldsymbol{J}_f. \tag{B.10}$$

Since the energy is supplied by working against the current due to the change of the magnetic field, the right-hand side gives the energy supplied to the magnet with the correct sign. Therefore, the work form for the work done by the magnetic field reads

$$\omega = \boldsymbol{H} \cdot d\boldsymbol{B}. \tag{B.11}$$

If we decompose as $\boldsymbol{B} = \mu_0 \boldsymbol{H} + \mu_0 \boldsymbol{M}$, (B.11) becomes

$$\omega = d\left(\frac{1}{2}\mu_0 \boldsymbol{H} \cdot \boldsymbol{H}\right) + \mu_0 \boldsymbol{H} \cdot d\boldsymbol{M}. \tag{B.12}$$

Here, $\boldsymbol{H}$ is the magnetic field created by the device, so it exists even without the magnet. The first term is the change of the vacuum magnetic field energy. Therefore, if we remove it and regard $\mu_0\boldsymbol{H}$ as the actual external field, we get

$$\omega = \boldsymbol{B} \cdot d\boldsymbol{M}. \tag{B.13}$$

However, this is not always correct. It is correct when the so-called *demagnetizing field* can be ignored as in the case of a long magnet with the magnetic field applied parallel to its long axis. It is totally different for a spherical magnet.

This difficulty is simply due to the magnetic interaction being long-ranged (→**2.11**).

B.3 Work done by electric field[144]

Since electric field does not enter inside conductors, the electric field energy does not change according to the state of the conductor, so the state of a conductor is not altered by the external electric field.

For dielectrics, the electric field goes into the bulk of the material. Therefore, the field has a strong thermodynamic effect. Electric work is done by displacing true charges, so in terms of the true charge density change $\delta\rho$ and electric potential φ, the work may be written as

$$\delta W = \int dV \varphi \delta\rho \tag{B.14}$$

The integration here is over the volume of the dielectric. Noting that

$$\boldsymbol{E} = -\mathrm{grad}\,\varphi, \;\; \mathrm{div}\,\delta\boldsymbol{D} = \delta\rho, \tag{B.15}$$

the integration result is given by

$$\begin{aligned} \delta W &= \int_V dV \varphi\, \mathrm{div}\,\delta\boldsymbol{D} = \int dV [\mathrm{div}\,(\varphi\,\delta\boldsymbol{D}) - \mathrm{grad}\,\varphi\cdot\delta\boldsymbol{D}] &\text{(B.16)}\\ &= \int_{\partial V} d\boldsymbol{S}\cdot\varphi\,\delta\boldsymbol{D} + \int_V dV \boldsymbol{E}\cdot\delta\boldsymbol{D} &\text{(B.17)}\end{aligned}$$

We may ignore the surface contribution for macroscopic systems. Only the second term is the extensive contribution. If the electric field is uniform, the work form reads

$$\omega = \boldsymbol{E}\cdot d\int_V dV\boldsymbol{D} = d\int dV \frac{\varepsilon_0}{2}\boldsymbol{E}^2 + \boldsymbol{E} d\int_V dV\boldsymbol{P}. \tag{B.18}$$

The first term exists even for non dielectrics, so $\boldsymbol{E}\cdot d\boldsymbol{P}$ is the work density. Note, however, that this conclusion applies only for macroscopic objects.

B.4 Our convention for the electromagnetic field

In these lecture notes, we follow the $\boldsymbol{E}$-$\boldsymbol{B}$ correspondence, which is the world standard, and use the SI unit system. That is, we assume all the magnetic fields are due to currents, and the Maxwell's equations in the vacuum reads

$$\mathrm{div}\,\boldsymbol{E} = 0, \qquad \mathrm{curl}\,\boldsymbol{E} = -\frac{\partial\boldsymbol{B}}{\partial t}, \tag{B.19}$$

$$\mathrm{div}\,\boldsymbol{B} = 0, \qquad \mathrm{curl}\,\boldsymbol{B} = \frac{1}{c^2}\frac{\partial\boldsymbol{E}}{\partial t}. \tag{B.20}$$

If we have materials. we introduce two auxiliary fields, the *electric flux density* $\boldsymbol{D}$ and the *magnetic field strength* $\boldsymbol{H}$:

$$\boldsymbol{D} = \varepsilon_0\boldsymbol{E} + \boldsymbol{P}, \;\; \boldsymbol{H} = \frac{1}{\mu_0}\boldsymbol{B} - \boldsymbol{M}. \tag{B.21}$$

Here, $\boldsymbol{P}$ is the *polarization* and $\boldsymbol{M}$is the *magnetization*. They must be determined from the bound charge density ρ_b and the bound current (localized loop currents) density $\boldsymbol{J}_b$ in the material:

$$\rho_b = -\mathrm{div}\,\boldsymbol{P} \tag{B.22}$$

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[144] following Landau-Lifshitz

and the macroscopic Maxwell's equation under the presence of material reads

$$\operatorname{div} \boldsymbol{D} = \rho_f, \qquad \operatorname{curl} \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t}, \tag{B.23}$$

$$\operatorname{div} \boldsymbol{B} = 0, \qquad \operatorname{curl} \boldsymbol{H} = \boldsymbol{J}_f + \frac{\partial \boldsymbol{D}}{\partial t}, \tag{B.24}$$

where $\rho - \rho_b = \rho_f$ (the free charge density) and $\boldsymbol{J} - \boldsymbol{J}_b = \boldsymbol{J}_f$ (the free current density).

4 Materials coordinates: Preliminary III

Those who do not wish to study thermodynamics with chemical reactions[145] need not read this section. They have only to understand the amount of chemicals in the system as mere subspecies of work coordinates already discussed in Section 3 (→**3.10**).

Many comments are aimed at people (e.g., instructors) who learned thermodynamics a long time ago from standard textbooks. The author believes that chemical thermodynamics must be critically reexamined. Physicists have never taken chemistry very seriously, and chemists appear to have assumed that the fundamental aspects of chemical thermodynamics must have already been established by physicists. Thus, it seems that chemical thermodynamics has been treated as a stepchild of thermodynamics proper. Therefore, we must proceed carefully step by step.

4.1 Materialistic stage of thermodynamics

Typically, thermodynamics textbooks discuss internal energy E and work coordinates such as volume V to describe a system. However, these textbooks often neglect the material basis of the system before introducing these thermodynamic coordinates. It is important to remember that even the *ordinary thermodynamic coordinates* E and $\boldsymbol{X}$ require materials for their existence and must be associated with them.[146]

Therefore, we have already referred to the materials stage (→**3.9**). On this stage, the quantities E and $\boldsymbol{X}$ are actors (→**3.9**), playing their roles in the thermodynamic processes.

However, the material stage of thermodynamics differs significantly from the ordinary stage in dramas, as it undergoes substantial changes when the actors perform.

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[145] ⟪**Significance of chemical reactions**⟫ What is the essential consequence of chemical reactions as physical phenomena? It is the possibility of the change of the system chemical composition due to the change of the internal energy and the work coordinates without any materials exchange between the system and its environment. That is, the amounts of chemicals of a closed system are mathematical variables not independent from the internal energy and work coordinates—ordinary thermodynamic coordinates—of the system.

[146] The author calls this the *no ghost principle*. Even information requires its carrying material. Needless to say, there are no zombies, either.

These changes often cause trouble and complications. For instance, changes in the quantities $(E, \boldsymbol{X})$, the ordinary thermodynamic coordinates, induce passive changes in the material composition of the system.[147] Even without any (materialistic or chemical) intervention from the experimenter, chemical changes are induced, if an equilibrium state must be maintained.

4.2 Conventional approaches with chemical reactions

Due to the trouble alluded in **4.1**, serious textbooks adopt one of the following two strategies to address this issue:

(1) To allow all chemical reactions to be halted at will, without disturbing the equilibrium state (→**4.15**) or to be in a special metastable equilibrium known as *frozen*

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[147] ⟪**Asymmetry between ordinary thermodynamic coordinates and 'chemical coordinates'**⟫ In physics, where there is action, there is reaction. If the stage changes, actors would be strongly affected. However, there is a notable asymmetry between the ordinary thermodynamic coordinates and the coordinates (variables) describing the amounts of chemicals in the system. We can fix E and $\boldsymbol{X}$ from outside the system, in principle, even when the chemical composition of the system changes. We can indeed fix the chemical composition with the aid of appropriate chemical reservoirs while altering E and $\boldsymbol{X}$. However, the maintained chemical composition is, generally speaking, not an equilibrium composition of the system with the altered E and $\boldsymbol{X}$. Instead, it is a nonequilibrium steady state. Generally, there is no way to keep equilibrium chemical composition variables fixed while altering the ordinary thermodynamic coordinates (E and $\boldsymbol{X}$).

equilibrium.[148]
(2) To acknowledge that chemical reactions exist in nonequilibrium states, while the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ still adhere to the ordinary equilibrium thermodynamics.[149]

Approach (2) is an eclectic strategy, and the consistency of its fundamental assumption, that only chemistry can be maintained in a non-equilibrium state without modifying ordinary equilibrium thermodynamics, raises concerns, so we will disregard this strategy.

Approach (1) may be realistic if all reactions proceed very slowly. However, it is worth noting that many reactions occur spontaneously at non-negligible rates. Negative catalysts are often invoked to inhibit such reactions, but this would require adding stoichiometric amounts of negative catalysts (reaction inhibitors) to the system (→**25.10**). Thus, although there are attempts to 'naturalize' strategy (1), there is no general hope. Remember that 'negative catalyst' is an oxymoronic concept.[150]

Therefore, in the present exposition, we will outline equilibrium thermodynamics without interfering with any natural chemical reactions in the system.

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[148] Authoritative sources may be:

J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, 1961), p.100:

> "The application of the general criteria for equilibrium to systems in which chemical reactions may occur involves the ability to freeze the chemical reactions at any desired point. Thus, a system containing r substances which may undergo a chemical reaction must be considered to be made up of r independent components."

E. A. Guggenheim, *Thermodynamics* (North-Holland, Fifth revised edition 1967), p.35:

> "We consider a system not in chemical equilibrium in which, however, the chemical reactions leading towards its attainment have been virtually suppressed. The system is then in a special kind of metastable equilibrium called frozen equilibrium. The several chemical species present are then virtually independent, and so we can suppose a chemical potential μ assigned to each such species.
>
> The final result may be described as follows. Instead of choosing a set of independent chemical species or components, we use the set of all the chemical species present, whether independent or not, and then obtain restrictive relations on their behavior."

However, these authors concern mainly with the mutual independence of chemical coordinates and not with the relation between the ordinary thermodynamic coordinates and chemical coordinates.

[149] I. Prigogine and R. Defay, *Thermodynamique Chimique* (Editions Desoer, 1950).

[150] It is interesting to recall that Pauli's last paper was on chemical reactions motivated by his rejecting negative catalysts.

4.3 Elementary chemistry thermodynamics relies on

Here, the elementary chemistry thermodynamics relies on is briefly summarized. Notice that it is provided by chemistry to thermodynamics; thermodynamics simply accepts it as a collection of empirical facts just as the case of nonthermal macrophysical facts:

(i) The law of definite proportions: This law states that a chemical compound always contains its component elements in fixed ratio (by mass).[151]

(ii) Chemical reactions occur: The amounts of chemicals the experimenter adds to the system are generally different from the actual changes of the amounts in the system.

We accept at least the following three principles:

(I) Mixing and separating of chemical compounds are possible quasistatically and reversibly.[152]

(II) There exists a chemical equilibrium state for every chemical reaction (for each $(E, \boldsymbol{X})$). The chemical equilibrium state is unique in the following sense: if the amounts of all chemical substances required to prepare a closed system (i.e., a materially closed system) are known,[153] the chemical composition of the system at the current moment is uniquely determined by this information along with the system's $(E, \boldsymbol{X})$ (which we refer to as the usual thermodynamic coordinates) at the current moment.[154]

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[151] However, in, e.g., mineralogy or geochemistry nonstoichiometric compounds are not at all rare, so this law must be relaxed: in a given equilibrium state, the available compounds in the system must exhibit a definite composition (that may depend on a particular equilibrium state, especially the ordinary thermodynamic coordinates, E and $\boldsymbol{X}$).

[152] That is, a mixing of chemicals can be undone without any trace in the 'world.' Here, if the chemicals are stable separately alone (as expected in the conventional expositions of chemistry and chemical thermodynamics), there is no problem. However, there are chemicals that cannot be isolated (→**25.11**). In this case (I) means that an inseparable equilibrium mixture may be separated out. The separated amount of the chemical in this case is expressed by a single materials coordinate (e.g., for the representative chemical among the equilibrium mixture). Notice that the expression in terms of the chemical composition coordinates is awkward even if possible.

[153] For this, it is sufficient to know the amounts of all compounds (i.e., the initial quantities) prepared when setting up the closed system.

[154] **⟪On the Uniqueness of Chemical Equilibrium⟫** Even if the initial equilibrium state is specified, there is no guarantee that the final state reached after a particular process will always be the same. However, the claim of (II) is that when the ordinary thermodynamic coordinates of the final state $(E, \boldsymbol{X})$ are the same, the chemical composition of the final equilibrium state is uniquely determined.

That said, a reader might argue that for chemical reactions carried out in a typical laboratory, even when the final state reaches the same temperature and pressure, the yield of a certain

(III) Any chemical reaction[155] may be realized as a redox reaction electrochemically (in principle). This fact is necessary to demonstrate (in principle) the equivalence of chemical and mechanical work (→**A.16**).

4.4 Trouble with expressions of amounts of chemicals

As is in (II) of **4.3**, for a closed system, if $(E, \boldsymbol{X})$, the set of all the ordinary thermodynamic coordinates (internal energy and work coordinates), is given, the moles of chemicals actually present in the system in equilibrium are uniquely determined. Generally speaking, if $(E, \boldsymbol{X})$ changes, the chemical equilibrium would shift. Therefore, even if we do not modify the system chemical composition $\tilde{\boldsymbol{N}} = \{\tilde{N}_i\}$ directly from outside the system (say, using a chemostat), $\tilde{\boldsymbol{N}}$ changes. That is, the chemical composition coordinates $\tilde{\boldsymbol{N}}$ are not independent from $(E, \boldsymbol{X})$.

However, the ith compound may be added to the system independently of other chemicals. In this sense the variables expressing the moles of chemicals should be handled as independent variables. Still, we must not forget that even if we add δN_i moles of the ith chemical to the system, the amount of chemical i present in the system may not increase by δN_i.

For example, consider the following reaction:

$$\mathrm{A} + \mathrm{B} \longleftrightarrow \mathrm{C}. \qquad (*)$$

Chemicals A, B or C may be added to the system freely and separately by the experimenter,[156] so the moles to express their amounts appear as independent variables. However, due to the chemical equilibrium, the actual amount of C present in the system is determined by the amounts of A and B in the system, so only two of A, B, and C are independent.[157]

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compound can vary significantly depending on the process, much like cooking. The variations described here are the result of non-equilibrium processes, as there are many reactions that proceed very slowly. Moreover, it is worth noting that most compounds we aim to synthesize are, depending on the time scale, not truly stable compounds. Therefore, when considering chemical equilibrium, it is crucial to keep in mind Feynman's caution in **2.6**."

[155] Even a simple conformational change that does not require any chemical bond changes is a kind of chemical reaction. In such cases, no bond need be dissociated or reconnected, but still we can realize it through bond dissociation/reconnection processes.

Here, radical reactions may be involved in the reaction, but any reaction between stable nonradical compounds may be realized as redox reactions. If a relatively stable radicals must be handled, they may be formed from ions electrochemically. As far as thermodynamics is concerned (i.e., thermodynamic relations between ordinary compounds), we may assume (III).

[156] Careful readers may wish to read **25.11**.

[157] For a closed system with fixed $(E, \boldsymbol{X})$, the chemical equilibrium is definite (→(II)). Conse-

4.5 Descriptions of experimental operations and of chemical composition of a system

4.4 tells us that there are two aspects for chemical quantities (moles of chemical compounds): (i) the operational aspect expressing the amounts of the chemicals the experimenter can add to the system, (ii) the descriptive aspect expressing the amounts of the chemicals actually in the system. Here, in case (i) all the amounts of distinct chemicals[158] may be understood as independently modifiable variables, but not so in case (ii).

4.6 Closed systems do not have independent variables describing amounts of chemicals

In particular, if the system is closed, there is no independent variable expressing the amount of chemicals.

Operationally in the sense of (i) in **4.5**, no such variable can exist, since no operation, i.e., adding or subtracting a chemical, is allowed; Descriptively in the sense of (ii) in **4.5**, although the amounts of compounds can change, e.g., by varying the internal energy, such changes are subordinate to or dependent on $(E, \boldsymbol{X})$, so there is no independent variable describing chemicals at all for a closed system (see the last footnote in **11.12**).

4.7 The moles of chemicals actually existing in the system are inconvenient thermodynamic variables

Let us denote as $\tilde{N}_i$ the mole number of the ith chemical that is actually present in the system and that the experimenter can add to the system separately (independently) from other chemicals. We denote $\tilde{\boldsymbol{N}} = \{\tilde{N}_i\}$, collectively. If we know $\tilde{\boldsymbol{N}}$, the chemical composition of the equilibrium state of the system at present is completely known to us.[159]

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quently, as will be explained in **4.6**, there is absolutely no amounts of chemicals the experimenter can change at will for any closed system.

[158] Here, ‘distinct chemical’ means a chemical we can isolate barring intrinsically accompanying compounds (→**25.3**).

[159] although not all the chemicals in the system can be operationally separately handled by the experimenter. See **25.11**.

Let us refer to $\tilde{\boldsymbol{N}}$ as the *chemical composition coordinates.*

If we adopt chemical composition coordinates $\tilde{\boldsymbol{N}}$ to describe the materials stage of the system as a part of thermodynamic variables as the conventional textbooks do, as already alluded above (→**4.1**), at least the following inconveniences follow:[160]
(i) The presence of chemical equilibria implies that $\tilde{N}_i$ are mutually related, so $\tilde{\boldsymbol{N}}$ cannot be a collection of independent variables.[161]
(ii) Even if the system is closed, if E and $\boldsymbol{X}$ (i.e., the ordinary thermodynamic variables) are changed, usually, $\{\tilde{N}_i\}$ also change. That is, $\tilde{\boldsymbol{N}}$ cannot be independent of $(E, \boldsymbol{X})$.[162] In particular, if the system is closed, $\tilde{\boldsymbol{N}}$ are completely subordinate to $(E, \boldsymbol{X})$ as noted in **4.6**.
(iii) Even if the experimenter add $\delta\tilde{\boldsymbol{N}}$ to the system, usually, its composition is not given by $\tilde{\boldsymbol{N}} + \delta\tilde{\boldsymbol{N}}$.

Consequently, the chemical composition coordinates $\tilde{\boldsymbol{N}}$ that are adopted as the standard chemical variables by all the textbooks are inadequate variables. Of course, as noted above, if we adopt an artificial assumption that all the chemical reactions can be halted freely at any moment while keeping the system in equilibrium (→**4.2**), the above difficulties disappear. However, as we will learn soon, we will have to swallow a far more dire consequence of this assumption (→**8.5**).

4.8 Materials coordinates and chemical composition coordinates[163]

4.5 tells us that the variables (i) to describe experimental operations and the variables (ii) to describe the actual composition of the system must be distinct variables. Furthermore, **4.7** tells us that variables (ii) (chemical composition coordinates) $\tilde{\boldsymbol{N}}$ are disqualified as the basic independent thermodynamic coordinates.

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[160] The ordinary chemical thermodynamic textbooks assume, as noted in **4.2**, that all the chemical reactions can be freely halted at any moment as an equilibrium state. If we assume this artificial (and unrealizable) assumption, the following problems disappear. However, we maximally avoid such an unnatural assumption.

[161] This has been stressed by Guggenheim and other textbook authors as noted in **4.2**. Freezing reactions is required mainly to avoid this difficulty (→**4.2** (1)).

[162] As can be guessed easily, $\tilde{\boldsymbol{N}}$ are partition additive but not additive (→**2.14**).

[163] It is generally believed that the amounts of chemicals are not continuous, so '$d\boldsymbol{N}$' does not make sense. However, according to the macroscopic observation at our scales (→**1.4**) no discrete nature of the matter shows up. Even the law of constant compositions (→**4.3** (i)) does not logically imply the discrete nature of matter, even though this is a natural interpretation. Also note that we cannot ignore nonstoichiometric compounds. Therefore, in thermodynamics, the amounts of chemicals are modeled by an interval of reals $\mathbb{R}$.

Let us use the ordinary symbol N_i for the variable (i) to describe the chemical operation (collectively, $\boldsymbol{N} = \{N_i\}$). $\boldsymbol{N}$ denote the amounts of chemicals the experimenter prepares to construct the system whose ordinary thermodynamic coordinates (i.e., internal energy and work coordinates) are $(E, \boldsymbol{X})$ and its chemical composition is $\tilde{\boldsymbol{N}}$. Let us call $\boldsymbol{N}$ the *materials coordinates*.[164]

The chemical composition of the equilibrium state (specified by) $(E, \boldsymbol{X}, \boldsymbol{N})$ is uniquely fixed (→**4.3** (II)).

Notice that the materials coordinates $\boldsymbol{N}$ are additive.[165] For example, for the system whose work coordinate is only the volume V, if we prepare two systems with the states $(E, V, \boldsymbol{N})$ and $(E', V', \boldsymbol{N}')$ and combine them into a single system, the resultant equilibrium state can be given by $(E + E', V + V', \boldsymbol{N} + \boldsymbol{N}')$. If the chemical composition coordinates of $(E, V, \boldsymbol{N})$ are $\tilde{\boldsymbol{N}}$ and that of $(E', V', \boldsymbol{N}')$ $\tilde{\boldsymbol{N}}'$, the chemical composition coordinates of $(E + E', V + V', \boldsymbol{N} + \boldsymbol{N}')$ are not necessarily $\tilde{\boldsymbol{N}} + \tilde{\boldsymbol{N}}'$.[166]

4.9 A simple illustration exhibiting the non-additivity of chemical composition coordinates

Let us allow the exchange of chemicals between the two systems. For simplicity, the systems are assumed to have only one work coordinate V, which is fixed. As a reaction in the system assume (∗) in **4.4**. In systems I and II the reactions must be in equilibrium. Combining these two systems, the materials coordinates for the combined systems are simply the sum: ${N_{\rm A}}^{\rm I} + {N_{\rm A}}^{\rm II}$ and ${N_{\rm B}}^{\rm I} + {N_{\rm B}}^{\rm II}$ (and for C ${N_{\rm C}}^{\rm I} + {N_{\rm C}}^{\rm II}$).

What happens to chemical composition coordinates such as $\tilde{N}_{\rm A}$? As shown in the following calculation example, the chemical composition of the resultant system is not $\tilde{\boldsymbol{N}}^{\rm I} + \tilde{\boldsymbol{N}}^{\rm II}$, which is not an equilibrium composition.

We rely on rudimentary chemistry. For the concentrations, there is a relation $[\mathrm{C}]/[\mathrm{A}][\mathrm{B}] = K$, where [X] implies the molarity of chemical X. For systems I and II, let the concentra-

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[164] In order to construct a system with the state $(E, \boldsymbol{X}, \tilde{\boldsymbol{N}})$ the chemicals the experimenter must prepare are generally not unique. For example, if a system is with the reaction A + B $\longleftrightarrow$ C, we can appropriately mix all A, B, C, or only A and C to construct the same equilibrium state (see **25.5** for detail).

We can also choose $\boldsymbol{N}$ so that they numerically agree with the current composition $\tilde{\boldsymbol{N}}$. However, if we add $\delta\boldsymbol{N}$ moles to this system, the resultant state has its materials coordinates $\tilde{\boldsymbol{N}} + \delta\boldsymbol{N}$, but of course its chemical composition is, generally speaking, *not* $\tilde{\boldsymbol{N}} + \delta\boldsymbol{N}$ due to chemical reactions.

[165] This is due to the conservation of elements and the law of constant compositions, but does not logically imply atomism. This fact is imported from elementary chemistry to thermodynamics.

[166] Here, it is assumed that the resultant total volume is just $V + V'$, so a special way of combining the two systems is assumed. That is, the total system before 'opening the gate' is enclosed in a rigid container of volume $V + V'$. Such a procedure can always be realized. In contrast, a procedure to maintain $\tilde{\boldsymbol{N}} + \tilde{\boldsymbol{N}}'$ after combining the systems is not always possible.

tions (molarities) of chemicals be a, b, c and A, B, C (respectively, using obvious notations). Assume I and II have the same volume and temperatures. K does not change before and after the combination of the systems, so the question is: if $c/ab = K$ and $C/AB = K$, can the same hold for the average concentrations: $[(c+C)/2]/[(a+A)/2][(b+B)/2] = K$? Needless to say, this holds only for very special choices. If $K = 1$, $A = 3a$, $B = 3b$ and $C = 9c$ imply $[10/2]/[4/2][4/2] = 5/4 \neq 1$. Thus, $\tilde{N}_{\mathrm{A}}^{\mathrm{I}} + \tilde{N}_{\mathrm{A}}^{\mathrm{II}} \neq \tilde{N}_{\mathrm{A}}^{\mathrm{I+II}}$, etc.

4.10 The significance of materials coordinates

Since materials coordinates are not very explicit in the ordinary thermodynamics, let us summarize the significance of introducing such coordinates.

As seen in **4.8** the materials coordinates are additive, but chemical composition coordinates are not (although still partition additive →**2.14**).

The materials coordinates are individually independent variables and are also independent from the ordinary thermodynamic coordinates E and $\boldsymbol{X}$. If the experimenter adds $\delta\boldsymbol{N}$ moles of chemicals, then the materials coordinates of the system changes as $\boldsymbol{N} \to \boldsymbol{N} + \delta\boldsymbol{N}$.[167] Note, however, in contrast to E or $\boldsymbol{X}$, the values of the materials coordinates do not immediately give the current state of the system, which is conveniently described in terms of $\tilde{\boldsymbol{N}}$. The equilibrium composition $\tilde{\boldsymbol{N}}$ are given in terms of $\boldsymbol{N}$ only when the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ are specified (→**4.11**).

4.11 Reaction map: $\boldsymbol{R}$

The relation between $\boldsymbol{N}$ and $\tilde{\boldsymbol{N}}$ may be described by the 'reaction map' R: R is the map that provides the equilibrium composition $\tilde{\boldsymbol{N}}$ for the system with the materials coordinates $\boldsymbol{N}$ when the ordinary thermodynamic coordinates are given by $(E, \boldsymbol{X})$: $R_{E,\boldsymbol{X}}(\boldsymbol{N}) = \tilde{\boldsymbol{N}}$. Its existence is guaranteed by the elementary chemistry **4.3** II.

If the experimenter adds $\delta\boldsymbol{N}$ moles of chemicals to the system (i.e., if the materials coordinates are changed as $\boldsymbol{N} \to \boldsymbol{N} + \delta\boldsymbol{N}$), $R_{E,\boldsymbol{X}}(\boldsymbol{N} + \delta\boldsymbol{N}) - R_{E,\boldsymbol{X}}(\boldsymbol{N})$ is the actual chemical composition change $\delta\tilde{\boldsymbol{N}}$ in the system.

If the system is closed, we can choose its materials coordinates $\boldsymbol{N}$ fixed, but its chemical composition coordinates $\tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$ depend on (actually, determined by) E and $\boldsymbol{X}$ and are not independent variables at all.

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[167] As noted later (e.g., **25.6**), the choice of the materials coordinates is not unique. Therefore, a precise statment is: "we can always choose the materials coordinates to satisfy additivity."

4.12 Materials coordinates and work

Mimicking the ordinary work coordinates in **3.10**, for reversible and quasistatic processes the energy change associated with the process to change materials coordinates is expressed as the following form (*chemical form* or *mass form*)

$$\zeta = \sum \mu_i dN_i \tag{4.1}$$

analogous to (3.11). Here, μ_i is an intensive variable called the *chemical potential* of chemical i.[168] When there is no change of work coordinates, for a reversible and quasistatic adiabatic process this form is exact, i.e., we can write $\zeta = dE$.

However, it is not obvious whether the materials coordinates may be treated just as described in the preceding paragraph as the ordinary work coordinates in thermodynamics (→**4.4**-**4.10**). If they may be, this is an empirical fact, so the relevant facts should be mentioned. This is empirically established at least for simple chemicals by electrochemistry (esp., by Faraday and Joule[169]) and the empirical equivalence of electric and mechanical energies (→**17.3**).

4.13 Operational coordinates and thermodynamic coordinates

If we do not distinguish electromagnetic and mechanical works and chemical works (the so-called mass action →**4.12**), they will be collectively called the *generalized work*. The work coordinates and materials coordinates will be collectively called *operational coordinates* (or generalized work coordinates) and written as Y_i (collectively $\boldsymbol{Y}$). The name is chosen because experimenters can vary them independently at their will, in principle. In particular, it should be noted that $\boldsymbol{Y}$ does not include chemical composition coordinates $\tilde{\boldsymbol{N}}$.

However, do not forget that work coordinates and materials coordinates, though bundled together, have significant distinctions (see esp. **4.7** (iii)).

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[168] There is an opinion that at the beginner level it is pedagogically advantageous to introduce the concept of chemical potential apart from thermodynamics [for example, G. Job and F. Herrmann, Chemical potential—a quantity in search of recognition, Eur. Phys. J., **27**, 353 (2006))]. A justification says that pressure, temperature, etc., may be introduced independent of thermodynamics. Of course for pressure this is all right, since P is a purely mechanical concept, but it is questionable as to T; its natural and proper introduction requires thermodynamics. Furthermore, chemical potential was initially introduced by Gibbs to thermodynamics, so the justification above may not be appealing, although its intuitive introduction as a quantity indicating the direction of changes involving chemicals may be pedagogically of some meaning.

[169] that is, Faraday's law of electrolysis (→**26.3**) and the presence of reversible electric cells (→**A.16**, e.g., **26.6**) make this possible (→**17.2**).

The basic variables to develop thermodynamics for a system are the internal energy E and the operational coordinates of the system. The set of coordinates $(E, \boldsymbol{Y}) = (E, \boldsymbol{X}, \boldsymbol{N})$ is called the *thermodynamic coordinates.*

4.14 Reversible and adiabatic change of materials coordinates

To make sense of the chemical form ζ (4.1) operationally we need quasistatic reversible and adiabatic changes of materials coordinates. Such changes are allowed due to the possibilities of reversible mixing/separating of chemicals and reversibility of chemical reactions (→**4.3**). The mechanical work-chemical work equivalence must have been self-evident for those who considered chemical reactions just as (classical) mechanical changes as Helmholtz (→**A.17**), but this is not any scientific proof of the equivalence.[170]

To define chemical potentials operationally, a cylinder with a piston closed by an appropriate semipermeable membrane is used (for more details →**17.5**). There are two potential problems here.

The first problem is the well-known realizability of semipermeable membranes (or selectively permeable membranes): it is only fictitious to assume a membrane that can segregate a selected chemical perfectly, so such a fancy device should be expelled from the theory.[171] However, a selective permeable membrane is a symbol to describe the reversible process (I) in **4.3**: mixing and separating chemicals can be realized reversibly; the separation process may use (appropriately idealized) reversible chromatography, fractionating column, etc.

The second problem is to realize exchange of finite amount of chemicals adiabatically. That is, whether $dE = \sum \mu_i dN_i$ can be realized. When the work coordinate is only V, the process is illustrated in Fig. 4.1. T he procedure is not very simple, so we will not use this process. A practically meaningful cases are under constant temperature and pressure, so we will discuss the cases with these conditions later

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[170] ⟪**How far apart classical mechanics and chemistry are**⟫ In 1922, while walking in Göttingen, Bohr told Heisenberg that the inability to explain chemistry with classical theory was the motivation behind quantum theory as mentioned in the footnotes of **A.17**. Bohr concluded his story by stating that the stability of matter is incompatible with the causal laws of classical mechanics, and it was this contradiction that had continually troubled him. Compare this with Helmholtz' talk (→**A.17**).

[171] This complaint may sound reasonable for critical people, BUT compared with the 'standing assumption' in the standard chemical thermodynamics textbooks that chemical reactions may be stopped at our will without destroying the system equilibrium is a much more drastic and fancy assumption than this.

(→**17.5**).

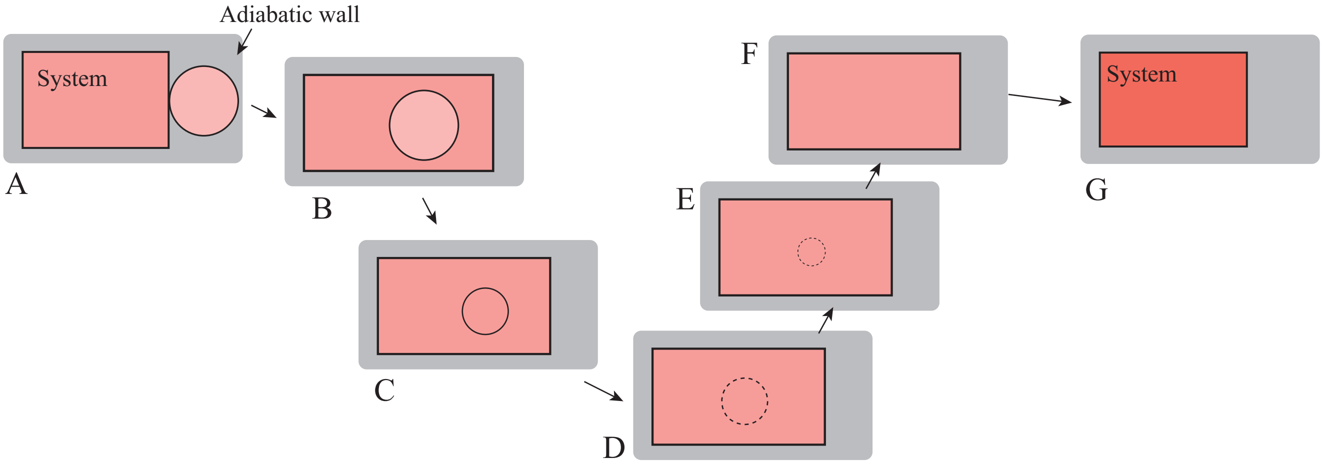

Figure 4.1: Adiabatic reversible addition of chemicals is possible, in principle.

Fig. 4.1 Adiabatic reversible addition of chemicals is possible, in principle.

The shade of red expresses the concentration of a particular chemical.

A: We assume that the total amount of each chemical we wish to add to the system is known. The pure chemical is in the round container, which is enclosed by a diathermal wall that does not exchange any work coordinates (i.e., no displacement to change the container volume in the present case). Thus the total system is with a uniform temperature, and is enclosed by adiabatic walls as a whole.

B: We embed the container into the system. During this process we may choose the work coordinates, e.g., the volume, of the system quasistatically appropriately. Accordingly, E and V may change.

C: Regulate the volume of the round container appropriately to make the chemical potential inside and that of the same material in the system identical. E may change during this process.

D: Then, change the wall of the container with the selective permeable membrane for the target chemical.

E-F: Appropriately changing the volume of the round container and the work coordinate of the system we can squeeze out the chemical in the round container quasistatically.

G: Finally, the work coordinates are returned to the original values reversibly and quasistatically. Thus, without changing the work coordinates we have added the chemical reversibly and adiabatically.

4.15 Why no distinction between materials coordinates and chemical component variables appears in any textbooks

Perhaps this may be clearly understood from Kirkwood-Oppenheim's book or Tasaki's book. In short, the situations in which $\boldsymbol{N}$ and $\tilde{\boldsymbol{N}}$ must be distinguished are avoided. That is, when chemicals are added (i.e., the operation by the experimenter), it is assumed that no chemical reactions are occurring at all. When chemical reactions occur and chemical compositions passively change even without direct material intervention by the experimenter, the system is considered closed. Therefore, in the former case we only need $\boldsymbol{N}$ and in the latter only $\tilde{\boldsymbol{N}}$.

In the conventional chemical thermodynamics the requirement for systems with chemical reactions is that "systems in which chemical reactions may occur involve the ability to freeze the chemical reactions at any desired point" as noted in **4.2**. While freezing reactions, the amounts of chemicals may be handled as our materials coordinates, and therefore, the convexity of E is preserved. As a result, the usual thermodynamic variational principle for equilibrium states may be demonstrated.

However, with the conventional variables (corresponding to our chemical composition coordinates), if you turn on chemical reactions, the convexity of E is lost (→**4.9** for an example), so the validity of the usual thermodynamic variational principle for equilibrium states is no longer guaranteed. Consequently, the variational principle for chemical reactions cannot be established in terms of the chemical composition variables $\tilde{\boldsymbol{N}}$.

Much more seriously, as we will see later, with the conventional material/chemical quantity expressions, the second law of thermodynamics with chemical reactions is hardly formalizable.

Under the so-called Mechanical Weltanschauung, there is no problem, since chemistry is mere special mechanics, as explained by Helmholtz (→**A.17**). Therefore, we can apply the second law with works alone to chemistry. However, 'Weltanschauung' is not science; it lacks empirical basis, no matter how plausible it may sound. Thus, the conventional (or at least the original) formulation of chemical thermodynamics does not properly adhere to the proper practice of science.

5 Thermodynamic space: Preliminary IV

5.1 Equilibrium states are distinguished by thermodynamic coordinates

Can we use the thermodynamic coordinates (→**4.13**) of a system to distinguish all the equilibrium states that we can macroscopically distinguish? Of course not. Note that, by definition (→**3.10**), thermodynamic coordinates cannot identify any changes that do not affect the internal energy, even if we can discern the change in the equilibrium state. For example, the difference in the three-dimensional shapes of a system (additive system →**2.11**) or the relative positions of coexisting phases (say, ice and water) in it are irrelevant to thermodynamics.

Some people might think there are likely more quantities that can be observed macroscopically, such as color, smell, or the sound produced when struck. Indeed, that is true. However, as long as color or smell can be changed independently of work coordinates without altering the energy density of the system, they do not need to be considered in thermodynamics.

Precisely speaking, a *thermodynamic state* (or *state*, for simplicity) is an equivalence class with respect to the thermodynamic coordinates of equilibrium states. Therefore, thermodynamics focuses on the changes of thermodynamic states rather than equilibrium states. From now on, however, we will not meticulously distinguish thermodynamic states and equilibrium states and use these words interchangeably

5.2 Thermodynamic space

The space spanned by the thermodynamic coordinates of a (simple[172]) system is called its *thermodynamic space*. The two equilibrium states that thermodynamics distinguishes correspond to two distinct points in this space (→**5.1**). Two equilibrium states whose thermodynamic coordinates agree are considered (thermodynamically) identical.

All thermodynamic coordinates may be measured in some energy unit,[173] so we may regard the thermodynamic space as the usual Euclidean space.[174] We may

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[172] This concept is not confined to simple systems. For a compound system its thermodynamic space may be the direct product of the thermodynamic spaces of the constituent simple systems or its convenient subspace.

[173] This is true even for materials coordinates.

[174] Or, any vector space whose metric is equivalent to that of the ordinary Euclidean space.

regard it as the ordinary linear vector space with the usual metric. Thus, we can use the ordinary calculus in this space.[175]

The thermodynamic space of a compound system is essentially the direct product of the thermodynamic spaces of the constituent simple subsystems.

5.3 Thermodynamic coordinates are privileged variables

For a given system its thermodynamic coordinates are the privileged coordinates with the following properties:
(1) They are extensive quantities that may be described and manipulated by non-thermal macrophysics and chemistry. In other words, thermodynamics is not needed to describe and to measure thermodynamic coordinates.
(2) They specify equilibrium states = thermodynamic states uniquely (by definition →**5.1**).

5.4 State quantity, state function

When the (thermodynamic coordinates of an) equilibrium state of a system is determined, the quantities that become fixed and measurable are called *state quantities*. Their values do not depend at all on the history of how the equilibrium state was achieved.

A function whose domain is a certain set in the state space is called a s *state function*. In other words, a function that has thermodynamic coordinates as its variables is called a state function. The quantities expressed by state functions are state quantities.

Naturally, a function of a state quantity is also a state function describing a state quantity. Therefore, a state quantity does not necessarily have to be a function with thermodynamic coordinates as independent variables. For example, temperature and pressure are not fundamental thermodynamic quantities (→**3.8**), but since they are state quantities, a function of temperature and pressure is also a state quantity.

5.5 Thermodynamic densities and fields

The fundamental variables of thermodynamics are extensive variables (→**3.2**). Con-

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[175] For sound basic knowledge of real analysis, the author recommends A. N. Kolmogorov and S. V. Fomin, *Elements of the Theory of Functions and Functional Analysis* [Two Volumes in One] (Martino Fine Books, 2012).

sequently, variables appearing in thermodynamics are extensive and intensive variables (→**3.2**). Also it was explained why theoreticians like to take the thermodynamic limit (→**2.15**), in which all the extensive quantities diverge and become meaningless. Therefore, to describe thermodynamics in this limit extensive quantities per unit volume, that is, the *thermodynamic densities* are used. Thus, in mathematical physics the key thermodynamic variables are the thermodynamic densities and their conjugate intensive variables (called *thermodynamic fields*).

The systems that we deal with at our scale (→**1.4**) are finite but they are typically very close to the thermodynamic limit; all the thermodynamic densities are virtually identical to their thermodynamic limit values.

In practice, it is often much more convenient to use the original extensive quantities rather than corresponding densities.[176] Therefore, in most cases, we will not use thermodynamic densities in the subsequent expositions.

5.6 The topology of the totality of equilibrium states

The totality of the equilibrium states $\mathcal{E}$ of a system under study need not be the whole thermodynamic space (→**5.2**) of the system. If $\mathcal{E}$ is not simply connected (→**5.7**), then two paths connecting two different equilibrium states may not be continuously deformed into each other within $\mathcal{E}$, so the results of line integrals can depend on the paths taken. The following part of this section explains that the topology of $\mathcal{E}$ is 'maximally' simple and such 'complications' never occur.

Remark In thermodynamics, as we will see there may be limits whose outcomes may not be in $\mathcal{E}$ (e.g., $T = 0$ state, or infinite thermodynamic coordinate limits (e.g., $V \to \infty$, $E \to \infty$)). However, $\mathcal{E}$ need not simply be an open set (e.g., the system volume may be bounded from above by a rigid container).

5.7 Some topological terms[177] (See Fig. 5.2)

⟨⟨Connected⟩⟩ An open set is *connected*, if it cannot be divided into two disjoint open sets. A set is connected, if there is no way to cover it by two disjoint open sets that both have intersections with the set.

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[176] For example, changing only the system volume while keeping all other operational coordinates is not so easy to describe in terms of densities.

[177] A superb introductory book is: I. M. Singer and J. A. Thorpe, *Lecture notes on elementary topology and geometry* (Scott, Foreman and Company, Glenview, IL, 1967). Every undergrad should read this.

⟪**Arcwise connected**⟫ A set is *arcwise connected*, if any two points in the set may be connected by a continuous curve in it. Note that connectedness does not imply arcwise connectedness.[178]
⟪**Simply connected**⟫ Suppose a set is arcwise connected and its any open set contains an arcwise connected open set.[179] If any closed continuous curve can be continuously contracted to a point in the set, we say the set is *simply connected*. Any closed continuous curve in a simply connected set is homotopic (see the following item) to a point.
⟪**Homotopic**⟫ A continuous curve $f(t)$: $t \in [0,1] \mapsto \mathcal{E}$ is *homotopic* to another continuous curve $g(t)$: $t \in [0,1] \mapsto \mathcal{E}$, if there is a continuous map $F(t,s) : [0,1] \times [0,1] \mapsto \mathcal{E}$ dependent not only on t but one more parameter $s \in [0,1]$ such that $F(t,0) = f(t)$ and $F(t,1) = g(t)$. In short, if we can continuously deform the graph of f to that of g without leaving $\mathcal{E}$, we say f and g are homotopic.
⟪**One-point contractible**⟫ If a set S is homotopic to a point P in S, the set is said to be one-point contractible: that is, if we can construct a continuous function $F(x,t) : S \times [0,1] \mapsto S$ such that $F(x,0) = x$ and $F(x,1) = P \in S$, we say S is one-point contractible. In short, if we can continuously shrink a set to a point within the set, we say the set is one-point contractible.

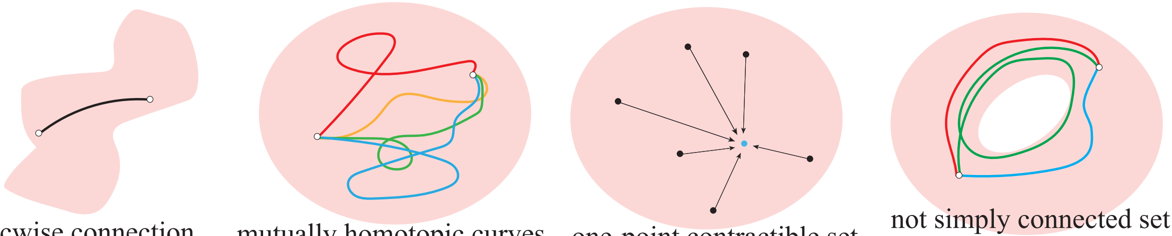
arcwise connection
mutually homotopic curves
one-point contractible set
not simply connected set; curves are not homotopic

Figure 5.1: Arcwise connection, homotopy, one point contractibility, simple connection (in 2-space)

5.8 Various equilibrium systems

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[178] For example, there is a counterexample in I. M. Singer and J. A. Thorpe, *Lecture Notes on Elementary Topology and Geometry* (Undergraduate Texts in Mathematics) (Springer; Reprint 1976). You should at least read such a book. The counterexample may be rather bizarre, because continuity does not exclude strange phenomena, but in physics, we usually consider curves with lengths (see, e.g., **9.13**), so we need not worry too much about such counterexamples.

[179] This condition says that the set is *locally arcwise connected* in the standard terminology.

The concept of 'simple system' was introduced earlier (→**2.10**) and it was stated that indefinitely complicated equilibrium systems may be conceived. Here, for simplicity, we assume all the simple systems are in spatially uniform equilibrium states.

If we prepare two simple systems and regard them jointly as a single system (Fig. 5.2A → B), even if there is no interaction between them, the resultant system is in equilibrium, since it satisfies the characterization of equilibrium states (→**2.8**). The resultant system is a compound system (→**2.10**).

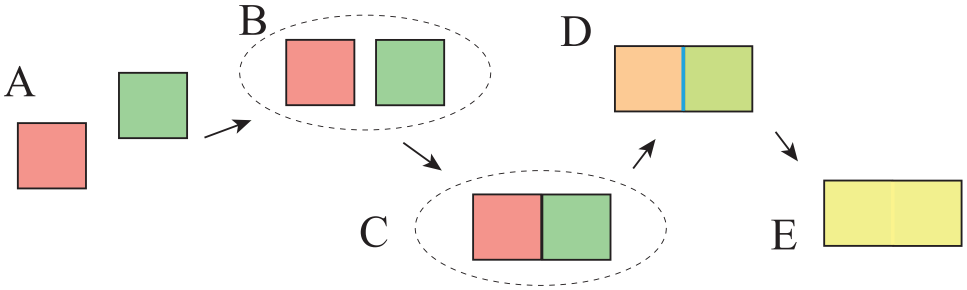

Figure 5.2: Various states of a compound system

Fig. 5.2 We can combine simple systems to make a compound system. The resultant compound system could be various, depending on the boundary conditions (walls) between the constituent simple systems.

A: Two simple systems in different equilibrium states.

B: It is of course possible to regard these simple systems as parts of a single system.

C: Even if these simple systems are connected through a wall that does not exchange any extensive quantities, there is no change of states from B.

D: Through varying the boundary conditions (i.e., wall properties →**2.1**), we can allow exchanges of some extensive quantities for a finite time span or forever to prepare various equilibrium states of a compound system.

E: We can further relax the constraints imposed by the wall; eventually, we could bring the compound system to a simple system (if both are made of the same materials).

As is illustrated in Fig. 5.2, by combining two simple systems, we can prepare various interpolative equilibrium states of a resultant compound system. Needless to say, we can start with as many simple systems as we wish, with walls of various types as we wish to separate them,[180] so we can make indefinitely complicated compound

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[180] ⟪**Requirement for walls**⟫ That we can do such things should be stated clearly as a theoretical requirement. In other words, when thermodynamics is 'axiomatized,' the existence of a "wall" must be postulated as one of the "axioms." To put it plainly, we assume that "there exists a wall

systems.

In thermodynamics, an inhomogeneous system may be understood as a compound system.[181]

5.9 $\mathscr{E}$ is a (smoothly deformed) convex set

For **5.8** there is no restriction on system A and system B; they need not share the same thermodynamic space.[182] Here, we assume that the two systems share the same thermodynamic space, but are in different equilibrium states.

The thermodynamic coordinates of A are $(E^{\mathrm{A}}, \boldsymbol{Y}^{\mathrm{A}})$ and those of B $(E^{\mathrm{B}}, \boldsymbol{Y}^{\mathrm{B}})$, where $\boldsymbol{Y}$ denotes the operational coordinates (→**4.12**) $(\boldsymbol{X}, \boldsymbol{N})$. Grafting these two systems in certain proportions as illustrated in Fig. 5.3, we make a compound system.

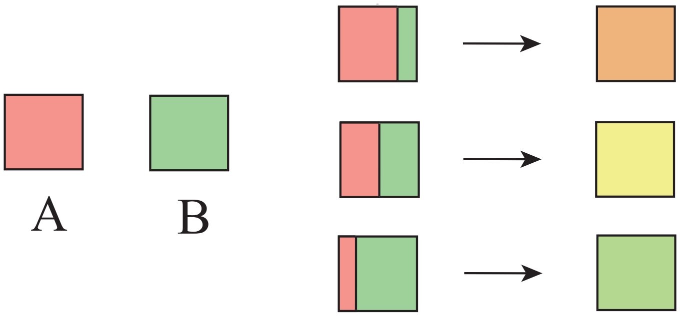

Figure 5.3: Making interpolated systems

Here, if the operational coordinates $\boldsymbol{Y}$ at equilibrium are all additive[183], then since

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that allows the exchange of only each thermodynamic coordinate of the system or any combination thereof." As this implies, merely assuming the so-called principles of conventional thermodynamics alone cannot possibly establish a sound theory. These points are collected in "summary."

The wall is assumed to have only local effects, except through the exchange of extensive quantities. If the reader knows phase transitions, she might question this, e.g., quoting Peierls' argument (for example, see Y. Oono, *Perspectives on Statistical Thermodynamics* (Cambridge, 2017) p419 and Q32.4 on p430). However, in this case the change in the order parameter has no energetic effect, so thermodynamically, we can ignore the effect (→**23.7**).

[181] As already noted (biological) 'cells' are sufficiently macroscopic. Remember that still no one imagined that we are made of cells before the cell theory by Theodor Schwann (1810-1882) and Matthias Jakob Schleiden (1804-1881). To regard spatially inhomogeneous macroscopic equilibrium systems as compound systems is sufficiently accurate.

[182] Needless to say, we can set up a single thermodynamic space for any set of systems through expanding the operational coordinate set.

[183] Note that being simply partition-additive is insufficient. See **5.13**. Whether an extensive quantity is additive or not is specified by macroscopic physical chemistry, and thus is decided prior to thermodynamics.

the material coordinates and energy are additive, as is clear from Fig. 5.3, for any $\lambda \in [0, 1]$, the thermodynamic coordinates can be formed by joining A and B in an appropriate ratio as follows:

$$\Lambda = (\lambda E^{\mathrm{A}} + (1-\lambda)E^{\mathrm{B}}, \lambda \boldsymbol{Y}^{\mathrm{A}} + (1-\lambda)\boldsymbol{Y}^{\mathrm{B}}). \tag{5.1}$$

This shows that any interpolated state with these thermodynamic coordinates Λ can be generated (although the resulting system may not be spatially uniform, it will reach equilibrium). In other words, an equilibrium state with thermodynamic coordinates Λ exists. Therefore, A, B $\in \mathcal{E} \Rightarrow \Lambda \in \mathcal{E}$. This implies that $\mathcal{E}$ is a convex set (→**5.11**).

Important remark The operation depicted in Fig. 5.3 gives the impression that simply bringing two systems into contact and then removing the wall between them will automatically result in a state corresponding to Λ. However, in reality, upon contact (e.g., due to mixing), the temperature may change, and thus, properties such as volume may not necessarily add up automatically. Nevertheless, since the additivity of $\boldsymbol{Y}$ is guaranteed, an equilibrium state defined by Λ exists and can be constructed from states A and B. The arrows in Fig. 5.3 represent this process. See **5.10**.

This means that, since materials coordinates are all additive,[184] if all the work coordinates are also additive, then $\mathcal{E}$ is a convex set.

However, the additivity is not guaranteed for all the work coordinates, so Λ may not be the thermodynamic coordinates of the final state. The true final equilibrium state 'C' $\{E^{\mathrm{C}}, \boldsymbol{Y}^{\mathrm{C}}\}$ is with $E^{\mathrm{C}} = \lambda E^{\mathrm{A}} + (1-\lambda)E^{\mathrm{B}}$, but its operational coordinates $\boldsymbol{Y}^{\mathrm{C}}$ must be a continuous function of $\lambda \boldsymbol{Y}^{\mathrm{A}} + (1-\lambda)\boldsymbol{Y}^{\mathrm{B}}$. Therefore, $\mathcal{E}$ may not be a convex set, but must be a set of a homeomorphic image of a convex set.[185]

Consequently, any continuous curves connecting two particular points in $\mathcal{E}$ are homotopic (→**5.7**). Furthermore, $\mathcal{E}$ is one-point contractible (→**5.7**).

REMARK However, non-additive work coordinates are usually never discussed in the conventional thermodynamics.[186] Therefore **in this book, we assume that $\mathcal{E}$**

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[184] Do not forget that the 'standard or conventional choice' adopted by all the textbooks, chemical compositions, $\tilde{\boldsymbol{N}}$, are *not* additive. However, this difficulty is conventionally evaded by the assumption that chemical reactions can be halted at any time as we wish.

[185] Since $\lambda \in [0, 1]$ is real, $\mathcal{E}$ must be arcwisely continuous (→**5.7**).

[186] except for chemical composition variables $\tilde{\boldsymbol{N}}$ as the standard description of the amounts of chemicals. However, in these lecture notes, the chemical variables are materials coordinates $\boldsymbol{N}$, so they are strictly additive.

is convex (→5.11).

5.10 What does an additive variable exactly mean?

In typical thermodynamic textbooks, the additivity of an extensive quantity X simply implies the relation (2.2) in **2.14**. For example, volume V is commonly understood as an additive quantity because combining systems with volumes V and V' would result in a new system with volume $V + V'$.

However, even for volume, this additivity is not automatic. If the container is not rigid, the total volume could change due to altered T, P, etc., through, e.g., materials mixing. In this case, additivity can be ensured by using a sufficiently rigid container. Thus, additivity implies that we can enforce the additivity of the quantity without changing the system energy adiabatically.

In short, additive extensive quantities are those for which we can enforce constancy without any (generalized) work under adiabatic conditions.

For chemical substances and volume, this is clearly possible.

5.11 Convex set

A set in a Euclidean space is a *convex set*, if the line segment connecting any two points in the set is in the set (Fig. 5.4).

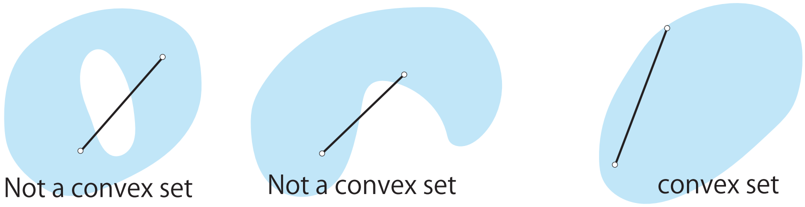

Figure 5.4: A convex set contains the line segment connecting two arbitrary points in the set.

Any common set of two convex sets is a convex set.

The direct product of two convex sets is a convex set.

Thus, the totality $\mathcal{E}$ of equilibrium states of a given system is a convex set in its thermodynamic space as demonstrated in **5.9**.

5.12 Convexity and the choice of thermodynamic coordinates

As we have learned from the expression of chemical amounts in a system that are state variables, convexity of $\mathcal{E}$ depends on the choice of the variables. This is stressed by Lieb and Yngvason on p33, "it is essential to note that the convex structure depends heavily on the choice of coordinates for" the thermodynamic space.[187] Thus, to cover chemical reactions thermodynamically, even within their 'axiomatic system,' how to describe amounts of chemical should have been discussed carefully.

5.13 Can we discuss the topology of $\mathcal{E}$ from partitioning of a system?

In **5.9** the nature of $\mathcal{E}$ was investigated through combining different equilibrium states. In contrast, Shimizu's *Principles of Thermodynamics* avoids 'dynamical changes due to making two systems in contact,' so his theoretical system does not allow to make a different equilibrium system through combining two arbitrary equilibrium systems. That is, his 'additivity' is not the true one but the partition additivity (→**2.14**). For example, when we write

$$X = \sum X_i, \tag{5.2}$$

the right-hand side permits any physically realizable partition of X, but it does not state anything about the range of X for the formula to hold. Of course, it is implicitly assumed that the range of X and X_i are the same single interval. However, the above formula is meaningful even if the range of X_i are two disjoint sets. It is obvious that the formula (5.2) cannot claim anything about the range of X.

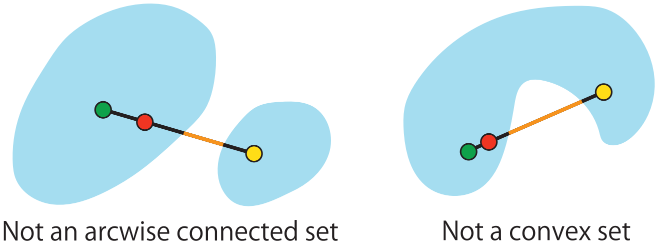

Figure 5.5: Additive constraints cannot determine whether $\mathcal{E}$ is convex or not. Suppose the red state is given beforehand. The red state may be the additivity consequence of the green and the yellow states. We can choose the ranges of these (green and yellow) states even if $\mathcal{E}$ is not convex to satisfy (5.2), if the red state is given beforehand (as in the case of partition additivity). If the green and the yellow states are given beforehand, Λ corresponds to any point on the segment connecting the green and the yellow states, so Λ may land on the 'orange' portion of the segment connecting the green and the yellow states. Thus, for $\Lambda \in \mathcal{E}$ to be true $\mathcal{E}$ must be a convex set.

Thus, the decomposability (or possibility of partitioning) of $(E, \boldsymbol{Y})$ does not properly impose any constraint on the topology of $\mathcal{E}$ [Actually, the decomposability is restricted by the geometry of $\mathcal{E}$]. See Fig. 5.5.

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[187] E. H. Lieb and J. Yngvason, "The physics and mathematics of the second law of thermodynamics," Phys. Rep. **310**, 1 (1999). Incidentally, they wrote already on p7, "It is well known, as Gibbs (1928), Maxwell and others emphasized, that thermodynamics without convex functions may lead to unstable systems." "In our treatment it (= convexity) is essential for the description of simple systems."

The convexity of $\mathcal{E}$ must be demonstrated separately from decomposability as we did (→**5.9**).[188]

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[188] Thus, Shimizu's 'proof' of the convexity of $-S$ is vacuous.

6 Quasistatic processes: Preliminary V

6.1 Points in the thermodynamic space

As we see in **5.3** any point $(E, \boldsymbol{Y})$ in the thermodynamic space of a system represents at most one equilibrium state (= thermodynamic state →**5.1**) of the system.

However, we cannot tell solely from the coordinate values whether the system is in equilibrium or not. The thermodynamic coordinates of a point in the thermodynamic space may also correspond to some states of the same system with the identical $(E, \boldsymbol{Y})$ but not in equilibrium.[189] For example, for a single component gas, its thermodynamic coordinate system is (E, V). However, the energy and the volume can also be defined for non-equilibrium states, such as a swirling gas in a box. As a result, a process that can be described by a continuous curve in the thermodynamic space is not guaranteed to express a quasistatic and/or a reversible process.[190] If the system is a compound system, the situation can be more complicated.

In short, a process along which thermodynamics can be applied corresponds to a definite continuous curve in the thermodynamic space, but a continuous curve in the thermodynamics space need not represent only processes consisting of states to which thermodynamics can be applied.

To minimize confusion we introduce the concept of 'quasiequilibrium state' in this section.

6.2 Quasiequilibrium states: simple systems

The state P of a simple system (→**2.10**), whose thermodynamic coordinates are well defined (thus, it has a well-defined representative point P in the thermodynamic space), satisfying the following conditions, will be called a *quasiequilibrium state*:[191]

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[189] In this exposition, we assume the point $(E, \boldsymbol{Y})$ describes any state (not necessarily an equilibrium state) with the internal energy and the operational coordinates given by $(E, \boldsymbol{Y})$. One merit of this choice may be that quasistatic process that is not really in equilibrium may be described mathematically without assuming all the states along any quasistatic process are in equilibrium (as explicitly declared in A. Arai, *Mathematics of thermodynamics* (Nihon-Hyoronsha, 2020)).

Furthermore, the values of the operational coordinates are often considered to be determined even if the system is not strictly in equilibrium states, especially when the degree of non-equilibrium is not significant.

[190] Needless to say, most nonequilibrium processes cannot even lie in the thermodynamic space.

[191] As a simple system with well defined thermodynamic coordinates, we require that the spatial structure of P is macroscopically close to homogeneous states.

(1) In a sufficiently small neighborhood[192] of P is an equilibrium state R of the system,[193] and
(2) State P eventually reaches R, if the system is left alone in the single uniform environment $\mathcal{B}$ that can maintain R.

That is, the state P may not be an equilibrium state, but there is a true equilibrium state R sufficiently close to P, and if the system in state P is left in an environment that maintains R, the system eventually reaches R (Fig. 6.1).[194]

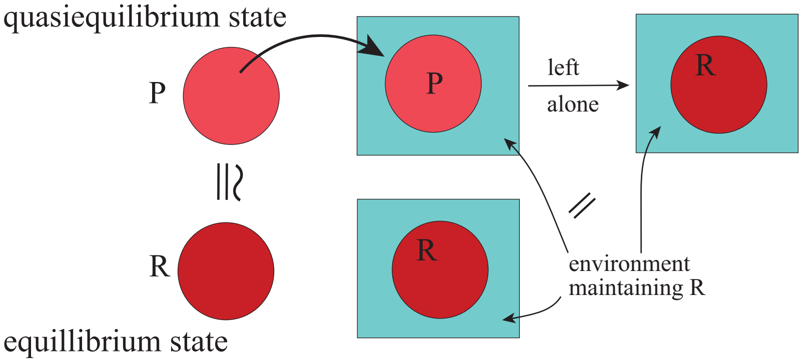

Figure 6.1: Quasiequilibrium state for simple systems

Suppose an irreversible change in a simple system is caused by a system-environment mismatch. For example, imagine a hot coffee in a thermos placed in a living room. If the thermos is of high quality, the state P of the coffee inside would be almost constant; there is a true equilibrium state R in the neighborhood, which is indistinguishable from P. That is, the state P is not a true equilibrium state, because it is cooling, but the thermodynamic coordinates of state P is, at every moment, located almost overlapping with equilibrium state R in the thermodynamic space. Thus, this state P is a quasiequilibrium state.

6.3 For compound systems quasiequilibrium states need not be defined

The purpose of introducing the quasiequilibrium state is to characterize the paths in the thermodynamic space along which we can use thermodynamics; especially, we can thermodynamically compute the state function changes between the initial and the final states of the

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[192] In mathematical terms, this means "contained in every neighborhood," and in this case, it is fine even if R = P. Informally, it is "infinitely close," but in reality, it means "the difference is negligibly small," and it can vary depending on the context.

[193] Point P in the thermodynamic space can agree with the point R. That is, a point representing an equilibrium state can also represent a quasiequilibrium state.

[194] R can be P itself.

path. Whether this is possible or not depends individually on the properties/states of simple systems making the compound system. Therefore, any compound system may be treated as a collection of simple systems separately. Thus, we need not define quasiequilibrium states (and quasistatic processes) for compound systems. To be complete, however, you can find a definition of quasiequilibrium states (that also leads to the definition of quasistatic processes for the compound system as a whole) at the end of this chapter (→**6.9**).

6.4 Quasistatic process

If at every moment of the process the state of the system (irrespective of its interacting exterior world—its environment, etc) is in a quasiequilibrium state (→**6.2**), we say the process is a quasistatic process.[195] Along a quasistatic process we can apply thermodynamics.[196]

Roughly speaking, when a system changes due to interactions with its environments, a process is a quasistatic process if any state along it can settle down to a very close equilibrium state if the system-environment interaction is severed.

By definition, the quasistatic process is about the system under consideration alone, because what matters is whether the system is always in quasiequilibrium states. Even if the system is interacting with something else, we do not care whether this other system is in (quasi)equilibrium or not. We also do not care whether the system is in equilibrium with it.

Informally speaking, at least for simple systems, if the process is sufficiently slow, it is a quasistatic process[197] for the system. For compound systems slowing down alone is not enough due to the possibility of pseudoequilibrium states (→**6.9**).[198]

Remark: Notice that a 'quasistatic process' is not simply a 'sufficiently slow process', distinct from Tasaki's explicit characterization. Historically, as can be seen

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[195] **Warning**: The definition of 'quasistatic process' may vary depending on the source. Many books require that not only the system itself, but its environment are quasistatic in our sense and that the system and its environment must be in equilibrium. [Notice that, according to this definition, the cooling process of hot coffee in a good thermos in the room is not a quasistatic process.] Then, they say that we can apply thermodynamics along quasistatic processes according to their definition. However, thermodynamics can be used under less strict conditions (e.g., no system-environment equilibrium is required (→**14.13**), so the definition is not suitable for this purpose.

A. Arai, ibid. defines a quasistatic process as a process consisting of equilibrium states.

[196] Needless to say, if the initial and the final states are in equilibrium, we can always use thermodynamics to compute the state quantity evolution. What is meant here is that along a quasistatic process at any point along the process we can use thermodynamics to compute the state quantities.

[197] This does not mean that the process is retraceable.

[198] Still, for individual subsystems we may use thermodynamics.

in **A.6**, the chief motivation to introduce a quasistatic process was to avoid any loss/dissipation. Therefore, to equate being quasistatic and being slow does not correctly capture the connotation of the word 'quasistatic' in the original spirit.

6.5 'Physics' of quasistatic process

The idea of quasistatic process first appeared in the theory of hydraulic machines (→**A.6**). Carnot adopted this idea in his reversible engine as a process with changes at an infinitesimal rate (→**A.7**). The idea was readily accepted thanks to the popularity of analysis in France at that time.

Macroscopic observations are observations ignoring (or averaging-out) fluctuations that are spatially small and temporally rapid (→**2.5**) according to the law of large numbers. In other words, the observational errors of macroscopic observation occur only when the errors significantly exceed (standard) deviations of fluctuations. Even if we ignore fluctuations, they do not cease to exist, but in equilibrium there is no systematic deviation in one direction caused by equilibrium fluctuations (the average vanishes). However,[199] by nudging these fluctuations gently externally, the averages of fluctuations can be made nonzero.[200] Thus, quasistatic processes can be realized at rates sufficiently small but finite. The mathematical infinitesimal rate is a theoretical idealization of such small but finite rates.

In other words, deviations from the law of large numbers, i.e., the deviations theoretically understandable by the large deviation principle can, realize quasistatic processes.[201]

6.6 Reversible quasistatic processes

During a process of a system, if its environment is in a quasiequilibrium state and if the compound system made of the system itself and its environment are "almost in equilibrium" (i.e., in a quasiequilibrium state →**6.9**), then the process is step-by-step retraceable, so it is reversible in particular.

6.7 Reversible process, quasistatic process and infinitesimal process

There is no direct logical relation among the concepts, 'reversible process,' 'quasistatic process,' and 'sufficiently slow infinitesimal process.' Here, some related remarks are collected.

(1) A quasistatic process is a process in which the system is in quasiequilibrium states (→**6.2**). For work coordinates, if there is no 'dry friction,' such a process is realizable

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[199] The discussion here essentially follows that of Koichi Ohno, *Learning Thermodynamics from Basics* (Iwanami 2001) p88 [In Japanese]

[200] This is the content of the so-called fluctuation-response relations in equilibrium statistical thermodynamics.

[201] Einstein's thermodynamic fluctuation theory exactly describes this large deviation theoretical framework as discussed in YO, *Perspectives on statistical thermodynamics* (Cambridge UP, 2017).

by sufficiently slowing down the changing rates (→**3.11**). Materials coordinates may be handled basically in the same fashion as the work coordinates, although some care is required. For heat see **14.12**.
(2) Even if the changing rate of operational coordinates or their conjugate variables is small, the change need not be reversible. It is possible to realize the situation analogous to the slowly cooling cup of coffee for work coordinates. A gas canistor with a pinhole is an example. For the gas in the canistor of volume V, its state, e.g., its pressure P, is almost constant. However, for the portion of the gas leaking from the hole, its volume expands very quickly from a tiny one to 'the whole world.'

Very similar to this, we could connect two containers containing gases of different pressures, respectively, with a small pin hole. Each container is in a quasiequilibrium state, so each container changes quasistatically. However, the whole system is not in equilibrium (not even in a pseudoequilibrium state →**6.9**). This is an example of irreversible changes of a compound system consisting of simple systems undergoing quasistatic changes.
(3) However small a change relative to the whole system, if the change itself is violent (not controllable), then even though the change is quasistatic for the system and may be infinitesimal, it may not be reversible. It may be easy to imagine such a situation with a gun powder ignited in small portions. Suppose a container of gas is with a piston, and its outside is a vacuum. If the piston is pulled out stepwisely very rapidly as $V \to V + dV \to V + 2dV \to \cdots$, then each step is a free expansion of the gas, so is irreversible. That is, even if the change as a whole (from the point of view of the whole system) is 'slow' and infinitesimal, it is irreversible.[202]

6.8 Why is thermodynamics useful?

Thermodynamics discusses only equilibrium states, even though this world is full of nonequilibrium phenomena. Why is thermodynamics still useful? Because:
(i) Equilibrium states do not depend how they are prepared (→**2.8**).
(ii) Equilibrium states may be realized with good approximation.
(iii) It is permissible to devise a convenient (reversible) quasi-static process to calculate the change of any state quantity between equilibrium states.

In particular, the starting state S of a process is very often a time independent

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[202] In this case, the gas is always in a quasiequilibrium state and so is its environment, but there is no (near) equilibrium relation between the system and its environment. That is why the process is not reversible.

state, and so is the destination state F. Therefore, often it is not a bad approximation to regard these states as equilibrium states; the changes of state quantities (→**5.4**) are completely determined by the thermodynamic coordinates of these two states.

To compute the change of state quantities without knowing the actual process from S to F, we have only to devise a convenient curve in the (operational) thermodynamic space connecting S and F. The process described by the curve can be realized as a quasistatic reversible process (→**C.5**). A simple example is in **11.14**.

6.9 Quasiequilibrium states: compound systems

As noted in **6.3**, we do not, in practice, have to define quasiequilibrium states for a compound system. Here, a definition is given, but the reader have only to realize how complicated quasiequilibrium states are and, consequently, quasistatic processes are for a compound system.

Since the case of general compound systems (→**2.10**) can be complicated, let us discuss a compound system consisting of two simple systems. If these simple systems are in quasiequilibrium states (→**6.2**) individually, the state P of the compound system corresponds to a point in its thermodynamic space (→**2.10**).

If we wish to say the compound system is in a 'quasiequilibrium state,' we must find a single uniform environment[203] $\mathcal{B}$ for the compound system such that the system in state P left alone in $\mathcal{B}$ eventually reaches an equilibrium state R of the compound system that is almost indistinguishable from P.

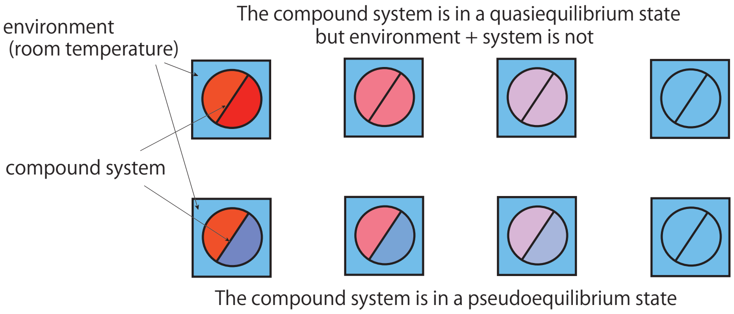

Figure 6.2: Quasi- and pseudoequilibibrium states for compound system

An obvious problem is that combining two (quasi)equilibrium simple systems may not create a compound system in equilibrium. Suppose one simple system is hot water and the other cold water, and the boundary does not allow easy exchange of energy (i.e., informally, 'approximately thermally insulating'). If the combined system is in a good thermos, then far before the whole system reaches a room temperature, the system would relax to an almost thermal equilibrium at some common temperature. Even during the relaxation

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[203] Here, the environment must be a single uniform one, because, if we allow multiple environments, the subsystems of a given compound system can have its own environment and the whole compound system may be maintained in a nonequilibrium steady state.

process the two simple systems can individually stay in quasiequilibrium states (at distinct temperatures), but there is no single uniform environment that can maintain this state of the compound system; as a state of a compound system, even though the change is slow, there is no equilibrium state close to the state.

A state represented by a point in the thermodynamic space, but without satisfying (1) of **6.2** may be called a *pseudoequilibrium state*.[204,205] See the bottom of Fig. 6.2. The example in the preceding paragraph is a pseudoequilibrium state.

If one simple system is hot water, and if the other is also hot water of similar temperature, then, although the state P of the compound system is not in equilibrium, both simple systems are in quasiequilibrium, so P is in the thermodynamic space of the compound system. Furthermore, there is a (uniform) equilibrium state R sufficiently close to P. Therefore, P is a quasiequilibrium state of the compound system, satisfying (1) and (2) of **6.2**. In this example, if the whole system is in a thermos, and cools gradually, P is not a true equilibrium state of the compound system. Thus it is called a quasiequilibrium state. See Fig. 6.2Top.

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[204] When we discuss a compound system, note that the boundary conditions (walls) between subsystems are included in the definition of the compound system, so we do not touch them.

In the case being discussed here, if the wall between the simple systems totally isolates them, the state is a quasiequilibrium state, because there is an environment to keep it as an equilibrium state of a compound system (e.g., an adiabatic environment). As seen from this example, the magnitude of the relaxation times is the key. If the internal relaxation is quicker than that of the external relation, the system cannot be in a quasiequilibrium state, but a pseudoequilibrium state. In the opposite case, we may regard the state of the compound system as a quasiequilibrium state. Recall the characterization of equilibrium states by Feynman **2.6**.

[205] A pseudoequilibrium state is a state that changes quasistatically, but there is no single bath to maintain an equilibrium state very close to it. We can apply thermodynamics to the process consisting of pseudoequilibrium states, but the process is not generally reversible.

7 ‘The first law’ of thermodynamics

7.1 Sign convention

When energy is added to the system in the ordinary sense of the word (that is, not in an algebraic sense), for example, when you perform work on a system and feel tired, we say that you have done work on the system and that the system has received a positive (+) amount of energy. We say that you have received a negative (−) amount of energy.

From now on, for any extensive quantity, if the system gains the quantity in the ordinary sense of the word, we assume a positive (+) amount of the quantity enters the system. If the system loses the quantity in the ordinary sense of the word, we say that a negative (−) amount of the quantity enters the system.

In other words, our algebraic sign convention is based on a system-centered point of view. [Note that this sign convention is the opposite of Clausius’ convention for his equivalents (→**A.12**).]

7.2 The so-called ‘first law of thermodynamics’

As stated in **A.9** the works of Mayer and Joule led to the recognition that the law of conservation of energy applies to energies beyond mechanical energy; specifically, the sum of (correctly converted) ‘heat’ Q and work W (→**4.12**) is conserved as energy. That is, the increase of the system energy ΔE may be written as $\Delta E = Q + W$. This relation has long been referred to as the *first law of thermodynamics*. Given the tradition of quantitative heat theory preceding Mayer’s and Joule’s works (→**A.2**), it was sensible to summarize the law of conservation of energy in this form.

Within non-thermal macrophysics, energy is a well-defined quantity in electromagnetism and mechanics, and so is work. In contrast, if ‘heat’ is to be quantitated independent of non-thermal macrophysics, as seen in **A.2**, we need ‘temperature.’ However, if we question what temperature is, its relation to the non-thermal macrophysics is quite opaque.[206]

Thus, ‘heat’ remains a mysterious concept in macrophysics unless it is directly

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[206] Needless to say, to understand thermal properties of gases, the kinetic theory of gases was devised according to classical mechanics. It directly connected temperature and kinetic energy, and certainly encouraged the mechanical Weltanschauung (→**1.3**). Still, such ‘speculations’ cannot be used to establish temperature within macrophysics.

related to work.[207]

The measurement of work W is already established in non-thermal macrophysics (→**3.11**). Therefore, the most direct way to define 'heat' is as $\Delta E - W$, provided a means of measuring ΔE is established.

7.3 Energetic equivalence of work coordinates and materials coordinates

The energy change due to any chemical reaction can, in principle, be converted

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[207] That temperature is a measure of extent of molecular motion is not only a meaningless explanation macroscopically, but also not conceptually correct. Quantum mechanically, temperature is not exactly the extent of molecular motion.

⟪How fundamental is scalar temperature as an empirical concept?⟫

Since thermodynamics must be based on macroscopic empirical facts (recall our basic discussions **1.5**-**1.8**), if we wish to construct thermodynamics in terms of the concept directly related to temperature (e.g., 'isothermy'), we must be able to establish the concept purely empirically without thermodynamics and nonempirical assumptions/particular Weltanschauungs.

Today, we believe that "temperature" is a concept that is one-to-one correspondent to a number line (or a part of it). However, it is quite dubious whether this is a purely empirical fact. Biologically, the "scale" of temperature is a synthesis of information obtained from various sensors, and it is not easy to conclude that the result corresponds to a numerical value called temperature. Note that this is very different from the concept of, e.g., "brightness" whose biological sensor can be understood as a photon counter.

We use words to relate the real material world to the world of concepts and mathematics/logic, but words do not exist at the boundary between these two worlds; they belong entirely to one of them. Therefore, no matter how sophisticated the concepts or mathematics we use, we cannot definitively specify the relationship between these two worlds without ambiguity. This is the essential reason why the models of a perfectly formalized logical system are not unique. The relationship between these two worlds is unique only when that relationship is 'God-given,' namely, the relationship between the activity within our nervous system and a property of the world is evolutionarily constructed through natural selection. Without such an intrinsic relation experiences cannot definitively provide concepts. The "temperature concept" lacks this fundamental relation.

Why, then, do we "naturally" think that there is a linear scale for temperature? The author believes that several non-empirical elements are deeply involved in this. Firstly, it is connected to the movement of "fire particles" and alchemical concepts (though it is clear from the history of thermodynamics that it was not considered the same as ordinary heat produced by things like combustion and gunpowder). When this is combined with the mechanical Weltanschauung, it leads to a thermodynamic interpretation of temperature and consequently, the one-dimensional temperature concept is seen as natural. There is a significant degree of implausibility in this being based purely on empirical facts. Subsequently, this temperature concept was established in relation to the second law of thermodynamics.

Therefore, it should not be forgotten that founding thermodynamics on the concept of temperature or the concept of isotherm, as often seen in elementary thermodynamics textbooks, likely involves circular (and at best self-consistent) reasoning and should be a cause for concern.

reversibly and quasistatically to electrical energy.[208] Any reaction, including biochemical reactions, may be understood as a redox reaction, that is, the exchange of electrons (→**26.4**). The energetic equivalence of the ordinary work and chemical work is empirically established by Faraday's law of electrolysis (→**26.3**) and the fact (e.g., **26.6**) that reversible cells can convert chemical energy to electrical energy qV reversibly, where q is the amount of charge involved in the reaction and V the electromotive force of the cell.

Here, 'in principle' is added to the statement, because devising a reversible cell is not always simple. This applies to any chemical reaction; realizing reactions in principle possible is usually hard, particularly if the reactions are interesting and practically important.

7.4 Generalized work done by the external systems to the system

For thermodynamics, the computation of generalized work forms (→**3.10** and **4.12**) for reversible quasistatic processes is dictated by non-thermal macrophysics and chemistry.

Ordinary macroscopic machines are designed to perform macroscopic work with high efficiency even at considerable speeds (→**3.10**). The work form may be computed according to the conventional macrophysics as illustrated in Appendix B after Section 4 (**B.1**, etc.).[209,210]

The energy change due to chemical changes (→**4.12**), the so-called mass action, may be reversibly converted to electrical work, so there is no new conceptual problem (→**7.3**).[211]

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[208] Usually no such general statement is given, but essentially, if all the chemical reactions can be realized as redox reactions, this is possible (→**4.3**III). Note that the 'equivalence' has two aspects. Faraday and Joule were concerned with the conversion rate when chemical energy is converted into work and vice versa. This can be shown even for heat and work, so this type of equivalence cannot say anything as to the asymmetry in the context of the second law (→**17.3**). Needless to say, Faraday and Joule preceded Clausius (before Clausius: BC for thermodynamics).

[209] This does not require that a complete theory for a particular work to be known. What is required is that the relevant work coordinate (extensive quantity) is operationally definable, and that the change of energy without dissipation due to the coordinate modification may be measurable (e.g., we can make a table of the conjugate variable empirically).

[210] Using a lossless generator or motor, mechanical potential energy may be reversibly converted to various forms of work, so ΔE based on (3.11) may be written as Mgh in terms of some mass M and a vertical displacement h, where g is the acceleration of gravity. Therefore, by measuring h, the (generalized) work done to the system by the external system can be, in principle, measured.

[211] Experimentalists took this fact for granted as seen in **A.16**, and theoreticians also did not

Thus, the generalized work done by the external systems to the system can be measured.

7.5 Energy change and work coordinate changes of the system

Even if the (generalized) work, whose amount is ΔE, is done on the system as described in **7.4**, there is no guarantee that the (generalized) work done by the external system was converted to reversible changes of operational coordinates (→**4.12**) of the system. A portion of the added external work ΔE may be dissipated inside the system, converted to 'heat.' Nevertheless, we can measure how operational coordinates of the system have been changed, and the total energy ΔE added to the system is also known. Therefore, if the thermodynamic coordinates of the initial equilibrium state are known, those for the final equilibrium state can also be known.

7.6 Necessity of adiabatic environment[212]

During the process described in **7.4**, the generated 'heat' should not leave the system, nor should 'heat' enter the system from outside. When the added generalized work ΔE (as described in **7.4**) is definite, the final energy of the system must also be increased by ΔE during the experiment. Furthermore, whether a condition for such an agreement (henceforth called an *adiabatic condition* →**7.7**) is met or not must be verifiable experimentally.[213] The environment where an adiabatic condition is met is called an *adiabatic environment*.

7.7 Adiabatic condition, adiabatic process

The wall that can place a system in an adiabatic environment by enclosing it is called an *adiabatic wall*.

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seem to have any questions about it as seen in Helmholtz's exposition (→**A.17**) and in Gibbs' basic thermodynamic paper quoted in **11.10**.

[212] There is an approach to define adiabaticity and energy conservation simultaneously (e.g., Tasaki defines energy through adiabatic work). However, energy was originally defined and its conservation law was established in mechanics (and is the backbone of mechanical Weltanschauung). No concept of adiabaticity is needed for the definition of mechanical energy. The concept of adiabaticity was required when we attempt to go beyond pure mechanics. Therefore, here, in line with our basic policy **1.8**), we presuppose energy before introducing adiabaticity.

[213] These lecture notes pay more attention to the experimental verifiability of concepts and the measurability of various quantities than ordinary thermodynamics textbooks. This is in response to operational criticisms made by Glenn Paquette.

An adiabatic environment refers to an environment in which the total sum of general work exchanged between the system and its surroundings during the process from the initial equilibrium state A to the final reachable[214] equilibrium state B becomes independent of how general work is added during the process (i.e., how energy is added via work), depending only on states A and B.[215]

Here, as long as the starting point A and the endpoint B are the same, any adiabatic process in between is allowed, without restrictions like being quasistatic or reversible. In this case, the general work can be dissipated within the system. The change in energy, ΔE, corresponds to the energy lost by the surroundings in the form of general work, $\tilde{W}$. If the process is quasistatic and reversible, ΔE can be found by integrating the general form of work $\omega + \zeta$ (the general work form for quasistatic processes, (3.11) and (4.1)) along the path

7.8 Adiabatic wall allowing no materials exchange

We may define adiabatic walls as in **7.7**, but to do physics the definition must be operational. That is, we must be able to check experimentally that 'the total sum of the generalized work is constant.'

If the total amount of work W added from outside the system and the total energy ΔE received by the system can be measured, then, in principle, the adiabatic nature of the wall can be verified. The measurement of the work added from outside the system is possible by using operations where non-thermal macroscopic physics can be applied. As for how much energy the system has received, if it can be confirmed that the initial and final equilibrium states A and B are always the same two states, then ΔE will be consistent, and even if its value cannot be directly measured, the adiabatic nature can still be verified.

As is clear from the term "adiabatic," an adiabatic wall means that it blocks the flow of energy in the form of heat. Therefore, in practice, it is sufficient to confirm that if the system enclosed by an adiabatic wall is left without doing any work, its energy remains unchanged regardless of external conditions. This can be verified if the state of the system can be monitored, though it is always preferable to quantify

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[214] Later, as we will see in **C.6** and **C.7**, since there exists an adiabatic process that leads from at least one of the two arbitrary equilibrium states to the other, when a transition from A to B is not possible here, we handle the reverse process.

[215] Later, we will see that in the case of an isothermal process, the work form becomes the complete form (→**18.1**) but this requires the process to be quasistatic and reversible. In the present case, however, there are no such restrictions.

the system's energy change.

7.9 Energy meter property

Let us say that a system has an *energy meter property*, if its intensive conjugate variables $\boldsymbol{y}$ of its operational coordinates $\boldsymbol{Y}$ depend on internal energy (density) injectively under fixed $\boldsymbol{Y}$ (more precisely, their densities).[216]

For example, all the thermometers are energy meters, meaning they have an energy meter property; the so-called gas thermometer has pressure that depends monotonically on the energy density under constant volume, so it is an energy meter.[217]As in this example, all the conjugate variables of operational thermodynamic coordinates are defined and measured within non-thermal macrophysics and chemistry, so we can measure them without knowing thermodynamics. In particular, whether ΔE is identical or not can be observed.

Just as not all the materials can make thermometers, there is no guarantee that all the materials/systems have an energy meter property, but it seems that most systems satisfy this property.

7.10 Non-adiabatic environment

If the system can exchange energy with its environment even without exchange of generalized work, the environment is not adiabatic. The energy exchange without any generalized work in a non-adiabatic environment is called 'heat.' More precisely, if energy transfer is possible without any generalized work, we say energy is transferred as *heat*. In other words, if the total energy change is not solely due to generalized work, the discrepancy $Q = \Delta E - W$ is said to be due to heat exchange.

Note that 'heat' is a mode of exchanging energy. It is not that something called 'heat' flows in or out (in contradistinction to 'caloric' →**A.2**). The energy entering a system as 'heat' and that as generalized work lose their distinction inside the system. However, informally, we say energy is gained as heat, when energy is transferred as heat.

7.11 Quantitating 'heat'

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[216] That is, if $\boldsymbol{y}(E, \boldsymbol{Y}) = \boldsymbol{y}(E', \boldsymbol{Y}) \Rightarrow E = E'$.

[217] The reader might think that the energy meter property is more conveniently defined by the difference in $\boldsymbol{Y}$ under constant $\boldsymbol{y}$. Perhaps. However, measuring $\boldsymbol{y}$ is generally easier than $\boldsymbol{Y}$.

How can we measure the energy exchanged as heat?

Suppose a system enclosed in a wall goes from its initial equilibrium state $(E, \boldsymbol{Y})$ to a final equilibrium state $(E + \Delta E, \boldsymbol{Y}')$ through performing generalized work $\tilde{W}$ on the system. $\Delta E - \tilde{W} = Q$ is the amount of heat the system exchanged with its environment (→**7.10**). $\tilde{W}$ is measurable, because it can be supplied by mechanisms that can be realized quasistatically (→**7.4**).[218]

Thus, for 'heat' Q to be operationally defined, the problem is how to measure ΔE. If the system is an energy meter (→**7.9**), measuring conjugate variables, we can determine ΔE.

7.12 Thermal contact, hotter/colder

A contact between two systems that is not adiabatic and that does not allow exchange of any operational coordinates (→**4.12**) is called *thermal contact*. Suppose two systems are in thermal contact but are isolated as a whole. After a long time the whole system (generally as a compound system) would reach an equilibrium state. We say the two systems reach a *thermal equilibrium*.[219] What happens during the thermal contact is that one system loses energy Q as heat, and the other gains energy Q as heat.[220] This Q may be measured as explained in **7.11**.

When two systems are in thermal contact, the system losing energy is called a *hotter system* and the other a *colder system*. The hotter-colder relation is solely determined by the individual states of the two systems before thermal contact. The final state is unique thanks to the zeroth law **2.9**, so the hotter-colder relation is a reproducible relation; Whenever the same experiment is repeated, the same side is always hotter or colder. Note that the concepts 'hotter' and 'colder' are so far not related to any kind of temperature.[221]

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[218] 'Quasistatically' for the environment or the external devices to supply work; this does not necessarily mean that the process is quasistatic for the system itself.

[219] Notice that this does not mean that the two systems are in equilibrium under any contact; they are in equilibrium only with respect to the exchange of heat.

[220] This is a figurative expression. Formally, it should be said that energy Q has been transferred in the form of heat conduction, rather than saying "heat was given or taken." Historically, Black recognized the importance of thermal equilibrium (→**A.2**).

[221] If we write that system A is hotter than B as $B <_H A$, this provides an order (however, here, we do not assume this): suppose there are three equilibrium systems A, B and C, with $C <_H B <_H A$. In this case, $A <_H C$ does not hold. This is one expression of the second law of thermodynamics.

7.13 Are work and heat always distinguishable?

Up to this point all the statements have assumed that, as a mode to transfer energy, heat and work can always be distinguished, but this is not always true. If the change of a state is violent, then the spatiotemporal scale of the system state inhomogeneity could range from microscopic to macroscopic, making the distinction between heat and work ambiguous. However, in thermodynamics, we assume the distinction is clear, or, we discuss only ‘slow’ changes with the clear distinction between work and heat.

Here, ‘distinction’ means that heat and work may be distinguished as different modes of transferring energy.[222] Once inside the system, the distinction is lost. It was once thought that heat was a flow of a special element called ‘caloric,’ so even after energy transfer as heat ‘caloric’ remained in the system. However, the idea lost popularity after Mayer and Joule (→**A.9**), especially after Joule’s detailed experiments demonstrated convincingly that heat and work quantitatively interchange.

However, if the heat-work conversion does not happen, the total amount of heat a system exchanges with its environment is conserved (due to energy conservation), so heat treated as a conserved quantity (just as thought in the caloric theory) is still effective (as Black originally assumed →**A.2**).

7.14 Conservation of energy in thermodynamics

The quantitative definition of heat in **7.11** determines Q to satisfy the conservation of energy. Therefore, the so-called first law of thermodynamics $\Delta E = W + Q$ is no longer considered as a law of physics.

Then, what is the core empirical fact intrinsic to thermodynamics? It is the principle to be called the *Mayer-Joule principle* (→**A.9**): “Work can always be converted to heat at a definite conversion rate.” Chemical work is a type of work (→**4.12**). The generated heat can be added to any system, so the Mayer-Joule principle should read precisely as:

> Generalized work can be converted to heat at a universal constant conversion rate and added to any system.[223]

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[222] Operationally, that is, we can invent an adiabatic wall (→**7.8**).

[223] In ordinary textbooks, it is almost never stated that “it can be added to any system.” However, without this statement, there is no guarantee that heat can be added to any system, no matter how high its temperature is. It is necessary to ensure that a heat source of any high temperature can be made possible through the dissipation of work.

The law of conservation of energy incorporating this principle is the so-called 'first law of thermodynamics.'[224]

In summary:

(i) Using generalized work (→**7.4**) and adiabatic processes (→**7.7**), the change of internal energy can be measured (→**7.9**). And
(ii) If the process is not adiabatic, the change of internal energy and the net generalized work added to the system can be different, and the discrepancy is defined as 'the energy transfer as heat' (→**7.11**).
(iii) Generalized work may always be converted to heat with a definite conversion rate (the Mayer-Joule principle), and
(iv) (ii) and (iii) are consistent with the law of conservation of energy of the non-thermal macrophysics and chemistry.

7.15 Comparison of mechanical energy and thermal energy

Suppose a mass of 1 kg is running at speed 100 km/h. Its kinetic energy is 386 J. If this mass is water and is heated with the thermal energy obtained by converting this kinetic energy, its temperature will not increase even by 0.1 K (actually about 0.092 K). This illustrates how thermal energy is 'much greater' than 'macroscopic mechanical energy.' Therefore, even the utilization of a 'tiny amount' of thermal energy can produce huge amount of work. This tells us how heat engine was revolutionary for humankind.[225]

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[224] However, in thermodynamics, we wish to restrict the number of coordinates as few as possible, so excessively violent changes must be avoided.

[225] It is understandable that the steam locomotive became a symbol of civilization. The opening of the final movement of Dvorák's Symphony No. 9 ("From the New World," 1893) is a depiction of a steam locomotive setting off (as heard in Abbado's performance with the Berlin Philharmonic: `https://www.youtube.com/watch?v=S5sB4B2lCaQ`).

8 The second law of thermodynamics

8.1 The second law of thermodynamics: preliminary

Clausius' work (→**A.10**) demonstrating Carnot's theorem (→**A.8**) in a consistent fashion with the Mayer-Joule principle (→**A.9**) clearly established that 'heat' is a special mode of energy transfer. Clausius' logical core, in his own words, goes 'through basically the same line of thought': if we deny Carnot's theorem, then we would have to accept a process that is highly improbable in reality.

Today, we demand that "a process highly improbable in reality" never happens as a principle called the *second law of thermodynamics*. As we will see below, there are various forms of the principle, but all are equivalent.[226]

8.2 The second law must explicitly consider materials coordinates as well

The ordinary electromagnetic and mechanical work may be reversibly and quasistatically converted to chemical energy through electrochemistry. This is possible due to Faraday's law of electrolysis and the existence of reversible electric cells (→**A.16**, e.g., **26.6**).

Consequently, there is no difficulty of principle nature to extend the first and the second laws of thermodynamics to handle materials coordinates (→**4.12**). Needless to say, however, the laws must clearly include chemistry as well.

There are two important points to pay special attention:

(1) The usual statement of the principles does not particularly quote any relevant empirical facts, but do not forget that the relation between the ordinary work and chemical work mentioned above requires empirical support.

(2) We must not forget the peculiar nature of 'chemical coordinates' (→**4.8**, **4.10**).

In steam engines and internal combustion engines, the generation of heat through combustion is essential for the conversion of 'chemical energy' into mechanical energy. If the transfer of energy in the form of heat were indispensable in this conversion process, we would have to acknowledge that the current system of thermodynamics is fundamentally altered.

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[226] If not, what would happen? As long as all the natural phenomena are related, we would be able to violate (or overcome) the second law.

8.3 Clausius' principle

Prepare a hotter system and a colder system (→**7.12**). *Clausius' principle* may be stated as:

> "It is impossible to transfer energy as heat from a colder system to a hotter system without leaving any trace in the surrounding world (environment)."

In thermodynamics what is not forbidden by its principles may happen. Thus, "It is allowed to transfer energy as heat from a hotter system to a colder system without leaving any trace in the surrounding world." Also, "It is possible to transfer energy as heat from a colder system to a hotter system with some trace left in the surrounding world." Such statements are absolutely required to make thermodynamics self-contained. However, it is unclear whether the above principle implies these 'positive statements' as well.

8.4 Metaprinciple of thermodynamics

In **8.3** is a rather strong statement, "anything that is not forbidden by its principles may happen," but since no exception to this statement is known, we should accept this statement as an empirical principle about all the principles of thermodynamics. Therefore, we demand *metapriciple of thermodynamics*:

> "Negation of anything that thermodynamic principles explicitly forbids is allowed."

Here, it is important not to ignore the word "explicitly" in the metaprinciple to prevent any misuse of the principle.[227]

8.5 Planck's principle

Planck's principle is conventionally stated as:

> If work coordinates do not change before and after the adiabatic process, the system internal energy cannot decrease.

However, there is no reason to exclude materials coordinates, so the law is revised as follows:

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[227] For example, while thermodynamics does not address anything about nonequilibrium phenomena, it should not imply anything can happen in nonequilibrium. Thermodynamic principles do not say anything about the relation between W (work) and Z (mass action →**17.1**), so the metaprinciple does not imply that there is no constraint between the mutual conversion of them. Thus, we must say something about their relation explicitly, if we adopt the conventional second laws that do not mention anything about chemistry.

> If operational coordinates (→**4.13**) do not change before and after the adiabatic process, the system internal energy cannot decrease.

As stated in **4.8**, note that this *does not fix* the chemical composition variables of the system. In fact, if work coordinates return to the original values, and if chemical composition variables also return to their original values, then, generally speaking, the system internal energy cannot change,[228] so this principle loses its significance considerably. Note further that the system need not be closed materially throughout the process; only before and after the process the materials coordinates of the system must be 'the same'[229] (→**4.8**).

This principle, together with the metaprinciple **8.4**, implies that as long as the state is in $\mathcal{E}$, the internal energy may be increased without altering the operational coordinates before and after the process.[230]

Remark 1 Note that this is not a principle solely for closed systems. Furthermore, chemical reactions may occur freely. The conventional thermodynamic textbooks never mention materials changes/chemical reactions in conjunction to the second law. When the second law is introduced, at least a clear statement about the 'equivalence' of work and mass action in contradistinction to heat must be made.

Remark 2: 'Halting chemical reactions at will' cannot save chemical thermodynamics The standard approach, when stated honestly, explicitly demands that we can halt chemical reactions at any time without disrupting the system equilibrium (→**4.15**). With this demand + the conventional Planck's principle mentioned at the beginning of this unit, can we develop chemical thermodynamics? Since reactions can be halted at any time, we can treat chemical composition variables and internal energy as independent variables. Thus, even with chemical reactions present in the system, the conventional Planck's principle can be made meaningful. However, the principle makes sense only while the reactions are suspended. To discuss the true chemical equilibria of the system we must release the chemistry from our artificial grip and allow the chemical reactions to proceed. Unfortunately, at that point, the conventional Planck's principle loses its significance considerably as already pointed out, since nothing is stated about chemical reactions. Thus, in the conventional thermodynamics framework in the textbooks, logically speaking, we are forced to

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[228] Recall $\tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$, so fixing $\boldsymbol{X}$ and $\boldsymbol{N}$ makes $\tilde{\boldsymbol{N}}$ a function of E.

[229] The choice of materials coordinates for a given state is not unique (→**4.8**, especially the footnote), so what is meant by 'the same' is that we can choose the identical materials coordinates before and after the process.

[230] This corresponds to S1: the existence of irreversible process of Lieb and Yngvason.

develop chemical thermodynamics without the second law.

8.6 Clausius' principle implies Planck's principle

If Planck's principle does not hold, we can decrease the system internal energy adiabatically without changing the operational coordinates. Since we cannot export energy as heat adiabatically, the system must have performed some (generalized) work on its environment. That is, we can extract work without modifying the operational coordinates.[231]

Prepare a colder heat bath (→**8.8**)[232] and a hotter heat bath (Fig. 8.1).

(i) Bring the system and the colder heat bath into thermal equilibrium through thermal contact (→**7.12**).

(ii) Then, thermally isolate the system from the heat bath and obtain work adiabatically from the system without changing its operational coordinates (violating Planck's principle).[233]

(iii) Next, bring the system into thermal contact with the colder heat bath; note that the procedure can bring the system completely to the original state as prepared in (i); here we have used the uniqueness of the equilibrium state **2.9**. If heat flows out from the system or there is no heat exchange at all, the first law (the conservation of energy) is violated, so to return to the original state given in (i) the heat must be brought to the system from the heat bath. Thus, the colder heat bath must have lost energy as heat, which was already converted to generalized work. Therefore,

(iv) We can then add this work as heat to any hotter heat source according to Mayer-Joule's principle (→**7.14**), violating Clausius' principle.

Therefore,[234] if Clausius' principle holds, Planck's principle must hold as well.

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[231] **⟪Need for proper description of the materials stage of the system⟫** [Remark 2 in **8.5** repeated] If we choose chemical composition variables $\tilde{\boldsymbol{N}}$ instead of $\boldsymbol{N}$ (→**4.15**) as basic thermodynamic coordinates just as in the conventional (i.e., all the existing) textbooks, no change of energy while fixing the chemical composition variables is generally possible; that is, Planck's principle loses its significance considerably. This difficulty cannot be removed even if chemical reactions may be halted at any time as assumed in the standard textbooks.

[232] The concept of 'heat bath' is discussed in **7.12**. A heat bath is a system making only thermal contact with another system and does not change its own thermal property: that is, its 'hotter' or 'colder' relation (→**8.3**) with any other systems does not change even if heat is exchanged with something else.

[233] Notice that this may not be a cycle for the chemical composition; the system may have done electrochemical work.

[234] Recall $(\neg B \Rightarrow \neg A) \iff (A \Rightarrow B)$. For example, "If not mortal, it is not alive." This means "if alive, it is mortal." This is the relation between a proposition and its contraposition. This

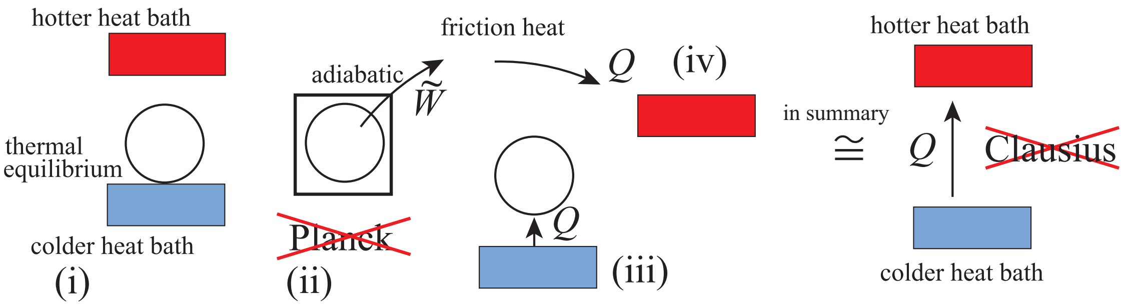

Figure 8.1: Clausius' principle implies Planck's principle

Fig. 8.1 Clausius' principle implies Planck's principle.

(i) Bring the system and the colder heat bath in thermal equilibrium through thermal contact.

(ii) Then, thermally isolate the system and obtain (generalized) work $\tilde{W}$ from the system without changing its operational coordinates (violating Planck's principle).

(iii) Next, bring the system in thermal contact with the colder heat bath again; Heat Q flows to the system, whose state returns to that in (i), but the heat Q was converted to $\tilde{W}$ in (ii). [Incidentally, Thomson's principle (→**8.7**) is also violated, so Thomson's principle is shown to imply Planck's principle.]

(iv) We can add $\tilde{W}$ as heat to any hot heat source according to Mayer-Joule's principle (→**7.14**), violating Clausius' principle.

8.7 Thomson's principle

Thomson's principle may be stated as[235]

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relation is always used in the demonstration of the equivalence of the principles in thermodynamics (→**8.9**, **8.10**, **8.13**).

[235] ⟨⟨**Thomson's and Planck's principles and chemical reactions**⟩⟩ The conventional Thomson's principle is stated without taking any chemical reactions into account, but we must explicitly state 'generalized work' in the principle to construct chemical thermodynamics properly.

Tasaki requires the following form of 'Kelvin's principle' (Premise 3.1):

> For any isothermal cycle at any temperature, the system cannot do any positive work to its environment.

This form of Kelvin's principle remains legitimate if the work is replaced with generalized work, including chemical reactions. That is, the presence of chemical reactions with the chemicals described in terms of chemical composition variables $\tilde{\boldsymbol{N}}$, as in all the existing textbooks, does not cause any problem.

However, to establish the presence of entropy, his isothermal system requires Planck's principle or its precursor premise 4.1 (in our notations):

> It is impossible to do generalized work without leaving any trace other than absorbing heat from a single heat bath.

Here, the condition “without leaving any trace” is quite important (Fig. 8.2); for example, if we warm a balloon, we can do some work with a single heat bath, but after doing the work, the balloon stays inflated, so the production of work with a single heat bath in this case does not violate Thomson’s principle.

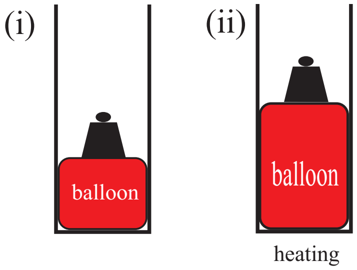

Figure 8.2: Doing work with a single heat source ‘with a trace’

Clausius regarded a ‘work source’ (a device to produce work) as the heat bath hotter than any ordinary heat baths (→**A.12**), so it cannot absorb heat from any heat bath. In this sense, Clausius’ principle implies Thomson’s principle.

The metaprinciple (→**8.4**) implies, for example, “If there are several heat baths not mutually in thermal equilibrium, we can make a device producing (generalized) work without leaving any trace other than exchanging heat with these heat baths.”

8.8 Heat source or heat bath

We have already used heat sources or heat baths. A heat bath is a constant temperature environment[236] in thermal contact with a system. While in modern times, it can

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> Let $(T, \boldsymbol{X})$ be an arbitrary equilibrium state with temperature T. For any T' such that $T' > T$ there is an adiabatic process that transforms $(T, \boldsymbol{X})$ to $(T', \boldsymbol{X})$. Furthermore, during this process the system must obtain positive work from its environment.

If we wish to study chemical reactions as well, we need not only $\boldsymbol{X}$ but also the variables designating the chemical composition of the system.

Needless to say, we know if $T \neq T'$, then, generally speaking, not both $(T, \boldsymbol{X}, \tilde{\boldsymbol{N}})$ and $(T', \boldsymbol{X}, \tilde{\boldsymbol{N}})$ can be equilibrium states due to chemical equilibrium shifts. Thus, his thermodynamic system does not generally handle chemical reactions.

[236] Precisely speaking, we do not know what temperature is. Therefore, although we continue to use this informal expression as in the text, to be logical, we must say that the heat bath is a system whose hotter/colder relation with any other systems never changes upon thermal contact.

be realized as a heat pad with high-speed feedback regulation of its temperature, it is essentially an idealized version of a constant temperature bath. We may imagine a sufficiently large well-stirred water tank, maintained at a constant temperature. However, a heat bath is assumed to be in an equilibrium state at a constant temperature despite interacting with a system. Hence, it cannot be of finite size. Therefore, math-inclined people argue that using such an unrealistic device in the foundational theory of physics is inappropriate.

Consequently, to be precise, theoreticians introduce an increasing sequence of baths and its limit is understood as the idealized heat bath. In practice, a sufficiently large well-stirred bath realizes the idealized heat bath quite accurately.[237]

An ingenious strategy is to use the first order phase transition (→**23.4**), exemplified by Laplace's ice calorimeter (Fig. 8.3). It is a good example, and also historically the first one. Some people criticize this idea as a cheat, since it relies on very special materials properties of particular substances. However, the materialistic diversity of our world is real and is its essential feature. Since continuous fine-tuning of phase transition temperatures is possible, we should note that any heat bath can be devised with Laplace's idea, in principle.

From the system's perspective, the heat bath assisted by first-order phase transitions cannot be distinguished from suitable heat pads when high-speed feedback control is employed.

In any case, since the idea of heat bath is quite natural, heat baths will be used freely without any hesitation throughout this book.

Fig. 8.3 Laplace's ice calorimeter

Left: According to the figure: "The Calorimeter of Lavoisier and La Place, 1801" in Wikipedia Calorimeter (however, the original has been cleaned). A contains ice-water and B contains 0 °C ice. A contains the ice to realize adiabaticity, so the formed water is discarded through the spout, if necessary. The water due to the melting in B is collected by the container and is weighed.

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[237] Mathematical limits in thermodynamics should be taken with a grain of salt. As discussed in **6.5**, thermodynamic infinitesimal is not really mathematical infinitesimal. Consequently, 'infinite' in thermodynamics should be understood as the reciprocal of 'thermodynamic infinitesimal.' That is, it is very big but finite, but the 'temperature fluctuation' of a heat bath is invisible from our scale.

In other words, mathematics (analysis) of thermodynamics is mathematics with errors, but those errors cannot be systematically collected to build something we cannot ignore at our scale.

However, no systematic and consistent development of 'thermodynamic math' is yet available, so we use the usual analysis.

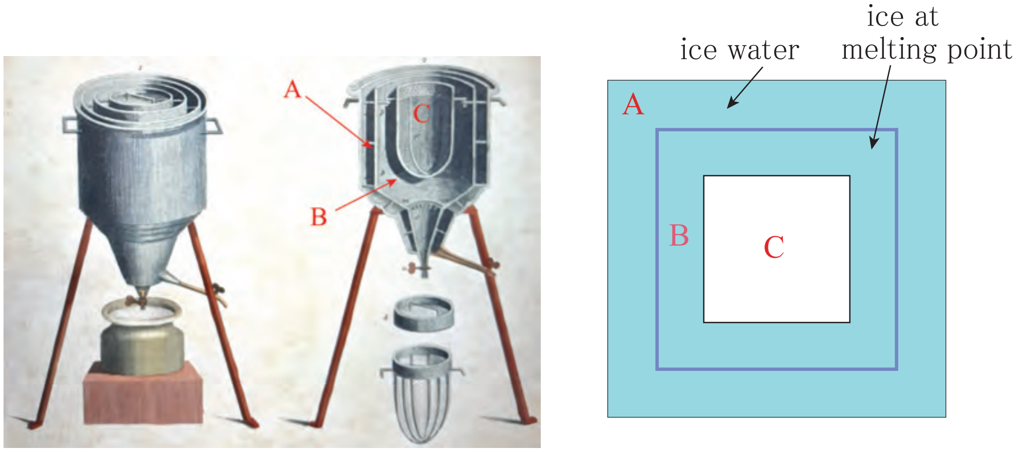

Figure 8.3: Laplace's ice calorimeter

Right: a schematic figure. Both A and B are maintained at 0 °C due to the melting ice, so no net heat exchange exists between them. That is, B+C is an adiabatic system. The melting of the 0 °C ice in B is used to measure the heat generated in C. A is used as a heat bath kept at 0 °C.

8.9 Planck's principle implies Thomson's principle

If Thomson's principle (→**8.7**) does not hold, we can prepare a single heat bath engine. This engine may be joined with a heat storage device that does not change its operational coordinates while absorbing or releasing heat.[238] After supplying heat to the heat storage, we can enclose the engine and the heat storage with adiabatic walls and consider the whole as a single adiabatic system. Operating the system we can produce work adiabatically without changing the operational coordinates of the system (→Fig. 8.4). Therefore, Planck's principle is violated. Thus, if Planck's principle holds, then Thomson's principle must also hold.

Fig. 8.4 Planck's principle implies Thomson's principle.

(i) Maintaining the operational coordinates of the heat storage, heat Q is introduced to it from the external heat source.

(ii) The total system is thermally isolated, and then the single-heat source engine is operated to convert heat Q to generalized work $\tilde{W}$.

As a single system, this process violates Planck's principle.

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[238] Precisely speaking, as noted in **C.3** explicitly, we must assume that we can, in principle, change the system internal energy without changing its operational coordinates. This assumption is not an artificial one and has already been used to state Planck's principle (→**8.5**).

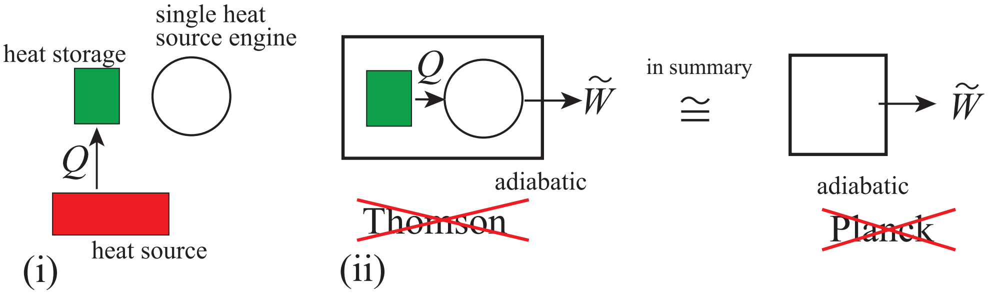

Figure 8.4: Planck's principle implies Thomson's principle

8.10 Thomson's principle implies Clausius's principle

Thomson's principle (+ metaprinciple **8.4**) allows us to prepare a heat engine that produces work W while absorbing heat Q from a hotter heat source and discarding (appropriate amount of) heat Q' to a colder heat source **8.7**).[239] If we assume that Clausius's principle can be violated, then heat Q' may be transferred to the hotter heat bath without leaving any trace other than this heat transfer (Fig. 8.5). Thus, we have realized a single heat source engine,[240] so Thomson's principle is violated. Thus, if Thomson's principle holds, so does Clausius' principle.

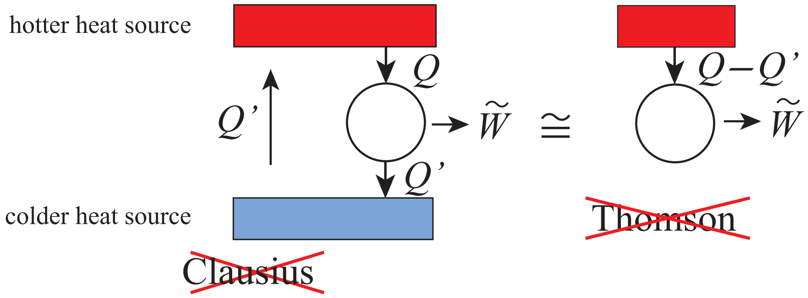

Figure 8.5: Thomson's principle implies Clausius' principle

Fig. 8.5 Thomson's principle implies Clausius' principle.
If we deny Clausius' principle, the exhaust Q' of engine may be returned to the hotter heat source, and we can realize the single heat source engine, violating Thomson's principle.

8.11 Three principles are equivalent

So far, we have demonstrated Clausius ⇒ Planck ⇒ Thomson ⇒ Clausius (→**8.6**, **8.9**, **8.10**). Therefore, all the principles are equivalent.

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[239] This does not mean that any choice of W, Q, Q' such that $W = Q - Q'$ is possible as Carnot's theorem (→**A.8**) implies.

[240] We could even transfer heat from the colder to the hotter heat bath, while producing work.

8.12 Isn't there any revision of Clausius' principle due to chemical reactions?

As already stated in **8.5** (especially Remark 2) and **8.7**, both Planck's and Thomson's principles, as presented in conventional textbooks, require revision in the world where chemistry is relevant. How about Clausius' principle?

Clausius' principle holds true in any world with or without chemistry, and thus does not require revision. However, the principle is equivalent to other principles in a particular world, so even if we can demonstrate the equivalence of Clausius' principle with, say, Planck's principle in a world without chemistry (that is the usual version of this principle), this demonstration is meaningful only in such a world.[241]

8.13 Carnot's principle

In the paper that established thermodynamics, Clausius demonstrated that if there were a heat engine that was more efficient than a reversible engine, (the so-called) Clausius' principle would be violated (→**A.10**) as explained in Fig. A.3. Since the second law of thermodynamics follows from Carnot's theorem that there is no engine more efficient than a reversible engine (see just below), We may call "There is no more efficient engine than a reversible engine," or more simply, "The efficiency of a heat engine has an upper bound less than 1" as Carnot's principle.

To derive Clausius' principle from Carnot's principle is trivial now. If we deny Clausius' principle, Thomson's principle is violated, so we can make a heat engine whose efficiency is 1, thus violating Carnot's principle. Therefore, all the principles so far stated are equivalent: Carnot $\equiv$ Clausius $\equiv$ Thomson $\equiv$ Planck.

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[241] A metaphor: in an additive group G the unit element '0' must satisfy $0 + x = x$ for any $x \in G$, so for a finite field, $\mathbb{Z}_p$ (p for a prime) the same law must hold, but the proof that something is equal to 0 in a finite field may not necessarily apply to the real field $\mathbb{R}$.

9 Partial derivatives and differential forms

From now on, we need rudiments of analysis of multivariable functions.[242] Thus, necessary mathematical topics are collected here for convenience. This is not a comprehensive introduction to the subject, so the reader is expected to have studied serious introductory textbooks on analysis. The reader may skip this section, and return to it later, if needed.[243]

9.1 Partial derivative and directional derivative

The reader is expected to be familiar with the rudiments of multivariable analysis, e.g., continuity of multivariable functions.[244] Partial differentiation is assumed to be well understood; for example, the partial differentiability of a two variable function $y = f(x_1, x_2)$ with respect to x_1 is the differentiability of f with fixed x_2 as a single variable function of x_1.[245]

Along a line we may interpret f as a single variable function. If it is differentiable, the derivative along the line is called the *directional derivative*. The directional derivative along a specific coordinate direction is the usual partial derivative.

One challenge with multivariable functions is that partial differentiability of a

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[242] Here, we perform multivariable analysis in the thermodynamic space, but for that, we need to introduce a topology into the thermodynamic space. For this purpose, the thermodynamic space is set up as a Euclidean space in **5.2**.

[243] Lieb and Yngvason [The physics and mathematics of the second law of thermodynamics, Phys. Rep. **310**, 1 (1999)] write on p10: “Giles’ work and ours use very little of the calculus. Contrary to almost all treatments, and contrary to the assertion (Truesdell and Bharata, 1977) that the differential calculus is the appropriate tool for thermodynamics, we and he agree that entropy and its essential properties can best be described by maximum principles instead of equations among derivatives. To be sure, real analysis does eventually come into the discussion, but only at an advanced stage (Section 3 and Section 5 in our treatment).”

The author agrees with them, if we do not worry about how work and energy are obtained in the macroscopic physics or how macroscopic physics is practiced. However, it is important to recognize that thermodynamics is not a standalone discipline separate from physics and chemistry (→**1.8**). Therefore, it is natural to express work in terms of the work form (→**3.10**). Consequently, analysis becomes an integral part of this exposition.

[244] In order to freely perform multivariable analysis in thermodynamic space, an appropriate topology must be defined for the thermodynamic space. Therefore, in **5.2**, Euclidean properties are assumed.

[245] Needless to say, for this to be possible, x_1 and x_2 must really be independent. It is a trivial statement, but, as we will see later, we must take it very seriously as alluded in **9.7**.

function at a point does not even guarantee its continuity there. Even if all the directional derivatives at the origin is well defined, the function may not be continuous at the origin. See

$$f(x,y) = \begin{cases} x^2y/(x^4+y^2) & \text{if } (x,y) \neq (0,0) \\ 0 & \text{if } (x,y) = (0,0) \end{cases} . \tag{9.1}$$

In this case, along any line going through the origin f goes to zero continuously, but along $(x,y) = (t,t^2)$ with $t \to 0$ f goes to $1/2$ at the origin.[246]

9.2 Notation for partial derivatives in thermodynamics

In mathematics, the partial derivative of $f(x,y)$ with respect to x and y are written, respectively, as

$$\frac{\partial f}{\partial x} \text{ and } \frac{\partial f}{\partial y}. \tag{9.2}$$

In this notation the former is understood that y is kept constant, and the latter x.

In the tradition of thermodynamics, however, the independent variables kept constant are explicitly designated as

$$\left(\frac{\partial f}{\partial x}\right)_y \text{ and } \left(\frac{\partial f}{\partial y}\right)_x. \tag{9.3}$$

The reason is that in thermodynamics, when f is differentiated with respect to x, what is fixed may not be y, but something else, say, $z = x - y$. In mathematics, in such a case f is regarded as another function g of x and z such that $f(x,y) = g(x,z)$ and the partial derivative must be written as

$$\left(\frac{\partial f}{\partial x}\right)_z = \frac{\partial g}{\partial x}. \tag{9.4}$$

Example: Let $f(x,y) = (x^2 - y^2)\tan y$ and $z = x - y$. Compute the following partial derivatives in the thermodynamic notation and express them in terms of x and y.

$$\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial x}\right)_z, \left(\frac{\partial f}{\partial z}\right)_x. \tag{9.5}$$

Answer:

$$\left(\frac{\partial f}{\partial x}\right)_y = \frac{\partial f}{\partial x} = 2x\tan y \tag{9.6}$$

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[246] taken from R. E. Gelbaum and J. M. H. Olmsted, *Counterexamples in Analysis* (Holden-Day, Inc., San Francisco, 1964). This is a very useful book.

is clear. To differentiate f with respect to x while keeping z constant means that $f(x,y)$ is rewritten as a function of x and z as $g(x,z)$:

$$g(x,z) = f(x, x-z) = z(2x-z)\tan(x-z) \tag{9.7}$$

and then partial differentiate it with respect to x. Therefore,

$$\left(\frac{\partial f}{\partial x}\right)_z = \frac{\partial g}{\partial x} = 2z\tan(x-z) + z(2x-z)/\cos^2(x-z) = 2(x-y)\tan y + (x^2-y^2)/\cos^2 y, \tag{9.8}$$

$$\left(\frac{\partial f}{\partial z}\right)_x = \frac{\partial g}{\partial z} = 2(x-z)\tan(x-z) - z(2x-z)/\cos^2(x-z) = 2y\tan y - (x^2-y^2)/\cos^2 y. \tag{9.9}$$

In passing, why don't you confirm the commutativity of partial derivatives below (**9.6**) in this case? Indeed, we have

$$g_{xz} = g_{zx} = 2\tan y - 2(x-2y)\sec^2 y - 2(x^2-y^2)\tan y \sec^2 y. \tag{9.10}$$

Why does not thermodynamics adopt an explicit function designation as in standard mathematics?

In mathematics f is a symbol for a function, and a function is defined including its independent variables (and the domain), but in thermodynamics the symbol f denotes a particular physical quantity such as internal energy E or pressure P and not simply a function. Therefore, its independent variables depend on various situations. For the above example f and g are distinct as functions, but if they denote the same physical quantity, they are denoted by the identical symbol f in thermodynamics. This can make it unclear what the independent variables are when partial derivatives are computed. That is why the notation as (9.3) is essential in thermodynamics.

9.3 Strong differentiability

For a multivariable function to have a tangent plane at a point, it is quite insufficient that the function is partial differentiable at the point (recall the example in **9.1**). If a multivariable function has a tangent plane at a point, it must be *strongly differentiable* there:[247] Let $\Delta f = f(x_1 + \Delta x_1, x_2 + \Delta x_2) - f(x_1, x_2)$. If we can choose

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[247] In mathematics, if we simply say a function is differentiable, it means strong differentiability. In these notes, however, to emphasize the distinction from the mere existence of all the partial derivatives the term 'strong differentiability' will be used to imply differentiability in the standard mathematics sense.

constants A and B such that

$$\Delta f = A\Delta x_1 + B\Delta x_2 + o\left[\sqrt{\Delta x_1^2 + \Delta x_2^2}\right] \tag{9.11}$$

holds,[248] then we say f is strongly differentiable at (x_1, x_2). That is, strong differentiability means that we can use a linear approximation of the function locally.

If f is strongly differentiable, A and B are given by partial derivatives, so we write

$$df = \frac{\partial f}{\partial x_1}dx_1 + \frac{\partial f}{\partial x_2}dx_2, \tag{9.12}$$

and call df the *total derivative* of f. Do not forget that for this to hold, partial differentiability is not enough, but we need strong differentiability of f.

9.4 Condition for strong differentiability

Theorem If all the partial derivatives of a function exist at a point and are all continuous there, then the function is strongly differentiable there.

Let us demonstrate this for a two variable function. If we apply the mean value theorem for x_1 and x_2, respectively, to

$$\begin{aligned}\Delta f &= f(x_1 + \Delta x_1, x_2 + \Delta x_2) - f(x_1, x_2) && (9.13)\\ &= [f(x_1 + \Delta x_1, x_2 + \Delta x_2) - f(x_1, x_2 + \Delta x_2)] + [f(x_1, x_2 + \Delta x_2) - f(x_1, x_2)], && (9.14)\end{aligned}$$

we can write with $\theta, \theta' \in (0, 1)$

$$\Delta f = f_{x_1}(x_1 + \theta\Delta x_1, x_2 + \Delta x_2)\Delta x_1 + f_{x_2}(x_1, x_2 + \theta'\Delta x_2)\Delta x_2. \tag{9.15}$$

Here, the standard abbreviations for partial derivatives are used:

$$\frac{\partial f}{\partial x} = f_x, \quad \frac{\partial^2 f}{\partial x \partial y} = f_{yx} \text{ [note the order of independent variables], etc.} \tag{9.16}$$

Since we have assumed that the partial derivatives are continuous, when Δx_1 and Δx_2 tend to zero, we see (9.15) converges to (9.12). It should be clear that even if the number of variables is more than two, the same logic applies.

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[248] o: A quantity $q(x)$ dependent on x satisfies $q(x) = o[x]$ near $x = 0$, if $\lim_{x\to 0} q(x)/x = 0$. In other words, $q(x) = o[x]$ means that q is a higher order infinitesimal than x. For example, $x^{1.01} = o[x]$.

9.5 The expression of total derivative in terms of gradient

For an n-variable function f that is partial differentiable

$$\mathrm{grad} f = \left(\frac{\partial f}{\partial x_1}, \cdots, \frac{\partial f}{\partial x_n} \right) \tag{9.17}$$

is called the *gradient* (or the *gradient vector*) of f at $x = (x_1, \cdots, x_n)$. In terms of the gradient vector, the total derivative (9.12) reads (if f is strongly differentiable →**9.3**)

$$df = \mathrm{grad} f \cdot dx. \tag{9.18}$$

The multivariable Taylor expansion of f around x_0 to the first order may be written as

$$f(x) = f(x_0) + \mathrm{grad} f(x_0) \cdot (x - x_0) + o[\|x - x_0\|], \tag{9.19}$$

where $\|\ \|$ implies the Euclidean metric.

9.6 Exchanging the order of partial differentiations

Since the partial derivative $\partial f/\partial x_1$ is a function of x_1 and x_2, we may conceive their partial derivatives (second order partial derivatives). The same applies to $\partial f/\partial x_2$ as well. Then, we can make two 'mixed' second-order partial derivatives, partial differentiation with x_1 first or that with x_2 first.

Theorem If $f_{x_1 x_2}$ and $f_{x_2 x_1}$ are both continuous in a domain, then $f_{x_1 x_2} = f_{x_2 x_1}$ in the domain.

We can show this as follows. In a neighborhood of a point (a, b) in the domain, let

$$\Delta = f(a + \Delta x_1, b + \Delta x_2) - f(a + \Delta x_1, b) - f(a, b + \Delta x_2) + f(a, b). \tag{9.20}$$

Applying the mean value theorem with respect to x_1 to $f(x_1, b + \Delta x_2) - f(x_1, b)$, we can choose $\theta \in (0, 1)$ such that

$$\Delta = \Delta x_1 [f_{x_1}(a + \theta \Delta x_1, b + \Delta x_2) - f_{x_1}(a + \theta \Delta x_1, b)]. \tag{9.21}$$

Applying the mean value theorem with respect to x_2, we can choose $\theta' \in (0, 1)$ such that

$$\Delta = \Delta x_1 \Delta x_2 f_{x_1 x_2}(a + \theta \Delta x_1, b + \theta' \Delta x_2). \tag{9.22}$$

Using the assumption about the continuity of the second order partial derivatives, we have

$$\lim_{(\Delta x_1,\Delta x_2)\to(0,0)} \Delta/\Delta x_1\Delta x_2 = f_{x_1x_2}(a,b). \tag{9.23}$$

If we repeat the same computation starting with x_2 instead of x_1, we get

$$\lim_{(\Delta x_1,\Delta x_2)\to(0,0)} \Delta/\Delta x_1\Delta x_2 = f_{x_2x_1}(a,b). \tag{9.24}$$

Remark In thermodynamics, the continuity of second-order partial derivatives cannot always be assumed. Therefore, $f_{x_1x_2} = f_{x_2x_1}$ is not guaranteed. W. H. Youngshowed that $f_{x_1x_2} = f_{x_2x_1}$ holds if all second-order partial derivatives exist and at least one of $f_{x_1x_2}$ or $f_{x_2x_1}$ is continuous, thereby relaxing the conditions somewhat. Nonetheless, the principles of thermodynamics and second-order differentiability alone do not suffice to conclude that $f_{x_1x_2} = f_{x_2x_1}$.[249]

9.7 Remark on the domain of the function and its partial derivatives

Note that the partial derivatives of f are not always well defined at the boundary of its domain. For example, if $f(x,y)$ is defined only on a smooth curve C: $(x(\alpha), y(\alpha))$ on the xy-plane parameterized by α,

$$\frac{df}{d\alpha} = f_x\frac{dx}{d\alpha} + f_y\frac{dy}{d\alpha} \tag{9.25}$$

is not meaningful if f is not defined on the tubular neighborhood of C. f may not be defined outside C. Therefore, neither f_x nor f_y may be defined.

The above is a trivial remark: it gives an example of f not differentiable with respect to, say, x if f is confined to C, but we encounter analogous situations in thermodynamics very often. For example, if we wish to express a thermodynamic quantity $S = S(E, V, \tilde{\boldsymbol{N}})$ in terms of the chemical composition $\tilde{\boldsymbol{N}}$, the partial derivative of S with respect to E is impossible, since fixing $\tilde{\boldsymbol{N}}$ usually fixes E as well.[250] If we write the totality of $\boldsymbol{N}$ as $\mathcal{C}$ and that of $\tilde{\boldsymbol{N}}$ as W, $R_{E,\boldsymbol{X}}$: $\mathcal{C} \mapsto W$ is a retraction,[251] so it is meaningful to introduce the materials coordinates as $S = S(E, V, R_{E,\boldsymbol{X}}(\boldsymbol{N}))$. We realize that the partial derivative of S with respect to E is possible, even if $\boldsymbol{N}$ is fixed.

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[249] I would like to acknowledge Mr. Shoki Koyanagi for drawing my attention to this point.

[250] This is a dire mathematical difficulty, if chemical reactions occur. Therefore, serious conventioal textbooks require that chemical reactions can be stopped freely at any time to avoid this problem (→**4.2**). Certainly, the difficulty mentioned here may be evaded, but as has already been pointed out in **4.15**, we will encounter much more fundamental difficulty.

[251] A retraction is a continuous map $f : X \to A \subset X$ such that f restricted on A is the identity on A. Here, X is a topological space.

9.8 Differential forms

Let $f_1, \cdots, f_n$ be functions of n variables. The following linear combination

$$\omega = \sum_{i=1}^{n} f_i dx_i \tag{9.26}$$

is called a *1-form*. (9.18) is an example.

9.9 Exact form

If a 1-form ω is written as the total derivative of a function f, that is, if, as (9.18), we can write $\omega = df$, ω is called an *exact form*.

9.10 External differentiation

For differential forms we can define an operation d called *external differentiation*:
(i) If operated on a (strongly differentiable) function f, it gives the total derivative (→**9.3**):[252]

$$df = \sum \frac{\partial f}{\partial x_i} dx_i. \tag{9.27}$$

(ii) d operated on the differential of independent variables gives 0: $d(dx_i) = 0$.

For the product of differentials, we use ∧ (wedge), and the following anti-commutativity is assumed:

$$dx_1 \wedge dx_2 = -dx_2 \wedge dx_1. \tag{9.28}$$

Consequently, the product of the same vanishes: e.g., $dx_1 \wedge dx_1 = 0$. Otherwise, just as the ordinary multiplication the combination and distributive rules hold.

$dx_1 \wedge dx_2$ may be interpreted intuitively as the area of a rectangle formed by two infinitesimal vectors: dx_1 along the x_1 axis and dx_2 along x_2. If we understand that the area changes its sign when the rectangle is flipped over, we can see that $dx_2 \wedge dx_1$ corresponds to the rectangle being flipped over.[253]
(iii) $d(f dx) = df \wedge dx$.[254]

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[252] In mathematics f is often assumed to be infinite times differentiable; in this unit we assume functions are as many times differentiable as needed.

[253] Recall the vector product.

[254] This is a very special case of the external differentiation of general products.

If we externally differentiate (9.12) using (iii) and assuming f is twice continuously differentiable, **9.6** implies $d^2 f = 0$:

$$\begin{aligned} d^2 f &= df_{x_1} \wedge dx_1 + df_{x_2} \wedge dx_2 && (9.29)\\ &= (f_{x_1x_1}dx_1 + f_{x_1x_2}dx_2) \wedge dx_1 + (f_{x_2x_1}dx_1 + f_{x_2x_2}dx_2) \wedge dx_2 && (9.30)\\ &= f_{x_1x_1}dx_1 \wedge dx_1 + f_{x_1x_2}dx_2 \wedge dx_1 + f_{x_2x_1}dx_1 \wedge dx_2 + f_{x_2x_2}dx_2 \wedge dx_2 && (9.31)\\ &= f_{x_1x_2}dx_2 \wedge dx_1 + f_{x_2x_1}dx_1 \wedge dx_2 && (9.32)\\ &= (f_{x_2x_1} - f_{x_1x_2})dx_1 \wedge dx_2 = 0. && (9.33) \end{aligned}$$

As can be seen from this, we generally have $d^2 = 0$.

9.11 Closed form

If a 1-form

$$\omega = \sum_i f_i(x_1, \cdots, x_n)dx_i \tag{9.34}$$

is externally differentiated to give $d\omega = 0$, ω is called a *closed form*. As can be seen readily by computation, if

$$\frac{\partial f_i}{\partial x_j} = \frac{\partial f_j}{\partial x_i}, \tag{9.35}$$

ω is closed. (9.35) is called *Maxwell's relation* in thermodynamics.

The relation implies the exchangeability of the order of partial differentiation, if $\omega = dF$ (→**??**):

$$\frac{\partial^2 F}{\partial x_i \partial x_j} = \frac{\partial^2 F}{\partial x_j \partial x_i}. \tag{9.36}$$

9.12 Poincaré's lemma

As we have seen in **9.11**, an exact form is a closed form. Is the converse true? That is, is there a function F such that $\omega = dF$, if $d\omega = 0$? This holds on a one-point contractible domain (→**5.7**). This is called *Poincaré's lemma*. The totality of equilibrium states $\mathcal{E}$ is a one-point contractible set in the thermodynamic space (→**5.9**), so Poincaré's lemma holds.

9.13 Line integration

Here, for simplicity, we discuss curves that can be parameterized with a (piecewise)

C^1-function.

Let C be a continuous curve with length[255] in n-space.[256] We assume that the curve C is parameterized by a (piecewise) C^1-function $c(t)$. Integrating the 1-form (9.34) with the parameterization $x = c(t)$ implies

$$\int_C \omega = \int_0^1 \sum_i f_i(c(t)) \cdot c'(t)dt. \tag{9.38}$$

In the domain where the 1-form is defined, to integrate an exact form $\omega = dF$ along a curve $x = c(t)$ connecting A and B gives, since $c(0) = A$ and $c(1) = B$,

$$\int_C \omega = \int_0^1 \frac{dF(c(t))}{dt}dt = F(B) - F(A). \tag{9.39}$$

That is, the result of the integral of an exact form depends only on the initial and the final points of the curve.

9.14 Path dependence of line integrals: examples

Since the differentials of state functions (→**5.4**) are exact, if the initial values are known, then the values at the final state can be computed along any path connecting the initial and the final states (→**9.13**). In particular, if the integration path is a closed curve, the integral vanishes.

To check the exactness of ω, checking its closedness is incomplete. However, as can be seen from **9.12**, if its domain is one-point contractible, we have only to check $d\omega = 0$. That is, we have only to confirm Maxwell's relations in the domain. For thermodynamics, the totality of equilibrium states $\mathcal{E}$ is one-point contractible (→**5.7**), so this is enough.

To confirm $d\omega = 0$ we have only to compute the external differentiation (→**9.10**)

Let us perform detailed calculations of line integrals of two variable examples.

$$\omega = y^2dx + 2x(y+1)dy. \tag{9.40}$$

(i) This is not closed: $d\omega \neq 0$.

To show this checking "Maxwell's relations" is one way, but (although actually exactly the same) to use external differentiation (→**9.10**) may be smarter:

$$d\omega = 2ydy \wedge dx + 2(y+1)dx \wedge dy = [2(y+1) - 2y]dx \wedge dy \neq 0. \tag{9.41}$$

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[255] ⟪**Continuous curve with length**⟫ If a curve may be parameterized in terms of a (piecewise) C^1-function, by writing $x = c(t)$, the length L of the curve reads

$$L = \int_0^1 \|c'(t)\|dt, \tag{9.37}$$

where $\| \ \|$ is the vector length.

[256] 'n-space' means n-dimensional space. Generally, a geometric object XXX of dimension n will be denoted as n-XXX.

(ii) The line integral of ω depends on the actual path: to integrate ω from the origin to $(1,1)$, let us compare the path A: along $y=x^2$, and B: along $x^2+(y-1)^2=1$.

To perform a line integral parameterizing the path is convenient.
A: Let us write $x=t$, $y=t^2$ $(t\in[0,1])$.

$$\int_{y=x^2 \text{ for } x=0\to 1}[y^2dx+2x(y+1)dy] = \int_0^1 dt\,[t^4dt+2t(t^2+1)2tdt] \tag{9.42}$$

$$= \int_0^1 dt\,(5t^4+4t^2)=1+4/3=7/3\approx 2.33. \tag{9.43}$$

B: Let us write $x=\sin t$, $y=1-\cos t$ $(t\in[0,\pi/2])$. Then,

$$\int_0^{\pi/2}[(1-\cos t)^2\cos tdt+2\sin t(2-\cos t)\sin tdt] \tag{9.44}$$

$$=\int_0^{\pi/2}dt\,[4-\cos t-6\cos^2 t+3\cos^3 t] \tag{9.45}$$

$$=2\pi-1-6\times\frac{\pi}{4}+3\times\frac{2}{3}=\frac{\pi}{2}+1\approx 2.57. \tag{9.46}$$

Certainly, the integral values depend on the paths.

(2) The following 1-form is exact:

$$\omega=y^2dx+2xydy. \tag{9.47}$$

(i) Let us confirm $d\omega=0$.

$$d\omega=2ydy\wedge dx+2ydx\wedge dy=[2y-2y]dx\wedge dy=0. \tag{9.48}$$

However, this is not generally enough to demonstrate the exactness of ω. For example, let us consider the following 1-form

$$\xi=(-ydx+xdy)/(x^2+y^2) \tag{9.49}$$

on the unit disk centered at the origin excluding the origin (its domain is not one-point contractible). $d\xi=0$ and formally we may compute $\xi=d\,\mathrm{Arctan}(y/x)$, but this is not a derivative of a single-valued function.
(ii) Along the same paths A and B above, let us integrate ω given by (9.47). For A

$$\int_{y=x^2 \text{ for } x=0\to 1}[y^2dx+2xydy] = \int_0^1 dt\,[t^4dt+2t(t^2)2tdt] \tag{9.50}$$

$$= \int_0^1 dt\,5t^4=1. \tag{9.51}$$

For B

$$\int_0^{\pi/2}[(1-\cos t)^2\cos tdt+2\sin t(1-\cos t)\sin tdt] \tag{9.52}$$

$$=\int_0^{\pi/2}dt\,[2-\cos t-4\cos^2 t+3\cos^3 t] \tag{9.53}$$

$$=\pi-1-4\times\frac{\pi}{4}+3\times\frac{2}{3}=1. \tag{9.54}$$

(iii) Since $\omega = d(xy^2)$, of course, $xy^2(x = y = 1) - xy^2(x = y = 0) = 1$.

9.15 Integral of 2-forms

A linear combination of the wedge products of differentials of two independent variables such as $dx_i \wedge dx_j$ is called a 2-form. In 2-space it is of the following form: $\omega = f dx \wedge dy$. Its integration on a 2-area m is defined as follows:

$$\int_m \omega = \int_m f dx dy. \tag{9.55}$$

The integrals of differential forms are linear with respect to the integrands ($a, b \in \mathbb{R}$):

$$\int_m (a\,\omega + b\,\omega') = a \int_m \omega + b \int_m \omega'. \tag{9.56}$$

The integral of $dy \wedge dx$ is negative of that of $dx \wedge dy$ (→**9.10** (ii)). If m is a small rectangle $\varepsilon_x \times \varepsilon_y$ around (x, y), and if f is continuous

$$\int_m \omega \simeq f(x, y)\varepsilon_x \varepsilon_y. \tag{9.57}$$

9.16 Change of independent variables of integrals: Jacobian

Suppose f is a function of (X, Y) and the map: $(X, Y) \mapsto (x, y)$ maps M to m.[257] Then,

$$\begin{aligned} \int_M f(X, Y) dX \wedge dY &= \int_m f(X(x, y), Y(x, y))(X_x dx + X_y dy) \wedge (Y_x dx + Y_y dy) \\ &= \int_m f(X(x, y), Y(x, y))(X_x Y_y dx \wedge dy + X_y Y_x dy \wedge dx) \\ &= \int_m f(X(x, y), Y(x, y)) \left[X_x Y_y - X_y Y_x\right] dx \wedge dy. \end{aligned} \tag{9.58}$$

This is a well-known formula for changing independent variables of integrals. The quantity in [ ] is the *Jacobian*:

$$X_x Y_y - X_y Y_x = \begin{vmatrix} \frac{\partial X}{\partial x} & \frac{\partial Y}{\partial x} \\ \frac{\partial X}{\partial y} & \frac{\partial Y}{\partial y} \end{vmatrix} \equiv \frac{\partial(X, Y)}{\partial(x, y)}. \tag{9.59}$$

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[257] For convenience, let us assume that the map is a diffeomorphism (one-to-one and differentiable in both directions).

That is,

$$dX \wedge dY = \frac{\partial(X,Y)}{\partial(x,y)} dx \wedge dy. \tag{9.60}$$

9.17 Maxwell's relations in terms of Jacobians

Let $\omega = \sum x_i dX_i$ be an exact 1-form (→**9.9**). Assume $\{x_i\}$ are differentiable with respect to $\{X_j\}$. Then,

$$0 = d\omega = \sum dx_i \wedge dX_i. \tag{9.61}$$

In particular, if only two independent variables are changed, we have

$$0 = \int_\varepsilon [dx_i \wedge dX_i + dx_j \wedge dX_j] \simeq -\left(\frac{\partial x_i}{\partial X_j}\right)_{X_j^c} \varepsilon_i \varepsilon_j + \left(\frac{\partial x_j}{\partial X_i}\right)_{X_i^c} \varepsilon_i \varepsilon_j. \tag{9.62}$$

Also we get

$$\begin{aligned} 0 &= \int_\varepsilon [dx_i \wedge dX_i + dx_j \wedge dX_j] = \int_\varepsilon \left[\frac{\partial(x_i, X_i)}{\partial(x_j, X_j)} + 1\right] dx_j \wedge dX_j && (9.63) \\ &\simeq \left[\frac{\partial(x_i, X_i)}{\partial(x_j, X_j)} + 1\right] \left(\frac{\partial x_j}{\partial X_i}\right)_{X_i^c} \varepsilon_i \varepsilon_j. && (9.64) \end{aligned}$$

Since $X \to x$ is diffeomorphic, the so-called Maxwell's relations[258] is, if Jacobians are continuous, equivalent to

$$\frac{\partial(x_i, X_i)}{\partial(x_j, X_j)} = -1. \tag{9.65}$$

Here, all the variables kept constants are not written for the partial derivatives; as the Jacobian, essentially the 2 × 2 portion need be considered.

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[258] As before, X_i^c in the suffix means that the variable X_i is removed from the total set of independent variables.

10 Structure of thermodynamic space

10.1 Possibility of reversible and quasistatic adiabatic processes

Let $\mathcal{E}$ be the totality of the equilibrium states of a system under consideration. Take a point $P \in \mathcal{E}$ and let its projection onto the operational coordinate hyperplane be P' (Fig. 10.1).

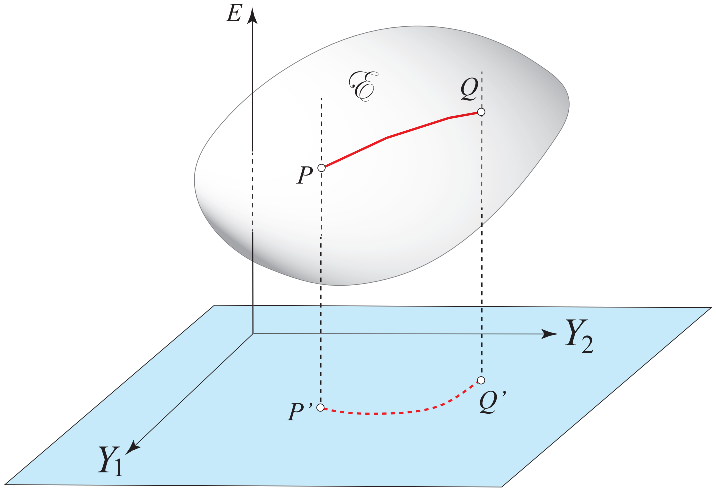

Figure 10.1: The totality $\mathcal{E}$ of the equilibrium states of a system and an adiabatic and reversible-quasistatic process in it (actually, $\mathcal{E}$ is not a finite set, but for convenience, it is illustrated as a finite set); The vertical broken lines denote constant operational coordinate lines. The adiabatic reversible and quasistatic change of operational coordinates from P' to Q' along the red broken curve on the operational coordinate hyperplane (the pale blue plane) results in the change of internal energy E according to $dE = \omega + \zeta$ (as illustrated by the red curve P to Q).

Our strategy is to elucidate thermodynamics based on the non-thermal macroscopic physics and chemistry (→**1.3**). We are allowed to change operational coordinates adiabatically and reversible-quasistatically as far as allowed by non-thermal macrophysics and chemistry. The system internal energy E changes according to the generalized work form (ω in **3.10** + ζ in **4.12**). Consequently, there exists a reversible quasistatic adiabatic process through an arbitrary state $P \in \mathcal{E}$ whose projection onto the $\boldsymbol{Y}$-plane may be specified as P'.[259]

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[259] This says for a curve C on the $\boldsymbol{Y}$-plane connecting P' and Q' (see Fig. 10.1), there is at least one adiabatic reversible and quasistatic process that is projected onto the curve C; the uniqueness of the process is not asserted; for a given C^∞ curve $\boldsymbol{Y}(\tau)$ connecting P' and Q' parameterized with

10.2 There is a region not accessible by adiabatic processes from an equilibrium state[260]

The following considerations rely on all the facts, principles, etc., we have so far discussed. In particular, we rely on Planck's principle (→**8.5**) as the second law of thermodynamics (stated here again for convenience):

τ on the $\boldsymbol{Y}$-plane. The curve corresponding to a reversible quasistatic adiabatic process through P may be constructed by integrating the generalized work form that corresponds to the following ODE:

$$dE = \sum_i y_i(\boldsymbol{Y}(\tau))Y_i'(\tau)d\tau.$$

By definition in this discussion Y_i' is C^∞, but $y_i(\boldsymbol{Y}(\tau))$ is 'as smooth as' $\boldsymbol{y}$, so we do not even know its continuity (we know only its existence as a function). Thus, mathematically, we cannot even claim the existence of a solution for the above differential equation. For example, Peano's theorem guaranteeing the existence of the solutions requires the continuity of $\boldsymbol{y}$. However, within the nonthermal physics/chemistry, at least the existence of E must be guaranteed. Thus, we accept the existence of the solution for E. In any case, it should be emphasized that the existence of quasistatic reversible adiabatic processes is given by the non-thermal physics, so, strictly speaking, any axiomatic thermodynamics must assume their existence,

Since no further condition (e.g., the Lipshitz continuity) as to the smoothness of $\boldsymbol{y}$ is generally guaranteed by macro physics, the solution may not be unique. For elementary facts about ODE, see, for example, P.-F. Hsieh and Y. Sibuya, *Basic theory of ordinary differential equations* (Springer, 1999).

If we use the second law of thermodynamics, we can demonstrate the uniqueness of the solution (→**10.3**). For the argument here we only need the existence of a process specified by the projection onto the $\boldsymbol{Y}$-plane.

Of course, the fact that all adiabatic quasistatic reversible processes passing through P and projected onto any curve on the operational coordinate plane from P' to Q' will reach the same Q cannot be asserted based on the uniqueness of the solution in this context (→**10.4**).

[260] From here up to **10.7** is roughly based on my memory of the geometric portion of Carathéodory's original: "Untersuchungen über die Grundlagen der Thermodynamik, Math. Ann. **67**, 355 (1909), which I read when I was an undergrad [now there is a translation: "Examination of the foundations of thermodynamics" By C. CARATHEODORY translated by D. H. Delphenich]. Very recently, I read Louis A. Turner, Simplification of Carathéodory's Treatment of Thermodynamics, Am. J. Phys., **28**, 781 (1960), whose geometric part seems similar; perhaps M. W. Zemansky, Kelvin and Caratheodory—a reconciliation, Am. J. Phys., **34**, 914 (1966) may be easier due to figures. Its Acknowledgements contain: "The author is very much indebted to Louis A. Turner for the opportunity to discuss these matters with him and for his helpful advice. All teachers of thermodynamics should be indebted to him for his pioneer work in (to use his words) "by-passing some of the more difficult mathematical nonessentials of Caratheodory."" However, in contrast to Zemansky's (or other such as Landsberg's) exposition, in this exposition no temperature (empirical or whatever) is utilized. The reason is of course that our exposition is strictly based on nonthermal physics, but, in any case, as is in (the footnote in) **3.8**, do not forget that the concept of temperature may not be independent of thermodynamics after all.

Planck's principle: By an adiabatic process with the identical initial and the final operational coordinates, the system internal energy cannot be reduced (Fig. 10.2). In paticular, along a line parallel to the energy axis, the system cannot go down adiabatically.

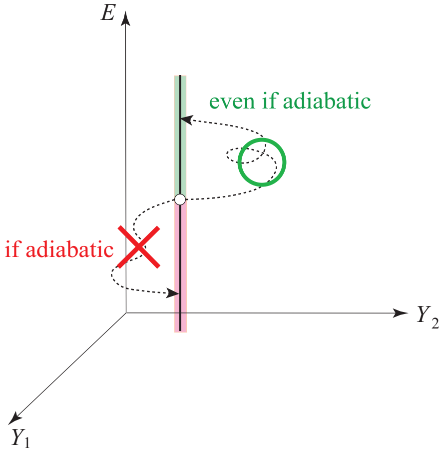

Figure 10.2: Planck's principle: from the state denoted by a small white disk on the vertical line the red-shaded portion cannot be adiabatically reached; the green-shaded portion may be accessible, but not reversibly (according to the metaprinciple **8.4**). The vertical line is a operational-coordinate constant line parallel to the energy axis.

Here, the 'adiabatic process' may be any realizable one whose initial and the final operational coordinates are identical (that is, the initial and the final work and materials coordinates agree).

Remark Planck's principle itself only forbids adiabatic reduction of internal energy. Therefore, it does not say anything about the green states in Fig. 10.2. We take the metaprinciple (→**8.4**) for granted.

10.3 Uniqueness of the internal energy change by a reversible and quasistatic adiabatic process I

Remark: Unlike the next **10.4**, this unit is not commonly written in regular books. Why? Because what is being shown here is considered unquestionable. If we assume that the conjugate variable $\boldsymbol{y}$ appearing in the generalized work form is differentiable as much as we like as a function of thermodynamic coordinates (for example, C^∞, although not necessarily that extreme—some people still assume C^2, and it is not uncommon to assume C^1), then what is shown here becomes trivial (no second law required). Furthermore, what is demonstrated in units like **10.8** and **10.9**, which are not easy to explain or hard to understand, also becomes trivial. The reason for avoiding that approach as much as possible is that the author wishes to clarify the justification for these convenient assumptions.

Take a point $P \in \mathcal{E}$ in the thermodynamic space $(E, \boldsymbol{Y})$ (Fig. 10.3Left). Let the curve P-Q be a result of integrating the generalized work form from P along P'-Q' on the $\boldsymbol{Y}$-plane as discussed in **10.1**.

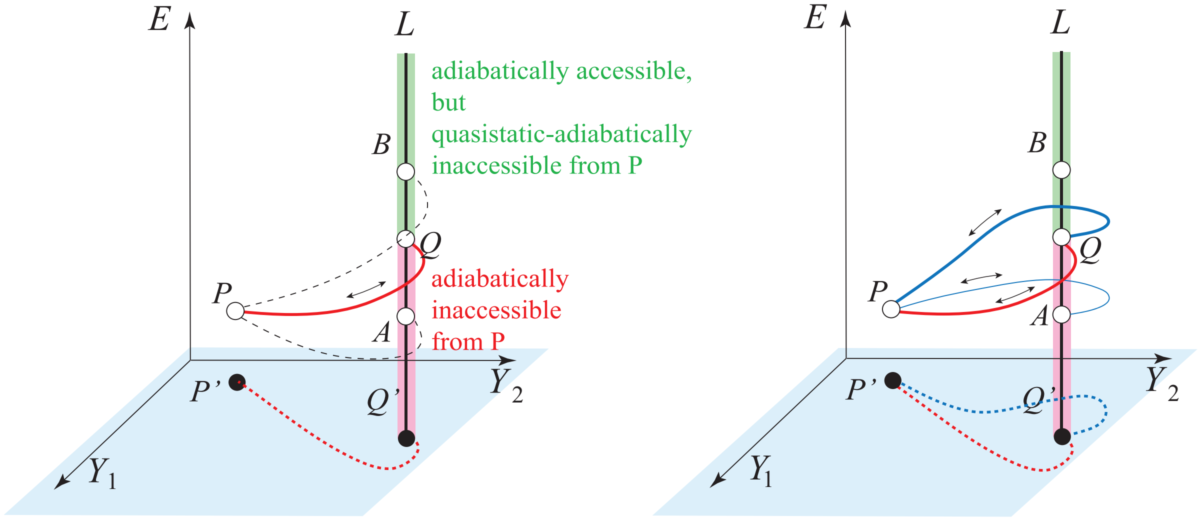

Figure 10.3: Left: The integral of the generalized work form along P'-Q' (the red dashed curve, same as in Figure 10.1) gives a uniquely determined solution curve (the red curve) thanks to the second law of thermodynamics. Here, the line L is the set of equilibrium states with the same operational coordinate Q' (a straight line parallel to the energy axis). Right: The integral of the generalized work form along P'-Q' (the red dashed curve, same as in Figure 10.1) and the integral along another P'-Q' (the blue dashed curve) both lead to the same Q starting from P, thanks to the second law of thermodynamics. In other words, the point Q on the vertical line L is uniquely determined by reversible and quasi-static processes starting from P; they will never go to a place like A.

Let L be the line going through Q' parallel to the energy axis (Fig. 10.3Left). In Fig. 10.3Left the broken red curve P'-Q' denotes a specified operational coordinate change for a reversible quasistatic adiabatic process (as in Fig. 10.1). Integrating the generalized work form along this curve has not yet been shown to give a unique solution, but the red curve in the figure is understood as a possible integration result as in Fig. 10.1.

Planck's principle tells us that we cannot go to state A that is below Q along L (in the red-shaded portion in Fig. 10.3Left) from P adiabatically; if possible, since $P \to Q$ is retraceable, we can adiabatically realize $Q \to P \to A$, but Q and A are on L, so this violates Planck's principle.

How about state B in the green-shaded portion above Q in Fig. 10.3Left? $P \to B$ is not forbidden adiabatically (→**8.4**), but cannot be realized reversibly; if possible $B \to P \to Q$ may be adiabatically realized and Planck's principle is violated.

Thus, we have found that if we integrate the generalized work form along any curve $P' \to Q'$ from P, the integration result is uniquely given by Q.

10.4 Uniqueness of the internal energy change by a reversible and quasistatic adiabatic process II

In **10.3**, it was shown that the result of integrating the generalized work form along any curve of finite length from P' to Q' (say, the blue dotted curve instead of the red one in Fig. 10.3 Right) uniquely determines Q when the 'initial state' P is fixed. In other words, any adiabatic, reversible, quasi-static process connecting P' and Q' will uniquely reach a certain state Q^* on line L as long as it starts from P.

Now, let us suppose that Q^* is located below Q on line L (see the right side of Figure 10.3). In this case, since both the P-Q and P-Q^* processes are reversible, one could move adiabatically from Q to Q^*, which would contradict Planck's principle. Similarly, it is not allowed for Q^* to be located above Q, as in the case of point B. Therefore, Q^* must coincide with Q.

Thus, it is concluded that all adiabatic, reversible, quasi-static processes starting from P and reaching line L will end at Q and only at that state.

10.5 Construction of reversible adiabatic hypersurface[261]

Notice that the argument in **10.4** (see Fig. 10.3Right) applies to any Q in $\mathcal{E}$ that can be reached from P adiabatically, quasistatically and reversibly. The energy of Q depends continuously on Q' (its $\boldsymbol{Y}$-coordinates),[262] so collecting all Q we can

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[261] A $(n-1)$-dimensional manifold in a n-dimensional space is called a *hypersurface* within the original space. This refers to a geometric object with one dimension less than the space itself, meaning it has a codimension of 1.

[262] This continuity originates from the general conclusions of macroscopic physics.

make a continuous hyperplane A_P consisting of all the curves (in $\mathcal{E}$) describing the quasistatic and reversible adiabatic processes starting from state P.[263] Let us call A_P the *reversible adiabatic hypersurface* going through P.

By construction the gradient vector for A_P at P is well defined, so A_P is strongly differentiable (→**9.3**) at P with the gradient given by $\boldsymbol{y}$.

10.6 Reversible adiabatic hypersurfaces foliate $\mathcal{E}$

Take a hypersurface A_P (curves in it are denoted by the red curves in Fig. 10.4) constructed as in **10.5** and choose an arbitrary point Q on it. Then, construct the adiabatic reversible hypersurface A_Q passing through Q (a curve in it is denoted by the green curve in Fig. 10.4) constructed just following the method in **10.5**. If A_P and A_Q do not agree, then there is a line parallel to the E-axis such that A_Q and A_P have distinct crossing points R and R', respectively, with it as illustrated in Fig.10.4. Then, we are allowed to go along $RQPR'$, where R' on A_P is just below R. Thus, Planck's principle would be violated.

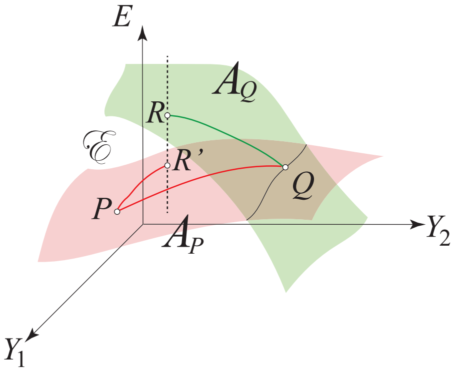

Figure 10.4: The red curves are on A_P and the green on A_Q. The illustration assumes that R on A_Q is above R' on A_P, where R and R' have the same operational coordinates. Along any curve the process is reversible, so $R \to Q \to P \to R'$ is adiabatically realizable, violating Planck's principle.

Therefore, A_P and any adiabatic reversible hypersurface sharing a common point must agree:

$$Q \in A_P \Rightarrow A_Q = A_P. \tag{10.1}$$

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[263] Q' is located within the convex set formed by the cross-section of $\mathcal{E}$ by the hyperplane parallel to the operational coordinate plane on which P' lies; hence A_P is contractible to a point; it is just a single hyper-surface with no holes or anything.

Therefore, A_P is anywhere strongly differentiable (see Fig. 10.4).

10.7 Adiabatic reversible surfaces do not switch their order along the energy axis

Given an equilibrium state, an adiabatic reversible surface through it is uniquely determined (→**10.5**). Furthermore, $\mathcal{E}$ may be decomposed into mutually exclusive adiabatic reversible surfaces like mille-feuille.[264] The stacking of these hypersurfaces is simple in the following (mathematically standard) sense. Take two adiabatic reversible hypersurfaces. If one is above the other along a line parallel to the E-axis, this ordering is kept along any line parallel to it. Switching ordering as in Fig. 10.5 is not allowed as explained below.

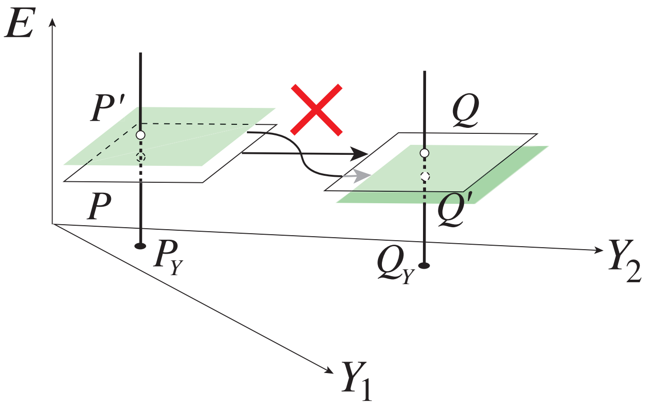

Figure 10.5: The adiabatic reversible surfaces do not switch their ordering along the energy axis. Here, vertical lines are parallel to the energy axis.

Suppose P' and P have the same operational coordinates (P_Y). We can go from P' to Q' and from P to Q adiabatically and reversibly. We can also go adiabatically from Q' to Q along the line parallel to the energy axis. Then, using the reversibility of P-Q, we can go $P' \to Q' \to Q \to P$ adiabatically. This violates Planck's principle.

10.8 How smoothly do adiabatic hypersurfaces depend on E?

Since all points on a straight line within $\mathcal{E}$, where the operational coordinates are constant (i.e., parallel to the energy axis), lie within one and only one adiabatic reversible hypersurface (10.1), it has been shown that there is a one-to-one corre-

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[264] Mathematically, we say $\mathcal{E}$ is *foliated* by adiabatic reversible hypersurfaces.

spondence, preserving order, between this set of adiabatic hypersurfaces and a certain interval of real numbers (a portion of the energy axis).

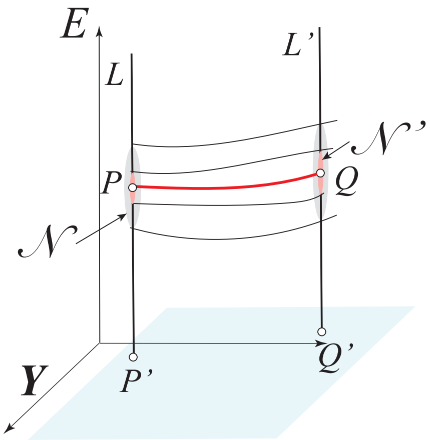

Figure 10.6: Adiabatic quasistatic reversible hypersurfaces depnd on E continuously.

It would not be ideal if the shape of the adiabatic hypersurface passing through a point changed drastically when the energy E at the intersection of a straight line parallel to the E-axis is slightly changed. How much can be asserted about this E-dependence?

Let us consider a reversible adiabatic path connecting P and Q in Fig. 10.1 (the red curve in Fig. 10.6. A reversible adiabatic path starting from any neighborhood $\mathcal{N}$ of P on the vertical line passing through P will uniquely reach a point on the vertical line L' passing through Q. Since the order of the solutions does not change, the closure of this set contains a neighborhood $\mathcal{N}'$ on L', which includes Q. Reversible adiabatic paths from Q to P certainly exist, and since the relative positions of solutions do not alter, the collection of reversible adiabatic paths returning from $\mathcal{N}'$ are all contained within $\mathcal{N}$. That is, there is a neighborhood of Q transferred by reversible adiabatic paths within an arbitrarily small neighborhood of P, and vice versa. Therefore, reversible adiabatic paths continuously depend on E. As a result, reversible adiabatic hypersurfaces also depend continuously on E.

To claim the same assertion with the aid of the theory of ordinary differential equations, we would need continuity of $\boldsymbol{y}$ with respect to E.[265]

10.9 Can we claim more smoothness?

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[265] We also need the curve P'-Q' to be C^1.

What can we say about the differentiability with respect to E of reversible adiabatic paths? Based solely on the assumptions we have explicitly mentioned, we likely cannot say more than that continuity is ensured (→**10.8**). As we will see later, it is convenient for reversible adiabatic hypersurfaces to depend smoothly on E. When entropy is introduced axiomatically, differentiability, and often even C^2-smoothness, is assumed. Lieb and Yngvason introduce an axiom called the Lipschitz tangent space (S2), which demands that the set of states adiabatically reachable from a state A has a tangent plane at A and furthermore that it is (locally) Lipschitz continuous. Of course, this is convenient but it seems neither clear in physics nor easy to explain mathematically its necessity.[266]

Here, we will anticipate that it is convenient for S to be partially differentiable with respect to E, and accordingly, consider the necessary conditions for this. As detailed in the footnotes of **10.2**, reversible adiabatic hypersurfaces are determined by reversible quasi-static work under adiabatic conditions, in other words, by the integral of the generalized work form. By using the differentiability of the initial conditions of the solution, we can understand how the solution depends on the change $E \to E + \delta E$. In this case, since a unique solution exists for all E in the neighborhood of P, if the conjugate variable $\boldsymbol{y}$ is partial differentiable with respect to E, the solution itself can also be partial differentiable with respect to E.

10.10 Adiabatic hypersurface and conjugate intensive variables

If $\boldsymbol{Y}(\tau)$ is a curve not crossing with itself starting from P' (as the red broken curve in Fig. 10.5), then the generalized work form becomes the following normal form differential equation in the hypersurface $\mathcal{S}$ defined by $\boldsymbol{Y} = \boldsymbol{Y}(\tau)$:

$$\frac{dE}{d\tau} = f(E, \tau). \tag{10.2}$$

If we make the totality of the solution set formed by changing the intial energy E_0, we obtain the set of curves $\{E = E(\tau, E_0)\}$ in $\mathcal{E} \cap \mathcal{S}$.

The problem of examining this group of curves is equivalent to considering the dependence of solutions on the energy coordinate E_0 of the starting point P, that is, the dependence on parameters.[267] According to the general theory, since the unique existence of solutions is guaranteed by the second law (→**10.3**), if $\boldsymbol{y}$ is a continuous function, it can be said that the solution curves also depend continuously on the initial values. Furthermore, if $\boldsymbol{y}$ is differentiable with respect to E in the first order, the solution curves depend smoothly on the initial

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[266] Of course, if entropy is defined by the differential form $dS = q/T$, differentiability is certainly required. However, there is no necessity that it must be defined using a differential form.

[267] A convenient reference is, for example, P.-F. Hsieh and Y. Sibuya, *Basic Theory of Ordinary Differential Equations* (Springer, 1999).

values.

Thus, it is important to understand the dependence of $\boldsymbol{y}$ on E under the condition that $\boldsymbol{Y}$ is fixed, but little is known about this.

However, if we assume that nothing unusual happens other than during phase changes, the continuity of $\boldsymbol{y}$ is guaranteed because $\boldsymbol{y}$ does not change discontinuously during phase changes.[268]Moreover, discussing the partial differentiability of $\boldsymbol{y}$ with respect to E may be possible to some extent.

10.11 Adiabatic reversible hypersurfaces: summary

Let us summarize the structure of the totality of the equilibrium states $\mathcal{E}$ of a simple system we have found so far.

The totality of the equilibrium states of a system $\mathcal{E}$ is separated into hypersurfaces consisting of equilibrium states that may be transformed into (reachable to and from) each other by quasistatic and reversible adiabatic processes (→**10.6**). These hypersurfaces have the same order (the same stacking order) along any line parallel to the E-axis (→**10.7**).

Any point in $\mathcal{E}$ on a line with constant operational coordinates (i.e., on a line parallel to the E axis) is in one and only one reversible adiabatic hypersurface, so the totality of these hypersurfaces and an interval of the real numbers are one to one continuously correspondent (i.e., homeomorphically correspondent[269]).

Each reversible adiabatic hypersurface may be constructed by integrating the generalized work form $dE = \sum y_i dY_i$ starting from any single equilibrium state on it. Thus, $(y_1, \cdots, y_m)$ defines a gradient vector field whose potential function is E, and reversible adiabatic hypersurface is strongly differentiable with respect to $\boldsymbol{Y}$.

Physicochemically speaking, a reversible adiabatic hypersurface A_P describes all the macrophenomena that can happen non-thermally without any dissipation, if the system is initially prepared in state P. In particular, if we forget about chemistry all together, it is the space where all the non-thermal macroscopic mechanical and electromagnetic phenomena occur, if the system is initially prepared in state P.[270] The phenomena that can occur within this hypersurface may be discussed without thermodynamics. Thermodynamics expands the realm of macrophysics/chemistry by allowing us to discuss the transitions between these hypersurfaces.

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[268] The conjugate extensive variables are equal between coexisting phases.

[269] We will discuss more smoothness later →**11.3**.

[270] However, do not forget the constraint that thermodynamics can handle only additive systems (→**2.11**).

C Appendix. Realizability of paths in the thermodynamic space

C.1 Why we consider the physical realizability of any path

For a given system, the totality $\mathcal{E}$ of its equilibrium states forms a convex set (or a homeomorphic image of a convex set →**5.9**). Therefore, for any two points P and Q in $\mathcal{E}$, there exists a continuous curve that connects them in $\mathcal{E}$. Is this curve realizable as an actual physico-chemical quasistatic reversible process (→**A.6**)?[271]

Thermodynamic textbooks often assume (though not always explicitly) that all processes connecting two equilibrium states in $\mathcal{E}$ are realizable as quasistatic reversible processes, so the following discussions may be taken for granted (and ignored). However, it is important to explicitly demonstrate the (experimental) realizability of all continuous paths in $\mathcal{E}$ as reversible and quasistatic processes. Then, we may guarantee the applicability of thermodynamics along any continuous curve in $\mathcal{E}$.

C.2 Adiabatic reversible processes

As discussed in **10.3**, if we integrate the generalized work form $(\omega + \zeta)$ along a continuous curve on $\mathcal{E}_P$ (the hyperplane with constant E passing through P) connecting P and Q' (Fig. 10.2), we obtain a unique solution curve connecting P and a certain point Q (on A_P →**10.5**) with the same operational coordinates as Q'. Therefore, there is an adiabatic reversible and quasistatic process between P and Q.

C.3 Changing E while keeping operational coordinates constant

Planck's principle (→**8.5**) discusses a state change vertically along a line parallel to the E axis. It states that it is impossible to decrease E along this line adiabatically, while increasing E along the line is adiabatically possible, but the process is practically achieved by heating the system with heat obtained from the dissipation of some work. Therefore, we may expect that reversibly heating the system should realize the same effect.

We make the following explicit assumption:[272]

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[271] Do not forget that being quasistatic does not guarantee the retraceability of a process. If there is no interaction with the environment, usually being quasistatic is enough to be retraceable.

[272] If we apply the metaprinciple (→**8.4**) to Planck's principle, we may claim that non-adiabatic

> A system may exchange heat reversibly and quasistatically, as long as its state is in $\mathcal{E}$, with its appropriate environment without modifying the operational coordinates.[273]

With this natural assumption, we may claim the existence of a reversible quasistatic process between any two equilibrium states P and Q as shown in **C.4**.

C.4 Any two equilibrium states may be connected by a reversible and quasistatic process

For a given system, the totality $\mathcal{E}$ of its equilibrium states is a convex set (or a homeomorphic image of a convex set →**5.9**). Therefore, any two points P and Q in $\mathcal{E}$ can be connected by a continuous curve in $\mathcal{E}$. Can we actually realize a physicochemical reversible quasistatic process (→**A.6**) connecting any two points P and Q in $\mathcal{E}$?

Choose a state Q^* on A_P (→**10.4**) with the same operational coordinates as Q (that is, Q^* is the crossing point of A_P and the line parallel to the E axis passing through Q). This construction, as discussed in **10.3**, yields an adiabatic reversible process from P to Q^* that has identical operational coordinates as Q. If $Q = Q^*$, then this adiabatic process is sufficient, but generally these two states are distinct. In that case, we may (→**C.3**) heat or cool the system reversibly to bring Q^* to Q while keeping the operational coordinates. Thus, we have shown that there is a reversible quasistatic process between any two equilibrium states.

C.5 Any continuous curve may be realized as a reversible quasistatic process

Since we may assume the thermodynamic space as a Euclidean space (→**5.2**), we can define a distance between two continuous curves connecting the same pair of points.[274] In $\mathcal{E}$ arbitrarily close to a continuous curve connecting P and Q, we can draw a physically realizable continuous process combining adiabatic and reversible continuous curves and line segments parallel to the E axis, so any continuous curve may be physically realized as a reversible quasistatic process.

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reversible changes may be allowed to move freely along any constant operational coordinate line, but here, to be clear this assumption is stated explicitly.

[273] However, if the chemical composition coordinates $\tilde{\boldsymbol{N}}$ are used, notice that this is generally impossible.

[274] There may be many ways, but for example, we can use the Frechét distance.

Therefore, we may connect any pair of states in $\mathcal{E}$ with a reversible quasistatic process that corresponds to any continuous curve in $\mathcal{E}$ connecting the two states.

C.6 There is an adiabatic process between any equilibrium states for a simple system

Remark As seen in the proof below, Planck's principle is used almost directly, so the irreversibility and adiabatic increase of internal energy are treated as inseparable. While this proof is valid for simple systems, it does not apply as-is to composite systems. Therefore, this is not yet a general proof of the statement that "an adiabatic process exists between any two equilibrium states." More generally, see **C.7**.

Thanks to Mayer-Joule's principle (→**7.14**), we can effectively add heat to the system adiabatically through supplying work to it. However, Planck's principle (→**8.5**) tells us that we cannot remove heat adiabatically through (generalized) work.

Therefore, if the situation is the Left of Fig. C.1, then there is an adiabatic process from P to Q, because we can adiabatically and irreversibly go from Q^* to Q. However, if the situation is the Right of Fig. C.1, then we cannot go from Q^* to Q adiabatically. In this case, we can go from Q to Q^* adiabatically, so an adiabatic process from Q to P is realizable.[275]

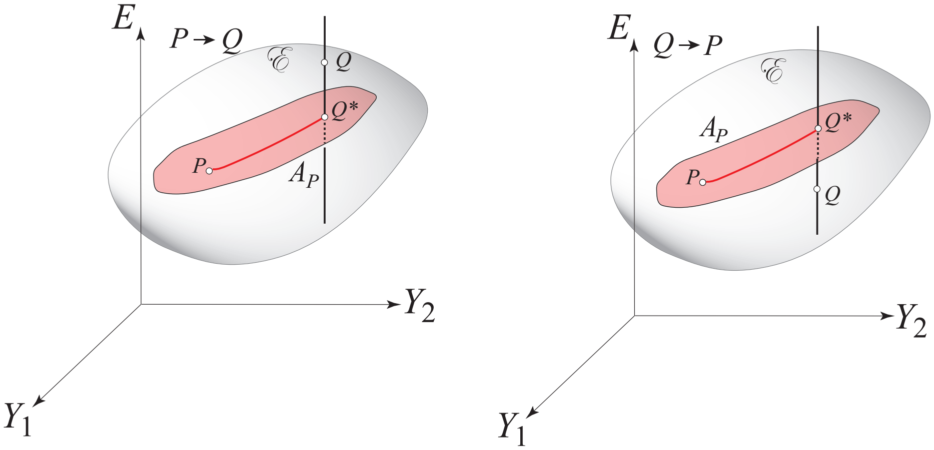

Figure C.1: Left: we can go from P to Q^* adiabatically, and if Q' has a smaller internal energy than Q we can go from Q^* to Q along the vertical line (irreversibly). Right: if Q is below Q^*, then we can never go to Q from Q^* adiabatically. However, we can adiabatically go from Q to Q^*. Since P-Q^* is reversible, we can adiabatically go from Q to P.

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[275] As noted repeatedly, the chemical compositions of Q and Q^* may not be identical.

Thus, we have shown that for any pair of equilibrium states of a simple system we can adiabatically go from at least one state to the other.

C.7 There is an adiabatic process between any equilibrium states

For simplicity, consider a compound system consisting of two simple systems, and represent its state as (A, B). For state A and state C of a simple system, let A^* (resp., C^*) denote the state that is adiabatically and reversibly connected to C (resp., A) with the same operational coordinates as A (resp., C) (See Fig. C.2 1 and 2).

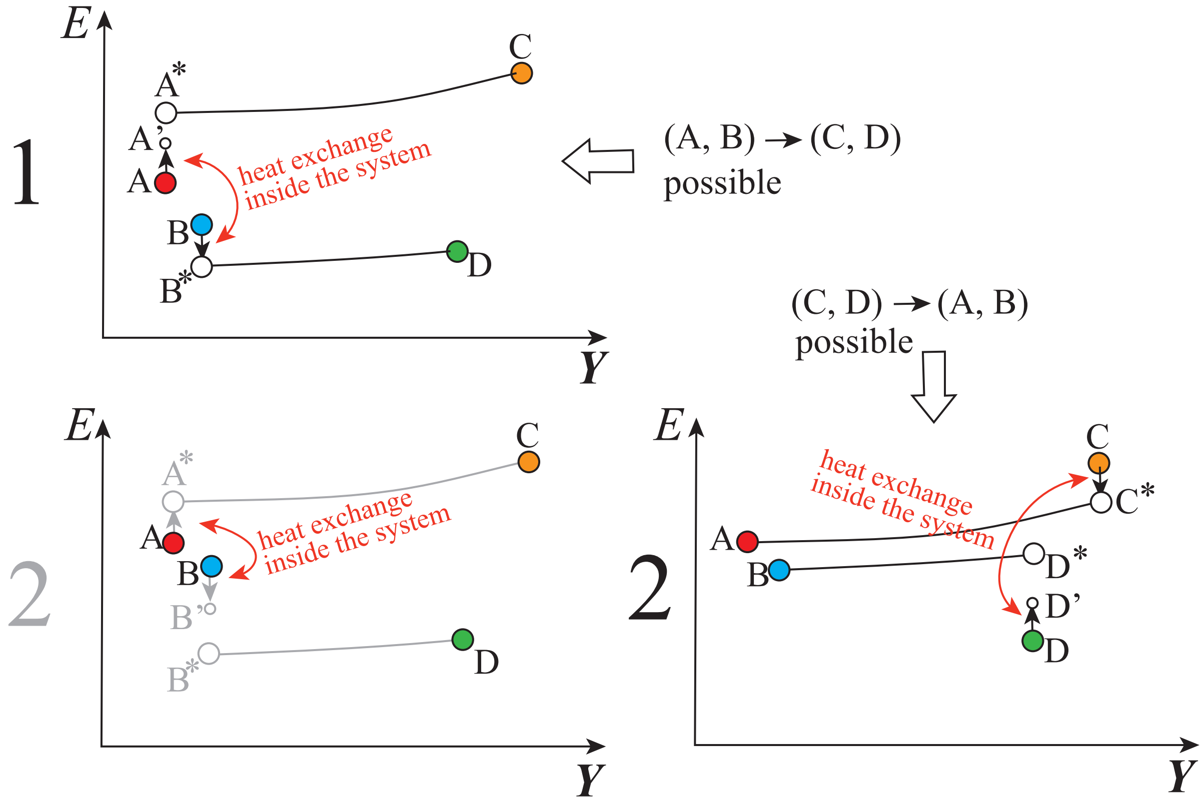

Figure C.2: Construction of adiabatic processes connecting two compound systems

Now, consider connecting two arbitrary equilibrium states (A, B) and (C, D) via an adiabatic process. See Fig. C.2. Construct the states (A^*, B^*) adiabatically and reversibly starting from (C, D). Then, try to 'move' A and B toward A^* and B^*, respectively, through a reversible exchange of heat between the simple systems.

In case 1 in Fig. C.2 B → B^* is realized and A → A' is also realized. Now, (A', B^*) can be adiabatically irreversibly altered to (A^*, B^*), from which we can go to (C, D).

In case 2, if we repeat the above strategy as 'gray 2' in Fig. C.2, unfortunately, the intermediate state accessible (A^*, B') through a reversible exchange of heat between the simple systems cannot realize (A^*, B^*). We must reverse the process. See 'black 2' in Fig. C.2. Construct the states (C^*, D^*) adiabatically and reversibly starting from (A, B). Then, try to 'move' C and D toward C^* and D^* through a reversible exchange of heat between the simple systems. The resulting state is (C^*, D'), which can be converted to (C^*, D^*). Thus, from (C, D) to (A, B) we can construct an adiabastic process.

As this shows, essentially, you need to bring each simple subsystem individually to the initial state from its (desired) final state through an adiabatic quasistatic reversible process (see C → A^* in Fig. C.2 1), adjusting the operational coordinates. Then, use quasistatic heat exchange among the sub simple systems to bring as many of the subsystems as possible to match the *-states. Finally, check whether the remaining states are all above their respective adiabatic reversible hypersurfaces starting from the target states. If this is not realizable, switch the starting states (1 - 2 switch in Fig. C.2.[276]

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[276] This is Lieb-Yngvason's comparison hypothesis (or theorem), their main result. The author believes it is perverse to try to show this solely within thermodynamics, since thermodynamics is actually 'physical' thermodynamics.

11 Construction of entropy

11.1 Outline of the logic introducing entropy

As summarized in **10.11** we can foliate $\mathcal{E}$ into strongly differentiable leaves (hypersurfaces called reversible adiabatic hypersurfaces) consisting of equilibrium states that can be mutually connected by adiabatic quasistatic reversible processes. These leaves stack smoothly along the E axis without altering the stacking order at any $\boldsymbol{Y}$ (→**10.8**, **11.4**).

Therefore, a differentiable function S that effectively captures this geometric structure (foliation structure) of $\mathcal{E}$ can be defined as follows: it takes a constant value 'S' on each leaf and is strictly monotonically increasing along the energy axis. That is, for each operational coordinates $\boldsymbol{Y}$, $E < E' \Rightarrow S(E, \boldsymbol{Y}) < S(E', \boldsymbol{Y})$, where $(E, \boldsymbol{Y})$ and $(E', \boldsymbol{Y})$ are both in $\mathcal{E}$.

Remark What we are doing here is defining a state function called entropy as conveniently as possible within the limits allowed. We are not proving that such a function already exists. In **10.11**, it is suggested that a convenient state function S can be constructed that captures the structure naturally inherent in $\mathcal{E}$. Our fundamental stance is that the "geometry" that the totality of equilibrium states is divided into leaves with a fixed ordering along the energy axis is the essence of natural phenomena, and entropy is 'merely' a means of expressing this or capturing this analytically.

11.2 Adiabatic accessibility and entropy

For simple systems, particularly as considered in **C.6**, it is impossible to reach adiabatically below an adiabatic reversible hypersurface, that is, a hypersurface of constant entropy. In other words, the equilibrium states that can be reached adiabatically from a given equilibrium state are only those where the entropy has not decreased from the initial state. Let $\mathcal{E}$ be the totality of equilibrium states of a system. If an equilibrium state $B \in \mathcal{E}$ can be reached from another equilibrium state $A \in \mathcal{E}$ under adiabatic conditions, it is said that B is *adiabatically accessible* from A. Let us denote this relation as

$$A \prec B. \tag{11.1}$$

Then, at least for simple systems we have the following equivalence relation

$$A \prec B \iff S(A) \le S(B). \tag{11.2}$$

We will see this a general equivalence relation not confined to simple systems in **12.5**.

11.3 Transition between adiabatic hypersurfaces through heat exchange

How can the value of this function S be changed? To see this, let us represent the adiabatic reversible hypersurface that is assigned a value S, which is a hypersurface of height E over at $\boldsymbol{Y}$, as follows:

$$E = E(\boldsymbol{Y}, S). \tag{11.3}$$

By definition, if it is possible to increase the internal energy while fixing the operational coordinates, then S will increase. This means that S increases when heat Q is added to the system (→**C.3**). Here, since this process occurs within thermodynamic space, "adding heat" refers to adding heat in a quasistatic reversible manner[277].

Since we have assumed that S is an increasing function of E, when a small amount of heat $\delta Q > 0$ is added to the system, S must increase (→**11.1**). Due to strict monotonicity, the corresponding change requires $\delta S > 0$. Now, can we say anything more than continuity regarding the dependence of δS on δQ, that is, on δE under the condition that $\boldsymbol{Y}$ remains constant? Since we can write:

$$E + \delta Q = E(\boldsymbol{Y}, S + \delta S) \tag{11.4}$$

and thus, at constant $\boldsymbol{Y}$ when heat is added:

$$\delta Q = E(\boldsymbol{Y}, S + \delta S) - E = E(\boldsymbol{Y}, S + \delta S) - E(\boldsymbol{Y}, S). \tag{11.5}$$

Since $E(\boldsymbol{Y}, S)$ is strongly differentiable with respect to $\boldsymbol{Y}$ as shown in **10.6**, if $\delta S \propto \delta Q$ for a certain $\boldsymbol{Y}$, we may assume $\delta S \propto \delta Q$ anywhere.

11.4 We may assume $\boldsymbol{\delta S \propto \delta Q}$

Thus, the problem is whether the dependence of the adiabatic reversible hypersurface on E is differentiable or not. In other words, the solution to (10.2) is differentiable with respect to its initial condition E (i.e., the E coordinate of P). As already discussed in **10.9**, this holds if $\boldsymbol{y}$ is partially differentiable with respect to E.

---

[277] We will see that such a process is actually possible in (→**14.12**), though in general, this is required by **C.3**.

Whether this holds or not must be determined by nonthermal physics and chemistry. Here, we require or assume this smoothness.[278] Thus, we may set $\delta S \propto \delta Q$.

> The standard argument since Carathéodory is as follows: Since $dS = 0$ and $dQ = 0$ are equivalent, on an adiabatic reversible hypersurface, the coefficients of the following two 1-forms
>
> $$dQ = dE - \sum y_i dY_i = 0, \tag{11.6}$$
>
> $$dS = \frac{\partial S}{\partial E} dE + \sum_i \frac{\partial S}{\partial y_i} dY_i = 0 \tag{11.7}$$
>
> must be proportional.[279] Consequently,
>
> $$dS = \frac{\partial S}{\partial E}\left(dE - \sum y_i dY_i\right) \tag{11.8}$$
>
> must hold, but S is (required to be) partially differentiable, $\delta S \propto \delta Q$.

Since Q is extensive, S must also be extensive. Therefore, we may require the partition additivity[280] (→**2.14**).

11.5 $S(E, \boldsymbol{Y})$ is partially differentiable with respect to thermodynamic coordinates

Let $E = E(\boldsymbol{Y})$ describe a leaf with constant S (i.e., a reversible adiabatic hypersurface). If we displace the operational coordinates from $\boldsymbol{Y}$ to $\boldsymbol{Y} + \delta\boldsymbol{Y}$ on this leaf, the state coordinates become $(E(\boldsymbol{Y} + \delta\boldsymbol{Y}), \boldsymbol{Y} + \delta\boldsymbol{Y})$, so we have, since S is constant on the leaf,

$$S(E(Y + \delta\boldsymbol{Y}), \boldsymbol{Y} + \delta\boldsymbol{Y}) = S(E(\boldsymbol{Y}), \boldsymbol{Y}). \tag{11.9}$$

Therefore, thanks to the partial-differentiability of S with respect to E and strong differentiability of the leaf $E = E(\boldsymbol{Y})$, we have[281]

$$S(E, \boldsymbol{Y} + \delta\boldsymbol{Y}) + \frac{\partial}{\partial E} S(E, \boldsymbol{Y} + \delta\boldsymbol{Y}) \frac{dE}{d\boldsymbol{Y}} \delta\boldsymbol{Y} = S(E, \boldsymbol{Y}) + o[\delta\boldsymbol{Y}]. \tag{11.10}$$

---

[278] Or, more directly, we could require the diffeomorphic relation between E and the adiabatic reversible hypersurfaces. This is true, if $\boldsymbol{y}$ is partial differentiable with respect to E as noted.

[279] The strong differentiability of S seems to be taken for granted.

[280] Precisely speaking, this to be hold for a system consisting of two noninteracting systems or a system in equilibrium.

[281] Here, E can be any realizable value; the following equality holds uniformly with respect to E.

That is,

$$S(E, \boldsymbol{Y} + \delta \boldsymbol{Y}) - S(E, \boldsymbol{Y}) = -\frac{\partial}{\partial E} S(E, \boldsymbol{Y} + \delta \boldsymbol{Y}) \frac{dE}{d\boldsymbol{Y}} \delta \boldsymbol{Y} + o[\delta \boldsymbol{Y}]. \tag{11.11}$$

Here, for each $\boldsymbol{Y}$ S is differentiable with respect to E, so the partial derivative is bounded. Therefore, we conclude that $S(E, \boldsymbol{Y})$ is partial differentiable (actually, strongly differentiable) with respect to $\boldsymbol{Y}$.

Thus, we may conclude that S is partial differentiable with respect to the thermodynamic coordinates.

11.6 Change of entropy due to thermal contact

Let us prepare two simple systems I and II individually in equilbrium. Keep I and II in thermal contact under an adiabatic condition as a whole. What is the final entropy $S_{\mathrm{I+II}}$ compared with the sum of the entropies S_{I} and S_{II} of the original systems I and II separately in equilibrium?

Because the change in entropy S for systems I and II requires $\delta S \propto \delta Q$ (→**11.3**), we can express the heat transfer using appropriate state functions θ_{I} and θ_{II} as $\delta Q_{\mathrm{I}} = \theta_{\mathrm{I}} \delta S_{\mathrm{I}}$, $\delta Q_{\mathrm{II}} = \theta_{\mathrm{II}} \delta S_{\mathrm{II}}$.

If system II obtains energy $\delta Q > 0$ as heat, and if system I loses the same amount of energy as heat, the entropy of the compound system changes as

$$\delta S = \delta Q \left(\frac{1}{\theta_{\mathrm{II}}} - \frac{1}{\theta_{\mathrm{I}}} \right), \tag{11.12}$$

because the entropy of a compound system is the sum of the entropies of its constituent simple systems. We have assumed II is colder and I hotter, but note that we still do not know which has larger θ, the cooler or the hotter system.

According to Thomson's principle **8.7** with the metaprinciple **8.4**, if we have two heat sources, there can be a system X that can produce work δW (> 0[282]) without any trace (X is an engine). Since system I is hotter and system II colder, heat δQ must flow from I to II to follow Clausius' principle. Conservation of energy (the so-called first law) implies that the heat flowing to the colder system II is $\delta Q - \delta W$. We assume everything is quasistatic and reversible, so the total entropy does not change for X (no trace)

$$\frac{\delta Q}{\theta_{\mathrm{I}}} = \frac{\delta Q - \delta W}{\theta_{\mathrm{II}}} \quad \Rightarrow \quad \delta Q \left(\frac{1}{\theta_{\mathrm{II}}} - \frac{1}{\theta_{\mathrm{I}}} \right) = \frac{\delta W}{\theta_{\mathrm{II}}} > 0. \tag{11.13}$$

---

[282] The sign convention here is opposite to our usual convention.

Therefore, $\theta_{\rm II} < \theta_{\rm I}$. That is, a hotter system has a larger θ.[283] Notice that if I (also II) is neither hotter nor colder, that is there is no heat transfer upon thermal contact between I and II $\theta_{\rm II} = \theta_{\rm I}$.

Thus, (11.12) is positive. That is, entropy increases due to thermal contact.

11.7 What is temperature?: absolute temperature and entropy

An intensive state quantity is called an *empirical temperature*, if it takes the same value between systems in thermal equilibrium and a hotter system (→**7.12**) exhibits a larger value (→**8.3**).[284]

Thus, the θ in **11.6** is an empirical temperature and, since it is thermodynamically natural and simple, is called the *absolute temperature*, which will henceforth be denoted by T. S will be called the *entropy* of the system.

Let dQ be the 1-form[285] expressing the amount of heat reversibly added to the system. Then, we have

$$dS = \frac{1}{T} dQ. \tag{11.14}$$

Since dS is a differential of a state function, it is an exact form (→**9.9**). Thus, T is an integrating factor of the non-exact form dQ.

Since dQ is the reversible energy change under constant operational coordinates $\boldsymbol{Y}$, we can write

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}} = T \tag{11.15}$$

and may regard this as the definition of the *absolute temperature.* The condition $\boldsymbol{Y}$ = const. implies that there is no exchange of matter between the system and its environment, we may also write

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},{\rm closed}}. \tag{11.16}$$

---

[283] Precisely speaking, what has been shown is that the system I that supplies heat has a larger θ. If system II is a hotter system than system II, then we can transfer heat from I to II without any trace (note that δW can be converted to heat) violating Clausius' principle **8.3**. Therefore, the supplier of the heat must be hotter.

[284] However, whether the existence of the so-called empirical temperature can really be empirically claimed is a delicate issue as noted in **3.8**. θ introduced here may well be the only unquestionable empirically constructed temperature.

[285] dQ is not meant to be the differential of Q, but dQ as a whole denotes a 1-form (→**9.8**). Probably writing it as q and call it the heat form may be better.

Since we have not chosen any unit of S, the unit of T is not determined at this point. As we will see later, if we choose the equation of state of the one-mole ideal gas as $PV \propto T$, then the T in this formula and that given by (11.15) are proportional (→**15.4**), so the choice of the proportionality constant $R = PV/T$ determines the unit of T and S (→**11.14**).

11.8 Change of entropy due to thermal contact

The following is essentially a repetition of the last portion of **??** in terms of absolute temperature. Let us consider what happens when two separate (simple) systems 1 and 2, each in equilibrium, are brought into thermal contact to form a composite system which is, as a whole, under an adiabatic condition.

Assume that temperatures T_1 and T_2 satisfy $T_1 > T_2$. According to Clausius' principle **8.3**, energy will irreversibly flow as heat from system 1 to system 2. Therefore, let us examine what happens when a small amount of energy $\delta E (> 0)$ is transferred from system 1 to system 2 through a thermally conducting barrier between them. According to **11.7**, after reaching equilibrium, the entropy decreases in system 1 by $\delta E/T_1$ and increases in system 2 by $\delta E/T_2$ during the energy transfer δE. Consequently, the entropy of the composite system under adiabatic conditions increases due to irreversible heat transfer:

$$\delta S = \delta E \left(\frac{1}{T_2} - \frac{1}{T_1} \right) > 0. \tag{11.17}$$

Thus, "it is impossible to decrease entropy in an adiabatic composite system through thermal contact." This is a rephrasing of Clausius' principle using entropy.

11.9 Gibbs' relation

For quasistatic processes generalized work may be expressed in terms of the generalized work form $\omega + \zeta$, so the first law of thermodynamics (→**7.14**) may be written as

$$dE = dQ + \sum_i y_i dY_i \tag{11.18}$$

in terms of operational coordinates (→**4.12**). Combining this with the entropy-reversible heat exchange relation $dQ = TdS$ (→**11.7**), we get

$$dE = TdS + \sum_i y_i dY_i = TdS + \sum_i x_i dX_i + \sum_j \mu_j dN_j. \tag{11.19}$$

Gibbs recognized this as the fundamental relation in thermodynamics and completed the foundation of thermodynamics (→**11.10**). Thus, this relation is called *Gibbs' relation*.

Remark. dS and $d\boldsymbol{Y} = (d\boldsymbol{X}, d\boldsymbol{N})$ are the differential between two infinitesimally adjacent equilibrium states; states $(E, \boldsymbol{Y})$ and $(E + dE, \boldsymbol{Y} + d\boldsymbol{Y})$ must be in the set of equilibrium states $\mathcal{E}$ for Gibbs' relation to be meaningful. This should be an obvious statement, but very often this is forgotten when chemical thermodynamics is considered.

The thermodynamics before Gibbs concentrated on the formulation of the second law, but Gibbs reformulated thermodynamics as an even practically useful versatile system in terms of entropy obtained by the efforts before Gibbs. The starting point of the reformulated thermodynamics is this Gibbs' relation. Each term takes the form: [an intensive quantity] × d[the corresponding (i.e., *conjugate*) extensive quantity].

Since entropy is the central quantity for thermodynamics, it is often natural and convenient to write Gibbs' relation for dS:

$$dS = \frac{1}{T}dE - \sum_i \frac{y_i}{T} dY_i. \tag{11.20}$$

Remark: As noted in **11.10**, Gibbs did not assume chemical reactions to occur in the system. Thus, there is no need to distinguish the materials coordinates and the chemical component variables. His dN_i are operational coordinates. That is, they are materials coordinates.

11.10 Gibbs' original formulation

Here, the original passage from Gibbs' classic paper[286] introducing Gibbs' relation is copied:

> (p62) Let us first consider the energy of any homogeneous part of a given mass, and its variation for any possible variation in the (p63) composition and state of this part. (By *homogeneous* is meant that the part in question is uniform throughout, not only in chemical composition, but also in physical state) If we consider the amount and kind of matter in this homogeneous mass as fixed, its energy E is a function of entropy S, and its volume V, and the differentials of these quantities are subject to the relation

$$dE = TdS - PdV, \tag{11.21}$$

---

[286] reprinted in *The Scientific Papers of J. Willard Gibbs V1* Thermodynamics (Kessinger's Legacy Reprints version; a reprint of 1906 Longmans, Green and Co. version). Notations of the thermodynamic variables have been replaced with the corresponding ones in these notes. The page numbers referred to are those in this version.

> T denoting the (absolute) temperature of the mass, and P its pressure. For TdS is the heat received, and PdV the work done, by the mass during its change of state. But if we consider the matter in the mass as variable, and write N_1, $N_2, \cdots, N_n$ for the quantities of the various substances 1, 2, $\cdots$, n of which the mass is composed, E will evidently be a function of $S, V, N_1, \cdots, N_n$, and we shall have for the complete value of differential of E
>
> $$dE = TdS - PdV + \mu_1 dN_1 + \cdots + \mu_n dN_n, \tag{11.22}$$
>
> $\mu_1, \cdots, \mu_n$ denoting the differential coefficients of E taken with respect to $N_1, \cdots, N_n$.
>
> The substances 1,$\cdots$, n of which we consider the mass composed, must of course be such that the values of the differentials $dN_1, \cdots, dN_n$ shall be independent, and shall express every possible variation in the composition of the homogeneous mass considered, including those produced by the absorption of substances different from any initially present. It may therefore be necessary to have terms in the equation relating to the component substances which do not initially occur in the homogenous mass considered, provided, of course, the substances, or their components, are to be found in some part of the whole given mass.[287]

Then, the original goes on to the phase rule (→**23.9**) discussion.
It is clear that chemical reactions are not in his scope at least in the book.

11.11 Gibbs' relation and chemical reactions

As warned in **4.10** (also noted in **11.9**) $d\boldsymbol{N}$ in $d\boldsymbol{Y}$ in this formula represents the amount of chemicals we add or remove from the system independently (operational coordinates). Therefore, due to chemical reactions (i.e., due to the shift of chemical equilibria) actual changes of the chemical composition variables may not be given by $d\boldsymbol{N}$ (for example, even if we add dN_i of chemical i, in the system the amount of chemical i may not increase by dN_i due to chemical reactions). The actual chemical composition changes $d\tilde{\boldsymbol{N}}$ are given by, when the ordinary thermodynamic coordinates E and $\boldsymbol{X}$ are specified,

$$d\tilde{\boldsymbol{N}} \equiv R_{E,\boldsymbol{X}}(\boldsymbol{N} + d\boldsymbol{N}) - \boldsymbol{N}, \tag{11.23}$$

where R is the reaction map (→**4.11**) giving the equilibrium composition under the condition specified by the ordinary thermodynamic coordinates E and $\boldsymbol{X}$.[288]

We can also express Gibbs' relation in terms of the chemical composition change

---

[287] Thus, chemical reactions are totally ignored; the changes of N_i are due to (algebraic) addition only.

[288] Needless to say, the system before addition must be in equilibrium: $R_{E,\boldsymbol{X}}(\boldsymbol{N}) = \tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N}^*)$. Here, $\boldsymbol{N}^*$ as the variable of R denotes the particular choice of the materials coordinates whose values agree with the chemical component variables: $\boldsymbol{N}^* = \tilde{\boldsymbol{N}}$.

(including the effects of chemical equilibrium shifts), i.e., $d\tilde{\boldsymbol{N}}$, as

$$dE = TdS + \sum_i x_i dX_i + \sum_j \mu_j d\tilde{N}_j. \tag{11.24}$$

This is because adding $d\boldsymbol{N}$ and adding $d\tilde{\boldsymbol{N}}$ (both as the increment of materials coordinates of the system; never misunderstand that $d\tilde{\boldsymbol{N}}$ here is the increment of the chemical composition variables) to the system result in the identical equilibrium state. Do not forget that not all the $\tilde{\boldsymbol{N}}$ are independently changeable due to chemical equilibrium relations. The resultant materials coordinates are given by $\boldsymbol{N} + d\tilde{\boldsymbol{N}}$ or equivalently by $\boldsymbol{N} + d\boldsymbol{N}$.[289] However, the actual system energy change may still be written in terms of $d\boldsymbol{N}$ as in (11.19).

In any case, the key point is that Gibbs' relation is an exact 1-form for E with the operational coordinates as independent variables.[290,291]

11.12 Partial derivatives with chemical reactions

Even though $\boldsymbol{N}$ and other variables are operationally independent, as variables for description of the chemical composition of the system, $\tilde{\boldsymbol{N}}$ cannot generally be independent of other variables; you cannot fix them freely while varying E and $\boldsymbol{X}$. It is important to recall that $\tilde{\boldsymbol{N}}$ is, unfortunately, the standard thermodynamic variable in the conventional textbooks.

Gibbs' relation tells us

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\boldsymbol{N}}, \tag{11.25}$$

---

[289] Simple illustration: consider A $\longleftrightarrow$ B with the equilibrium condition to be the identity of the amounts of A and B. Let us add δN_{A} and δN_{B} to the system. Then, obviously, $\delta\tilde{N}_{\mathrm{A}} = \delta\tilde{N}_{\mathrm{B}} = (\delta N_{\mathrm{A}} + \delta N_{\mathrm{B}})/2$.

[290] In traditional thermodynamics, the chemical composition variables are regarded as the basic chemical coordinates. However, they are not independent variables, in general, so Gibbs' relation may not be written in terms of them. For example, if $\tilde{\boldsymbol{N}}$ is fixed, in most cases, no state change can occur, because chemical equilibria depend on the internal energy and the work coordinates. Thus, we must distinguish the operational change of $\boldsymbol{N}$ and the actual change (along the actual quasistatic path) of $\tilde{\boldsymbol{N}}$ as stressed in **4.4-4.10**.

[291] One might introduce the so-called extent of chemical reactions (or reaction coordinates) $\boldsymbol{\xi}$ that are supposedly independent of each other by introducing appropriate catalysts. However, even if you introduce (orthogonal) reaction coordinates, still you cannot fix the reaction coordinates at your will while changing E and $\boldsymbol{X}$, because the chemical equilibria shift, meaning $\boldsymbol{\xi}$ changes.

but the conventional formula

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\tilde{\boldsymbol{N}}} \tag{11.26}$$

is usually meaningless.[292] (11.25) is equivalent to

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\mathrm{closed}}. \tag{11.27}$$

Also, we may write

$$x_i = \left(\frac{\partial E}{\partial X_i}\right)_{S,X_i^c,\boldsymbol{N}}, \tag{11.28}$$

but the conventional formula

$$x_i = \left(\frac{\partial E}{\partial X_i}\right)_{S,X_i^c,\tilde{\boldsymbol{N}}} \tag{11.29}$$

is, generally, meaningless.

We can fix S and $\boldsymbol{X}$ while changing some of the materials coordinates. Therefore,

$$\mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,\boldsymbol{X},N_i^c} \tag{11.30}$$

is meaningful, but with the chemical composition variables, an analogous expression in the standard textbooks is meaningless.[293]

---

[292] To avoid this difficulty, honest textbooks explicitly demand that $\tilde{\boldsymbol{N}}$ can be fixed at our will while changing other thermodynamic coordinates. We have already noted in Remark 2 of **8.5** that this *ad hoc* convention cannot rescue chemical thermodynamics.

[293] In this 'unit' there are several statements about meaningless nature of the conventional textbook expressions. However, we must note that not all the textbooks are imprecise. For example, Kirkwood and Oppenheim, *Chemical Thermodynamics* (McGraw-Hill, 1961) clearly states that the usual Gibbs' formula for open systems applies when there is no chemical reaction (p52 for homogeneous systems, p56 for inhomogeneous systems). It is also stated clearly on p48 that, for a closed system, the changes due to chemical components do not appear at all in the expression of the first law.

However, on p101 we find the following statement: 'In a closed system in which the masses of the components are changed,

$$dE = TdS - PdV + \sum \mu dN \tag{8.4}$$

From this the chemical equilibrium condition under constant S and V is discussed. Thus, clearly there is a confusion.

11.13 Fundamental equations

Describing a system thermodynamically involves setting up its thermodynamic space and giving its entropy S as a function of its thermodynamic coordinates $(E, \boldsymbol{Y})$. Therefore, $S = S(E, \boldsymbol{Y})$ is referred to as the *fundamental equation* of the system.

A fundamental equation is specific to a particular system and is not a universal function that applies to all systems. As a result, thermodynamics cannot provide it for a given system. Instead, it may be an empirical result or a product of theories outside thermodynamics.[294]

To describe a system or a material, equations of state are often used. For example, the relation among the pressure P, volume V and temperature T for a gas is a famous example. However, since non-fundamental variables (→**3.2**) such as P and T appear, such an equation of state is insufficient to determine the fundamental equation; we need knowledge of E. Let us see the problem for an ideal gas (→**11.14**).

11.14 Fundamental equation of ideal gases

The relation between pressure P, volume V and temperature T for an N mole ideal gas is usually called the equation of state of an ideal gas:

$$PV = NRT. \tag{11.31}$$

Here, R is the gas constant.[295] This relation is, like all other equations of state, not a result of thermodynamics, but a result of experiments or some other theories.

To describe an ideal gas thermodynamically, we must first set up its thermodynamic space, and then provide its entropy as a function of thermodynamic coordinates or give its internal energy as a function of entropy and operational coordinates.

For an ordinary gas with a fixed amount its thermodynamic coordinates are only V in addition to E. Therefore, its fundamental equation takes the form: $S = S(E, V)$, which is not provided by thermodynamics, but requires empirical data. One such piece of data is the so-called equation of state (11.31), while the other is a relation between E and some other variables (called a *thermal equation of state*). For an ideal

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[294] For example, if thermodynamics is applied to chemical industry, almost always detailed experimental data are used, while detailed steam tables (e.g., found in this) are employed for steam engines.

[295] $R = 8.314\,462\,618\,153\,24$ m^2·kg/s^2·K·mol.

gas, we use the 'fact' that E depends only on T linearly.

If we heat the gas without any work (i.e., at constant V), all the added heat would be converted to the internal energy. Thus, under constant volume, we assume (based on empirical results)

$$E = NC_VT, \tag{11.32}$$

where C_V is a constant (later called the constant volume heat capacity →**14.6**) per mole (molar heat capacity). Gibbs' relation (→**11.9**)

$$dS = \frac{1}{T}dE + \frac{P}{T}dV \tag{11.33}$$

and (11.32) tell us that under a constant volume condition

$$dS = \frac{NC_V}{E}dE. \tag{11.34}$$

Since entropy is a state quantity, dS is exact (→**9.9**). Therefore, the entropy of an equilibrium state F $= (E, V)$ is obtained from that of the initial state I $= (E_0, V_0)$ by any process described by any continuous curve[296] connecting I and F (→**9.13**). Therefore, let us line-integrate (11.33) along the path first going from I to state M $= (E, V_0)$ and then from M to F (Fig. 11.1). For a 1 mole gas $P/T = R/V$, so the fundamental equation for a 1 mole ideal gas reads

$$S = S_0 + \int_{E_0}^{E} \frac{C_V}{E}dE + \int_{V_0}^{V} \frac{R}{V}dV = S_0 + C_V \log\frac{E}{E_0} + R\log\frac{V}{V_0}. \tag{11.35}$$

From this, we can get everything we wish to know thermodynamically:

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E = \frac{R}{V},\ \ \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{C_V}{E}. \tag{11.36}$$

---

[296] Actually, 'continuity' alone is inconvenient, so throughout these lectures, we assume that any curve has a length (→**9.13**).

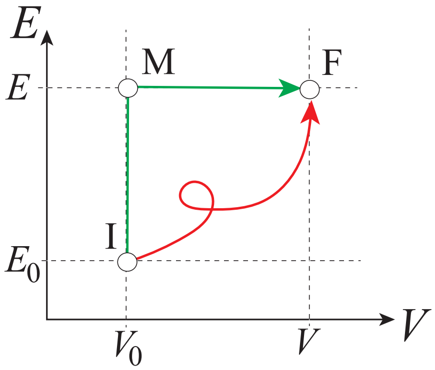

Figure 11.1: The green path is the integration path for (11.35). We may use any curve (say, the red curve) connecting I and F in the thermodynamic space, but a practical path must be something like the green one.

The premises of themodynamics—a summary

The key assumptions to develop thermodynamics have been mentioned up to this point. Let us have a summary. We will avoid, however, a reckless attempt to establish an axiomatic system for thermodynamic (see **1.8** and a footnote there). Accordingly, as can be understood from the numbers of the cited units, we do not pay much attention to the ordering of the "premises." However, if you follow and understand the units marked with $*$ in the appropriate order (i.e., in the order of the explanations given so far), it should be possible to construct thermodynamics fairly logically.

As discussed in **1.9**
$*$ We accept the established facts and basic principles of macroscopic nonthermal physics and chemistry. All the basic variables (thermodynamic coordinates) are completely defined within this premise. For instance, the integrability of work forms even without continuity of conjugate variables, and the existence of adiabatic reversible processes **10.1**, **C.2** are presupposed by macroscopic physics. However, although it may be somewhat artificial, we assume the differentiability of the conjugate variables $\boldsymbol{y}$ with respect to E (→**10.9**). Furthermore, the Euclidean nature of the space spanned by thermodynamic coordinates (→**5.2**) also arises from macroscopic physics and similar sources.
$*$ The systems under consideration are restricted to additive systems (→**2.11**).

$*$ It is possible to change the operational coordinates without involving thermal phenomena (→**3.11**). The postulate dual to this is the possibility of thermal contact (→**7.12**).
$*$ The systems are constrained to have non-fractal 3-dimensional boundaries, and it is permissible to set boundary conditions within their interior as "walls" (→**2.1**). There are walls allowing the exchange of any set of thermodynamic coordinate components for any prescribed time span (→**5.8**).
$*$ Any system can be in an equilibrium state (→**2.8**). "A state of a system is an equilibrium state, if there is a constant environment in which we can embed the system with an appropriate boundary condition (wall) without causing any change of the state of the system and without any dissipation."
$*$ "Uniqueness of Equilibrium States" **2.9**: Equilibrium states reached under identical conditions are unique (thermodynamically indistinguishable).

$\ast$ Equilibrium states are partitioning-rejoining invariant (→**2.13**).
$\ast$ "Equivalence of Work Coordinates and Material Coordinates" **7.3**: The equivalent relationship between the energy associated with the exchange of material and the energy in ordinary non-thermal physics has been empirically established. These coordinates may be collectively referred to as "Operational Coordinates."
$\ast$ The change in internal energy of the system is measurable [**7.9** energy meter property of the system].
$\ast$ "Principle of Mayer-Joule" **7.14**: Generalized work can always be converted into heat at a constant conversion rate and add to any system. It is presupposed that heat and work can be distinguished (→**7.13**).
$\ast$ "Planck's Principle" **8.5**: If operational coordinates do not change before and after an adiabatic process, the internal energy of the system is non-decreasing.

We also assume the Meta Principle **8.4**: "Negation of anything that thermodynamic principles explicitly forbids is allowed."

$\ast$ "Possibility of Reversible Quasistatic Heating and Cooling" **C.3**: A system can reversibly and quasistatically exchange heat with its environment without changing its operational coordinates as long as the state is in $\mathcal{E}$.

Additionally, though secondary, the following two are assumed:

$\ast$ For any substance (or collection of substances) selective permeable membranes exist (→**17.5**).
$\ast$ Heat baths exist (→**8.8**).

12 Principle of increasing entropy

12.1 The principle of increasing entropy: introduction

In simple systems, as shown in **11.2**, entropy never decreases during adiabatic processes. In such systems, as reflected in Planck's principle, irreversible processes and increases in internal energy within adiabatic systems are inseparable. Therefore, it should be noted that the claim in **11.2** is based on this understanding, and thus the equivalence between adiabatic reachability and non-decreasing entropy has not been demonstrated generally.

Thus, we must consider how entropy changes in an adiabatic compound system when a prepared equilibrium state ultimately reaches another equilibrium state irreversibly after walls (constraints) between subsystems are removed or relaxed.[297] Since thermodynamics can only deal with the relationship between equilibrium states, to begin with, it is essential to precisely define the initial equilibrium state from which irreversible changes start (→**12.2** and **12.3**).

12.2 How to make various non-homogeneous equilibrium states

We have seen in **5.8** that we can prepare an equilibrium state of a compound system (→**2.10**) by combining simple systems in equilibrium through various walls (boundary conditions →**2.1**) and then leave the resultant state for a sufficiently long time in a fixed environment that does not cause any dissipation even after any time dependence subsides. Here, a wall (= boundary condition) is specified by a set of extensive quantities allowed to be exchanged across it.

In thermodynamics, only equilibrium systems that can be constructed as described in the preceding paragraph are discussed. Note that the component simple systems appearing in the construction of a compound system are macroscopic (→**1.4**) but can be extremely small relative to our size. Thus, as stages for the usual macrophysics (fluid dynamics, rheology, etc.) such compound systems provide sufficiently detailed macroscopic description of a system.[298]

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[297] The changes caused by external operations, as long as they do not alter the relationships between subsystems, may be treated similarly to the case of simple systems and are not addressed separately.

[298] Needless to say, this does not mean in fluid dynamics, rheology, etc., small macroscopic parts of a system are always in equilibrium.

12.3 Constrained equilibrium states

If we remove all the walls between any simple subsystems defining a compound system (→**12.2**) in equilibrium (i.e., if all the boundary constraints on intrasystem exchanges of extensive quantities are abolished), the system would eventually settle down to an equilibrium state of a simple system.[299]

Since the system as a whole was in equilibrium[300] even before abolishing walls, the original system should be regarded as in an equilibrium state but is not allowed to reach the unconstrained equilibrium state by constraints (walls). Therefore, let us call the original equilibrium state of the compound system a *constrained equilibrium state*. Since all the walls need not be abolished at once, there are many different constrained equilibrium states for a given (compound) system.

To (partially) remove constraints may be expressed as reducing or weakening the constraints.

The devices imposing constraints (in many cases, walls) themselves do not contribute thermodynamic quantities to the system; they exert thermodynamic effects only through interfering the exchange of extensive quantities. Therefore, as stated before (→**2.1**), such devices (walls) are very often identified with particular mathematical boundary conditions imposed there.[301]

12.4 Reducing constraints does not decrease entropy

Take two simple systems in equilibrium with the thermodynamic coordinates being $(E_1, \boldsymbol{Y}_1)$ and $(E_2, \boldsymbol{Y}_2)$, respectively. We combine[302] these two systems without any constraint on the 'wall (meaning that exchange of any extensive quantities is allowed without any restrictions at the boundaries of both systems[303]) between the two sys-

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[299] Usually; always, especially if all the component simple systems are made of the same chemical components.

[300] According to our definition of 'equilibrium' **2.8**.

[301] Needless to say, this identification is allowed only when (sub)systems are macroscopic. Nowadays, systems with a very few microscopic particles or microscopic mechanical degrees of freedom are discussed as thermodynamic systems, and their boundaries are often mathematical boundary conditions. Whether such an idealization is meaningful or not should be critically considered case by case.

[302] When two equilibrium systems are combined, it is not always automatically guaranteed that the additivity of extensive quantities holds, but we can realize additivity without any net work to the whole system under an adiabatic condition. That is, there is a way to realize the idealized additivity to hold. See **5.10**.

[303] Needless to say, there would be no difference, even if there is restrictions in exchange as can be seen from the argument below.

tem, and leave them alone (isolated from ‘the world’). The resultant new equilibrium states would be written as $(E_1+\Delta E, \mathbf{Y}_1+\Delta\mathbf{Y})$ and $(E_2-\Delta E, \mathbf{Y}_2-\Delta\mathbf{Y})$, respectively. Of course, these two systems are individually in equilibrium and in equilibrium with each other. Furthermore, each system has its own definite entropy. The sum of the entropies of individual systems after combining is the entropy S_{1+2} of the equilibrium state reached after combining the two systems.

First, make the wall between the two systems adiabatic but allowing arbitrary exchange of operational coordinates. If the combined system is left undisturbed, both the simple systems perform adiabatic works on each other. The resultant equilibrium state of the individual system, which is adiabatic, will have non-decreasing entropy as seen in **11.2**.

Next, make the wall between the systems diathermal but allow no exchange of any operational coordinates. Leaving the combined system under this condition will result in heat exchange and a new equilibrium state will be reached. As seen in **11.6**, the entropy in this new state will not decrease compared to the initial state.

If we alternate these two types of operations, the entropy of the combined system will increase monotonically, so it converges to a finite value or definitely diverges to infinity. However, the divergence is impossible for a finite system.[304] Then, the entropy must converge to S_{1+2}.[305]

Since entropy did not decrease in any step of gradually removing the constraints, we have $S_{1+2} \geq S_1 + S_2$.

As can be seen from the demonstration, the essence is, informally, Planck’s principle (or entropy cannot be reduced adiabatically) and Clausius’ principle (or entropy increases by thermal contact).

12.5 The principle of increasing entropy

A system, under an adiabatic condition, transitions from one equilibrium state to another (for instance, when constraints are reduced or operational coordinates are altered by the experimenter →**12.3**). We now know from **11.2** and **12.4** that entropy does not decrease in such transitions. In other words, if we denote that state $B \in \mathcal{E}$ is adiabatically accessible from state $A \in \mathcal{E}$ as $A \prec B$ as before, then generally the

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[304] because the relation between an interval of E and the corresponding interval of S is diffeomorphic (→**10.8**). Here, E is finite.

[305] Note that the resultant system is a simple system (without any internal constraints). Therefore, if the states have distinct S for a definite $\boldsymbol{Y}$, their internal energy must be distinct. This of course contradicts the isolated nature of the total system.

following equivalence holds:

$$A \prec B \iff S(A) \le S(B). \tag{12.1}$$

This is referred to as the *principle of increasing entropy*.[306] In a closed system under an adiabatic condition, if a change occurs spontaneously from an initial to a final equilibrium state,[307] the system entropy can never decrease.

However, this only means that if the initial entropy and the entropy of the final equilibrium state is compared, the latter cannot be smaller. Even if we say the entropy increases with a process through relaxing constraints, it does not mean the system entropy at any time point increases during the process. Do not forget that entropy is defined only for equilibrium states.[308]

12.6 The entropy maximization principle

Due to **12.5**, if the entropy of a closed adiabatic system becomes maximum under given constraints, the system cannot change any further, so the system is in (constrained) equilibrium.[309]

The converse also holds under the metaprinciple of thermodynamics (→**8.4**). If the system entropy is not max, then there is no thermodynamic proposition (or principle) that is violated even if a spontaneous change happens to increase its entropy. Therefore, the system cannot be in equilibrium, if its entropy is not maximum. Thus, 'entropy max' and 'equilibrium' are equivalent. This is called the *maximum entropy principle* or *entropy maximization principle*.

12.7 Adiabatic accessibility and entropy

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[306] ⟪**$\Delta S > 0$ shown?**⟫ Note that what is actually demonstrated up to this point is only $\Delta S \not< 0$; that is, we have only demonstrated that, if $\Delta S < 0$, then the second law would be violated. $\Delta S > 0$ has never been demonstrated, so, logically speaking, 'increasing' is an exaggeration. However, *within the thermodynamic framework*, we have examples in which actually $\Delta S > 0$ can be demonstrated under the condition for $\Delta S \not< 0$, so it is admissible to use this name for the principle.

The situation is quite different from the so-called pure mechanical demonstration of the second law (e.g., using Jarzynski's inequality).

[307] As emphasized later (→**12.11**) equilibrium states are all stable against (thermodynamically meaningful) small perturbations, so in this case the initial state must be prepared by relaxing some constraints.

[308] Thus, it is meaningless to mention the thermodynamic entropy of the universe.

[309] Here, the uniqueness of the state with max entropy is true as long as the thermodynamic coordinates are additive.

Let $\mathcal{E}$ be the totality of equilibrium states of a given system. For $A, B, C \in \mathcal{E}$, $A \prec B$ and $B \prec C$ imply $A \prec C$ (transitivity). It is also antisymmetric (if $A \prec B$ and $A \neq B$, then $B \not\prec A$) and reflexive $A \prec A$). Mathematically such a relation is called a partial ordering relation (or *partial order*). If for any $A, B \in \mathcal{E}$ at least one of $A \prec B$ and $B \prec A$ holds, $\prec$ is called a *total order*.

If a set U is totally ordered with respect to some ordering $\prec$, we can define a function f on U such that

$$x \prec y \Rightarrow f(x) \leq f(y). \tag{12.2}$$

We have seen that the adiabatic accessibility is a total order in **11.2** and **12.4**, so we can define a state function that increases by adiabatic processes. Entropy S is just such a function.

It is easy to recognize that irreversibility somehow orders the initial and the final equilibrium states. Thus, you might regard the existence of entropy is obvious. However, the nontrivial part is to show that this ordering is total.[310]

Also to see, for example, the differentiability of entropy we must assume some analytic properties of the state space, which may not be obvious from physics. Thus, in these lecture notes, the above mentioned approach has been totally avoided.

12.8 Structure of the thermodynamic space and entropy: a summary

Let us summarize the structure of the thermodynamic space which is captured analytically by the entropy S.

(1) The thermodynamic space is foliated by the adiabatic and reversible hypersurfaces on each of which entropy S is constant. These hypersurfaces are strongly differentiable with respect to $\boldsymbol{Y}$ (→**11.1**).

(2) Under the condition keeping all the operational coordinates constant (i.e., along a line parallel to the energy axis) entropy is a strictly monotone increasing function of E (→**11.3**), and $dS = dQ/T$, if heat dQ is added reversibly (→**11.7**).

(3) Thanks to (1) and (2) we can show (→**11.5**) that S is partial differentiable with respect to the thermodynamic coordinates.

(4) Entropy never decreases under adiabatic conditions (→**12.6**). This leads to the

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[310] Read Elliott H. Lieb and Jakob Yngvason, The physics and mathematics of the second law of thermodynamics Phys. Rep **310**, 1 (1999). They call this totality the *comparison principle*, and regard its demonstration as their chief contribution. As can be seen from this, the existence of entropy concept from irreversibility is actually highly nontrivial. This is why even for steady states the concept of entropy cannot be extended.

principle of increasing entropy **12.5** and the entropy maximization principle **12.6**.

12.9 Entropy max does not imply entropy extremum

Even if a system is in equilibrium, its entropy need not be maximum due to entropy being extremal. This is simply because the maximum of a continuous function occurs at an extremum or at the domain boundary (see, for an example, **16.6**).[311]

12.10 Thermodynamic variations

Variations of a thermodynamic state of a system are not simple displacements of the corresponding point in the thermodynamic space (more precisely in $\mathcal{E}$) of the system.[312]

What happens, under an adiabatic condition, if we perturb a system in an equilibrium state? Immediately after the perturbation, generally speaking, the system ceases to be in equilibrium, so the point describing the system disappears from the thermodynamic space. After a sufficiently long time, the system reaches an equilibrium state (→**2.9**). We only know that its entropy cannot be less than the original value before the perturbation. The realized equilibrium state after the perturbation is generally distinct from the original state. There is no way, generally, to predict the final state thermodynamically. Therefore, we only consider perturbations that may be handled within thermodynamics. That is the perturbation due to the thermodynamic variation.

A thermodynamic variation requires a partition $\mathcal{P}$ of the system under study into macroscopic pieces.[313] The thermodynamic coordinates of the resultant macroscopic pieces are chosen under the condition that the total sum of the extensive quantities of these subsystems agrees with the original total amounts.[314] The boundary conditions between subsystems may be chosen appropriately so that the state of the resultant compound system can stay in equilibrium (in order to use thermodynamics). Unless

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[311] Recall that $\mathcal{E}$ need not be an open set. If it is open, then a maximum if realized must always be an extremal.

[312] Since all the points in $\mathcal{E}$ are equilibrium states, the results of the perturbations never spontaneously return to the unperturbed state. If a variation pushes the state out of $\mathcal{E}$, we cannot use thermodynamics to discuss its effect.

[313] Here the partition may be understood as fictitious or virtual, but there is a way to actually realize it albeit complicated and impractical.

[314] If you wish to consider non-additive extensive quantities, the combined extensive quantities must be consistent with the amount in the original state as noted in the next footnote.

otherwise stated, the walls (boundary conditions) in the original compound systems are maintained and the imposed constraints are respected when thermodynamic variations are constructed (Fig. 12.1).

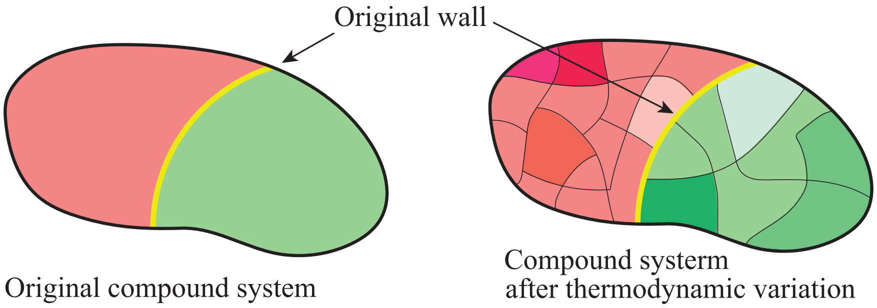

Figure 12.1: Unless otherwise stated, the walls (boundary conditions) in the original compound system are maintained and the imposed constraints are respected when thermodynamic variations are constructed.

For a function of thermodynamic coordinates $J(E, \boldsymbol{Y})$, its variation δJ due to the given thermodynamic variation is computed as

$$\delta J(E, \boldsymbol{Y}) = \sum_{i \in \mathcal{P}} J(E_i, \boldsymbol{Y}_i) - J(E, \boldsymbol{Y}), \tag{12.3}$$

where $\mathcal{P} = \{i\}$ denotes the set of subsystems i by a particular partition of the original system into subsystems satisfying $E = \sum_{i \in \mathcal{P}} E_i$ and $\boldsymbol{Y} = \sum_{i \in \mathcal{P}} \boldsymbol{Y}_i$.[315] That is, a *thermodynamic variation*, which may sonetimes called a *thermodynamic perturbation*, is defined by a particular spatial partition $\mathcal{P}$ (with appropriate boundary conditions and a particular distribution of thermodynamic coordinates $\{E_i\}$ and $\{\boldsymbol{Y}_i\}$).

The quantities with δ are often called virtual variations. This means that we do not worry too much about actual realizability of the variations. Here, δ does not mean that the variation is small in any sense. Still, we can say a thermodynamic perturbation δ is small if the thermodynamic densities (→**5.5**) change only slightly. **Remark**. δJ above is *not* defined as the difference between the original state and any result just after modification. Do not forget that we are discussing equilibrium thermodynamics. It is defined by comparing two equilibrium states, the original state that is in equilibrium and the final *equilibrium* state that the system reaches in a sufficiently long time after modification/variation is imposed.

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[315] If there are work coordinates that are not additive, then the choice of the values for each piece is complicated, but still we may assume the distribution of variables compatible with $\mathcal{P}$ is possible.

12.11 What happens if thermodynamic variations are applied?

For an equilibrium state of a system, if there were a thermodynamic variation for which $\delta S > 0$, then even if we remove all the constraints required to realize the variation, the resultant equilibrium state must show $\delta S > 0$ relative to the original 'unperturbed' state thanks to the principle of increasing entropy. This simply means that the original state was not an equilibrium state, contradicting our starting premise. In other words, for any thermodynamic variation, any equilibrium state must satisfy:

$$\delta S \le 0. \tag{12.4}$$

Traditionally, (12.4) is called the (thermodynamic) *stability criterion* of an equilibrium state, but as the above discussion tells us, it is a universal property of any equilibrium state of any simple system.[316]

However, if the variation does not respect the original constraints in the system (contrary to the situation illustrated in Fig. 12.1), then the variation can remove the original contraints, so the principle of increasing entropy **12.5** may apply, and $\delta S > 0$ can occur, implying the original state was not stable against some perturbations. In such a case the system evolves to a new equilibrium state. Therefore, (12.4) may generally be interpreted as the stability condition of the equilibrium state. However, still the reader must clearly recognize that for a simple system (12.4) must hold, and has nothing to do with the state stability.

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[316] As we will learn soon, it is equivalent to $-S$ being convex. See **13.5**.
Thus, an equilibrium state satisfying $\delta S > 0$ is oxymoronic.

13 Convexity

13.1 Convex analysis and thermodynamics

We have seen that the thermodynamic space of a system is a Euclidean space spanned by the internal energy E and the operational coordinates $\{Y_i\}$ (→**4.13**). The thermodynamic space is (trivially) foliated by reversible adiabatic hypersurfaces on which entropy is constant. If a certain point in $\mathcal{E}$ (= a certain thermodynamic state) is given, its entropy is determined as a state quantity by the fundamental equation (→**11.13**). Or, if the operational coordinates and entropy S are fixed, the internal energy of the system is determined, so internal energy is given as a state function of S and operational coordinates as $E = E(S, \boldsymbol{Y})$.

As we will see soon, E and S (precisely, $-S$) are (under certain reservations but substantially[317]) convex functions. Convexity imposes strong constraints on the mathematical structure of thermodynamics. For example, a convex function is a C^1-function if it is strongly differentiable. This implies that absolute temperature is continuous with respect to operational coordinates.[318]

The subfield of analysis discussing convex functions is called *convex analysis*.[319] It is highly desirable that any physicist has rudimentary knowledge of convex analysis, but it is not covered by the standard math courses for physics students. In this set of lecture notes, convex functions are defined in this section with some of their elementary properties explained. Other crucially important topics on convex analysis will be discussed later in Section 18.

13.2 Epigraph and convex function

Let us write a function f with n independent variables $x_1, \cdots, x_n$ as $y = f(\mu)$

---

[317] If there is no non-additive work coordinates

[318] However, do not forget that T may not be differentiable.

If chemicals are described in the conventional fashion as in the textbooks, then we cannot thermodynamically claim that chemical potentials are continuous as functions of thermodynamic coordinates.

[319] The standard reference may be R. T. Rockafellar, *Convex Analysis* (Princeton Landmarks in Mathematics 1997; original 1970). For us this is more than enough, but V. M. Tikhomirov, Convex Analysis (Chapter 1 of *Analysis II* edited by R. V. Gamkrelidze, Springer Berlin 1990 (Original 1987)) summarizes newer developments. This is included in *Encyclopaedia of Mathematical Sciences* Vol. 14.

($\mu = (x_1, \cdots, x_n)$).[320] Then, the *graph* of f is, if continuous, a n-hypersurface in $n+1$ space (y, μ) any of whose point is at height y at position μ in the n-hyperplane $(0, \mu)$. The point set above this graph including the graph (i.e, the hypersurface describing $y = f(\mu)$) itself is called the *epigraph* of function f (Fig. 13.1). More precisely:

> Let C be the domain of f. Its epigraph epi f is defined by
>
> $$\mathrm{epi}\, f = \{(y, \mu) \,|\, y \geq f(\mu), \mu \in C\}$$

Note the equality sign in $y \geq f(\mu)$ in the definition.

A function f defined on a convex set (→**5.11**) whose epigraph epi f is a convex set is called a *convex function.*

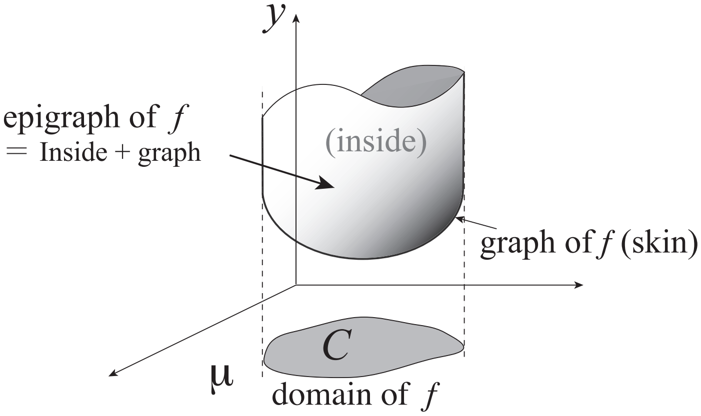

Figure 13.1: An epigraph and the corresponding convex function

A function that is convex upward is called a *concave function.* Convex functions are convex downward in mathematics.

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[320] The domain of f is assumed to be convex (→**5.11**). In standard textbooks of convex analysis such as Rockafellar's *Convex Analysis* for any function f its value outside its usual domain is set $f = +\infty$ and its domain is extended to the whole space. Here, we will not use this convention which is standard for convex analysis, but adopt the usual convention for functions. This will not be stated explicitly.

If the domain is not convex, then function f cannot be a convex function. Therefore, some people claim that the convexity of the domain of a convex function need not be stated explicitly. This opinion is logically flawed, because convexity can be verified only on a convex set. However, many physicists do not seem to think this way. Needless to say, if a convex function is provided beforehand, its domain must be convex, but if you wish to define a convex function anew, the domain must be provided in advance. A function cannot be defined without a domain, and its convexity cannot be checked if the domain is not convex.

13.3 Jensen's inequality

A crucial inequality for convex functions is:

Theorem [Jensen's inequality]

For a function $f : C \mapsto \mathbb{R}$ to be a convex function a necessary and sufficient condition is

$$f\left(\sum_i \lambda_i \mu_i\right) \le \sum_i \lambda_i f(\mu_i), \tag{13.1}$$

for any $\{\lambda_i\}$ such that $\lambda_i \ge 0$ and $\sum_i \lambda_i = 1$. This inequality is called *Jensen's inequality*. In other words, if we write a general weighted average as $\langle\ \rangle$

$$f(\langle \mu \rangle) \le \langle f(\mu) \rangle \tag{13.2}$$

is a necessary and sufficient condition for f to be a convex function. Its meaning should be clear from the following Fig. 13.2 (for two variables $\mu = (x_1, x_2)$). (13.2) means epi$f$ (→**13.2**) is a convex set.

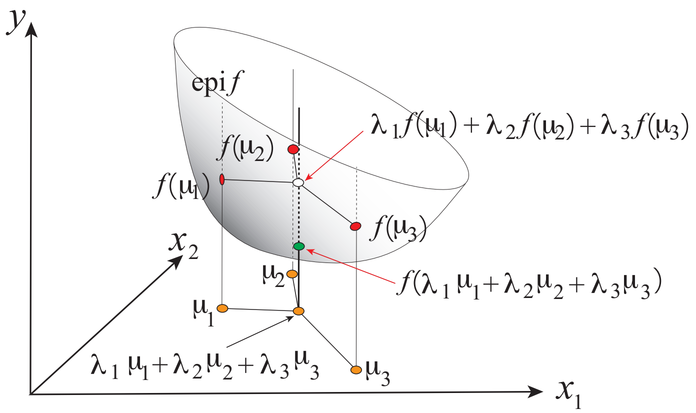

Figure 13.2: A convex function with two independent variables; Jensen's inequality (in this illustration for three points) means that the green dot on the graph is below the white dot (inside the epigraph). Thus, epi$f$ (→**13.2**) is a convex set.

13.4 Analytic properties of convex functions

Some important properties of a convex function are summarized without proof.

(1) A convex function is Lipshitz continuous.[321]
(2) A convex function is directionally continuously differentiable (→**9.1**) along any line in its domain except for countably many points.
(3) A convex function is continuously differentiable at a point where it is strongly differentiable (→**9.3**).

13.5 Entropy is a concave state function

Consider two equilibrium systems 1 and 2 whose thermodynamic coordinates are $(E_1, \boldsymbol{Y}_1)$ and $(E_2, \boldsymbol{Y}_2)$, respectively. Both states are assumed to be in the same set $\mathcal{E}$ of equilibrium states of a simple system. From these two systems we make a compound system, and then remove the wall between 1 and 2. Before removing the isolating wall the entropy of the (juxtaposed) compound system is

$$S(E_1, \boldsymbol{Y}_1) + S(E_2, \boldsymbol{Y}_2) \tag{13.3}$$

due to partition additivity. After removing the wall constraints, if work coordinates satisfy additivity,[322] the entropy of the resultant combined system[323] is $S(E_1 + E_2, \boldsymbol{Y}_1 + \boldsymbol{Y}_2)$. According to the principle of increasing entropy (→**12.5**) we have

$$S(E_1 + E_2, \boldsymbol{Y}_1 + \boldsymbol{Y}_2) \geq S(E_1, \boldsymbol{Y}_1) + S(E_2, \boldsymbol{Y}_2). \tag{13.4}$$

If we apply the extensivity of entropy (→**11.3**) for $\lambda \in [0, 1]$

$$\lambda S(E, \boldsymbol{Y}) = S(\lambda E, \lambda \boldsymbol{Y}), \tag{13.5}$$

so, combining the two relations, we get

$$S(\lambda E_1 + (1-\lambda)E_2, \lambda \boldsymbol{Y}_1 + (1-\lambda)\boldsymbol{Y}_2) \geq \lambda S(E_1, \boldsymbol{Y}_1) + (1-\lambda)S(E_2, \boldsymbol{Y}_2). \tag{13.6}$$

That is, $-S$ is a convex function according to the theorem in **13.3**; in other words, S is a concave function.[324]

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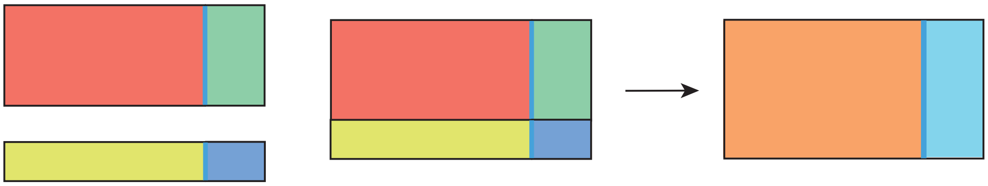
[321] $f(x)$ is Lipshitz continuous at x, if in a neighborhood of x we can choose a positive number K such that $|f(x) - f(y)| < K|x - y|$. For the ordinary continuity, no bound for K is required.

[322] Note that partition additivity (→**2.14**) is not enough (→**5.13**).

[323] As noted before (→**5.10**), this is not automatic, but the point is that we can enforce the combined system to have the thermodynamic coordinates $(E_1 + E_2, \boldsymbol{Y}_1 + \boldsymbol{Y}_2)$ reversibly and adiabatically without any generalized work.

[324] **Warning**. With the conventional expression of chemicals entropy is not a concave function. If we follow the *ad hoc* convention of freely freezing chemical reactions, while reactions are frozen, entropy is concave. That is, generally speaking, only if there is no chemical reaction, S is concave in the usual formulation of thermodynamics.

Let us extend the above convexity argument to compound systems. We assume (as schematically illustrated in Fig. 13.3) two systems are with the identical internal constraints (walls/boundary conditions), and when two systems are combined, we assume that the choice of the two states respect the constraints and the combination is realized between the corresponding pieces of the subsystems defining the compound systems. Then, an inequality analogous to (13.6) holds.[325]



Two original compound system
with the identical internal wall

Combined and equilibrated while respecting the internal wall

Figure 13.3: Convex combinations of compound systems must respect internal boundary conditions a schematically illustrated here.

13.6 The so-called stability criterion $\delta S \le 0$ and convex analysis

We have shown for any equilibrium state for a simple system its entropy does not increase by any thermodynamic variation in **12.10**. It is copied here for convenience:

$$\delta S \le 0. \tag{13.7}$$

First of all notice that this inequality is, for simple systems, simply Jensen's inequality applied to $-S$, since $-S$ is convex. As remarked just below (12.4), it is the property of any equilibrium state of a simple system. Convex analysis confirms this statement for simple systems.

For a compound system, (13.7) holds, if all the original internal constraints (walls/boundary conditions) in the system are respected when thermodynamic variations are constructed. Here, we assume that any imposed thermodynamic variation never alters the internal constraints (if any for compound systems). Then, again, (13.7) is a convexity result that is due to the nature of entropy.

13.7 Entropy is C^1 with respect to thermodynamic coordinates

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[325] If we combine two compound systems without paying attention to the (mis)matching of boundaries, then the procedure virtually nullifies many internal constraints. However, there are very many ways to combine the systems, so, generally speaking, (13.6) would not hold.

We have demonstrated that $S(E,\boldsymbol{Y})$ is partially differentiable (→**11.5**[326]) concave function. This and **13.4** (2) imply that all the partial derivatives are continuous. Therefore, the theorem shown in **9.4** implies that $S(E,\boldsymbol{Y})$ is strongly differentiable.[327] Thus, we may conclude that entropy as a function of thermodynamic coordinates is strongly and continuously differentiable (strongly C^1).

Consequently, conjugate intensive variables (the so-called thermodynamic fields →**5.5**) are all continuous functions of thermodynamic coordinates. In particular, temperature and chemical potentials are continuous functions of thermodynamic coordinates.[328]

Haven't the conjugate variables of the work coordinates been introduced from outside thermodynamics, due to the nonthermal macrophysics? Why, then, are their properties constrained by thermodynamics? One way to understand the situation is that thermodynamics does not alter the properties of conjugate variables, but the systems that do not have continuous conjugate variables do not realize proper equilibrium states for which thermodynamics holds or some members of the thermodynamic coordinates are not additive.

13.8 The inverse function of a monotone decreasing convex function is also a monotone decreasing convex function

Let x and y be reals and $y = f(x,Z)$ be a convex function defined on $C \subset \mathbb{R} \times \mathbb{R}^n$ ($x \in \mathbb{R}, Z \in \mathbb{R}^n$). Furthermore, we assume for each $Z \in \mathbb{R}^n$ f is a strictly monotone decreasing function of $x \in \mathbb{R}$ (that is, $x_1 < x_2 \Rightarrow f(x_1,Z) > f(x_2,Z)$). At each Z we can uniquely solve $y = f(x,Z)$ for x, so we can define the function $x = g(y,Z)$ on $(y,Z) \in f(C) \times \mathbb{R}^n$. The resultant g is convex. This assertion should be clear from the following illustration Fig. 13.4:

13.9 Internal energy is convex

13.5 tells us that $-S = -S(E,\boldsymbol{Y})$ is a convex function, and when $\boldsymbol{Y}$ is fixed, $-S$

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[326] There, we showed that S is strongly differentiable with respect to $\boldsymbol{Y}$ (not with respect to $(E,\boldsymbol{Y})$).

[327] Since we did not show previously that $S(E,\boldsymbol{Y})$ is strongly differentiable, we cannot use **13.4** (3).

[328] Here, the continuities are shown only when the independent variables are the thermodynamic coordinates or those with E being replaced by S.

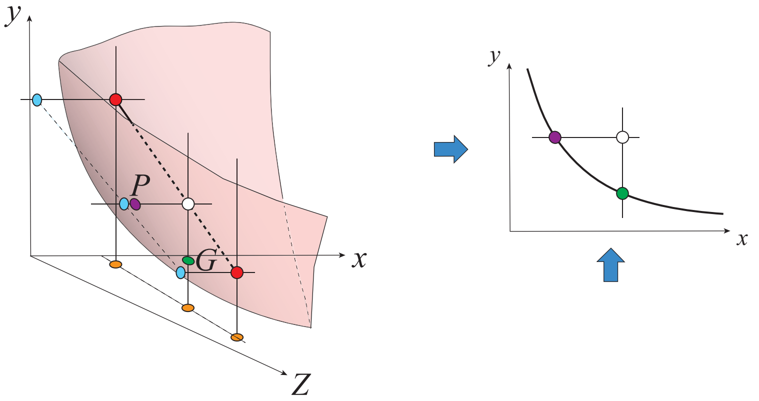

Figure 13.4: A strictly decreasing convex function with respect to one coordinate: Red dots (green and purple dots also) are on the graph of the function (the pale red surface). Jensen's inequality is illustrated by the white dot above green dot G or right of purple dot P. The blue dots are on the yZ hyperplane and the orange on the xZ-hyperplane. The essence may be exhausted by the right diagram, exhibiting, "The inverse function of strictly decreasing convex function is also a strictly decreasing convex function"; the graph seen along either arrow is convex.

is strictly decreasing function of E, since its derivative is $-1/T < 0$. Therefore, as shown in **13.8**, E is convex as a function of $(-S, \boldsymbol{Y})$. Thus,[329] $E = E(S, \boldsymbol{Y})$ is convex.

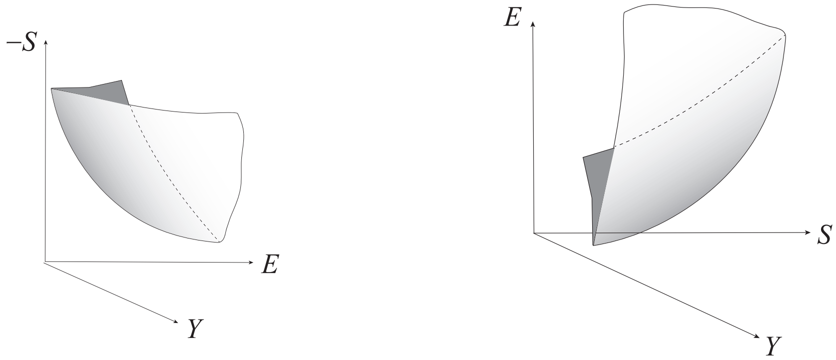

Figure 13.5: $-S$ is a strictly decreasing convex function of E when $\boldsymbol{Y}$ is fixed, so E is a convex function of $(S, \boldsymbol{Y})$.

From this a similar argument as **13.7** shows that E is a continuous strong-differentiable function of the thermodynamic coordinates. Since E is convex, combining systems I and II in equilibrium to make a new system (by relaxing some constraints between I and II), we have an analogous inequality (i.e., Jensen's inequality

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[329] For example, if $y = f(x)$ is convex, then if $y = f(-x)$ (the mirror image with respect to the plane perpendicular to x) is defined, it is convex as well.

for E) as (13.6)

$$E(\lambda S_1 + (1-\lambda)S_2, \lambda \boldsymbol{Y}_1 + (1-\lambda)\boldsymbol{Y}_2) \le \lambda E(S_1, \boldsymbol{Y}_1) + (1-\lambda)E(S_2, \boldsymbol{Y}_2). \quad (13.8)$$

In particular, if we apply a thermodynamic variation (→**12.10**), since E is convex, we have[330]

$$\delta E \ge 0. \quad (13.9)$$

This is a universal property of the internal energy of any equilibrium state under any thermodynamic variation just as the counterpart for entropy already discussed in **13.6**.

13.10 Internal energy minimization principle

If there is no contribution of generalized work, then energy conservation implies

$$\delta E = \delta Q. \quad (13.10)$$

Combining this with Clausius' inequality, if the heat bath temperature and the system temperature are identical, we have

$$\delta E \le T\delta S. \quad (13.11)$$

Under this condition, if we require entropy is constant, we obtain

$$\delta E < 0. \quad (13.12)$$

This implies that under $(S, \boldsymbol{Y})$ constant condition, if the system spontaneously changes, say, after reducing the internal constraints, the internal energy decreases.[331] This is called the *principle of decreasing internal energy*, but the condition $S =$ constant would make the principle not so usable. If there is no spontaneous change, we have

$$\delta E \ge 0. \quad (13.13)$$

That is, the internal energy must be minimum in equilibrium, under the $S =$ constant condition.

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[330] To verify this experimentally, we must fix the sum of the operational coordinates without work (which is possible) under reversible adiabatic condition.

[331] Intuitively, a spontaneous change is accompanied with dissipation that would increase the system entropy, but to maintain S, the system must be cooled, so the internal energy must be reduced.

Let us define the thermodynamic variation for the case with $(S, \boldsymbol{Y})$ as independent variables, following **12.10** as

$$\delta J(S, \boldsymbol{Y}) = \sum_{i \in \mathcal{P}} J(S_i, \boldsymbol{Y}_i) - J(S, \boldsymbol{Y}), \tag{13.14}$$

where $\mathcal{P} = \{i\}$ is the partition of the system in to pieces i while satisfying $S = \sum_{i \in \mathcal{P}} S_i$ and $\boldsymbol{Y} = \sum_{i \in \mathcal{P}} \boldsymbol{Y}_i$. The convexity of E implies, for thermodynamic variations of simple systems and compound systems with internal constraints respected (13.13) is nothing but Jensen's inequality. If internal constraints are not respected thermodynamic variations applied to compound systems may give $\delta E < 0$, showing the unstable nature of the constrained equilibria. In this sense, the sign of the variational change can indicate the stability of the equilibrium state. However, do not forget the condition that $S =$ constant.

14 Heat and entropy

14.1 Entropy: summary[332]

Let us summarize the properties of entropy S.
(1) The thermodynamic space is foliated by strongly differentiable hypersurfaces defined by reversible adiabatic accessibility (→**10.11** for a summary) on which entropy is constant.
(2) Entropy is a continuously (strongly) differentiable concave function of the internal energy and operational coordinates $\boldsymbol{Y}$ (→**11.3**). This implies that the internal energy is a continuously (strongly) differentiable convex function of entropy S and $\boldsymbol{Y}$ (→**13.7 13.9**).
(3) If we add heat dQ quasistatically to the system under constant work coordinates without material exchanges (that is, while keeping all the operational coordinates constant), the system entropy changes by $dS = dQ/T$ (→**11.7**). Consequently, the differential form for the first law of thermodynamics may be written as Gibbs' relation: $dE = TdS + \sum ydY$ (→**11.9**).
(4) Entropy can never decrease under adiabatic conditions. This leads to the principle of increasing entropy **12.5** (and the entropy maximizing principle **12.6**).

14.2 Heat bath and heat exchange

A system is called a *heat bath*, if it is in thermal contact (→**7.12**) with a system and is kept at a constant temperature (→**8.8**). Note, however, that even if a system is

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[332] As already mentioned in **1.7** Guggenheim's *Thermodynamics* seems to be the first textbook of thermodynamics that adopted to state the second law in terms of entropy: 'The enunciation of the properties of entropy and of thermodynamic temperature together constitute the *second law of thermodynamics*.' (§1.20)

Entropy is characterized in §1.16 as follows: There exists an function S of the state of a system called the *entropy* of the system having the following properties:
(1) The entropy S^{Σ} of a system Σ is the sum of the entropies of its parts, $\alpha, \beta, \cdots$ so that $S^{\Sigma} = S^{\alpha} + S^{\beta} + \cdots$.
(2) The entropy S^{α} of a closed phase α is determined by the energy E^{α} and the volume V^{α} of the phase so that
(3) $(\partial S^{\alpha}/\partial E^{\alpha})_{V^{\alpha}}$ is always positive.
(4) The entropy of an insulated closed system Σ increases in any natural change,
(5) remain constant in any reversible change, and is maximum at equilibrium.

Then, how does Guggenheim handle chemicals? His §1.27 simply states that for an open system the usual Gibbs relation is extended with the additional $\sum \mu dN$.

in contact with a single heat bath, if there is no net exchange of heat with it, the system is adiabatic.

If a heat bath of temperature T_B exports energy Q (> 0) as heat, the entropy of the heat bath decreases by Q/T_B:

$$\Delta S_{\text{bath}} = -\frac{Q}{T_B}. \tag{14.1}$$

If energy $|Q|$ is released by the system to the heat bath, that is, if the system gains heat Q (< 0) from the heat bath, the heat bath gains heat $-Q$ (> 0) from the system, so (14.1) can always be used with the sign of Q understood algebraically.

14.3 The existence of intrinsic heat bath

Suppose a system is in equilibrium. Is there any heat bath that does not change the system state even when in thermal contact with it? In other words, is there always a heat bath that is in thermal equilibrium with a given equilibrium system? Recall that thermal equilibrium $\iff$ identity of temperatures (→**??**).

For a system in equilibrium, we can define its temperature. The concavity of entropy and its differentiability implies temperature is a continuous quantity (→**13.7**), so there must be a heat bath at the same temperature of a given system. Let us call such a heat bath an *intrinsic heat bath* of the system. In particular, even if a system is in thermal contact with its intrinsic heat bath, the system state does not change. Even if the system is adiabatic before this thermal contact, its state does not change.

The existence of the intrinsic heat bath tells us that thermodynamic equilibrium states need not be describable in terms of mechanics and electrodynamics alone.[333]

14.4 Clausius' inequality

Suppose a system is in thermal contact with a heat bath of temperature T_B, and the compound system consisting of the system and the heat bath as a whole is under an adiabatic condition. If energy Q is transferred as heat from the heat bath to the system and if the whole system reaches an equilibrium, (14.1) tells us that the total

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[333] Can a system in thermodynamic equilibrium be fully described solely in terms of pure mechanics? Statistical mechanics assumes it is possible, but the reader should not forget that despite being called statistical "mechanics," this framework does not actually rely on mechanics (be it classical, quantum, or any other form). For instance, it does not require the fundamental element of mechanics: equations of motion. From the empirical science perspective, there is no way to verify that a many-body system obeys mechanics.

entropy change ΔS_{total} is given by

$$\Delta S_{\text{total}} = \Delta S - \frac{Q}{T_B}, \tag{14.2}$$

where ΔS is the system entropy change. Since the whole system is adiabatic, the total entropy cannot decrease (the principle of increasing entropy→**12.5**), so we must have $\Delta S_{\text{total}} \geq 0$. Consequently,

$$\Delta S \geq \frac{Q}{T_B}. \tag{14.3}$$

This is called *Clausius' inequality*. Here, note that the temperature in the inequality is not the system temperature (though it is the final temperature of the system)

14.5 More general Clausius' inequality

Suppose a system is in thermal contact with more than one heat baths and obtains heat Q_i from heat bath i at temperature T_i.[334] If the system and all the heat baths are collectively under adiabatic conditions, the total entropy change may be written as (cf. (14.2))

$$\Delta S_{\text{total}} = \Delta S - \sum_i \frac{Q_i}{T_i}. \tag{14.4}$$

During the process the system can do work as long as the whole system is adiabatic. Again, the principle of increasing entropy (→**12.5**) implies

$$\Delta S \geq \sum_i \frac{Q_i}{T_i}. \tag{14.5}$$

This is also called Clausius' inequality. For the equality to hold, the heat exchange with each heat bath must be quasistatic, so the system temperature must be adjusted each time it exchanges heat with different heat baths (as in **15.1**).

For any cycle for the system (a process whose intial and final system states are identical), since entropy is a state quantity, (14.5) becomes

$$0 \geq \sum_i \frac{Q_i}{T_i}. \tag{14.6}$$

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[334] The contacts with various heat baths may be simultaneous, allowing heat transfer from a heat bath to another via the system. What matters here is the total amount of heat (net heat) Q_i for each bath i, which maintains equilibrium. Needless to say, during the heat exchange, the system is not in equilibrium.

The equation equivalent to this was derived by Clausius before he reached the entropy concept (→**A.13**).

14.6 Heat capacity

For simplicity, let us consider a system with a single temperature in equilibrium. We add heat δQ reversibly and quasistatically (under a certain condition), and the system temperature changes as $T \to T + \delta T$. The proportionality constant $C(T)$ (which may depend on T) in the following formula:

$$\delta Q = C(T)\delta T \tag{14.7}$$

is called the *heat capacity* of the system (under a specific condition at temperature T).

There are many heat capacities under various conditions (e.g., under constant volume). The condition 'cond' is attached as C_V for the capacity under constant volume condition.

The amount of required heat causing a uniform change in a system scales with the system volume (or mass), so the heat capacity is an extensive quantity.

If heat is added reversibly (→**14.10**), then δQ may be written in terms of entropy. Therefore, generally we may write (if S is differentiable with T[335])

$$C_{\text{cond}}(T) = T\left(\frac{\partial S}{\partial T}\right)_{\text{cond}}. \tag{14.8}$$

However, no entropy is needed to define the heat capacity.

14.7 The relation between internal energy and heat capacity

If we apply Gibbs' relation (11.19) to (14.8), generally, we have,

$$C_{\text{cond}}(T) = \left(\frac{\partial E}{\partial T}\right)_{\text{cond}} - \sum_i y_i \left(\frac{\partial Y_i}{\partial T}\right)_{\text{cond}}. \tag{14.9}$$

The chain rule gives (here, Y_i^C implies that only Y_i is removed from $\boldsymbol{Y} = \{Y_i\}$)[336]

$$\left(\frac{\partial E}{\partial T}\right)_{\text{cond}} = \left(\frac{\partial E}{\partial T}\right)_{\boldsymbol{Y}} + \sum_i \left(\frac{\partial E}{\partial Y_i}\right)_{\text{cond},Y_i^c} \left(\frac{\partial Y_i}{\partial T}\right)_{\text{cond}}, \tag{14.10}$$

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[335] Remember that the strong differentiability of S is guaranteed only for thermodynamic coordinates (→**13.7**).

[336] If the condition includes some Y_i, the derivative with 'cond, Y_i^c' kept constant should be removed or set 0.

so we have[337]

$$C_{\rm cond}(T) = \left(\frac{\partial E}{\partial T}\right)_{\boldsymbol{Y}} + \sum_i \left\{\left(\frac{\partial E}{\partial Y_i}\right)_{{\rm cond},Y_i^c} - y_i\right\}\left(\frac{\partial Y_i}{\partial T}\right)_{\rm cond}. \tag{14.11}$$

If the thermodynamic coordinates are only E and V as for the ordinary gas, (14.11) gives

$$C_P = C_V + \left\{\left(\frac{\partial E}{\partial V}\right)_P + P\right\}\left(\frac{\partial V}{\partial T}\right)_P. \tag{14.12}$$

For an ideal gas (→**11.14**) the internal energy E is a function of T only, and for 1 mole of an ideal gas $PV = RT$, so the above formula reduces to Mayer's relation (→**14.8**):

$$C_P = C_V + R. \tag{14.13}$$

Here, C_P and C_V are constant pressure and constant volume molar specific heat, respectively.

14.8 Mayer's relation

(14.13) was the relation used by Mayer to determine the work equivalent of heat (→**A.9**). Needless to say, however, the relation was not derived with the aid of thermodynamics, but by using *Mayer's cycle* illustrated in Fig. 14.1. Here, one mole of an ideal gas is used.

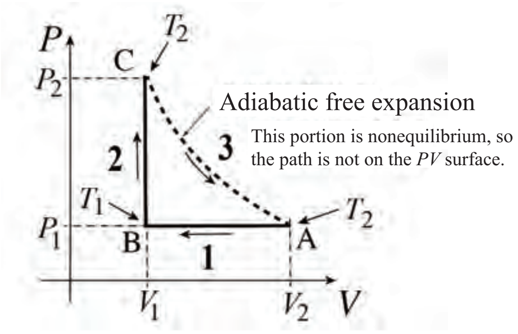

Figure 14.1: Mayer's cycle

Fig. 14.1 Mayer's cycle consists of three processes: Reversible and quasistatic compression under

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[337] Note that if the conventional chemical coordinates—the chemical composition variables $\tilde{\boldsymbol{N}}$—are used as the usual thermodynamic textbooks, the corresponding formula becomes complicated.

constant pressure **1**, reversible and quasistatic heating under constant volume **2**, and adiabatic free expansion **3**. Mayer knew Gay-Lussac's 'law of constant temperature': no temperature changes under adiabatic free expansion. British scientists did not know this law, so Mayer's assertion was regarded as a speculation, so they did not easily acknowledge Mayer's priority.

The gas does not do any work and adiabatic during Process **3** in Fig. 14.1, so its internal energy is constant. During Process **1** the system is compressed under constant pressure, and energy is obtained by the system as work:

$$W = P_1(V_2 - V_1) = R(T_2 - T_1) > 0. \tag{14.14}$$

During this process the system temperature goes down from T_2 to T_1 under constant pressure so the system obtains negative heat Q_1:

$$Q_1 = C_P(T_1 - T_2) < 0. \tag{14.15}$$

Process **2** is heating under constant volume, and the system absorbs heat Q_2:

$$Q_2 = C_V(T_2 - T_1) > 0. \tag{14.16}$$

After one cycle, the system must return to the original state, so the internal energy must return to its original value:

$$W + Q_1 + Q_2 = 0 \;\Rightarrow\; R(T_2 - T_1) + C_P(T_1 - T_2) + C_V(T_2 - T_1) = 0. \tag{14.17}$$

Thus, Mayer's relation (14.13) has been obtained.

$Q_1 + Q_2$ may be thermally measured and W can be mechanically obtained, so the conversion factor of the unit of heat cal and unit of work J, that is, the work equivalent of heat cal/J should be determined.

The data for Mayer's original computation in 1842 were:

$C_P = 0.267$ cal/g·deg, the specific heat ratio $\gamma = C_P/C_V = 1.421$ and the thermal expansion coefficient $\alpha = 1/274\ \mathrm{K}^{-1}$ to compute the volume expansion.

From these values we can obtain cal/J=3.59. Get this number, using the gas of 1 cm^3; Mayer adopted the mass of the 1 cm^3 gas to be 0.0013 g, and the pressure to be 1 atm: $P = 1033 \times 980$ dyn/cm^2 (Answer[338]).

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[338] Choose $T_2 - T_1 = 1$ deg.

$$\begin{aligned} Q_1 &= -0.0013 \times 0.267 = -0.0003471 \text{ cal}, && (14.18)\\ Q_2 &= 0.0013 \times 0.267/1.421 = 0.0002443 \text{ cal} && (14.19)\end{aligned}$$

14.9 "Emden's problem"[339]

Suppose a leaky room of volume V is maintained at pressure P as the outside. If air is regarded as an ideal gas $PV = NRT$, and $E = NC_VT$ hold, so the following ratio is constant (the constant volume specific heat of diatomic ideal gas is $5R/2$):

$$E/PV = C_V/R = 5/2. \tag{14.22}$$

Since this ratio does not depend on temperature, the internal energy of the air in the room is, as long as the air pressure does not change, constant even if the room is heated.[340]

Even if the room is perfectly thermally insulated, the energy loss still occurs with the air leaking from the room as a result of thermal expansion. If the room temperature is T, the number of moles $N(T)$ of air in the room is fixed by $PV = N(T)RT$, so the heat dQ needed for $T \to T + dT$ is given by

$$dQ = N(T)C_PdT = \frac{PVC_P}{RT}dT. \tag{14.23}$$

Therefore, the required energy to warm the room from T_1 to T_2 is obtained as

$$Q = \int_{T_1}^{T_2} dT\,\frac{PVC_P}{RT} = \frac{PVC_P}{R}\log\frac{T_2}{T_1} = C_PN_0T_1\log\frac{T_2}{T_1}, \tag{14.24}$$

where N_0 is the initial amount of air in the room.

To warm the N_0 mole air from T_1 to T_2, if the volume is constant, then the needed heat is $Q_V = N_0C_V(T_2 - T_1)$; if the pressure is constant, then the needed heat is $Q_P = N_0C_P(T_2 - T_1)$. What is the order of the magnitude of these needed heats, Q,

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$$\Rightarrow \quad Q_2 - Q_1 = 0.0001028 \text{ cal}. \tag{14.20}$$

On the other hand, the work is obtained as $W = P\Delta V = 1033 \times 980 \times (1/274) = 3695$ erg $= 0.0003695$ J, so the work equivalent of heat is given by

$$0.0003695 \text{ J} = 0.0001028 \text{ cal} \;\Rightarrow \text{cal/J} = 3695/1028 = 3.59. \tag{14.21}$$

This should be 4.18, but the Mayer could not get very accurate source data.

[339] taken from Prof. J. Kishine's lecture notes (U. Tokyo, 2022).

[340] R. Emden, Why do we have winter heating? Nature **141**, 908 (1938). Still, heating is costly despite (14.22). Where is all the money gone? The original discussion focused on the reason why the Earth does not heat up despite the Sun's radiation, and concluded that it is due to radiation emitted by the Earth.

Q_V and Q_P?[341]

14.10 Reversible quasistatic and adiabatic process for ideal gas: Poisson's relation

For reversible quasistatic and adiabatic processes an ideal gas satisfies PV^γ = constant. This is called *Poisson's relation*. Here, γ is the specific heat ratio as in **14.8**: $\gamma = C_P/C_V$.

For an ideal gas $dE = C_V dT$ under any condition (→**11.14**), so the P, V, T-relation in an adiabatic reversible and quasistatic process always satisfies

$$dE = -PdV = C_V dT \ \Rightarrow C_V dT + PdV = 0. \tag{14.25}$$

Combining this with the equation of state $PV = RT$, we get

$$C_V dT + PdV = C_V d\left(\frac{PV}{R}\right) + PdV = \left(\frac{C_V}{R} + 1\right) PdV + \frac{C_V}{R} V dP. \tag{14.26}$$

Then, use Mayer's relation (14.13) and divide the result with PV:

$$C_P d\log V + C_V d\log P = 0 \ \Rightarrow \ d\log P + \gamma d\log V = 0. \tag{14.27}$$

Integrating this, we obtain Poisson's relation.

There should not be any entropy change before and after adiabatic, reversible and quasistatic processes. Confirm this (Answer[342]).

14.11 Temperature-altitude relation

When air ascends, we may approximate its thermal phenomenon by adiabatic, reversible and quasistatic expansion. Approximating air as an ideal gas, find how

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[341] $Q_V < Q < Q_P$. The second inequality is physically obvious. The first inequality maybe understood as follows: Increase the temperature by dT under constant volume first. Then, to reduce the pressure to the original value, increase the volume. This process does work, so the temperature goes down. Therefore, to get the dT increase, we need a bit more energy. Thus, even if we take the reduction of the total amount of air due to leakage into account, we need more energy than the case of strictly constant volume.

[342] The entropy of an ideal gas is given by its fundamental equation (11.35). Let us rewrite this with the aid of Mayer's relation (14.13) as:

$$S = S_0 + C_V \left[\log \frac{E}{E_0} + (\gamma - 1)\log \frac{V}{V_0}\right]. \tag{14.28}$$

Poisson's relation PV^γ with $P = RT/V$ gives $PV^\gamma \propto (T/V)V^\gamma = TV^{\gamma-1}$ = constant. For an ideal gas $E \propto T$ (→(11.32)), so we get $EV^{\gamma-1}$ = constant. Thus, (14.28) implies $S = S_0$.

many kelvins the air temperature goes down per 1 km ascending. This question is equivalent to the following:
At altitude z let the pressure, temperature and density, $P(z)$, $T(z)$, $\rho(z)$, respectively. The average molecular weight of air is M. Obtain $dT(z)/dz$.

The molar volume is $M/\rho(z)$, so the equation of state reads

$$P(z)M/\rho(z) = RT(z). \tag{14.29}$$

The force balance in the vertical direction for a horizontal disk of unit area with thickness dz (Fig. 14.2) tells us

$$P(z) + dP(z) + g\rho(z)dz = P(z). \tag{14.30}$$

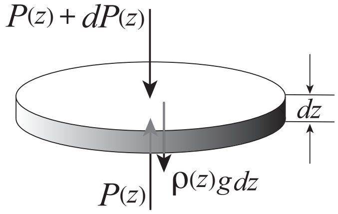

Figure 14.2: The force balance in the vertical direction for a horizontal disk of unit area with thickness dz

Therefore,

$$\frac{dP(z)}{dz} = -\rho(z)g. \tag{14.31}$$

If we eliminate the density with the aid of the equation of state (14.29), we get

$$\frac{dP(z)}{dz} = -Mg\frac{P(z)}{RT(z)}. \tag{14.32}$$

We wish to have a differential equation for $T(z)$, so we use $P(T/P)^\gamma = P^{1-\gamma}T^\gamma =$ constant, which is obtained from Poisson's relation PV^γ(→**14.10**) and the equation of state, to write $P(z)$ in terms of $T(z)$. This relation gives $(1-\gamma)dP/P + \gamma dT/T = 0$, so (14.32) becomes

$$\frac{1}{P(z)}\frac{dP(z)}{dz} = -\frac{\gamma}{1-\gamma}\frac{1}{T(z)}\frac{dT(z)}{dz} = -Mg\frac{1}{RT(z)}. \tag{14.33}$$

That is,

$$\frac{dT(z)}{dz} = -\frac{Mg(\gamma-1)}{\gamma R}. \tag{14.34}$$

$M = 29$ g/mol, $\gamma = 1.41$, $R = 8.314 \times 10^7$ erg/K, and $g = 980$ cm/s^2 give about 10 K/km.

14.12 Reversible and quasistatic heat exchange

For simplicity, let us assume that the heat capacity of the system is constant C. The system has an initial temperature $T - \delta T$. It is placed in thermal contact with a heat bath of temperature T_B ($\geq T$), and the temperature changes from $T - \delta T$ to T. Let us also assume that the system is sufficiently small with good heat conductance and that δT is sufficiently small. Then, there is no irreversible process inside the system due to the inhomogeneity of the system temperature. The entropy change of the system is given by

$$\delta S_S = \int_{T-\delta T}^{T} \frac{CdT}{T} = C \log \frac{T}{T-\delta T} = C\left[\frac{\delta T}{T} + \frac{1}{2}\left(\frac{\delta T}{T}\right)^2 + O[\delta T^3]\right]. \tag{14.35}$$

The heat bath loses energy $C\delta T$ as heat, so its entropy change is given by

$$\delta S_B = -\frac{C\delta T}{T_B}, \tag{14.36}$$

since the heat bath temperature does not change. The total entropy change of the system + heat bath reads

$$\delta S = \delta S_S + \delta S_B = C\left(\frac{1}{T} - \frac{1}{T_B}\right)\delta T + \frac{C}{2T^2}\delta T^2 + O[\delta T^3]. \tag{14.37}$$

Therefore, as long as $T < T_B$, however slowly the temperature is changed, still the term first order in δT remains, so the total entropy increases. Actually, if $\delta T > 0$, $T < T_B$ and if $\delta T < 0$, $T > T_B$ (Clausius' principle **8.3**), so the first term of (14.37) is always[343] positive unless $\delta T = 0$.

Consequently, only if $T = T_B$, and if the change is slow (is quasistatic), entropy does not change.

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[343] With the aid of a good thermal insulating wall, you can indefinitely slow down the temperature change. Still after the temperature reaches the final value, the final (eventual) entropy increase does not depend on how slowly you perform the change.

14.13 Stepwise heat exchange

14.12 suggests that if we reduce the temperature difference between the two systems in thermal contact, the increase of entropy is reduced. Suppose we wish to change the system temperature from T_1 to T_2 ($> T_1$). This suggestion implies that the entropy change due to the heat exchange by using a single heat bath of temperature T_2 should be larger than that due to the heat exchange in two steps, first $T_1 \to T_m$ by using a heat bath of an intermediate temperature T_m ($T_1 < T_m < T_2$), and then $T_m \to T_2$ by using a heat bath of temperature T_2. As long as $T_m \in (T_1, T_2)$ the total entropy change should be smaller. Is this true?

As 14.12 let us assume the system heat capacity C is constant and it is in thermal contact with a heat bath, but system + heat bath is isolated. First, the system temperature is initially T_1 and the heat bath is at temperature T_m. The total entropy change is given by

$$\Delta S + \Delta S_B = \int_{T_1}^{T_m} dT\,\frac{C}{T} - \frac{C(T_m - T_1)}{T_m} = C\log\frac{T_m}{T_1} - C\frac{T_m - T_1}{T_m}. \tag{14.38}$$

In the second step, the initial system temperature is T_m and the heat bath is at temperature T_2, so

$$\Delta S + \Delta S_B = C\log\frac{T_2}{T_m} - C\frac{T_2 - T_m}{T_2}. \tag{14.39}$$

Therefore, the total entropy change due to two steps is

$$\Delta S^{(2)} = C\log\frac{T_2}{T_1} + C\left[\left(\frac{T_1}{T_m} + \frac{T_m}{T_2}\right) - 2\right]. \tag{14.40}$$

The total entropy change due to one step is

$$\Delta S^{(1)} = C\log\frac{T_2}{T_1} + C\left[\left(\frac{T_1}{T_2}\right) - 1\right] = C\log\frac{T_2}{T_1} + C\left[\left(\frac{T_1}{T_2} + 1\right) - 2\right]. \tag{14.41}$$

Suppose A and B are positive numbers. Then the following function satisfies $f(A) = f(B)$ and strictly convex ($f''(T) = 2A/T^3 > 0$):

$$f(T) = \frac{A}{T} + \frac{T}{B}. \tag{14.42}$$

Therefore, $f(A) = f(B) > f(T)$ for any T between A and B ($\min f(T) = f(\sqrt{AB})$), implying $\Delta S^{(2)} < \Delta S^{(1)}$.

If we repeat this logic, we should be able to reduce the entropy change further. For M steps with the temperature increment $\tau = (T_2 - T_1)/M$, the contribution of the heat bath (the second term of (14.40)) reads as follows to give the $M \to \infty$ limit:

$$C\left[\left(\frac{T_1}{T_1+\tau} + \frac{T_1+\tau}{T_1+2\tau} + \cdots + \frac{T_2-\tau}{T_2}\right) - M\right] \tag{14.43}$$

$$= \quad -C\left(\frac{\tau}{T_1} + \frac{\tau}{T_1+\tau} + \cdots + \frac{\tau}{T_2} + O[\tau^2]\right) \to -C\int_{T_1}^{T_2}\frac{dT}{T} = -C\log\frac{T_2}{T_1}. \tag{14.44}$$

Thus,

$$\lim_{M\to\infty} \Delta S^{(M)} = 0. \tag{14.45}$$

As we expected, the process is reversible and quasistatic.

14.14 Reversible and quasistatic heat exchange for fluid systems: *rete mirabile*

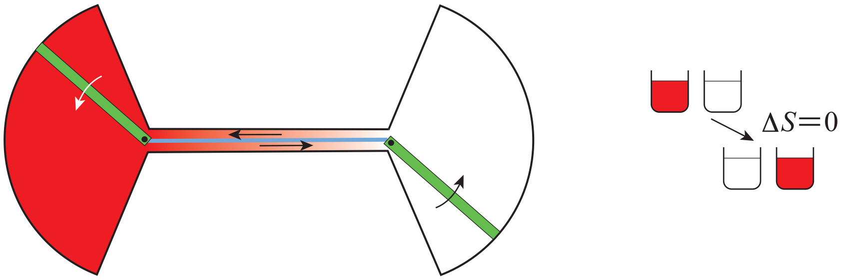

Figure 14.3: Two fan-shaped containers are connected by thin flat tubes in the middle. The containers have rotating adiabatic pistons (green bars) and the two fluids do not mix. The thin tube is divided by a diathermal membrane (denoted by a blue line) to realize the so-called *countercurrent exchange*. The heat exchange becomes closer to quasistatic exchange if the tube becomes thinner. In this thin limit, the right and the left portions of the figure exchange matter, but there is no heat exchange at all, resulting reversible heat exchange between the two fluids. What happened is virrually the exchange depicted in the right, so ΔS should be zero.

For fluids, we can change its temperature reversibly, for example, by exchanging the temperatures between two fluids as shown in Fig. 14.3.

As shown in the small figure in Fig. 14.3, if we prepare two identical liquids at different temperatures, and then exchange their temperatures, thermodynamically there is no state change at all, so thermodynamics does not forbid the exchange of temperatures reversibly. Thus, our metaprinciple (→**8.4**) asserts the existence of such a process.

A wiser method is to prepare numerous thin countercurrent exchange tubes and connect the two containers with these tubes as in Fig. 14.4.

Such an ingenious mechanism cannot be ignored by organisms. Such a device (organ) is called '*rete mirabile*' (pl. *retia mirabila*). For example, for water fowls *retia mirabila* in the legs and feet transfer heat from the outgoing (hot) blood in the arteries to the incoming (cold) blood in the veins. The same mechanism is utilized to maintain mammalian testes at low temperature (pampiniform plexus).[344]

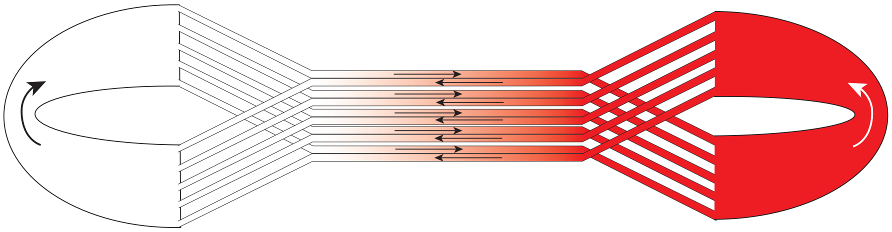

Figure 14.4: A schematic diagram of *rete mirabile*. If there is a mechanism to circulate fluid, fluids can be exchanged forever while separating the temperatures of the both parts.

Not only heat but small ions and ATP exchange can use similar mechanisms (`https://en.wikipedia.org/wiki/Rete_mirabile`).

Lesson: Anything thermodynamics does not forbid may be realized. Trust the metaprinciple **8.4**.

14.15 Can we equate temperatures reversibly and quasistatically?

Two blocks with identical heat capacities C are initially at temperature T_1 and T_2 $(> T_1)$, respectively. If we bring them to thermal contact while isolating the whole system, they eventually reach a thermal equilibrium. The final temperature is $T_m = (T_1 + T_2)/2$ according to the first law. Therefore, the total entropy change is given by

$$\Delta S = \int_{T_1}^{T_m} \frac{CdT}{T} + \int_{T_2}^{T_m} \frac{CdT}{T} = C \log \frac{T_m}{T_1} + C \log \frac{T_m}{T_2} = 2C \log \frac{T_m}{\sqrt{T_1 T_2}}. \quad (14.46)$$

Needless to say, (since $-\log x$ is convex, due to Jensen's inequality **13.3**) $T_m = (T_1 + T_2)/2 > \sqrt{T_1 T_2}$, so $\Delta S > 0$; the process is neither quasistatic nor reversible.

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[344] cf. B. R. Robinson, J. K. Netherton, R. A. Ogle, and M. A. Baker, Testicular heat stress, a historical perspective and two postulates for why male germ cells are heat sensitive, Biological Review **98**, 603 (2023).

If the final temperature is $\sqrt{T_1T_2}$, there is no entropy change, so we may bring the two blocks to the same temperature reversibly and quasistatically. However, $T_1+T_2 > 2\sqrt{T_1T_2}$ implies that the total energy of the blocks must be reduced. Since the whole system is adiabatic, the internal energy must be reduced with a reversible work.

That is, between two heat sources whose temperatures are initially T_1 and T_2, respectively, we can operate a reversible engine (e.g., the Carnot engine **A.8**) (→**15.1**) until the temperature difference of the two sources disappears to realize the above situation. To check this explicitly may be a nice exercise of elementary thermodynamics.

15 Heat engine and heat pump

15.1 The efficiency of a reversible engine

A device that converts heat obtained from heat sources to work is called a *heat engine*. Thomson's principle **8.7** tells us that no engine works with only one heat source. Therefore, the metaprinciple **8.4** tells us that with two heat sources at different temperatures we can make a heat engine.

Suppose there are a high temperature heat source (→**8.3**) of temperature T_H and a low temperature heat source (→**8.3**) of temperature T_L ($< T_H$). Consider a heat engine that obtains heat Q_H from the high temperature heat source and Q_L from the low temperature heat source to deliver work $-W$ (> 0) (that is, the engine obtains work $W < 0$) during a single cycle. After one cycle the engine state returns to the original state, so the internal energy of the engine does not change:

$$W + Q_H + Q_L = 0. \tag{15.1}$$

To make a 'lossless' engine, according to the father and the son Carnot, the heat exchange between the engine and heat source must be performed quasistatically (→**A.6**-**A.8**), so the heat exchange must be done reversibly and quasistatically (i.e., isothermally →**14.12**). Due to the heat from the high-temperature heat source, the entropy of the engine changes by

$$\Delta S_H = \frac{Q_H}{T_H}. \tag{15.2}$$

Similarly, due to the heat from the low-temperature heat source, the entropy of the engine changes by

$$\Delta S_L = \frac{Q_L}{T_L}. \tag{15.3}$$

After the completion of a single cycle, the state of the engine returns to the original state, so there must not be any change in state quantities, in particular, in the engine entropy. Therefore,

$$0 = \Delta S_H + \Delta S_L = \frac{Q_H}{T_H} + \frac{Q_L}{T_L}. \tag{15.4}$$

An '*efficiency*' η is always considered as the ratio of 'gain'/'expenditure,' so for an engine the expenditure is the heat Q_H we supply from the high-temperature heat bath (a furnace), and the gain is the work $|W|$ engine produces. Notice that $W < 0$, since the energy balance is considered from the engine-centered point of view. Therefore, the efficiency of the engine is defined by

$$\eta = \frac{|W|}{Q_H} = -\frac{W}{Q_H}. \tag{15.5}$$

(15.1) implies

$$\eta = -W/Q_H = (Q_H + Q_L)/Q_H = 1 + Q_L/Q_H. \tag{15.6}$$

(15.4) gives

$$Q_L/Q_H = -T_L/T_H, \tag{15.7}$$

so that we get the efficiency of the reversible engine:

$$\eta = 1 - T_L/T_H. \tag{15.8}$$

15.2 Carnot's theorem: A reversible engine gives the efficiency upper bound

Consider a general engine functioning between the two heat sources as in **15.1**. What is its efficiency? That the efficiency of the reversible engine is the maximum is Carnot's theorem (→**A.8**, which is equivalent to other second laws →**8.13**). To demonstrate the theorem here we use Clausius' inequality **14.4**. If we remove the reversibility condition, (15.2) and (15.3) become

$$\Delta S_H \geq \frac{Q_H}{T_H}, \quad \Delta S_L \geq \frac{Q_L}{T_L}. \tag{15.9}$$

Except for this change, the remaining argument is the same as **15.1**. The overall change of entropy after one cycle is zero, so (15.4) is replaced by

$$0 = \Delta S_H + \Delta S_L \geq \frac{Q_H}{T_H} + \frac{Q_L}{T_L}. \tag{15.10}$$

Now, (15.7) is, since Q_H is positive, replaced by

$$Q_L/Q_H \leq -T_L/T_H. \tag{15.11}$$

This implies Carnot's theorem:

$$\eta = 1 + Q_L/Q_H \leq 1 - T_L/T_H. \tag{15.12}$$

15.3 Thermodynamic determination of absolute temperature scale

Absolute temperature is defined by (→(11.27))

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}} = T. \tag{15.13}$$

Usually, the concept of absolute temperature is associated with Thomson, but do not forget that absolute temperature is essentially the temperature scale introduced by Carnot far before entropy.

Carnot (and Clapeyron) clearly recognized that the efficiency of the heat engine can be used as a thermometer. Especially, Carnot defined $\Theta(\theta)$ (later called the Carnot function) from the efficiency $\delta\eta$ of the Carnot engine functioning between two heat baths of empirical temperatures θ and $\theta - \delta\theta$:[345] $(\delta\theta > 0)$

$$\frac{\delta\eta}{\delta\theta} = \frac{1}{\Theta(\theta)}. \tag{15.14}$$

If absolute temperature T is a strictly increasing differentiable function of empirical temperature θ, (15.12) gives

$$\delta\eta = 1 - \frac{T(\theta - \delta\theta)}{T(\theta)} = \frac{T'(\theta)}{T(\theta)}\delta\theta. \tag{15.15}$$

That is,

$$\Theta(\theta) = 1 \Bigg/ \frac{d\log T(\theta)}{d\theta} \tag{15.16}$$

It is convenient to use θ satisfying the equality $\Theta(\theta) = T(\theta)$. If this is required, (15.16) becomes $\Theta'(\theta) = 1$, so this is equivalent to demanding $\theta = \Theta = T$ (choosing the common origins for convenience). This was emphasized much later by Thomson: this relation allows us to define temperature solely by the principle of thermodynamics independent of particular materials such as mercury or ethanol.[346]

In this exposition T already appeared in the equation of state of an ideal gas. Therefore, we need to demonstrate that this T is indeed the thermodynamically defined absolute temperature T defined by (15.13) (→**11.7**)

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[345] $\delta\eta = 1 - (T - \delta T)/T = \delta T/T = \delta \log T$.

[346] This was a rather serious problem in the first half of the 1800s. See H. Chang, Inventing Temperature: measurement and scientic progress (Oxford Studies in Philosophy of Science, Oxford University Press, 2004).

15.4 *T* in the ideal gas equation of state is absolute temperature

Carnot conceived the following reversible engine that uses (1 mole of) an ideal gas as its working substance (Fig. 15.1):

(i) The engine does work through expansion while absorbing heat from the high temperature heat source (at T_H) (A→B in Fig. 15.1).

(ii) Then, it continues to expand while doing work and cools from T_H to T_L (B→C). Notice that this portion was Watt's novelty in his engine appreciated highly by Carnot as noted in **A.4**.

(iii) Next, the engine volume isothermally shrinks (i.e., the engine is done some positive work) while discarding heat to the low temperature heat source at T_L (C→D).

(iv) Finally, the system is compressed adiabatically (the engine is done some positive work as well) and its temperature goes up from T_L to the original T_H (D→A).

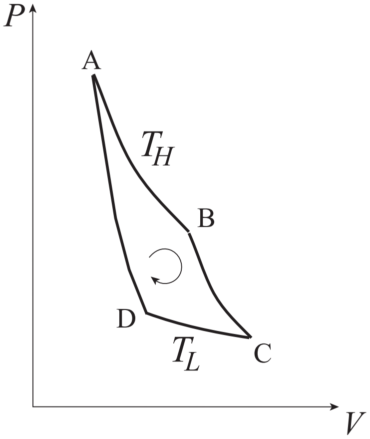

Figure 15.1: The Carnot cycle: AB and CD are quasistatic isothermal processes, and BC and DA are quasistatic adiabatic processes. The working substance is an ideal gas, so during the isothermal process its internal energy is constant. This implies that during isothermal processes the work the system does (or is done to the system) and the heat it absorbs (or it discards) must be identical.

The work added to the system (= the engine) is given by (note that $W < 0$, since the engine gives us work $|W|$)

$$W = -\oint_{\mathrm{ABCDA}} PdV \tag{15.17}$$

That is, the work $|W|$ done by the engine per cycle is given by the area enclosed by the figure in Fig. 15.1.

During the isothermal process A→B the engine does work, but the internal energy of the ideal gas does not change without temperature change (→(11.32)). Therefore, this work must be supported by the heat Q_H absorbed from the heat bath at temperature T_H. Therefore,

$$Q_H = \int_{\mathrm{A}\to\mathrm{B}} PdV = \int_{\mathrm{A}\to\mathrm{B}} \frac{RT_H}{V} dV = RT_H \log \frac{V_B}{V_A} > 0. \tag{15.18}$$

According to the similar logic, the heat $|Q_L|$ released to the low temperature heat bath (the system absorbs heat Q_L (< 0)) during the isothermal process C→D must be the same as the work done to the system:

$$|Q_L| = -\int_{\mathrm{C}\to\mathrm{D}} PdV = \int_{\mathrm{C}\to\mathrm{D}} \frac{RT_L}{V} dV = RT_L \log \frac{V_C}{V_D}. \tag{15.19}$$

To relate these two heats we need the volume relations during the reversible adiabatic process. From Poisson's relation (→**14.10**) PV^γ = constant, so we see $TV^{\gamma-1}$ = constant. Therefore, we have $T_H V_{\mathrm{A}}^{\gamma-1} = T_L V_{\mathrm{D}}^{\gamma-1}$ and $T_H V_{\mathrm{B}}^{\gamma-1} = T_L V_{\mathrm{C}}^{\gamma-1}$. Thus, $T_H/T_L = V_{\mathrm{D}}^{\gamma-1}/V_{\mathrm{A}}^{\gamma-1} = V_{\mathrm{C}}^{\gamma-1}/V_{\mathrm{B}}^{\gamma-1}$, that is, $V_{\mathrm{B}}/V_{\mathrm{A}} = V_{\mathrm{C}}/V_{\mathrm{D}}$ holds, since $\gamma > 1$. Using this relation in (15.18) and (15.19), we obtain (15.4). The remaining argument is just as in **15.1** and we obtain (15.8). Hence, T in the ideal gas equation of state is (proportional to[347]) the thermodynamic absolute temperature.

15.5 The efficiency of reversible engine with more than two heat sources

For a reversible engine working with heat Q_i supplied by the i-th heat bath of temperature T_i there is no entropy change for a cycle, so the general Clausius' equality (→**14.5**) holds:

$$\sum_i \frac{Q_i}{T_i} = 0. \tag{15.20}$$

To be clear, if $Q_i > 0$ (resp., $Q_i < 0$), then Q_i will be marked with + (resp., with −) as Q_i^+ (resp., Q_i^-). Then, (15.20) reads

$$\sum_{+i} \frac{Q_i^+}{T_i} + \sum_{-i} \frac{Q_i^-}{T_i} = 0. \tag{15.21}$$

---

[347] That is, 'identical apart from the choice of the units'.

Now, let us replace the temperatures of the heat source supplying + heat with the highest temperature $T_{\max}$ among the temperatures of the heat baths. We get

$$\sum_{+i} \frac{Q_i^+}{T_i} \geq \frac{\sum_{+i} Q_i^+}{T_{\max}}, \tag{15.22}$$

Similarly, let us replace the temperatures of the heat source supplying − heat with the lowest temperature $T_{\min}$. We get (since $Q_i^- < 0$)

$$\sum_{-i} \frac{Q_i^-}{T_i} \geq \frac{\sum_{-i} Q_i^-}{T_{\min}}. \tag{15.23}$$

Adding these two inequalities and write $Q^\pm = \sum Q_i^\pm$. (15.20) implies

$$\frac{Q^+}{T_{\max}} + \frac{Q^-}{T_{\min}} \leq 0. \tag{15.24}$$

Notice that this inequality has the same structure as (15.10).

The conservation of energy implies $W + Q^+ + Q^- = 0$. The efficiency of the engine η should be defined as work/total expenditure, so its calculation becomes exactly the same as the calculation of the efficiency of an engine working with two heat sources:

$$\eta = \frac{W}{Q^+} \leq 1 - \frac{T_{\min}}{T_{\max}}. \tag{15.25}$$

"More general" Carnot's theorem[348] The proof of Carnot's theorem in **15.2** requires, strictly speaking, equilibration of the engine after every cycle. To remove (or reduce the effect of) this restriction, we may use n ($\gg 1$) cycles as a single cycle. Furthermore, during this long operation of an engine, the source temperatures need not be constant. Note that this variable source temperature problem can be cast as the many heat source problem just discussed (→**15.5**), so the available max and min temperatures are written T_H and T_L, respectively, and the overall efficiency is given by (15.25).

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[348] This is emphasized by H Tasaki in an Appendix of his *Thermodynamics*.

16 Equilibria between two systems

16.1 Equilibrium condition between two systems

Let us prepare two systems I and II whose equilibrium states may be expressed in terms of an identical set of thermodynamic coordinates $(E, \boldsymbol{Y})$. Assume that these two systems as a whole are isolated and in contact with each other through various walls (= various boundary conditions). Allow the exchange of an operational coordinate between I and II.[349] Then, the entropy of I + II cannot be less than the sum of the original entropies before coming into contact according to the principle of increasing entropy (→**12.5**):

$$S_{\mathrm{I+II}} \geq S_{\mathrm{I}} + S_{\mathrm{II}}. \tag{16.1}$$

In particular, the entropy maximization principle **12.6** implies that after reaching the new equilibrium state $S_{\mathrm{I+II}}$ must be maximized for the exchanged coordinate. This is the most general equilibrium condition. Note that the max value of $S_{\mathrm{I+II}}$ is given by the max value of the sum $S_{\mathrm{I}} + S_{\mathrm{II}}$ (cf. **16.3**).

$-S_{\mathrm{I+II}}$ is (substantially →**13.1** footnote) convex, so its minimum is unique and global.[350] Thus, the local maximum of $S_{\mathrm{I+II}}$ is global, and the max value is unique.

However, the max value may not be given by the extremal value of $S_{\mathrm{I+II}}$. Therefore, for example, if an operational coordinate Y is exchanged between I and II, and if Gibbs' relation is

$$dS = \frac{1}{T}dE - \frac{y_1}{T}dY_1 - \cdots - \frac{y}{T}dY - \cdots, \tag{16.2}$$

the equilibrium condition need not be obtained from the extremal principle:[351]

$$\frac{\partial}{\partial Y_{\mathrm{I}}}S_{\mathrm{I}} - \frac{\partial}{\partial Y_{\mathrm{II}}}S_{\mathrm{II}} = 0. \tag{16.3}$$

or the identity $y_{\mathrm{I}}/T_{\mathrm{I}} = y_{\mathrm{II}}/T_{\mathrm{II}}$. For each thermodynamic coordinate, we must check whether (16.3) is admissible.

---

[349] The process is assumed to keep the total amount of thermodynamic coordinates. As to additive quantities see **5.10**.

[350] Any level set of a convex function is a convex set. Therefore, if the minimum is unique, it is a global minimum. However, strictly speaking, the uniqueness of the minimum point is not guaranteed by convexity. It only tells us that eh minimum value is taken in a convex set. Most practical examples seem to have unique minima, so we will not consider this very general situation.

[351] As noted already, we allow chemical reactions to occur.

16.2 Equilibrium due to thermal contact

Let us consider the case where only E can be exchanged among the thermodynamic coordinates $(E, \boldsymbol{Y})$.[352] This implies that only heat exchange can occur between I and II (or, I and II are in thermal contact →**7.12**). (16.1) becomes

$$S_{\mathrm{I+II}}(E) \geq S_{\mathrm{I}}(E_{\mathrm{I}}) + S_{\mathrm{II}}(E - E_{\mathrm{I}}), \tag{16.4}$$

and the E_{I} that maximizes the right-hand side gives the equilibrium condition. However, whether the condition is an extremal condition or not is not automatically clear.

Temperature is defined so that (1) the temperatures of two systems in thermal contact are equal if and only if they are in thermal equilibrium (→**7.12**), a nd that (2) the 'high' or 'low' of temperature is defined consistently with the direction of heat flow (consistent with Clausius' principle **8.3**) (→**11.7**). Therefore, in particular, thermal equilibrium is equivalent to temperature equilibrium (equality), so (→**11.12**)

$$\left(\frac{\partial S_{\mathrm{I}}(E_{\mathrm{I}})}{\partial E_{\mathrm{I}}}\right)_{\boldsymbol{Y}_{\mathrm{I}}} + \left(\frac{\partial S_{\mathrm{II}}(E - E_{\mathrm{I}})}{\partial E_{\mathrm{I}}}\right)_{\boldsymbol{Y}_{\mathrm{II}}} = \frac{1}{T_{\mathrm{I}}} - \frac{1}{T_{\mathrm{II}}} \tag{16.5}$$

must vanish in thermal equilibrium. That is, the thermal equilibrium condition is an extremal condition.

Note that the equality of temperature is not the consequence of the entropy maximization principle (→**12.6**). The logic is the other way around: the fact that thermal equilibrium is the temperature equality (and the concavity of entropy) implies that the entropy is extremized in thermal equilibrium. Thus, we may say that the thermal equilibrium condition may be written as an extremal principle for entropy, but it is not derived logically from the requirement for entropy.

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[352] Needless to say, the chemical equilibria shift, so the chemical composition of the system cannot be fixed, generally speaking. Therefore, with the conventional choice of the chemical coordinates as in most text books, changing E while fixing all the thermodynamic coordinates is generally impossible. Thus, for example in the chemical thermodynamics book by Kirkwood and Oppenheim, no chemical reaction is permitted when Gibbs' relation is discussed. Furthermore, reactions are halted when partial derivatives with respect to the ordinary thermodynamic coordinates are computed to avoid mathematical difficulties of keeping chemical composition variables constant. After entropy maximization with frozen reactions, do they allow reactions to proceed? Then, the states of I and II change, so the equilibrium temperature would also change. [Thus, would they discuss iterative way to determine the equilibrium condition?]

16.3 Infimal convolution

When a certain thermodynamic coordinate is exchanged between two systems, the entropy after reaching equilibrium between the two systems is determined by the principle of maximizing entropy (→**12.6**). The entropy of the compound system thus formed is again a concave function, if coordinates are additive (not merely partition additive →**2.14**).

The general theorem behind this fact is the theorem of *infimal convolution.*

Let f and g be convex functions: $\mathbb{R}^n \to \mathbb{R}$. Then, the following construction

$$h(x) = \inf_{x=x_1+x_2} [f(x_1) + g(x_2)] \equiv (f \,\Box\, g)(x) \tag{16.6}$$

is called *infimal convolution.* The resultant function is also convex.

[Demonstration] Let us demonstrate Jensen's inequality (→**13.3**) directly:

$$\begin{aligned}
\lambda h(x) + (1-\lambda)h(x') &= \lambda \inf_{x=x_1+x_2} [f(x_1) + g(x_2)] + (1-\lambda) \inf_{x'=x_1'+x_2'} [f(x_1') + g(x_2')] \\
&= \inf_{x=x_1+x_2, x'=x_1'+x_2'} \{\lambda[f(x_1) + g(x_2)] + (1-\lambda)[f(x_1') + g(x_2')]\} \\
&= \inf_{x=x_1+x_2, x'=x_1'+x_2'} \{[\lambda f(x_1) + (1-\lambda) f(x_1')] + [\lambda g(x_2) + (1-\lambda) g(x_2')]\} \\
&\ge \inf_{x=x_1+x_2, x'=x_1'+x_2'} [f(\lambda x_1 + (1-\lambda)x_1') + g(\lambda x_2 + (1-\lambda)x_2')] \qquad (16.7) \\
&\ge \inf_{\lambda x+(1-\lambda)x' = \lambda(x_1+x_2)+(1-\lambda)(x_1'+x_2')} [f(\lambda x_1 + (1-\lambda)x_1') + g(\lambda x_2 + (1-\lambda)x_2')] \qquad (16.8) \\
&= h(\lambda x + (1-\lambda)x'). \qquad (16.9)
\end{aligned}$$

Here, in (16.8) note that fixing x and x' independently is conditionally more constrained than fixing $\lambda x + (1-\lambda)x'$ as a whole.

16.4 Equilibrium states attained through ordinary operational coordinate exchanges

Generally speaking, if exchange of ordinary operational coordinates ($E\boldsymbol{X}$) between system I and system II is allowed, the realized equilibrium entropy is given by (→**16.1**) (is obtained by Infimal convolution →**16.3**)

$$S(E, \boldsymbol{X}, \boldsymbol{N}_{\mathrm{I}}, \boldsymbol{N}_{\mathrm{II}}) = \sup_{\boldsymbol{X}=\boldsymbol{X}_{\mathrm{I}}+\boldsymbol{X}_{\mathrm{II}}, E=E_{\mathrm{I}}+E_{\mathrm{II}}} [S_{\mathrm{I}}(E_{\mathrm{I}}, \boldsymbol{X}_{\mathrm{I}}, \boldsymbol{N}_{\mathrm{I}}) + S_{\mathrm{II}}(E_{\mathrm{II}}, \boldsymbol{X}_{\mathrm{II}}, \boldsymbol{N}_{\mathrm{II}})] \tag{16.10}$$

is automatically concave. However, the condition sup need not be realized by an extremal condition. As noted already in **16.1**, this depends on the domain of the entropy function, so there is no general theory as we will see in **16.6**.

If the max condition can be obtained from the extremal condition, the equilibrium condition reads

$$\left(\frac{\partial S_{\mathrm{I}}}{\partial X_{\mathrm{I}}}\right)_{X^c{}_{\mathrm{I}}} + \left(\frac{\partial S_{\mathrm{II}}}{\partial X_{\mathrm{II}}}\right)_{X^c{}_{\mathrm{II}}} = \frac{x_{\mathrm{I}}}{T_{\mathrm{I}}} - \frac{x_{\mathrm{II}}}{T_{\mathrm{II}}}, \tag{16.11}$$

where X^c means to remove X from the totality of the operational coordinates $\boldsymbol{Y}$.

16.5 Equilibrium states attained through contacts allowing chemical exchanges

Let us keep E and the operational coordinates $\boldsymbol{Y}$ other than the mole number N of one chemical, and exchange only this chemical substance between two systems I and II to obtain a new equilibrium. Assume the two systems as a whole is adiabatic and materially closed for simplicity:

$$S(E, N, \boldsymbol{Y} \setminus N) = \sup_{N_{\mathrm{I}}+N_{\mathrm{II}}=N} [S_{\mathrm{I}}(E, N_{\mathrm{I}}, \boldsymbol{Y}_{\mathrm{I}} \setminus N_{\mathrm{I}}) + S_{\mathrm{II}}(E, N_{\mathrm{II}}, \boldsymbol{Y}_{\mathrm{II}} \setminus N_{\mathrm{II}})]. \tag{16.12}$$

Here, N and $\boldsymbol{Y}$ on the left-hand side are given by the sum of $N_{\mathrm{I}}, N_{\mathrm{II}}$ and $\boldsymbol{Y}_{\mathrm{I}}, \boldsymbol{Y}_{\mathrm{II}}$, respectively. The actual material exchange process may be imagined as illustrated here (Fig. 16.1):

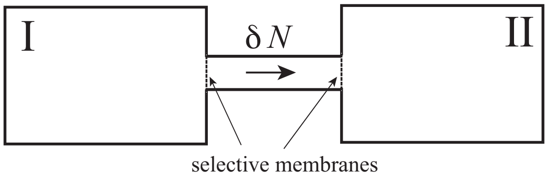

Figure 16.1: The two systems are connected via selective membranes allowing only the designated chemical to go through. The central connecting portion is not needed, but is here to clearly show that only the target component is exchanged.

Chemical potentials are defined in conjunction to the variation of operational variables, so they must be determined how much substances are imported to or exported from the system. Whether there are chemical reactions or not is irrelevant.[353]

Consider the case a certain compound can be exchanged between systems I and

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[353] We must also pay attention to the existence of chemicals that cannot be isolated as a pure substance. For such compounds we may consider the import/export of the mixtures consistent to the compounds stoichiometrically (→**25.11**). In such cases the changes of materials coordinates are not affected by the instantaneous actual chemical compositions of the mixtures.

II as in Fig. 16.1.[354] What happens at the ends of the connecting pipe is exactly the same phenomenon as the experimenter does to add or to subtract the chemical. Therefore, if I and II are in equilibrium, the chemical potentials on the both sides of the pipe must agree. That is,

$$\left(\frac{\partial S_{\mathrm{I}}}{\partial N_{i\mathrm{I}}}\right)_{E_{\mathrm{I}},\boldsymbol{X}_{\mathrm{I}},\boldsymbol{N}_{\mathrm{I}}^{i}}+\left(\frac{\partial S_{\mathrm{II}}(N_i-N_{i\mathrm{I}})}{\partial N_{i\mathrm{I}}}\right)_{E_{\mathrm{II}},\boldsymbol{X}_{\mathrm{II}},\boldsymbol{N}_{\mathrm{II}}^{i}}=\frac{\mu_{i\mathrm{I}}}{T_{\mathrm{I}}}-\frac{\mu_{i\mathrm{II}}}{T_{\mathrm{II}}}. \tag{16.13}$$

Here, superfix ^{i} means to remove N_i from the set of materials coordinates.

16.6 Pressure equilibrium

If two systems interact through a wall that allows exchange of volume (that is, through a movable piston) only, and if there is no restriction for the range of the piston (except for the nonnegativity of the volumes), (16.3) becomes

$$\left(\frac{\partial S_{\mathrm{I}}}{\partial V_{\mathrm{I}}}\right)_{\boldsymbol{X}_{\mathrm{I}}\backslash V_{\mathrm{I}},\boldsymbol{N}_{\mathrm{I}}}=\left(\frac{\partial S_{\mathrm{II}}}{\partial V_{\mathrm{II}}}\right)_{\boldsymbol{X}_{\mathrm{II}}\backslash V_{\mathrm{II}},\boldsymbol{N}_{\mathrm{II}}} \tag{16.14}$$

This implies

$$\frac{P_{\mathrm{II}}}{T_{\mathrm{I}}}=\frac{P_{\mathrm{II}}}{T_{\mathrm{II}}}. \tag{16.15}$$

If the wall is not adiabatic, this means that the pressures must agree.

However, in this case it is easy to restrict the range of the volume; we have only to place stoppers for the piston (Fig. 16.2). Needless to say, the agreement of P/T does not hold. Still, the total entropy is maximized under the presence of stoppers.[355,356] The value is not extremum, but is on the boundary of the domain of the volume variable.

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[354] If the compound cannot be isolated as a single substance, the mixture consistent with the compound are exchanged.

[355] Even in this case we can directly apply infimal convolution (→**13.2**). The reader might be worried about the range of the variables, but there is no difficulty, if we redefine our convex function f whose domain is C as a convex function f whose domain has no boundary but $f=+\infty$ outside C (the standard choice in convex analysis as noted in the footnote of **13.1**).

[356] Complication due to dry friction: If there is dry friction between the piston and the cylinder, it is hard to determine the final position of the piston. Therefore, the final equilibrium states are not unique. In this case, can we control the final state precisely by fine-tuning the initial condition? Since the mechanism of dry friction is rather microscopic, the author is pessimistic.

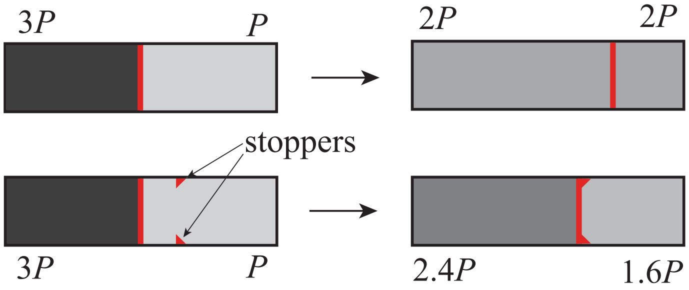

Figure 16.2: Pressure equilibria of ideal gases with and without stoppers; the red wall is movable and diathermal. In both cases, the entropy is maximized under the conditions.

It seems to be possible to 'impose stoppers' to work coordinates. This is quite different from the heat exchange.[357]

16.7 Adiabatic piston

Consider an adiabatic box with an adiabatic piston as illustrated in Fig. 16.3.

Figure 16.3: An adiabatic box equipped with an adiabatic piston (blue)

Suppose, for example, System II is initially at a higher pressure than System I. Releasing the piston, we wait for a long time. What is the eventually reached equilibrium state?

To determine the states of the system, we must determine all the thermodynamic coordinates of both systems. If both the boxes are filled with gases, we must determine the following four extensive variables: $E_{\rm I}, E_{\rm II}, V_{\rm I}$, and $V_{\rm II}$. The sum of internal energies and volumes are conserved. Furthermore, the pressures must be identical. Thus, we have three equalities. With one more equation, the states are completely determined. The relation may be a relation holding for System I only (for example,

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[357] Generally speaking, it seems very hard to invent stoppers for extensive quantities whose exchanges are due to accumulations of 'microscopic exchanges.' That is, to invent (macroscopic) stoppers for materials coordinates seems almost impossible.

the gas in I undergoes a polytrope change[358]).

If we can perform the experiment reversibly and quasistatically, then the total entropy must also be preserved, so the final equilibrium state must be unique. For example for an ideal gas, Poisson's relation uniquely determine the final temperatures and the piston position.

What happens, then, if the process is not quasistatic? Since the process is not quasistatic, dissipations of the kinetic energy of the piston must occur in the systems. The details of the process, such as friction between the piston and the wall, determine how the kinetic energy is distributed between I and II, making the resultant equilibrium state an open set in $\mathcal{E}$.

For example, if there is no friction at all between the piston and the walls, the piston starts to oscillate, and irreversible expansions and compressions of the gases occur.[359] Thus, the kinetic energy is distributed to I and II through heating of the gases. In general, however, there is a friction between the piston and the wall, so heat is also generated at the piston-wall contact as well.[360] This depends on the details of the piston and the wall, and we must also consider how the generated heat is distributed between I and II. Thus, even macroscopically many different outcomes can occur, so the resultant equilibrium state cannot be unique.[361]

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[358] A polytropic process is a process for which PV^n is constant for some $n > 0$. This is used to approximately describe various actual processes. The final state depends on n; This implies that the final equilibrium state depends sensitively to the actual process.

[359] In an ideal gas, since there are no "intermolecular interactions," one might wonder if dissipation does not occur. However, in thermodynamics, even for an ideal gas, it is assumed that it reaches an equilibrium state. This suggests that, although these interactions can be ignored statically, dynamically they cannot be ignored, indicating an idealization that acknowledges the presence of interactions that are significant in dynamics.

[360] When friction is the so-called dry friction, where the frictional force remains constant. Consequently, even the condition that the pressure in the final equilibrium state must be equal between I and II does not hold.

[361] We can make examples like the adiabatic piston for many other situations. For example,. consider an adiabatic wall allowing the exchange of chemical B. Assume for simplicity the volume does not change. If we can determine E and $N_{\rm B}$ the states are determined. There are four quantities we must determine for the two systems. The total energy and the total amount of B are fixed without chemical reaction. Furthermore, the chemical potential of B must agree. We have three relations. We must worry about the method to transfer B between the two systems; there can be numerous different ways.

17 Mixing entropy

17.1 Review: Open systems and closed systems

Up to this point for simple and compound systems, the usual electromagnetic/mechanical works and the chemical works are treated basically without much distinction. However, we already know 'chemical coordinates' (= variables to describe the amounts of various materials in the system) are not as simple as the usual work coordinates (esp., see Section 5).

A system is said to be *closed*, if it does not exchange any material with its environment. In conventional thermodynamics, closed systems are first considered, and then the so-called mass action Z (= ζ in **4.12**) due to materials exchange is taken into account. The conservation law of energy (the so-called first law →**7.14**) is extended to include the Z term:

$$\Delta E = Q + W + Z. \tag{17.1}$$

Based on this equation the thermodynamics of open systems is developed traditionally. That is, once the 'first law' is generalized as (17.1), the thermodynamics of open systems is constructed without any new empirical facts or principles.

However, since thermodynamics is a phenomenology, clear supporting empirical statements are desirable that the general theory of open systems based on (17.1) can be constructed even if chemical reactions occur.

This book attempts to minimize the deviation from conventional textbooks while correcting them. Still, it is worth noting that chemistry is not straightforward. For the convenience of those who may have avoided chemistry until this point, an explanation of how to choose 'chemical coordinates' and their controllability will be repeated.

17.2 Amount of materials as thermodynamic coordinates

The conservation of energy may be assumed to hold as (17.1), but what about the second law? Does it remain intact even with 'chemical coordinates'? Since thermodynamics began with the study of the relationship between heat and work, the second law more or less explicitly mentions work and work coordinates, but 'chemical coordinates' and 'chemical energy' are not mentioned until open systems are considered.

The problem we must consider is whether we may handle the work coordinates and the 'chemical coordinates' as the quantities of the same nature. Heat and work are, even if energetically their amounts are the same, thermodynamically fundamentally different quantities (→**A.10**, **8.3**). How about chemical work (mass action) thermodynamically?

To assert that work coordinates and 'chemical coordinates' are the quantities of the same nature, we must verify that no constraints as stated by the second law is imposed on the mutual conversion of work and 'chemical coordinates' [or, if we adopt Clausius' expression (→**A.11**), without any compensation].

17.3 What is the meaning of non-existence of restrictions due to the second law?

Let us review the relationship between heat and work: According to Mayer and Joule, we can convert work W to heat Q at temperature T (without any other trace) (→**7.14**). Then, we cannot recover W from the resultant heat Q to restore the original 'world' state as shown by Carnot [We must consume a part q of Q for compensation (→**A.11**; Fig. 17.1 I)].[362]

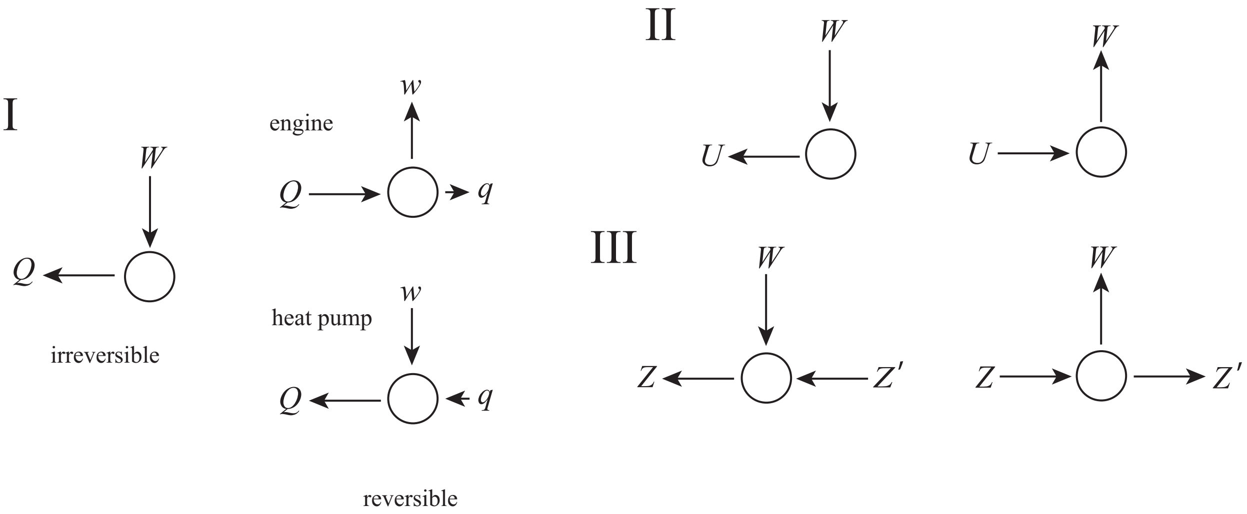

Figure 17.1: Possible constraints due to the second principle: Q, q $(< Q)$ heats; W, w $(< W)$: works; U: potential energy; Z, Z': chemicals (the so-called mass actions). For all cases the state of the device denoted by a circle must return to the original state after the process.

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[362] Needless to say, we can convert heat 100% to work utilizing an isothermal expansion process of a gas, but in this case the gas changes its volume, so it is not without trace as illustrated in **8.7**.

In contrast, there is no such restriction on the relationship between mechanical potential energy and work (without any friction and all the processes must be quasistatic; Fig. 17.1 II). If work W is converted to potential energy U, it is possible to convert U to work W exactly without leaving any trace; this is the meaning of 'without the restriction imposed by the second law [i.e., no compensation in Clausius' sense (→**A.11**) is required].'

Needless to say, the U-W relation is a fact established in macroscopic mechanics and/or electromagnetism.[363]

How about chemical energy Z and work W? Is there any restriction imposed by the second law or something similar? To convert chemical energy carried by chemical compounds, usually, material exchange is inevitable, although all the reactions may happen in a closed system. Here, the circles in Fig. 17.1 denote 'converters' (an engine, a motor, etc.), In the conversion between W and Z the device may be a (reversible) electric cell, so W may be electric potential energy. 'Chemical fuel' with energy Z is introduced and then 'chemical exhaust' with energy Z' is discarded ($W = Z - Z'$).

We must establish the W-Z relation empirically as well: switching the exhaust Z' and the fuel Z, 'W' can 'restore' the fuel perfectly. To study this what kind of experiments should we perform? Perhaps, the most effective experiments are electrochemical experiments, using electric cells. The importance of electrochemistry is not only because of recent practical applications, but also from a fundamental science point of view (as utilized by Faraday and Joule →**A.16**).

In essence, the reversible relation between electric cell reactions and electrolytic reactions demonstrates the equivalence of chemical work and ordinary work (see, for example, **26.6**).

In summary, it is empirically justified to extend Thomson's principle **8.7** and Planck's principle **8.5** to versions that include not only ordinary works but also generalized works, such as chemical works. Work coordinates and 'chemical coordinates' (more precisely, materials coordinates) can be considered thermodynamic coordinates (and are collectively referred to as operational coordinates →**4.13**). Our second laws have already been extended to cover chemical reactions[364] (Section 8).

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[363] The relation is amply verified empirically.

[364] However, as emphasized repeatedly, do not forget that the changes of 'chemical coordinates' must be handled with care.

17.4 Why the conventional chemical thermodynamics is problematic?

As noted in **17.2**, the conventional approach is to complete the thermodynamics without any chemical reaction and then graft chemistry to it. For this approach to be admissible, the basic principles of thermodynamics, especially the second law, must also apply to chemical reactions. Unfortunately, however, Thomson's principle and Planck's principle must be augmented to this end. If the work-chemical work equivalence (→**17.3**) is explicitly stated, we do not need to revise Thomson's principle. However, for Planck's principle (→**8.5**), the fundamental difference between the work coordinates and chemical composition variables (→**4.8**) must be taken into account as in **8.5**.

Clausius' principle (→**8.3**) remains unchanged even with chemical reactions. This is because the principle retains the same form in any restricted world (say, the world where chemical reactions are forbidden). Thus, even if Planck's principle can derive Clausius' principle, this proof is in the world where a particular version of Planck's principle holds, e.g., in a world where chemical reactions are prohibited.

The construction of the foliations of the thermodynamic space requires a principle equivalent to Planck's principle.[365] Therefore, to construct entropy that can cover chemical reactions, it must be based on Planck's principle revised to include chemical reactions explicitly (→**8.5**).

In a world where chemical reactions take place, if we want to halt the progress of a reaction, we generally have to fix the ordinary thermodynamic coordinates $(E, \boldsymbol{X})$. Therefore, in order to discuss chemical reactions within thermodynamics, entropy must also be constructed in a way that accommodates the world where chemical reactions occur.

Thus, the 'rootstock' for chemical thermodynamics must be specially prepared to graft chemistry; chemical reactions should be incorporated into thermodynamics from the beginning. See **4.15** about the problems of the conventional chemical thermodynamics.

17.5 Selectively permeable membrane and mass action

There are numerous distinct materials (chemicals). We must assume that we can distinguish them, since they are considered distinct. While distinguishing distinct chemicals is the job of chemistry, in thermodynamics, we must assume that we can

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[365] As emphasized repeatedly, for each version of Planck's principle is a thermodynamics for the corresponding restricted world.

(at least in principle) specify/identify the chemicals that may be exchanged between the system and its environment. This assumption is equivalent to the one that we can specify the properties of the walls enclosing the system accordingly.

The idealized device that enables this procedure is the *selectively permeable membrane* (henceforth, *selective membrane* to be short), which allows only a specified set of chemicals to be exchanged across it. In principle, it can distinguish stereoisomers and isotope-replaced compounds.[366] The amount of a compound may be measured in any manner, but it is convenient to use mole numbers to describe chemical reactions. Therefore, unless stated otherwise, mole numbers will be used to describe the amount of a compound. If the amount of a chemical is changed by dN adiabatically and quasistatically, the system energy change will be written as[367]

$$dZ = \mu dN. \tag{17.2}$$

Here, N is an extensive quantity. Generally, there are many different compounds;

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[366] The selectively permeable membrane is equivalent to the commonly used ‘semipermeable membrane’ in elementary thermodynamics. Some authors try to avoid the use of such a device, arguing that it “cannot exist” in reality. However, here, our basic attitude is that such objections to semipermeable membranes arise due to misunderstanding of the concept of ‘selective membrane’ (→**4.14**).

The selective membrane is a black box that represents high precision separating processes. Selective membranes appear everywhere in organisms with high precision (for isotope replacement the precision is limited but still not non-selective). They may not be passive, so to use them in thermodynamics is often claimed to be illegitimate. However, since equilibrium thermodynamics does not impose any limit on the conversion of work to chemical work, even active separation processes can be realized quasistatically, so where there is separability (= distinguishability) of compounds, we may assume that we can separate them quasistatically and reversibly. Therefore, wherever compounds are separable (= distinguishable), we can separate them quasistatically and reversibly, and the process may be summarized as a selective membrane. For example, pure substance A can be separated by distillation (e.g., multi-stage distillation) from a mixture. The needed phase transitions can be reversibly and quasistatically realized. We can add pure A to another system reversibly and quasistatically as well. Describing such processes in terms of selective membranes as black boxes should be perfectly consistent with thermodynamics (recall, e.g., adiabatic walls). In the case of biomembranes, a selective transport of a particular compound across it could be accompanied by the consumption of ATP or by the countercurrents of other compounds, but even active transport can be described in terms of (chemical) works and should be possible to realize as a reversible and quasistatic process; it is a matter of ingenuity since thermodynamics does not forbid it.

Thus, in short, any distinguishable compounds maybe reversibly and quasistatically separable. This should be a chemical principle (→**4.3** (I)), and its materialization is the selective membrane (like an ohmic resistor, a gyrator, etc., in the circuit theory).

[367] Here, dZ is, as dQ, a symbol for a 1-form and does not imply the differential of Z.

they are distinguished by suffixes as

$$dZ = \sum_i \mu_i dN_i. \tag{17.3}$$

μ_i is called the *chemical potential* of chemical i. dN_i is the amount of chemical i added by the experimenter to the system (the increment of the materials coordinate for chemical i as discussed in **4.12**).

Remark: Probably, it is no more necessary by now to repeat, but the actual amount of chemical i in the system may not change by dN_i due to chemical reactions.

17.6 Thermodynamic space for open systems

To describe thermodynamics we need the internal energy and operational coordinates consisting of work coordinates and materials coordinates (as 'chemical coordinates'). As stated in **17.2** thermodynamically work and materials coordinates are 'equivalent' with respect to the second law.

Thus, we write Gibbs' relation **11.9** as

$$dE = TdS + \sum_i x_i dX_i + \sum_i \mu_i dN_i. \tag{17.4}$$

Or, if we wish to regard entropy as the central quantity to organize thermodynamics,

$$dS = \frac{1}{T}dE - \sum_i \frac{x_i}{T}dX_i - \sum_i \frac{\mu_i}{T}dN_i. \tag{17.5}$$

17.7 Chemical potential

A basic (albeit not practical) operational method to determine the chemical potential μ_i of chemical i (as a function of $(S, \boldsymbol{Y})$) is illustrated in Fig. 17.2.

A small cylinder containing only chemical i is attached to the system.[368] A selectively permeable and hard membrane that allows only i to pass is placed between the cylinder and the system. While adding chemical i to the system, the system volume is kept constant with an appropriate adjusting of the left piston. The total

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[368] For chemicals that cannot be isolated, appropriate equilibrium mixtures replace the chemicals as discussed in **16.5**. See **25.11** as well.

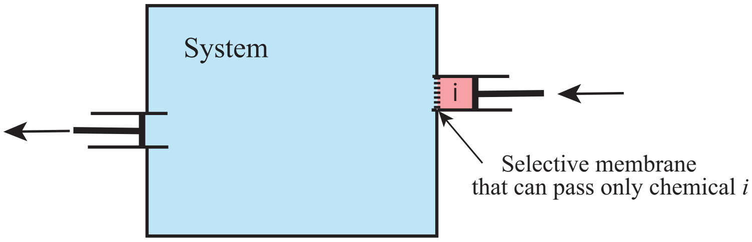

Figure 17.2: An operational definition of chemical potential. The left piston is for maintaining the total volume of the system.

work required for this process can determine μ_i.[369]

As can be seen from Gibbs' relation, it is possible to keep all work coordinates constant while pushing the piston, such as by suppressing the associated volume change.[370] Although how to add chemicals adiabatically to the system has already been discussed (→**4.14**), it is complicated. To avoid such procedures, as will be discussed in Section 18, we may use an isothermal process. $\Delta A \equiv W - Q$ may be measured, where W is the work added to the system due to pushing in the chemical, and Q is the exchanged heat to keep the system temperature constant. Both are measurable. Therefore,

$$dA = -SdT + \boldsymbol{x}d\boldsymbol{X} + \mu_i dN_i + \cdots. \tag{17.6}$$

implying that $dA = \mu_i dN_i$ can be used to measure μ_i. However, the chemical potential obtained this way is a function of T and $\boldsymbol{Y}$ (not E and $\boldsymbol{Y}$).

17.8 The Gibbs-Duhem relation

Since $E = E(S, \{X_i\}, \{N_i\})$ is a first-degree homogeneous function (→**3.5**), (3.6) implies

$$E = S\frac{\partial E}{\partial S} + \sum_i X_i \frac{\partial E}{\partial X_i} + \sum_i N_i \frac{\partial E}{\partial N_i} = ST + \sum_i X_i x_i + \sum_i N_i \mu_i. \tag{17.7}$$

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[369] Needless to say, the process must be reversible and quasistatic. However, whether such a process is realizable or not cannot be decided by speculation. For example, one must determine whether the magnitudes of the force needed to push in and pull out the piston is identical. Of course, we usually assume they are identical, but that can be guaranteed only by empirical evidence.

Still, it is natural to expect that the quasistatic motion of the piston is reversible, if chemical reactions are in equilibrium.

[370] Notice that the chemicals pushed into the system can carry some other quantities such as 'magnetization' or 'electric charge.' If these properties are inseparable, it is not convenient to keep related work coordinates constant. Instead, the chemical potential should be extended to include these quantities as electric chemical potential (→**26.11**) we will see later.

Taking the total differential of the above formula, we get

$$\begin{aligned} dE &= TdS + SdT + \sum_i (x_i dX_i + X_i dx_i) + \sum_i (\mu_i dN_i + N_i d\mu_i) && (17.8) \\ &= \left[TdS + \sum_i x_i dX_i + \sum_i \mu_i dN_i \right] + \left[SdT + \sum_i X_i dx_i + \sum_i N_i d\mu_i \right]. && (17.9) \end{aligned}$$

However, we have Gibbs' relation (17.4), so this implies

$$SdT + \sum_i X_i dx_i + \sum_i N_i d\mu_i = 0.[371] \tag{17.10}$$

This is called the *Gibbs-Duhem relation*. Notice that this is nothing but a result of Euler's theorem applied to degree zero homogeneous functions (intensive quantities) (→**3.5**). If there is only one chemical, this formula gives the differential of its chemical potential as

$$d\mu = -\frac{S}{N} dT - \sum_i \frac{X_i}{N} dx_i. \tag{17.11}$$

17.9 Chemical potential of an ideal gas

(17.11) reads for an ideal gas

$$d\mu = -\frac{S}{N} dT + \frac{V}{N} dP = -\frac{S}{N} dT + \frac{RT}{P} dP \tag{17.12}$$

due to the equation of state $PV = NRT$. Therefore, if the temperature is constant we can integrate this as

$$\mu(T, P) = \mu(T, P^{\ominus}) + RT \log \frac{P}{P^{\ominus}}. \tag{17.13}$$

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[371] We are aware that there are many equivalent choices of materials coordinates. For example, $\boldsymbol{N}$ in this formula may be replaced with $\tilde{\boldsymbol{N}}$ as

$$SdT + \sum_i X_i dx_i + \sum_i \tilde{N}_i d\mu_i = 0.$$

In other words, even though $\tilde{\boldsymbol{N}}$ is not a set of independent variables in contrast to $\boldsymbol{N}$ (in other words, even though the result (3.7) of Euler's theorem cannot be used), the same result is obtained thanks to chemical equilibrium. However, it is important to remember that this does not mean that the chemical composition variables are being used as independent coordinates. The $\tilde{N}_i$ in these equations represent specific values taken by the material coordinates N_i; they are not adopting the chemical composition variables as independent variables. Note that μ_i is <u>not</u> given by $\partial E/\partial \tilde{N}_i$. The chemical composition variables are not being used in the calculations. Rather, it is as if, 'after all the calculations are completed,' the values of the material coordinates are substituted with the values of the chemical composition coordinates at that point in time.

In particular, if the chemical potential at the standard pressure $P^\ominus = 1$ (in chemistry, pressure is often measured in atm, and this implies $P^\ominus = 1$ atm, but 10^5 Pa these days) is $\mu(T, P^\ominus) = \mu^\ominus(T)$, then we may write[372]

$$\mu(T,P) = \mu^\ominus(T) + RT\log P. \tag{17.14}$$

17.10 Dalton's law of partial pressures

The pressure of a mixture of two distinct gases 1 and 2 with mole numbers N_1 and N_2, respectively, is given by

$$P = (N_1 + N_2)RT/V, \tag{17.15}$$

if we assume both gases are ideal. Dalton understood this formula as the sum of the 'partial pressures' of individual gases, denoted by P_1 and P_2 respectively as $P = P_1 + P_2$:

$$P_1 = N_1RT/V, \tag{17.16}$$

$$P_2 = N_2RT/V. \tag{17.17}$$

This is called Dalton's *law of partial pressures*. If we introduce the *mole fraction* x of gas 1 as

$$x = \frac{N_1}{N_1 + N_2}, \tag{17.18}$$

the partial pressures read

$$P_1 = xP, \;\; P_2 = (1-x)P. \tag{17.19}$$

17.11 Understanding partial pressures in terms of selective membranes

Partial pressure may be understood as follows (Fig. 17.3). Assume the temperature is constant.

Let the mole numbers of component gases 1 and 2 be N_1 and N_2, respectively. Under pressure P their volumes are $V_1 = xV$ and $V_2 = (1-x)V$, respectively, where x is the mole fraction of gas 1. The sum $V_1 + V_2$ is exactly V as illustrated

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[372] The convention for defining standard states, which sets the reference quantities, will be summarized later in simpler cases (**25.18**).

in Fig. 17.3A.[373] Assuming that the containers are adiabatic, we allow each gas to freely expand to volume V as Fig. 17.3B. Since the temperature does not change, the pressures are P_1 and P_2 in **17.10**, respectively. If we 'superpose' these two gases (B→C→D), the pressure in D is $P = P_1 + P_2$, since they do not interact.

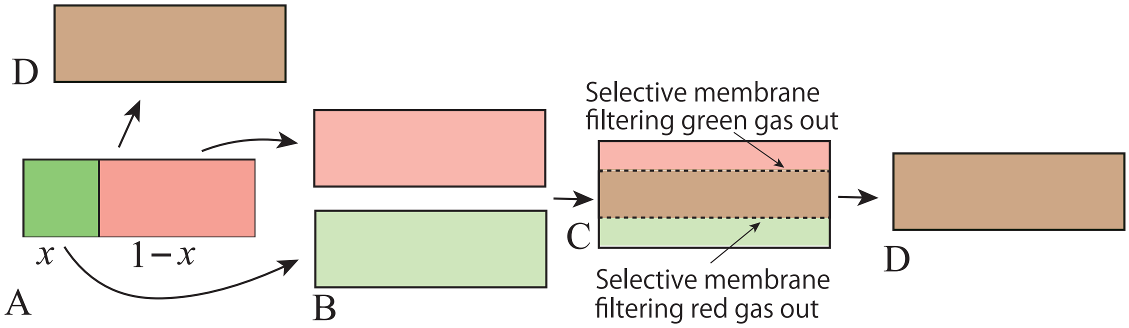

Figure 17.3: Dalton's law of partial pressures

Fig. 17.3 A: Let the mole numbers of the component gases 1 (green) and 2 (red) be N_1 and N_2, respectively. The individual volumes are $V_1 = xV$ and $V_2 = (1-x)V$, respectively, under pressure P, and the total volume is exactly V. If we remove the separating wall between 'green' and 'red' and wait for equilibration, the resulting mixture of ideal gases is shown in D. The temperature does not change.

If we use the selective membranes, Dalton's law of partial pressures may be understood in terms of the adiabatic free expansion of the gases.

B: If we adiabatically and freely expand each gas in the compartments of A to volume V, each will become a gas with its corresponding partial pressure.

C: Replace the bottom wall of the box with the red gas (resp., the upper wall of the box with the green gas) with a selective membrane that excludes the red gas (resp., the green gas) and merge the two boxes quasistatically. Since two gases do not interact, no work is needed for the merging process B→D. Thus, the total internal energy is constant throughout the process.

Needless to say, we assume that the processes using selective membranes are reversible, but the assumption is empirically supported by chemistry (→**4.3**).

17.12 Mixing entropy

Mixing two substances usually makes the substances hard to separate, so our com-

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[373] This is a dual of the law of partial pressure and is called *Amagat's law*. That is, the volume of a gas mixture at (T, P) is the sum of the volumes of the component gases at (T, P).

mon sense tells us that the process A→D in Fig. 17.3 is irreversible. Indeed, A→B in A→B→C→D is irreversible due to the free expansion, so the entropy of the whole system should increase by the process A→D. This increase of entropy is called the *mixing entropy*. The process B→C→D is reversible thanks to the selective membranes, so this entropy increase should be due to the process A→B (see Remark below).

The entropy of an ideal gas (i.e., the fundamental equation of an ideal gas) is given by (11.35). Adiabatic free expansion keeps the internal energy, so the system temperature does not change. Therefore, the fundamental equation tells us that for the N mole of an ideal gas the entropy change due to the volume change $V \to V'$ is given by

$$S(V') = S(V) + NR\log\frac{V'}{V}. \tag{17.20}$$

Therefore, for gas 1 and gas 2 the entropy changes are given by

$$S_{1\mathrm{B}} = S_{1\mathrm{A}} - N_1R\log x, \tag{17.21}$$

$$S_{2\mathrm{B}} = S_{2\mathrm{A}} - N_2R\log(1-x), \tag{17.22}$$

respectively, and the total entropy change reads

$$\Delta S = -NR\{x\log x + (1-x)\log(1-x)\}, \tag{17.23}$$

where the total mole number is written as $N = N_1 + N_2$.

Remark As we have seen, the mixing itself is a reversible process if performed quasistatically. Therefore, some authors assert that the irreversibility of the mixing process is due to diffusion (i.e., the expansion through other materials). However, the irreversibility is between A and B in Fig. 17.3. Thus, even 'diffusion' through something is irrelevant. The crux of mixing entropy is simply the irreversible expansion. Notice that this is consistent with **4.3** (I). See the last paragraph of **17.16**.

17.13 Raoult's law and ideal liquid mixtures

Consider a mixture of liquid A and liquid B at temperature T. The liquids have vapor pressures (the pressure of the vapor in equilibrium with its liquid →**??** as well) $P_{\mathrm{A}0}$ and $P_{\mathrm{B}0}$, respectively, at T, when they are pure. Raoult found for many liquid mixtures, approximately:

> The vapor pressure of the mixture is the sum of individual partial pressures given by $P_{\mathrm{A}} = xP_{\mathrm{A}0}$ and $P_{\mathrm{B}} = (1-x)P_{\mathrm{B}0}$, where x is the mole fraction of A in the liquid mixture.

This empirical law is called *Raoult's law.*

The liquid mixture for which Raoult's law hold exactly is called an *ideal liquid mixture* (for a more direct definition, see the end of **17.14**).

17.14 The chemical potentials of the components of an ideal liquid mixture

Let us write the chemical potentials of pure liquids A and B at temperature T and pressure 1 (atm) be $\mu_{\mathrm{A}}^{\ominus}$ and $\mu_{\mathrm{B}}^{\ominus}$. Also let us write the chemical potentials of vapor A and vapor B at temperature T and pressure 1 (atm) be $\mu_{\mathrm{AG}}^{\ominus}$ and $\mu_{\mathrm{BG}}^{\ominus}$, respectively. If we assume the vapors are ideal gases, their chemical potentials have the form of (17.14), so the equilibrium relation for each component between the liquid and the vapor phases read, as given in **17.9**,[374]

$$\begin{aligned}\mu_{\mathrm{A}}^{\ominus} &= \mu_{\mathrm{AG}}^{\ominus} + RT\log P_{\mathrm{A0}}, &(17.24)\\ \mu_{\mathrm{B}}^{\ominus} &= \mu_{\mathrm{BG}}^{\ominus} + RT\log P_{\mathrm{B0}}, &(17.25)\end{aligned}$$

where P_{A0} and P_{B0} are the vapour pressures of liquid A and liquid B, respectively, at temperature T as in **17.13**. If we denote the chemical potentials of the components in the mixture as μ_{A} and μ_{B}, respectively, each component must be in equilibrium with the corresponding vapor component with its partial pressure:

$$\begin{aligned}\mu_{\mathrm{A}} &= \mu_{\mathrm{AG}}^{\ominus} + RT\log(xP_{\mathrm{A0}}), &(17.26)\\ \mu_{\mathrm{B}} &= \mu_{\mathrm{BG}}^{\ominus} + RT\log((1-x)P_{\mathrm{B0}}). &(17.27)\end{aligned}$$

Comparing the above two sets of equations, the chemical potentials of the components may be given by

$$\begin{aligned}\mu_{\mathrm{A}} &= \mu_{\mathrm{A}}^{\ominus} + RT\log x, &(17.28)\\ \mu_{\mathrm{B}} &= \mu_{\mathrm{B}}^{\ominus} + RT\log(1-x). &(17.29)\end{aligned}$$

A mixed liquid with these component chemical potentials is called an *ideal liquid mixture.*

---

[374] In the following formulas, precisely speaking, the chemical potentials of the pure liquids must be at their respective vapor pressures (→**??**), but the chemical potential of the ordinary liquid is insensitive to the pressure if it is not very high (say, 10 atm).

17.15 Mixing entropy of ideal liquids

(17.7) tells us, generally for a two component liquid mixture,

$$E = ST - PV + \mu_A N_A + \mu_B N_B. \tag{17.30}$$

Before mixing the two components, the term $\mu_A N_A + \mu_B N_B$ reads

$$xN\mu_A^\ominus + (1-x)N\mu_B^\ominus, \tag{17.31}$$

where $N = N_A + N_B$. After mixing, we have

$$xN[\mu_A^\ominus + RT\log x] + (1-x)N[\mu_B^\ominus + RT\log(1-x)]. \tag{17.32}$$

For ideal liquids, it is assumed that mixing does not change the internal energy or volume, so the entropy change ΔS reads, under the constant temperature-pressure condition,

$$T\Delta S = -\Delta(\mu_A N_A + \mu_B N_B). \tag{17.33}$$

Comparing (17.31) and (17.32), we conclude

$$\Delta S = -NR[x\log x + (1-x)\log(1-x)], \tag{17.34}$$

which is the increase in entropy due to mixing and is called the mixing entropy. Notice that this formula is exactly the same as the one for ideal gas mixing case (17.23).

17.16 Meaning of the mixing entropy

For simplicity, we consider a one-to-one mixing, i.e., the $x = 1/2$ case.

Let us consider an experiment to eject a particle from the left half of the system[375] (Fig. 17.4). Before mixing, always green particles are detected; we know this even before performing any experiments. But, what about after mixing? We would detect both red and green particles evenly, so we cannot predict the outcome of each experimental run (Fig. 17.4Right).

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[375] According to the official standpoint of thermodynamics, we do not (cannot) inquire whether a substance is made of particles or not. However, it is a macroscopic fact that if a macroscopic object is irradiated by appropriate beam, particles are ejected. We cannot know the 'actual' structure of the object—even for a gas; it must be quite different from the collection of flying ball bearings. In reality, nobody knows what is going on.

Note that we are only using a macroscopically verifiable fact here: if we mix similar substances with a definite mole ratio, and then eject a particle, the probability to get a particular molecular species is proportional to the mole fraction.

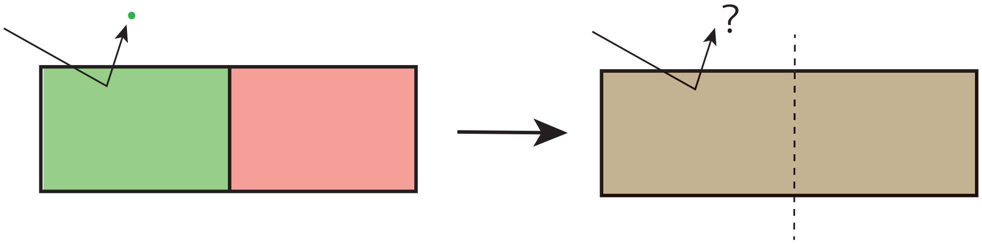

Figure 17.4: Experiment to eject a particle from a one-to-one mixture

What question should we ask to know the outcome of a particular run? We have only to make one question that can be answered by YES or NO: "Is it green?"[376] By "mixing," what we knew without asking any questions becomes uncertain, and we need to obtain new knowledge that can be obtained from a single YES-NO question to restore "perfect knowledge" about the system.

The required knowledge may be quantitated by the number of questions to obtain it. The amount of knowledge we can obtain from a single unbiased YES-NO question (called the *information* we can obtain) is called '1 bit of information'.

For the case with $x = 1/2$, the mixing entropy is given by $\Delta S = NR\log 2$. To obtain complete information about the left half, we must keep asking the question till the half becomes empty. How many times must we ask? Since 1 mole is exhausted if ejection experiments are repeated N_A (Avogadro's constant) times, through the mixing process we lose NN_A bits of information. This means entropy per particle $NR\log 2/NN_A = k_B \log 2$ corresponds to 1 bit, where k_B is the *Boltzmann constant*.

Next, let us consider doubling the volume of a gas by adiabatic free expansion (Fig. 17.5). Once again, we will consider particle ejection experiments.

Before the volume is doubled, particles always come out from the left side, but after doubling the volume, we cannot predict whether a particle will come out from the left or the right half. In this case, we have lost the information that could be obtained from a single unbiased YES-NO question, "Is it from the left?". Notice that the entropy increase is exactly the same as the above mixing problem: $\Delta S = NT\log 2$.

---

[376] It goes without saying that the answer to the YES or NO question must be totally unpredictable ('*unbiased YES-NO question*'). However, is the condition "totally unpredictable" a perfectly unambiguous prerequisite? There is ambiguity here, because 'randomness' is a tricky concept, usually, for example, tied to the total symmetry of the space.

It is often said that randomness is guaranteed only by quantum mechanics, but this depends on its theoretical structure and Born's probability interpretation. The assertion is a convention; it sounds obvious to some people according to their world view.

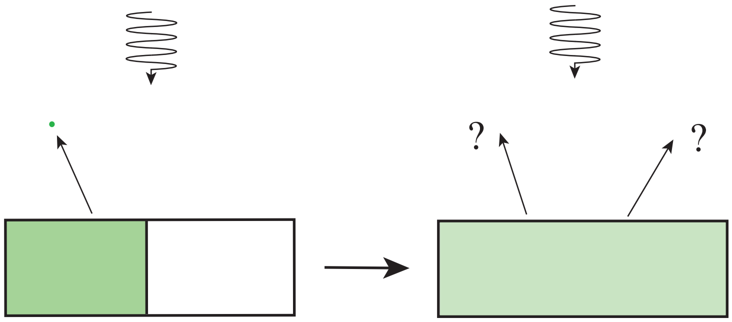

Figure 17.5: Doubling the volume of a gas by adiabatic free expansion

These two examples teach us two lessons:
The entropy increase due to a process looks quantitatively connected to the amount of knowledge we need to describe the system after the process as precisely as before the process. Additionally, as noted before (→**17.12**), the entropy increase by mixing is solely due to expansion.

We may summarize the distinction of chemicals as follows: we distinguish chemicals macroscopically, or we should say that we recognize distinct chemicals that we can distinguish macroscopically. The key point is that the macroscopic distinction of chemicals cannot be erased by any macroscopic means. Thus, even if we mix distinct chemicals, there always remains a macroscopic means to separate them. The distinction any macroscopic means cannot erase may be usually interpreted as microscopic properties, but macroscopic experimental methods cannot verify this interpretation.

17.17 Entropy and phase transition

Phase transitions and related topics will be discussed later (Section 23). For now, let us consider the changes we encounter daily such as freezing of water or boiling to produce water vapor. Such changes are called phase transitions. For water liquid phase (water coming out of a faucet), gas phase (vapor) and sold phase (ice) are distinct at our daily temperature and pressure. During phase transitions, water exchanges the so-called *latent heat* such as melting heat or boiling heat with its environment without changing the system temperature.[377]

Let L be the latent heat absorbed by the system when it turns from phase A to phase B, then the entropy change due to the phase transition A→B is given by

$$\Delta S_{\mathrm{A}\to\mathrm{B}} = \frac{L}{T}. \tag{17.35}$$

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[377] Thus, T is not partially differentiable with respect to the internal energy.

For example, 1 mole of ice melts at 0 °C = 273 K under 1 atm to become liquid water. The latent heat is 5940 J/mole. Therefore, 1 mole of liquid water at 0 °C has a larger entropy by $\Delta S = 6010/273 = 22.0$ J/K·mol = $2.65R$ ($R = 8.314$ J/K·mol) than 1 mole of ice. What does this mean from the information standpoint?

As we have seen in **17.16** 1 bit/molecule corresponds to entropy change of $R \log 2 = 0.693R$ J/K per mole. Therefore, the melting entropy is $2.65/0.693 \approx 3.8$ bits/molecule. To understand the state of a single molecule in liquid water as accurately as in ice, we must ask about 4 more YES-NO questions.[378]

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[378] If we may use a detailed molecular model, this number may be interpreted as follows: in cold water a water molecule still cannot move freely due to hydrogen-bonding networks, but can rotate relatively freely than in a crystal. To specify its rotation axis by its residing octant, we already need 3 bits.

18 Isothermal process and Legendre-Fenchel transformation

18.1 Thermodynamics of isothermal processes

A process in which initial and the final states have the same temperature is called an *isothermal process*. As is usual in thermodynamics, we do not care whatever happens during the process. To begin with during the process the system need not be in equilibrium, so even mentioning temperatures during the process is meaningless. However, the most practical way to achieve an isothermal process is to maintain the system in thermal contact with a heat bath (→**8.8**). This guarantees that the initial and the final equilibrium states are at the same temperature; Of course, we cannot say anything about the system temperature in between, even if the system remains in thermal contact with a heat bath of temperature T.

To utilize thermodynamics we must connect the intial and the final states with a reversible quasistatic process. For isothermal processes it is convenient to devise an appropriate reversible quasistatic isothermal process. Let us consider Gibbs' relation (→**17.6**) for an isothermal process. To keep the system temperature, free exchange of heat between the system and its environment should be allowed, so instead of dE, we should consider

$$dE - dQ = dW + dZ = \sum y_i dY_i = \sum x_i dX_i + \sum \mu_i dN_i. \tag{18.1}$$

Reversibly and quasistatically $dQ = TdS$ and the system temperature T is constant. Therefore, it is convenient to rewrite (18.1) as

$$dE - TdS = d(E - TS) = dW + dZ = \sum x_i dX_i + \sum \mu_i dN_i. \tag{18.2}$$

Thus, to introduce

$$A = E - TS, \tag{18.3}$$

called the *Helmholtz energy*, is convenient. For isothermal reversible quasistatic processes (17.1) implies

$$dA = dW + dZ. \tag{18.4}$$

Here, just as dQ previously, dW and dZ are symbols for 1-forms and do not necessarily imply exact forms (→**9.8**).

If the system is materially closed (i.e., without the dZ term), $dA = dW$, so, as adiabatic processes, quasistatic work form is exact for isothermal processes.[379]

18.2 The change of Helmholtz energy for isothermal but not quasistatic processes: work principle

First, let us consider a closed system (thus there is no Z, although chemical reactions or chemical equilibrium shifts may occur in the system). For isothermal reversible quasistatic processes (18.4) implies

$$\Delta A = W, \tag{18.5}$$

where W is the work done to the system from outside reversibly and quasistatically.

What happens, if the work is not reversible and generally involves some dissipation (→**2.3**) (in the system)? Naturally, the system heats up (before equilibration), but the generated heat would escape to the attached heat bath. That is, not all the added work is converted to the system energy:

$$\Delta A \leq W. \tag{18.6}$$

This is called the *principle of minimum work*. That is, to cause a given change ΔA the minimum work specified by (18.5) is possible if the work is added quasistatically and reversibly.

If a system does work on the external world, if that is done without loss (i.e., reversibly without dissipation) the maximum work should be taken out. This is called the *maximum work principle*. In this case A is reduced, and the system loses energy as work, so both ΔA and W are negative according to our sign convention. The argument (18.6) is algebraic, so it should always be correct. Therefore,

$$|\Delta A| \geq |W|. \tag{18.7}$$

This is the maximum work principle: we can take out the largest work (i.e., $|\Delta A|$) if reversible.

For the general cases with mass actions (that is, for the system being no more closed), we have only to replace W with $W + Z$:

$$\Delta A \leq W + Z. \tag{18.8}$$

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[379] As we saw in **7.7**, in an adiabatic process, the work W itself was a conserved quantity, but in the current case, this holds true only in the quasi-static case.

If there is no work, but chemical energy could be extracted by chemical reactions, we have $|\Delta A| \geq |Z|$ as (18.7). However, in practice, not only the constant temperature, but also the constant pressure condition becomes important. This topic will be postponed to the section discussing the Gibbs energy (→**19.6**).

18.3 Clausius' inequality and work principle

The derivation of the work principle in **18.2** may be admissible in physics, but it may not sound like a formal demonstration. Therefore, here, the principle is rederived by using Clausius' inequality (→**14.4**). To realize an isothermal process, we may assume that the system is always in thermal contact with a heat bath at a constant temperature T. Needless to say, the system may not be in equilibrium during the process, so its temperature may be meaningless. If we apply Clausius' inequality

$$\Delta S \geq \frac{Q}{T} \tag{18.9}$$

to $Q = \Delta E - W$, we have

$$T\Delta S = \Delta(TS) \geq \Delta E - W \;\;\Rightarrow\;\; W \geq \Delta(E - TS) = \Delta A. \tag{18.10}$$

This is just (18.6).

18.4 Principle of Helmholtz energy minimization

If a closed simplesystem does not exchange work with its environment, the inequality (18.6), which holds under constant temperature, reads

$$\Delta A \leq 0. \tag{18.11}$$

That is, under constant temperature, if a change can actually happen without any net generalized work contribution of operational coordinate change, then its Helmholtz energy should decrease.

Here, Δ implies the result due to a certain actual perturbation of the intial state (equilibrium state) that has no energetic contribution. If it can destabilize the original state, then the system free energy must not increase. This is called the *principle of decrease of Helmholtz energy*. If (18.11) never happens, then the equilibrium state is stable. Since (18.11) never happens for simple systems, the Helmholtz free energy of the equilibrium state must be the smallest possible. This is called the *Helmholtz energy minimization principle*, which is a global principle for a state to be in equilibrium.

18.5 Thermodynamic variation under constant temperature

The isothermal thermodynamic variation is defined as follows, just as the variation under adiabatic conditions **12.10**: for a function $J(T, \boldsymbol{Y})$ of T and operational coordinates $\boldsymbol{Y}$,

$$\Delta J(T, \boldsymbol{Y}) = \sum_{i \in \mathcal{P}} J(T, \boldsymbol{Y}_i) - J(T, \boldsymbol{Y}), \tag{18.12}$$

where $\mathcal{P}$ denotes the set of subsystems by a particular partition of the original system into subsystems, and $\boldsymbol{Y} = \sum_{i \in \mathcal{P}} \boldsymbol{Y}_i$.

For any variation respecting the internal constraints, if any,

$$\Delta A \geq 0 \tag{18.13}$$

holds for any equilibrium state due to the convexity of A with respect to $\boldsymbol{Y}$ (just Jensen's inequality). That is, (18.13) has nothing to do with the stability of the equilibrium state. However, if the variation does not respect the internal constraints, (18.11) may happen for compound systems.

18.6 Legendre transformation

The transformation: $E \to A = E - ST$ is called the *Legendre transformation*, which changes the independent variables $S, \boldsymbol{X}, \boldsymbol{N}$ of E to $T, \boldsymbol{X}, \boldsymbol{N}$. Certainly,

$$dE = TdS + \boldsymbol{x}d\boldsymbol{X} + \boldsymbol{\mu}d\boldsymbol{N} \;\Rightarrow\; dA = -SdT + \boldsymbol{x}d\boldsymbol{X} + \boldsymbol{\mu}d\boldsymbol{N}. \tag{18.14}$$

However, the formula alone does not explain the meaning of the Legendre transformation at all.

When we write

$$E(S, \boldsymbol{X}, \boldsymbol{N}) \to A(T, \boldsymbol{X}, \boldsymbol{N}) = E(S, \boldsymbol{X}, \boldsymbol{N}) - TS,$$

the T in the formula is not arbitrary but is determined by $E(S, \boldsymbol{Y})$:

$$T = \left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}}. \tag{18.15}$$

Let us consider the relationship between E and A geometrically. Since the other variables are unaffected, let us suppress $\boldsymbol{Y}\boldsymbol{N}$ from now on.

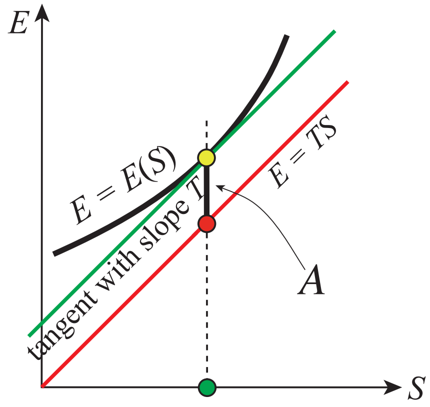

Figure 18.1: Legendre transformation

Consider a state whose entropy is given by the green dot (Fig. 18.1). Its temperature T is the slope of the tangent line to E at that point, since E is a (strictly monotone increasing) convex function of S (→**13.9**). Draw a line (red line) with the same slope passing through the origin, $E = TS$. Then, $A = E - TS$ is the E-coordinate value of the yellow dot subtracted that of the red dot. This implies that the minimum of the (signed) distance measured along the E-axis between the curve $E = E(S)$ and the line $E = TS$ is A. Thus, we have the following expression (the conditions are written to the right of a vertical bar):

$$A = \min_S |_{\boldsymbol{Y}} [E(S, \boldsymbol{Y}) - TS]. \tag{18.16}$$

The suffix $\boldsymbol{Y}$ to the right of | implies that the minimum $\min_S$ is taken under the condition that the operational coordinates $\boldsymbol{Y}$ are fixed. Since E is differentiable with respect to S, the conditional minimization indeed gives

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{Y}} - T = 0, \tag{18.17}$$

so (18.16) agrees with the elementary Legendre transformation.

Now, rewrite (18.16) as

$$-A = \max_S |_{\boldsymbol{Y}} [TS - E(S, \boldsymbol{Y})]. \tag{18.18}$$

Since E is a convex function, in particular, a convex function of S, this formula is just the (partial) *Legendre-Fenchel transformation* (→**18.7**, **18.8**).

From now on, in these notes any Legendre transformation will be discussed as the Legendre-Fenchel transformation partly to emphasize that transformation is a tool of convex analysis (→**13.1**) and that the differentiability of functions (as appearing in (18.17)) is not required. The second point is crucial when we discuss phase transitions (→**23.11**).

18.7 Legendre-Fenchel transformation

For a convex function $f : \mathbb{R}^n \to \mathbb{R}$ (→**13.2**)

$$f^*(x) = \sup_y [x \cdot y - f(y)] \tag{18.19}$$

is called the *conjugate function* of f. [Here, sup and max may not be fastidiously distinguished.[380]] The transformation $f \to f^*$ is called the *Legendre-Fenchel transformation*. If f is everywhere differentiable, as we have seen in **18.6**, the Legendre-Fenchel transformation agrees with the conventional Legendre transformation.[381]

Pay special attention to the following two theorems:

(1) The conjugate function f^* of a convex function f is convex [Proof →**18.10**].

(2) The conjugate of the conjugate of a convex function is the original convex function: $(f^*)^* = f^{**} = f$ [Proof→**18.11**].

These two theorems imply for E and A:

(1) $-A$ is a convex function of T (That is, A is convex upward as a function of T for each $\boldsymbol{Y}$).

(2) If we know A, we can completely recover E.

Remark 1. The Legendre-Fenchel transformation (or Legendre-Young-Fenchel transformation) is a standard terminology in convex analysis. Although non-differentiable

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[380] ⟪**sup and max**⟫ 'max' denotes the maximum value. $M = \max_{y\in C} f(y)$ implies that the function f assumes at a point in C actually the largest value M. In contrast, $M = \sup_{y\in C} f(y)$ implies that M is the least upper bound of the values of f on C (that is, the least upper bound of the set $f(C)$ is M), so there need not actually be a point in C where f takes the value M. For example, on $C = (-1, 1)$ for $f(y) = 1 - y^2$ $\max_{y\in C} f = \sup_{y\in C} f = 1$, but for $g = y^2$ there is no $\max_{y\in C} g(y)$. Still, $\sup_{y\in C} g(y) = 1$, so sup and max must be distinguished, but for many cases we will discuss, max exists intuitively, so we may consider sup as max.

[381] These days, it has become common to define the Legendre transformation using the sup (supremum), including non-differentiable situations. However, in physics, differentiability is always conspicuous. Therefore, in this book, we deliberately use the term "Legendre-Fenchel transformation" to highlight this distinction. See Remark below.

cases are also discussed as the Legendre transformation these days, the use in partial differential equations and mechanics (symplectic dynamics) is traditionally restricted to differentiable cases as the original due to Legendre. As seen in **23.11** the applications to nondifferentiable cases are essential to understanding phase transitions (→**23.11**). To guarantee the completeness (→**18.13**) of thermodynamic functions this generalization is crucial, and hence the name 'Legendre-Fenchel transformation' will be used throughout the book.

Remark 2. The sign choice in (18.19) is the mathematically standard choice. However, as seen in (18.16) and (18.18) thermodynamically convenient formulas have different sign or sup/inf switch. For the inverse transformation, as seen in (18.30), again there is a sign flip. The author wishes to remember only one formula (18.19). Note that the inverse transformation has exactly the identical form. Therefore, the readers are strongly recommended to stick to the mathematically standard formula, even if minus signs $(-)$ may show up in thermodynamics.[382]

18.8 Partial Legendre-Fenchel transformation

As we have already seen in **18.6**, the Legendre-Fenchel transformation of E to A is with respect to the variable S and its conjugate T for each fixed $\boldsymbol{Y}$. Such transformation should be called a *partial Legendre-Fenchel transformation*. Its mathematics is almost the same as is explained in **18.7**: we fix all the remaining variables, and at each fixed value, we can define its Legendre-Fenchel transformation. We will use the following notation (as already used):

$$f^*(x,z) = \sup_y|_z[x \cdot y - f(y,z)]. \tag{18.20}$$

Its inverse transformation is

$$f(y,z) = \sup_x|_z[x \cdot y - f^*(x,z)]. \tag{18.21}$$

In the context of thermodynamics, E is certainly a convex function with respect to all variables. However, for an isothermal process, we focus only on S and treat E as a single-variable function of S and apply the partial Legendre-Fenchel transformation.

We will emphasize this later again, but it is important to note that the functions obtained through such partial Legendre-Fenchel transformations (in this case, $-A$)

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[382] Recall that the relation between Hamiltonians and Lagrangians in classical mechanics uses the standard convention.

are convex functions with respect to the variable of interest (in this case, T), but remain the same as the original function (in this case, E) with respect to other variables. In other words, $-A$ is convex with respect to T (for each $\boldsymbol{Y}$) but concave with respect to $\boldsymbol{Y}$ (for each T) (as it involves putting a negative sign and flipping the convex function). Therefore, it is important to note that $A(T, \boldsymbol{Y})$ is neither entirely convex nor entirely concave as a whole.

18.9 What happens if E is totally Legendre-Fenchel transformed?

In thermodynamics, the Legendre-Fenchel transformation is always with respect to a genuine subset of the coordinates (→**18.8**). Since E is a first-degree homogeneous function (→**3.5**) of extensive variables, obviously we have

$$0 = \sup_{S,\boldsymbol{Y}}[ST + \boldsymbol{y} \cdot \boldsymbol{Y} - E], \tag{18.22}$$

which may seem like a meaningless result, but is it? Since 0 is obviously a convex function, $f^{**} = f$ (→**18.7** (ii)) implies $0^* = E$:

$$E = \sup_{T,\boldsymbol{y}}[ST + \boldsymbol{y} \cdot \boldsymbol{Y}]. \tag{18.23}$$

This formula implies that if all the extensive quantities are measured, the most important thermodynamic quantity can be determined. Thus, an apparently self-evident formula (18.22) could be regarded as a foundation of thermodynamics. That is, 0 as a function of T and $\boldsymbol{y}$ is a complete thermodynamic function (→**18.13**).

18.10 Conjugates of convex functions are convex

As the following computation demonstrates, if f^* is defined as (18.19), whatever f may be, f^* satisfies Jensen's inequality (→**13.3**), so it is convex. For any $\lambda \in [0,1]$

$$\begin{aligned}
\lambda f^*(x_1^*) + (1-\lambda) f^*(x_2^*) &= \lambda \sup_{x_1}[x_1 \cdot x_1^* - f(x_1)] + (1-\lambda) \sup_{x_2}[x_2 \cdot x_2^* - f(x_2)] \\
&= \sup_{x_1,x_2} \{\lambda[x_1 \cdot x_1^* - f(x_1)] + (1-\lambda)[x_2 \cdot x_2^* - f(x_2)]\} \\
&\geq \sup_{x_1=x_2} \{\lambda[x_1 \cdot x_1^* - f(x_1)] + (1-\lambda)[x_2 \cdot x_2^* - f(x_2)]\} \\
&= \sup_{x} \{\lambda[x \cdot x_1^* - f(x)] + (1-\lambda)[x \cdot x_2^* - f(x)]\} \\
&= \sup_{x}[x \cdot (\lambda x_1^* + (1-\lambda) x_2^*) - f(x)] \\
&= f^*(\lambda x_1^* + (1-\lambda) x_2^*).
\end{aligned} \tag{18.24}$$

Therefore, f^* is convex irrespective of f. In particular, the conjugate of a convex function is again convex.

18.11 $f^{**}=f$, if f is convex

Let $f:\mathbb{R}^n\to\mathbb{R}$ be a convex function. Then, $f^{**}=f$.

By definition for $\forall x$ and for $\forall y$

$$f^*(x)\geq x\cdot y-f(y). \tag{18.25}$$

If f is convex, then for each y there is x such that the equality holds.[383] Therefore, for each y in the inequality below left there is x satisfying the equality. That is, the equation in the right holds:

$$f(y)\geq x\cdot y-f^*(x)\ \Rightarrow\ f(y)=\sup_x[x\cdot y-f^*(x)]. \tag{18.26}$$

This is the definition of f^{**}, and implies $f^{**}=f$.

18.12 Helmholtz energy in terms of Legendre-Fenchel transformation

This unit is a summary repeat of the last portion of **18.7**. Let us rewrite (18.16) as

$$-A(T)=\max_S|_{\boldsymbol{Y}}[TS-E(S,\boldsymbol{Y})]=\sup_S|_{\boldsymbol{Y}}[TS-E(S,\boldsymbol{Y})]. \tag{18.27}$$

Since $E(S)$ is convex, the above formula is a (partial) Legendre-Fenchel transformation **18.7** (or **18.8**) of a convex function. That is,

$$-A=E^*. \tag{18.28}$$

Thus, we immediately know that $-A$ is a convex function of T; $A(T)$ is a concave function of T, Also, we have

$$(-A)^*=E^{**}=E. \tag{18.29}$$

More explicitly, this reads

$$E=\sup_T|_{\boldsymbol{Y}}[TS-(-A)]=\sup_T|_{\boldsymbol{Y}}[TS+A]. \tag{18.30}$$

The implication of this formula is important. $E=E(S,\boldsymbol{Y})$ is a function completely describing the thermodynamics of a given system (→**18.13**). Since Helmholtz energy A allows the construction of E as seen in (18.30), A is, though dependent on non-thermodynamic coordinate T, also a function that completely describes the thermodynamics of the system.

18.13 Complete thermodynamic functions

A thermodynamic function that can reconstruct or restore the internal energy $E=E(S,\boldsymbol{Y})$ as a function of S and operational coordinates $\boldsymbol{Y}$ through a (partial)

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[383] To understand this really intuitively we need geometry of a convex function and its supporting planes. This is explained in Appendix D at the end of this section (→**D.2**).

If f is not convex, for each y there is no guarantee for x giving the equality to exist, so $f^{**}=f$ need not hold. As seen in **18.10**, f^{**} is convex and agrees with f where it is convex, but $f>f^{**}$ (since there is no x satisfying the equality in (18.26)), so f^{**} is called the *convex hull* of f.

Legendre-Fenchel transformation is called a *complete thermodynamic function*. The Helmholtz energy is an example as seen in **18.6**.

18.14 Gibbs-Helmholtz equation for the Helmholtz energy

Since the Helmholtz energy is a complete thermodynamic function **18.13**, there should be a formula obtaining the internal energy from the Helmholtz energy. Since $E = A + TS$ and $dA = -SdT + \boldsymbol{y}d\boldsymbol{Y}$,

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_{\boldsymbol{Y}} = A + \frac{1}{T}\left(\frac{\partial A}{\partial 1/T}\right)_{\boldsymbol{Y}} = \left(\frac{\partial A/T}{\partial 1/T}\right)_{\boldsymbol{Y}}. \tag{18.31}$$

This formula is, historically, a rehash of (19.7) for the Gibbs energy.

D Appendix D: Geometrical meaning of the Legendre-Fenchel transformation

D.1 Convex functions are supported by hyperplanes from below

Let $f : \mathbb{R}^n \to \mathbb{R}$ be a convex function. Since its epigraph epi f (→**13.2**) is a convex set, there is a hyperplane $\mu = h(x) = x \cdot b - \beta$ below it. That is, we can choose $b \in \mathbb{R}^n$ and $\beta \in \mathbb{R}$ so that

$$f(x) \geq x \cdot b - \beta \tag{D.1}$$

holds.[384] See Fig. D.1 Left. In particular, for each b we can choose β as small as possible so that the hypersurface $y = x \cdot b - \beta$ touches epi$f$. A hyperplane tangent to epi f is called a *supporting hyperplane* of f. Thus, we see that the graph of f is enveloped by all the supporting hyperplanes of f itself (Fig. D.1 Right). That is, f can be reconstructed from the totality of the parameters (b, β) characterizing the supporting hyperplanes of epi f (→**D.2**). This is the essence of the Legendre-Fenchel transformation **18.7**.

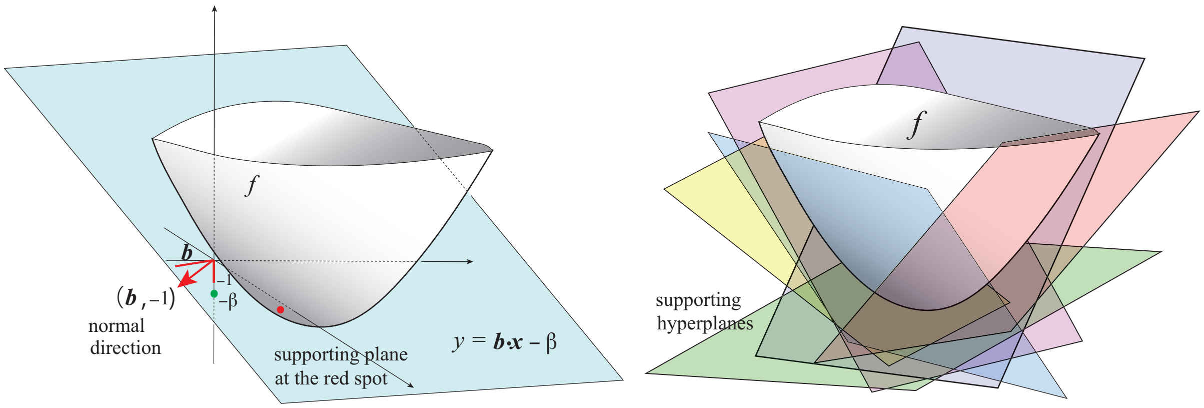

Figure D.1: Examples of supporting planes of f. If we collect all the supporting planes of f, their envelop is f.

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[384] Notice that $y = x \cdot b - \beta$ expresses a hyperplane in $\mathbb{R}^n \times \mathbb{R}$ passing through $(0, -\beta)$ and perpendicular to $(b, -1)$:

$$(b, -1) \cdot (x, y + \beta) = 0 \;\Rightarrow\; b \cdot x - y - \beta = 0 \;\Rightarrow\; y = b \cdot x - \beta. \tag{D.2}$$

D.2 Reconstruction of a convex function from its supporting planes

Let $f : \mathbb{R}^n \mapsto \mathbb{R}$ be a convex function. Let $\mu = x^* \cdot x - \mu^*$ be a hyperplane that has $\mathrm{epi}\, f$ on its upper side (allowing tangential contacts) and F^* be the set of totality of the parameters (x^*, μ^*) allowed for such hyperplanes:

$$F^* = \{(x^*, \mu^*)\} \,|\, f(x) \geq x^* \cdot x - \mu^* \text{ for } \forall x \in \mathbb{R}^n\}. \tag{D.3}$$

That this set is a closed convex set may be demonstrated as follows:
Suppose (x_1^*, μ_1^*) and (x_2^*, μ_2^*) belong to F^*. For $\forall x \in \mathbb{R}^n$

$$\begin{aligned} f(x) &\geq x_1^* \cdot x - \mu_1^*, && \text{(D.4)} \\ f(x) &\geq x_2^* \cdot x - \mu_2^*, && \text{(D.5)} \end{aligned}$$

so for any $\lambda \in [0, 1]$

$$f(x) \geq (\lambda x_1^* + (1 - \lambda) x_2^*) \cdot x - (\lambda \mu_1^* + (1 - \lambda) \mu_2^*). \tag{D.6}$$

holds. That is, $(\lambda x_1^* + (1 - \lambda) x_2^*, \lambda \mu_1^* + (1 - \lambda) \mu_2^*) \in F^*$.

For $\forall x \in \mathbb{R}^n$

$$f(x) \geq x^* \cdot x - \mu^*, \tag{D.7}$$

so for $\forall x \in \mathbb{R}^n$

$$\mu^* \geq x^* \cdot x - f(x) \tag{D.8}$$

holds. Therefore,

$$\mu^* \geq \sup_x [x^* \cdot x - f(x)]. \tag{D.9}$$

That is, $(x^*, \mu^*) \in F^*$ implies that this is the epigraph of f^* defined as

$$\mu^* \geq f^*(x^*) = \sup_x [x^* \cdot x - f(x)]. \tag{D.10}$$

or $F^* = \mathrm{epi} f^*$. F^* is a closed convex set, so f^* is a convex function, which is the conjugate of f.

Notice that f^* is the upper bound of the affine function $g(x^*) = x \cdot x^* - \mu$ at each x^* under the condition: $(x, \mu) \in F = \mathrm{epi} f$.

D.3 Gradient inequality

Let f be a convex function. If for $\forall z$ x^* satisfies

$$f(z) \geq f(x) + x^* \cdot (z - x) \tag{D.11}$$

for a given x, x^* is called the *subgradient* of f at x, and the inequality (D.11) is called the *subgradient inequality* (see Fig. D.2):

$$\partial f(x) = \{x^* \mid f(z) \geq f(x) + x^* \cdot (z - x) \text{ for } \forall z\}, \tag{D.12}$$

which is a convex set and is called the *subdifferential* of f at x.

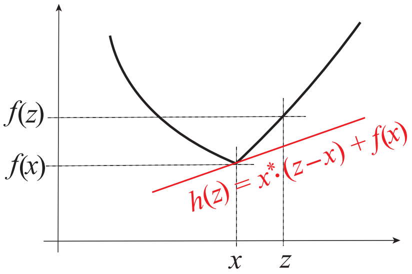

Figure D.2: Subgradient x^* and subgradient inequality illustrated

This inequality implies that the following affine function illustrated in Fig. D.2

$$h(z) = x^* \cdot (z - x) + f(x) \tag{D.13}$$

expresses the supporting hyperplane (→**D.1**) of epi$f$ that is in contact with it at $(x, f(x))$.

If f is not differentiable at x, its subgradients are not unique. That is, the subdifferential $\partial f(x)$ (D.12) consists of more than one point.

If a convex function f is differentiable at x, (D.11) reads

$$f(z) \geq f(x) + \nabla f(x) \cdot (z - x). \tag{D.14}$$

Let us call this the *gradient inequality*.

D.4 A consequence of the gradient inequality

If we write (D.14) around x and around x', for any point z

$$\begin{aligned} f(z) &\geq f(x) + \nabla f(x) \cdot (z - x), && \text{(D.15)} \\ f(z) &\geq f(x') + \nabla f(x') \cdot (z - x'). && \text{(D.16)} \end{aligned}$$

Therefore, we obtain

$$\begin{aligned} f(x') &\geq f(x) + \nabla f(x) \cdot (x' - x) \ \Rightarrow f(x') - f(x) \geq \nabla f(x) \cdot (x' - x), \quad \text{(D.17)} \\ f(x) &\geq f(x') + \nabla f(x') \cdot (x - x') \ \Rightarrow f(x) - f(x') \geq \nabla f(x') \cdot (x - x'). \quad \text{(D.18)} \end{aligned}$$

Adding these two inequalities we obtain

$$0 \geq \nabla f(x) \cdot (x' - x) + \nabla f(x') \cdot (x - x') = (\nabla f(x) - \nabla f(x')) \cdot (x' - x). \tag{D.19}$$

That is, we have obtained

$$(\nabla f(x) - \nabla f(x')) \cdot (x - x') \geq 0. \tag{D.20}$$

If we apply this to E, we get an inequality for differences between any two points in the thermodynamic space:

$$\Delta S \Delta T + \sum \Delta x_i \Delta X_i + \sum \Delta \mu_i \Delta N_i \geq 0. \tag{D.21}$$

19 Constant temperature-pressure processes and Gibbs energy

19.1 Thermodynamics of isothermal and isobaric processes

Experiments are often conducted in environments with constant temperature and pressure due to their relative ease. For systems in which chemical reactions are of primary interest, Gibbs' relation may be written as

$$dE - TdS + PdV = d(E - TS + PV) = \sum_{V^c} x_i dX_i + \sum_i \mu_i dN_i, \tag{19.1}$$

where $\sum_{V^c} x_i dX_i$ denotes the works other than the volume work. Therefore, similar to the case of the Helmholtz energy (→**18.1**), it is convenient to define the *Gibbs energy* as

$$G = E - TS - (-P)V = E - TS + PV. \tag{19.2}$$

This is also a Legendre transformation as the Helmholtz energy (→**18.1**) in elementary thermodynamics. To make its mathematical properties explicit the following (partial) Legendre-Fenchel transformation is recommended (→**18.7**, **18.8**):

$$-G = \sup_{S,V} |_{\boldsymbol{Y}\setminus V} [TS + (-P)V - E]. \tag{19.3}$$

The conditions (what to keep const, etc.) are written after |. Do not forget that the conjugate of V is $-P$. From the general theory of the Legendre-Fenchel transformation (→**18.7**) $-G$ is a convex function of T, P (while keeping all the work coordinates other than V fixed under a materially closed condition). Therefore, we can recover E:

$$E = \sup_{T,P} |_{\boldsymbol{Y}\setminus V} [ST + (-P)V - (-G)] = \sup_{T,P} |_{\boldsymbol{Y}\setminus V} [TS - PV + G]. \tag{19.4}$$

This is similar to the case of the Helmholtz energy A (→**18.12**). Therefore, the Gibbs energy G is also a complete thermodynamic function (→**18.13**).

19.2 Results of partial Legendre-Fenchel transformation

E is a convex function[385] of S, $\boldsymbol{X}$ and $\boldsymbol{N}$. If we (partial) Legendre-Fenchel-transform

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[385] if there are no non-additive extensive quantities

E with respect to S, the resulting $-A$ is a convex function of T if all other variables are fixed under materially closed conditions. Although E is a convex function of all its variables, as already noted in **18.8**, A is concave only with respect T; if T is fixed, as a function of $\boldsymbol{X}$ it is a convex function; A itself is neither convex nor concave.

A similar remark applies to G. $-G$ is a convex function of T and P, which means G is a two-variable concave function of T and P when all the operational coordinates are fixed except for V; G itself is neither a convex nor convex function.

19.3 Enthalpy

The Legendre-Fenchel transformation in **19.1** may be understood in two steps; first the transformation with respect to V, then with respect to S:

$$-H = \sup_V |_{S,\boldsymbol{Y}\backslash V}[-PV - E], \tag{19.5}$$

$$-G = \sup_T |_{P,\boldsymbol{Y}\backslash V}[TS - H]. \tag{19.6}$$

Combine these two equations gives us (19.3). H is called the *enthalpy*. It is a complete thermodynamic function, since inverse transformation(s) recovers E. Under a constant pressure condition, ignoring the exchange of energy due to volume change, the remaining energy change is ΔH. For an ordinary chemical experiment in a lab, this corresponds to the exchange of heat due to chemical reactions (the *reaction heat* →**25.19**).

Comparing (19.6) and (18.27) we get the equation corresponding to (18.31):

$$H = \left(\frac{\partial G/T}{\partial 1/T}\right)_{P,\boldsymbol{Y}\backslash V}. \tag{19.7}$$

This is the *Gibbs-Helmholtz equation*, which allows us to calculate the Gibbs energy change from the reaction heat (→**24.1**).

19.4 Chemical potential and Gibbs energy

In chemistry there are often no work coordinates other than volume V. This means that there is no work contribution to the system other than the volume work. Thus, we have $dG = dZ$:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i. \tag{19.8}$$

Therefore, under constant temperature and pressure we have

$$dG = \sum_i \mu_i dN_i. \tag{19.9}$$

Consequently, if we add a chemical under constant temperature and pressure following the procedure illustrated in Fig. 17.2, the required work $\mu_i dN_i$ should directly give its chemical potential. However, note that, in contrast to the chemical potential explained in **17.7**, here, its independent variables are T, P ans $\boldsymbol{Y}$ except for V.

The meaning of the materials coordinate (→**4.8**) change dN_i is that the experimenter (algebraically) adds dN_i moles of chemical i to the system. Since this addition may be through a selective permeable membrane for i, the chemical potential of i in the system must be identical to the measurable chemical potential μ_i itself. However, the system has its own chemical reactions, so the amount of chemical i in the system need not (algebraically) increase by dN_i moles.

19.5 Chemical composition coordinates in a closed system

Let the chemical composition coordinates of the equilibrium state before adding dN_i are $\tilde{\boldsymbol{N}}$. Adding of dN_i alters the chemical composition coordinates by $d\tilde{\boldsymbol{N}} = \{d\tilde{N}_i\}$. The energy required for this changes (under constant T, P) is given by

$$\sum_j \mu_j d\tilde{N}_j. \tag{19.10}$$

Addition of dN_i to the system reversibly and quasistatically changes the system Gibbs energy by $\mu_i dN_i$. These two formulas must give the same results under constant T, P and $\boldsymbol{Y} \setminus V$:

$$\mu_i dN_i = \sum_j \mu_j d\tilde{N}_j. \tag{19.11}$$

In short, we must generally have the following equality under constant T, P and $\boldsymbol{Y} \setminus V$:

$$\boldsymbol{\mu} \cdot d\boldsymbol{N} = \boldsymbol{\mu} \cdot d\tilde{\boldsymbol{N}}. \tag{19.12}$$

Such a formula never appears in the ordinary thermodynamics textbooks, but the essence is, as we have already seen from a simple example in **4.9**, that there are many ways to express the changes in materials coordinates of the system. If the actual chemical composition changes by $d\tilde{\boldsymbol{N}}$ due to adding chemicals $d\boldsymbol{N}$, we can realize the same state by adding $d\tilde{\boldsymbol{N}}$ as well. Therefore, these two operations realizing the identical equilibrium state must vary the Gibbs energy identically. This is the meaning of (19.12).

Therefore, in particular, if chemical reactions occur in the closed system under constant T, P and $\boldsymbol{Y} \setminus V$, we must have

$$0 = \boldsymbol{\mu} \cdot d\tilde{\boldsymbol{N}}. \tag{19.13}$$

As is pointed out in the textbook by Kirkwood and Oppenheim, if a system is closed, chemical potentials never show up in its Gibbs' relation. (19.13) is, as we will see later (→**19.9**), the equilibrium condition for chemical reactions, but we will discuss only the situations without chemical reactions in this section.[386]

19.6 'Chemical work' minimization principle

In many chemical experiments, systems have no work exchange except for the volume work. Since

$$dG = -SdT + VdP + \sum_i \mu_i dN_i, \tag{19.14}$$

$dG = dZ$ (→**17.1**) under constant temperature and pressure conditions; materials exchanges only change the Gibbs energy. Under reversible and quasistatic conditions, we have

$$\Delta G = Z. \tag{19.15}$$

Then, what happens if the process is not reversible? Since $G = A + PV$, if W consists only of volume work, then

$$\Delta G = \Delta A - W = \Delta A + P\Delta V, \tag{19.16}$$

However, the (extended) minimum work principle (18.8) implies

$$\Delta G \le Z. \tag{19.17}$$

This inequality may be called the *minimum chemical work principle.*

In electrochemistry this principle gives the minimum electric energy required to charge an electric cell. Also, exactly the same logic used in deriving the maximum work principle (18.7) implies

$$|\Delta G| \ge |Z|. \tag{19.18}$$

That is, the electric energy taken out from a cell is maximum if the process is reversible. Thus, this should be called the *maximum chemical work principle.*

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[386] Chemical reactions are discussed in Chapter 25.

19.7 Principle of Gibbs energy minimization

If a closed system does not exchange any work except for the volume work with its environment, (19.17) that holds under constant T and P reduces to

$$\Delta G \leq 0. \tag{19.19}$$

What follows is quite parallel to the case of the Helmholtz energy **18.4**.

Under constant T and P if there is no net contribution to the change of operational coordinates (except or the volume work), but still the system changes, then its Gibbs energy should decrease. D in (19.19) denotes the change from the initial equilibrium state due to some external operation that does not require any net generalized work except for the volume work. Combining two systems in equilibrium to produce a single system with some operation without net work is an example. The change is an actual change due to some operation in contradistinction to the variation due to thermodynamic variation that redistribute extensive quantities to the pieces according to the system partition. (19.19) is called the *principle of decrease of Gibbs energy.*

From this we see that if a state under constant T and P is with the smallest Gibbs energy allowed, the state is an equilibrium state. This is called the *principle of minimum Gibbs energy.*

19.8 Principle of Gibbs energy minimization and thermodynamic variation

Let $\boldsymbol{Y}'$ be the totality of the operational coordinates $\boldsymbol{Y}$ except for V. The change δJ of a function $J(T, P, \boldsymbol{Y}')$ under constant T and P due to a thermodynamic variation is computed as:

$$\delta J(T, P, \boldsymbol{Y}') = \sum_{i \in \mathcal{P}} J(T, P, \boldsymbol{Y}'_i) - J(T, P, \boldsymbol{Y}'). \tag{19.20}$$

Here, the partition $\mathcal{P} = \{i\}$ is a partition of the original system into pieces i with distribution of extensive quantities satisfying $\boldsymbol{Y}' = \sum_{i \in \mathcal{P}} \boldsymbol{Y}'_i$.

The system is assumed to be a simple system or a compound system with the internal constraining conditions (walls) satisfying isobaric and isothermal conditions.

If a thermodynamic variation is imposed on its equilibrium state, as long as the internal constraints are respected, the convexity of G (→**19.1**) always implies

$$\delta G \geq 0. \tag{19.21}$$

This is a universal property of equilibrium states under constant T and P.

For a compound system, if the thermodynamic varation does not respect its internal constraints, the variation can remove the constraints, so the sign of δG is indefinite. Thus,

$$\delta G \leq 0 \tag{19.22}$$

is possible, and we conclude that the original equilibrium state was not really stable.

From this point of view, it is understandable that (19.21) is called the stability condition (cf. (19.19)).

19.9 Chemical equilibrium condition

Consider a chemical reaction in a closed system under constant T and P. Since we are doing thermodynamics, both the initial and the final states must be in equilibrium. For a simple system as seen in (19.21) any thermodynamic varition cannot decrease the Gibbs energy, so

$$\boldsymbol{\mu} \cdot d\boldsymbol{N} = \boldsymbol{\mu} \cdot d\tilde{\boldsymbol{N}} = 0 \tag{19.23}$$

is the equilibrium condition.

For the initial and the final states to be different, since both must be in equilibrium and distinct, at least the initial state must be a compound system with an internal constraint (separating walls) preventing chemical reactions.[387] If we relax the constraints and if reactions proceed, then, as seen in **19.8**, we get (19.22). In this case, if the system reaches a chemical equilibrium, the system Gibbs energy must be minimum. Therefore, for any variation of chemical composition variables, we have

$$\boldsymbol{\mu} \cdot \delta\tilde{\boldsymbol{N}} \geq 0, \tag{19.24}$$

and the equilibrium composition is given by the equality in (19.24).[388]

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[387] Usually textbooks use ‘negative catalysts’ in a simple system, but clearly recognize that the concept ‘negtaive catalyst’ is an oxymoron. See the remark in **25.10**.

[388] This is a standard result taught in chemical thermodynamics. However, it should be noted that in standard chemical thermodynamics, when there is a chemical reaction, even entropy cannot be considered, and of course, it is not possible to define things like Gibbs energy. Thus, this “standard

19.10 Phase equilibrium under constant temperature and pressure

When two distinct phases[389] of a pure substance coexist (as ice floating in liquid water), we can interpret the two phases A and B in contact through an interface as two systems A and B in contact through a wall that allows free exchange of matter, heat and volume. The condition that these two systems are in equilibrium under constant T and P is the principle of Gibbs energy minimization (→**19.7**). The Gibbs energy of the total system is the sum of the Gibbs energies of A and B. Thus, if there is only one chemical substance (or without any chemical reaction), the chemical composition variable is identical to the materials coordinate, so the minimization principle gives:

$$G_{\mathrm{A+B}}(T,P,N) = \min_{N'}[G_{\mathrm{A}}(T,P,N-N') + G_{\mathrm{B}}(T,P,N')]. \tag{19.25}$$

Differentiating this with respect to N', we get (see **16.5**)

$$-\mu_{\mathrm{A}} + \mu_{\mathrm{B}} = 0. \tag{19.26}$$

That is, the chemical potentials must be the same between the two phases in equilibrium.

19.11 Clapeyron-Clausius equation

Understanding how the boiling point changes as pressure changes is a practically important question (recall the vacuum distillation). To this end, we need to know how the chemical potential changes as a function of pressure. If the system has the volume as the only work coordinate, then (17.11) becomes

$$d\mu = v dP - s dT, \tag{19.27}$$

where v is the molar volume $v = V/N$ and s is the molar entropy $s = S/N$.

Let Δ denote the change due to the transition A→B. Take dT and dP along the white arrow in Fig. 19.1. $\Delta\mu = 0$ becomes

$$\Delta v\, dP = \Delta s\, dT, \tag{19.28}$$

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result" is not a derived result. In the mechanical worldview (→**A.17**) advocated by Helmholtz, chemical reactions are merely mechanical changes, so, by blindly accepting the view, the results can be derived without issue.

[389] For a precise definition of 'phase,' see **23.2**.

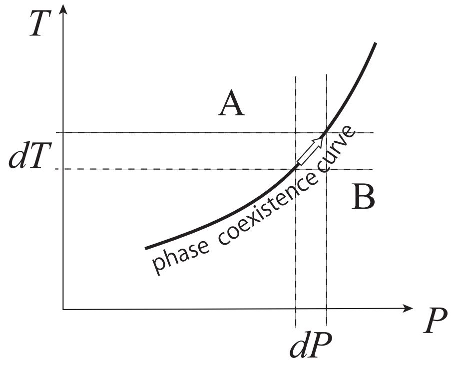

Figure 19.1: How does the coexistence temperature change, when the pressure is changed along the coexistence curve? We wish to know the slope of the white arrow.

where $\Delta v = v_{\rm B} - v_{\rm A}$ and $\Delta s = s_{\rm B} - s_{\rm A}$. dT/dP is the slope of the white arrow:

$$\left.\frac{dP}{dT}\right|_{\rm coexistence} = \frac{s_{\rm B} - s_{\rm A}}{v_{\rm B} - v_{\rm A}}. \tag{19.29}$$

This is called the *Clapeyron-Clausius equation.*[390] If we write the latent heat of A→B as L, the relation between the latent heat and Δs is given by (17.35), so (19.29) becomes

$$\left.\frac{dP}{dT}\right|_{\rm coexistence} = \frac{L}{T\Delta v}. \tag{19.30}$$

Vapor pressure is the pressure exerted by a vapor in equilibrium with its condensed phases (solid or liquid) at a given temperature T in a closed system. Thus, if phase B is a condensed phase (liquid or solid), and if A is a gas phase in the above, P is the vapor pressure of this substance at temperature T.

19.12 Ideal dilute mixture

In **17.14**, we considered an ideal liquid mixture of any proportion based on two empirical laws, Dalton's law of partial pressures and Raoult's law. Dalton's law may be more reliable than Raoult's law, which is not so reliable for real liquids of comparable component ratios. However, if the mole fraction x is sufficiently close to 0 or 1, Raoult's law is fairly accurate. Therefore, the chemical potential formulas for the ideal liquid mixtures (17.28) and (17.29) are fairly reliable for small x. If this is the case, the mixture is called an *ideal dilute mixture.*

If a gas dissolves with only a small amount in a certain liquid, the mole fraction

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[390] For Clapeyron, see **A.5**.

x of the gas in the liquid is proportional to the gas pressure, known as *Henry's law.* This law is closely related to Raoult's law if we accept Dalton's law, but much more reliable than Raoult's law.

19.13 Melting point depression

Suppose material A is desolved in liquid B with a small mole fraction x. The chemical potential of B at temperature T (P is not varied, so it is not written) reads (see (17.29)) as in ideal dilute mixture (→**19.12**)

$$\mu_L(T) = \mu_L^{\ominus}(T) + RT\log(1-x). \tag{19.31}$$

Here, $\mu_L^{\ominus}(T)$ is the chemical potential of pure liquid B.[391] If the mixture is cooled sufficiently, crystals (i.e., the solid phase) of almost pure B will separate out. If we write the chemical potential of pure solid B as $\mu_S^{\ominus}(T)$, then, at the melting point T_m of pure B, as we have already seen in **19.10**,

$$\mu_L^{\ominus}(T_m) = \mu_S^{\ominus}(T_m). \tag{19.32}$$

If an impurity mixes with a melt, its freezing point goes down: $T_m \to T_m - \Delta T$. In this situation the pure crystal is in equilibrium with the impurity-containing liquid B whose chemical potential is (19.31). Thus, the equilibrium condition is

$$\mu_S^{\ominus}(T_m - \Delta T) = \mu_L^{\ominus}(T_m - \Delta T) + R(T_m - \Delta T)\log(1-x). \tag{19.33}$$

Assume x is small. Taylor expanding this formula in x (note that $\Delta T = O[x]$), we obtain

$$\frac{\partial}{\partial T_m}[\mu_S^{\ominus}(T_m) - \mu_L^{\ominus}(T_m)]\Delta T = RT_m x. \tag{19.34}$$

The partial derivative of μ is computed according to (17.11), so we get

$$[s_L(T_m) - s_S(T_m)]\Delta T = \frac{L}{T_m}\Delta T = RT_m x, \tag{19.35}$$

where L is the melting heat (→**17.17**). From this the extent of the *melting point depression* is given by

$$\Delta T = \frac{RT_m^2}{L}x. \tag{19.36}$$

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[391] Throughout this section $\ominus$ implies quantities for pure substances.

Even if we dissolve x mol of a solute, its ‘molecule’ might separate into several pieces to increase the effective molarity of the solute. This results in the melting point depression larger than the expected value (19.36). This observation is historically important, because it gave an evidence for ionization of electrolytes (→**26.2**).

19.14 Boiling point elevation

If material A that hardly vaporizes is dissolved in a liquid, its boiling point T_b increases by ΔT. At this elevated boiling point the pure vapor of the liquid and the liquid containing A by x mole fraction are in equilibrium. Therefore, the formula corresponding to (19.33) reads

$$\mu_G^{\ominus}(T_b + \Delta T) = \mu_L^{\ominus}(T_b + \Delta T) + R(T_b + \Delta T)\log(1 - x). \tag{19.37}$$

Using a similar logic leading to (19.36), we obtain the *boiling point elevation*

$$\Delta T = \frac{RT_b^2}{L}x, \tag{19.38}$$

where L is the evaporation heat of the pure liquid.

The reason why the boiling point increases due to the impurity from T_b is that its vapor pressure at T_b is not P but is reduced by ΔP. To estimate this amount we have only to write down the agreement of the chemical potentials at T_b under pressure $P - \Delta P$:

$$\mu_G^{\ominus}(T_b, P - \Delta P) = \mu_L^{\ominus}(T_b, P - \Delta P) + RT_b\log(1 - x). \tag{19.39}$$

We need the pressure dependence of the chemical potential that may be obtained from (19.27). Taylor-expanding the equality around P, we get

$$-v_G\Delta P = -v_L\Delta P - RT_bx. \tag{19.40}$$

In the present case the molar volume v_G of the gas is overwhelmingly larger than that of the liquid v_L, so we may ignore v_L. Furthermore, the gas can be approximated as an ideal gas, so we may use $v_G = RT/P$. Thus, we get

$$\Delta P = Px. \tag{19.41}$$

19.15 Osmotic pressure: van't Hoff's law

Suppose there is a pure solvent and a solution consisting of the solvent and a solute in contact through a selective membrane that only allows the solvent to go through. Since the chemical potential of the solvent is smaller in the solution than in the pure solvent as seen in (19.31), the solvent pushes into the solution. To prevent this influx, we must apply pressure on the solution side. The minimum pressure π required to prevent this influx is called the *osmotic pressure* (Fig. 19.2).

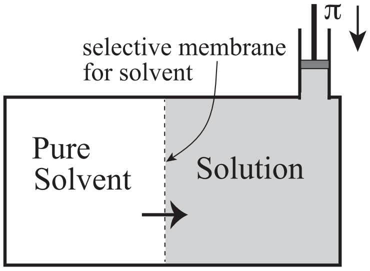

Figure 19.2: The horizontal arrow indicates the tendency for solvent to invade.

If the pressure of the solvent is P, the solution must be maintained at pressure $P+\pi$ to prevent any flow. The equilibrium condition for the solvent reads

$$\mu^{\ominus}{}_{\rm solv}(P+\pi,T)+RT\log(1-x)=\mu^{\ominus}{}_{\rm solv}(P,T). \tag{19.42}$$

By the Taylor expansion just as (19.33), we get *van't Hoff's law*:

$$-v\pi=-RTx \;\Rightarrow\; \pi=nRT, \tag{19.43}$$

where n is the molarity of the solute: since x is a molar fraction, and $x \ll 1$, x is almost identical to the solute moles per one mole of the solvent, whose volume is v, so the molarity n of the solute is given by $n=x/v$.

19.16 The colligative properties

Raoult's law (→**17.13**), Henry's law (→**19.12**), melting point depression (→**19.13**), boiling point elevation (→**19.14**) and van't Hoff's law (→**19.15**) are all independent of the peculiarities of individual substances and all due to the terms $\log x$ or $\log(1-x)$ in the chemical potential (that is, due to the mole fraction), so they can be understood in a unified fashion (or all at once as a bunch). Therefore, they are called the *colligative properties*.[392]

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[392] colligative ⇐ co + ligate = tying up together.

20 Making full use of Jacobians

20.1 Strong differentiability of internal energy: a review

Internal energy is a strongly differentiable convex function of entropy S, work coordinates $\boldsymbol{X}$ and materials coordinates $\boldsymbol{N}$. Therefore,

$$dE = TdS + \sum x_i dX_i + \sum \mu_i dN_i \tag{20.1}$$

is an exact form. From the convexity of E, the intensive conjugate variables, T, x_i and μ_i are (Lipshitz) continuous functions of thermodynamic coordinates (→**13.4** (1)). However, the thermodynamic principles cannot show greater smoothness of conjugate intensive variables, such as the differentiability of T, from its principles.

Empirically, as long as there is no phase transition, fairly high-order partial differentiability seems to hold. Therefore, let us assume that the internal energy is a C^2 function of the thermodynamic coordinates in this section.[393]

Those who feel uneasy about the notation of partial derivatives in thermodynamics should read **9.2**.

20.2 Legendre-Fenchel transformation and changing independent variables

The independent variables of complete thermodynamic functions obtained from E by Legendre-Fenchel transformation (→**18.7**) are not necessarily extensive quantities. Therefore, if the dimension of the thermodynamic space of a system is $\mathcal{D}$, we encounter situations requiring a set of $\mathcal{D}$ thermodynamic variables to be replaced by another set of $\mathcal{D}$ thermodynamic variables. For example, the independent variables of the Gibbs energy are $T, P, \boldsymbol{X} \setminus V$ and $\boldsymbol{N}$, so it is required to express this set of variables in terms of $S, \boldsymbol{X}, \boldsymbol{N}$ to use the fundamental equation (→**11.13**). We have already differentiated chemical potentials with respect to T, for example.

Thus, to determine the outcome of twice differentiability of internal energy, it is

---

[393] Equilibrium statistical mechanics can demonstrate that E is C^ω if there is no phase transitions (rather, phase transitions are defined as the states where the C^ω-nature of free energy is lost). Remember that this is only a model result; not empirical at all. However, we should clearly recognize that the statistical mechanics framework is a consequence of thermodynamics, if we accept the typicality argument of the microstates. Thus, statistical mechanics is so good a model of thermodynamics that one may wish to regard it more basic than thermodynamics under the prejudice that smaller scales are closer to the fundamental.

convenient to be able to compute freely the results of the derivatives of any thermodynamic variable with respect to another thermodynamic variable.

20.3 Chain rule

Let us differentiate an n variable function $f(\boldsymbol{X})$ of variables $X_1, \cdots, X_n$ (collectively denoted as $\boldsymbol{X}$) with another set of n variables $x_1, \cdots, x_n$ (collectively denoted as $\boldsymbol{x}$).
Remark From this unit to unit **20.6** $\boldsymbol{X}$ and $\boldsymbol{x}$ are not work coordinates and their conjugates but general variables. Uppercase (resp., Lowercase) letters need not mean extensive (resp. intensive) variables.

Here, we assume that the transformation $\boldsymbol{X} \to \boldsymbol{x}$ is diffeomorphic.[394] The following formal calculations are reliable as long as the smooth map $\boldsymbol{X} \to \boldsymbol{x}$ is bijective.

Let us assume that f be a function of $\boldsymbol{x}$, and apply the chain rule:

$$\left(\frac{\partial f}{\partial x_i}\right)_{x_i^c} = \sum_{j=1}^{n} \left(\frac{\partial X_j}{\partial x_i}\right)_{x_i^c} \left(\frac{\partial f}{\partial X_j}\right)_{X_j^c}. \tag{20.2}$$

Here, the superscript c means that from the relevant set of variables we remove the one with this mark. If we define a column vector

$$\frac{\partial}{\partial \boldsymbol{X}} = \left(\left(\frac{\partial}{\partial X_1}\right)_{X_1^c}, \cdots, \left(\frac{\partial}{\partial X_n}\right)_{X_n^c}\right)^t, \tag{20.3}$$

etc., where superscript t implies the transposition, (20.2) can be succinctly expressed as

$$\frac{\partial f}{\partial \boldsymbol{x}} = \left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right] \frac{\partial f}{\partial \boldsymbol{X}}. \tag{20.4}$$

Here, the following $n \times n$ matrix is used:

$$\left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right] = \operatorname{matr}\left(\left(\frac{\partial X_j}{\partial x_i}\right)_{x_i^c}\right) \tag{20.5}$$

---

[394] One to one and differentiable in both directions; More intuitively, a map that is 'smooth' and that maps any sufficiently small cube around each point $\boldsymbol{X}$ to another nondegenerate n-dimensional shape around its image $\boldsymbol{x}$; the map linearized at any point becomes a regular, i.e., invertible, linear map.

$$= \begin{pmatrix} \left(\frac{\partial X_1}{\partial x_1}\right)_{x_1^c} & \left(\frac{\partial X_2}{\partial x_1}\right)_{x_1^c} & \left(\frac{\partial X_3}{\partial x_1}\right)_{x_1^c} & \cdots & \left(\frac{\partial X_n}{\partial x_1}\right)_{x_1^c} \\ \left(\frac{\partial X_1}{\partial x_2}\right)_{x_2^c} & \left(\frac{\partial X_2}{\partial x_2}\right)_{x_2^c} & \ddots & \cdots & \left(\frac{\partial X_n}{\partial x_2}\right)_{x_2^c} \\ \left(\frac{\partial X_1}{\partial x_3}\right)_{x_3^c} & \ddots & \ddots & \ddots & \left(\frac{\partial X_n}{\partial x_3}\right)_{x_3^c} \\ \vdots & \vdots & \ddots & \ddots & \vdots \\ \left(\frac{\partial X_1}{\partial x_n}\right)_{x_n^c} & \left(\frac{\partial X_2}{\partial x_n}\right)_{x_n^c} & \cdots & \cdots & \left(\frac{\partial X_n}{\partial x_n}\right)_{x_n^c} \end{pmatrix}. \tag{20.6}$$

If we further apply a diffeomorphism from $\boldsymbol{x}$ to n variables $a_1, \cdots, a_n$ (collectively denoted as $\boldsymbol{a}$), we can write

$$\frac{\partial f}{\partial \boldsymbol{a}} = \left[\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{a}}\right]\left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right]\frac{\partial f}{\partial \boldsymbol{X}}, \tag{20.7}$$

and the variable changes may be written in terms of the matrix multiplication:

$$\left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{a}}\right] = \left[\frac{\partial \boldsymbol{x}}{\partial \boldsymbol{a}}\right]\left[\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right]. \tag{20.8}$$

You should explicitly write the two-variable case to confirm the relation.

20.4 Jacobian

The determinant of the matrix introduced in (20.6), which is called the Jacobi matrix, is known as the *Jacobian*. We use the following notation:

$$\frac{\partial(X_1, \cdots, X_n)}{\partial(x_1, \cdots, x_n)} = \frac{\partial(\boldsymbol{X})}{\partial(\boldsymbol{x})} = \det\left(\frac{\partial \boldsymbol{X}}{\partial \boldsymbol{x}}\right) = \det\left(\left(\frac{\partial X_j}{\partial x_i}\right)_{x_i^c}\right). \tag{20.9}$$

In this notation, the variables upstairs represent dependent variables and the variables downstairs represent independent variables.

In particular, if we have only two variables

$$\frac{\partial(X, Y)}{\partial(x, y)} = \begin{vmatrix} \left(\frac{\partial X}{\partial x}\right)_y & \left(\frac{\partial Y}{\partial x}\right)_y \\ \left(\frac{\partial X}{\partial y}\right)_x & \left(\frac{\partial Y}{\partial y}\right)_x \end{vmatrix} = \left(\frac{\partial X}{\partial x}\right)_y \left(\frac{\partial Y}{\partial y}\right)_x - \left(\frac{\partial X}{\partial y}\right)_x \left(\frac{\partial Y}{\partial x}\right)_y. \tag{20.10}$$

20.5 Computational rules due to Jacobians being determinants

To take advantage of the Jacobian formulation of partial derivatives, we only need to memorize a few simple rules (as summarized in **20.12**), some of which are direct consequences of Jacobians defined as determinants.

If we exchange two columns or two rows, a determinant switches its sign. From its definition (20.9), if we change the orders of two dependent or independent variables, the Jacobian switches its sign. In particular, for the two variable case we can explicitly write

$$\frac{\partial(X,Y)}{\partial(x,y)} = -\frac{\partial(Y,X)}{\partial(x,y)} = \frac{\partial(Y,X)}{\partial(y,x)} = -\frac{\partial(X,Y)}{\partial(y,x)}. \tag{20.11}$$

If we multiply a constant b to a column or row of a determinant, the determinant itself is multiplied by b. We only need the case where $b = -1$. In particular, for the two variable case we can explicitly write

$$\frac{\partial(-X,Y)}{\partial(x,y)} = \frac{\partial(X,-Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(-x,y)} = \frac{\partial(X,Y)}{\partial(x,-y)} = -\frac{\partial(X,Y)}{\partial(x,y)}. \tag{20.12}$$

20.6 The chain rule in terms of Jacobians

The determinant of (20.8) reads

$$\frac{\partial(X_1,\cdots,X_n)}{\partial(a_1,\cdots,a_n)} = \frac{\partial(x_1,\cdots,x_n)}{\partial(a_1,\cdots,a_n)}\frac{\partial(X_1,\cdots,X_n)}{\partial(x_1,\cdots,x_n)}. \tag{20.13}$$

Determinants are just numbers, so we can exchange the order of multiplication to write

$$\frac{\partial(X_1,\cdots,X_n)}{\partial(a_1,\cdots,a_n)} = \frac{\partial(X_1,\cdots,X_n)}{\partial(x_1,\cdots,x_n)}\frac{\partial(x_1,\cdots,x_n)}{\partial(a_1,\cdots,a_n)}. \tag{20.14}$$

Notice that this implies an algebraic rule: if we have the same factors in the numerator and the denominator, we can cancel them. In the calculation utilizing Jacobians, differential calculus turns into algebra. In thermodynamics such a formal calculation invariably gives correct results.

In the two-variable case, this formal calculation rule may be illustrated as follows. First, separate the two factors in the upstairs and downstairs (the numerator and the denominator), and then throw in identical factors in the open slots:

$$\frac{\partial(X,Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{\qquad}\frac{\qquad}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)}. \tag{20.15}$$

Here, A and B may be anything that can be used as a set of independent variables. That is, (A,B) are at least locally diffeomorphic to (X,Y) and to (x,y).

20.7 Partial derivatives in terms of Jacobians

In the Jacobian expression, the variables downstairs are independent variables for a function F of $\boldsymbol{x}$

$$\frac{\partial(F, x_2 \cdots, x_n)}{\partial(x_1, x_2, \cdots, x_n)} = \det \begin{pmatrix} \left(\frac{\partial F}{\partial x_1}\right)_{x_1^c} & 0 & 0 & 0 & \cdots & 0 & 0 \\ \left(\frac{\partial F}{\partial x_2}\right)_{x_2^c} & 1 & 0 & 0 & \cdots & 0 & 0 \\ \left(\frac{\partial F}{\partial x_3}\right)_{x_3^c} & 0 & 1 & 0 & \cdots & 0 & 0 \\ \vdots & \vdots & 0 & 1 & \ddots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ \vdots & \vdots & \vdots & \ddots & \ddots & \ddots & \vdots \\ \left(\frac{\partial F}{\partial x_n}\right)_{x_n^c} & 0 & 0 & \cdots & \cdots & 0 & 1 \end{pmatrix} = \left(\frac{\partial F}{\partial x_1}\right)_{x_1^c}. \tag{20.16}$$

In particular, for the two-variable case

$$\frac{\partial(F, y)}{\partial(x, y)} = \det \begin{pmatrix} \left(\frac{\partial F}{\partial x}\right)_y & 0 \\ \left(\frac{\partial F}{\partial y}\right)_x & 1 \end{pmatrix} = \left(\frac{\partial F}{\partial x}\right)_y. \tag{20.17}$$

Even for cases with many variables, if we wish to consider only two variables among them, we may manipulate the formulas as if there are no other variables, as can be guessed from the structure of the matrix in (20.16).

20.8 Basic relations obtained from the chain rule

Let X and Y be thermodynamic variables. Then, trivially,

$$\frac{\partial(X, Y)}{\partial(X, Y)} = 1. \tag{20.18}$$

If we apply (20.15) to this formula, we obtain

$$1 = \frac{\partial(X, Y)}{\partial(X, Y)} = \frac{\partial(X, Y)}{\partial(A, B)} \frac{\partial(A, B)}{\partial(X, Y)}. \tag{20.19}$$

That is,

$$\frac{\partial(X, Y)}{\partial(A, B)} = 1 \bigg/ \frac{\partial(A, B)}{\partial(X, Y)}. \tag{20.20}$$

Combining this formula and the partial derivatives expressed in terms of Jacobians (→**20.7**), for example, we obtain

$$\frac{\partial(X,Y)}{\partial(x,Y)} = 1\Bigg/\frac{\partial(x,Y)}{\partial(X,Y)} \;\Rightarrow\; \left(\frac{\partial X}{\partial x}\right)_Y = 1\Bigg/\left(\frac{\partial x}{\partial X}\right)_Y. \tag{20.21}$$

Although this relation may appear trivial from an algebraic point of view, analytically, it is not so trivial. On the left-hand side, both X and Y are regarded as functions of x and $Y(x,y)$, and the derivative is with respect to x with $Y(x,y)$ being fixed. On the right-hand side both x and y are regarded as functions of X and Y and the derivative is with respect to X with Y being fixed. An example of this is (for specific heats such as C_V →**14.6**)

$$\left(\frac{\partial T}{\partial S}\right)_V = 1\Bigg/\left(\frac{\partial S}{\partial T}\right)_V = \frac{T}{C_V}. \tag{20.22}$$

Since algebraic calculations are allowed, we can perform, for example,

$$\frac{\partial(x,X)}{\partial(y,X)} = \frac{\partial(x,X)}{\quad}\Bigg/\frac{\partial(y,X)}{\quad} = \frac{\partial(x,X)}{\partial(y,x)}\Bigg/\frac{\partial(y,X)}{\partial(y,x)} = -\frac{\partial(X,x)}{\partial(y,x)}\Bigg/\frac{\partial(X,y)}{\partial(x,y)}. \tag{20.23}$$

In terms of partial derivatives, this reads

$$\left(\frac{\partial x}{\partial y}\right)_X = -\left(\frac{\partial X}{\partial y}\right)_x\Bigg/\left(\frac{\partial X}{\partial x}\right)_y. \tag{20.24}$$

If we set $x = P$, $y = T$, $X = V$, we obtain

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P\Bigg/\left(\frac{\partial V}{\partial P}\right)_T = \frac{\alpha}{\kappa}, \tag{20.25}$$

where α is the isobaric thermal expansion coefficient and κ is the isothermal compressibility:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P, \quad \kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T. \tag{20.26}$$

20.9 Maxwell's relations

9.6 states that if all the twice partial derivatives of E exist and continuous, their results do not depend on the order of differentiation. That is, if we use Y_i to represent, entropy, work coordinates or materials coordinates[395]

$$\frac{\partial^2 E}{\partial Y_i \partial Y_j} = \frac{\partial^2 E}{\partial Y_j \partial Y_i}. \tag{20.27}$$

That is,

$$\left(\frac{\partial y_i}{\partial Y_j}\right)_{Y_j^c} = \left(\frac{\partial y_j}{\partial Y_i}\right)_{Y_i^c}. \tag{20.28}$$

This relation is called *Maxwell's relations* in thermodynamics. For example, for a gas with only volume as its work coordinate

$$dE = TdS - PdV \tag{20.29}$$

yields the following Maxwell's relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \tag{20.30}$$

Physically, this is remarkable; it quantitatively relates the temperature change due to a volume change under adiabatic conditions to the pressure change when entropy is changed (i.e., heat is added) under constant volume. It should be hard to understand the relation intuitively.[396]

20.10 Unified Maxwell's relation in terms of Jacobians

Maxwell's relations hold not only for internal energy, but for any sufficiently smooth twice differentiable quantities. Therefore, for example, for complete thermodynamic functions there are many Maxwell's relations. However, the only formula that needs to be memorized is the following:

$$\frac{\partial(X,x)}{\partial(y,Y)} = 1. \tag{20.31}$$

Here, uppercase letters denote extensive quantities, and lowercase letters denote intensive quantities, and the alphabetical correspondence implies the conjugate relation: the pair (X, x) denotes, for example, pairs (S, T), $(V, -P)$, (N, μ), etc.

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[395] If we choose the conventional chemical coordinates (= chemical composition variables), then this is true only without any chemical reaction.

[396] Or, even by statistical mechanics alone.

This formula has been demonstrated in **9.17**.[397] An algebraic formal 'derivation' is in **20.11**.

20.11 Unification of Maxwell's relations: algebraic 'explanation'

Let us rewrite (20.28) as

$$\left(\frac{\partial x}{\partial Y}\right)_{X,\cdots} = \left(\frac{\partial y}{\partial X}\right)_{Y,\cdots}, \tag{20.32}$$

denoting with $\cdots$ the other extensive variables than X and Y. The essence of this equation is

$$\frac{\partial(x,X)}{\partial(Y,X)} = \frac{\partial(y,Y)}{\partial(X,Y)}. \tag{20.33}$$

Therefore,

$$\frac{\partial(x,X)}{\partial(y,Y)} = \frac{\partial(Y,X)}{\partial(X,Y)} = -1. \tag{20.34}$$

By combining this with (20.11), we immediately obtain (20.31). Needless to say, this is not a proof, but rather a mnemonic.

20.12 Summary of Jacobian technique

The definition of the Jacobian is provided in **20.4**, esp., (20.9). Thus, the partial derivative can be written as (→**20.7**)

$$\left(\frac{\partial A}{\partial B}\right)_{\cdots} = \frac{\partial(A,\cdots)}{\partial(B,\cdots)}. \tag{20.35}$$

All the calculations required when we use Jacobians are algebraic and are based only on the following three rules:

(i) The rule for signs (→**20.5**): horizontal exchange of letters[398] or changing the sign of a letter switches the sign:

$$\frac{\partial(X,Y)}{\partial(x,y)} = -\frac{\partial(Y,X)}{\partial(x,y)} = \frac{\partial(Y,X)}{\partial(y,x)} = -\frac{\partial(X,Y)}{\partial(y,x)}, \tag{20.36}$$

---

[397] To derive the formula considering its physical meaning is with poor taste, but thus derived

$$\frac{\partial(P,V)}{\partial(T,S)} = 1$$

is known for a long time. Mike Stone informed me of this fact. However, the existing derivation is in poor taste and does not capture the essence of the formula (it is found in Am. J. Phys., but not cited here for the sake of the reputation of those involved). As seen in **9.17**, physics is irrelevant.

[398] which may be called 'transposition.'

$$\text{for example, } \frac{\partial(-X,Y)}{\partial(x,y)} = -\frac{\partial(X,Y)}{\partial(x,y)}. \tag{20.37}$$

(ii) Chain rule (→**20.6**): The same factors $\partial(\cdots)$ may be inserted/removed:

$$\frac{\partial(X,Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{}\frac{}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)}. \tag{20.38}$$

(iii) Maxwell's relation (→**20.10**): for arbitrary conjugate pairs (X,x) and (Y,y)

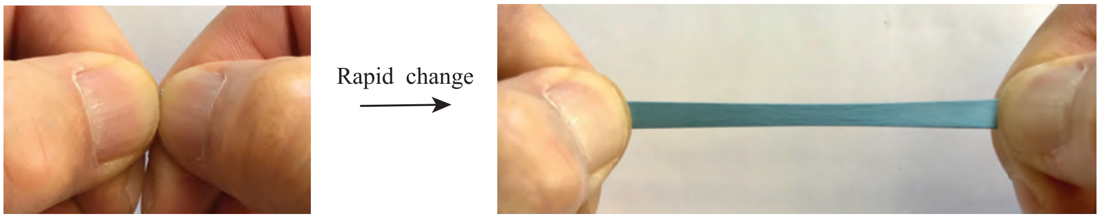
$$\frac{\partial(X,x)}{\partial(y,Y)} = 1. \tag{20.39}$$

Practice the usage of Jacobians through the examples in the next section.

21 Entropic elasticity

21.1 Experiments with a rubber band[399]

Prepare a wide rubber band (for bundling broccoli and asparagus). As a temperature sensor use your lips. First, lightly touch the rubber band with your lips to confirm that it is at room temperature; it should feel somewhat cool. Next, as illustrated in the photo 21.1 Left, hold both ends of a very small portion of the band tightly between your thumbs and fingers, and quickly and strongly stretch it (Fig. 21.1 Right).



Hold firmly

Stretch at once

Figure 21.1: If we stretch a small portion of a wide rubber band quickly and strongly, we can approximately realize an adiabatic reversible quasistatic stretching of a rubber band.

Immediately after stretching, put the stretched portion to your lip. It should feel warm. Keep stretching the rubber band strongly for a while to allow it to equilibrate roughly with the room temperature, and then suddenly stop stretching. The shrunk portion of the rubber band should now feel cool, which you can confirm by touching it with your lips.

Although we use the term "quickly" to describe the stretching process, the actual stretching speed is relatively slow compared to the relaxation rate of the rubber polymers, resulting in a reversible quasistatic process. Furthermore, the heat flow from the ambient air and our hands during the stretching process is limited, allowing for an adequate adiabatic condition. In other words, we have approximately realized an adiabatic reversible and quasistatic stretching of the rubber band.

21.2 Summary of empirical observations about rubber bands

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[399] Feynman starts his thermodynamics lecture with rubber in Lecture 44 of *The Feynman Lectures on Physics* Vol. I. We can find a rubber band engine illustrated in Fig. 44-2. Also a rubber band fridge may be made: `https://www.youtube.com/watch?v=1fmrvxB154w&t=51s`.

From the experiment in **21.1** and related ones, we can observe the following:
(1) An adiabatic and reversible quasistatic stretching increases the temperature of the stretched portion.
(2) Adiabatic and reversible quasistatic shrinking decreases the temperature of the shrunk portion. This is just the reversal of (1), and is not surprising, but still a notable fact.
(3) If we suspend a weight with a rubber band and warm it, the weight is raised.
(4) To prevent the warming of the rubber band from raising the weight, we must increase the weight.
The effects of (3) and (4) are not large and are not as easily observed as (1) and (2),[400] but see Fig. 21.2.

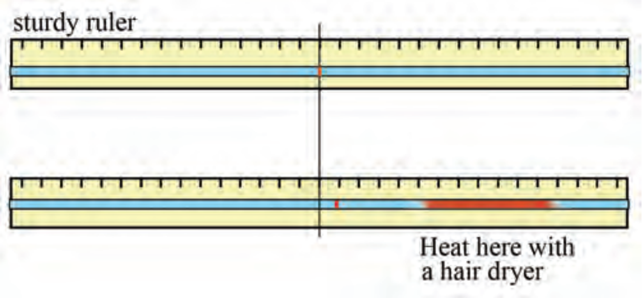

Figure 21.2: An experiment demonstrating (3). When a rubber band strongly stretched along a sturdy ruler is marked, and a part of it is heated, the mark moves slightly towards the heated side.

An obvious fact we must note is that increasing the length L of the rubber band requires a stretching force F and, consequently, we must do some work.

21.3 Thermodynamics of a rubber band

To develop the thermodynamics of any system, we must first set up its thermodynamic space. That is, we must choose its thermodynamic coordinates. To describe the state of a rubber band, we need its internal energy and the length L. When stretched, a rubber band becomes thinner, but it is empirically known that its volume is approximately constant, so, for example, its width is not an independent coordinate.[401] Therefore, we adopt L as its work coordinate. The work required to

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[400] According to Shixian Zhang, Quanling Yang & Qing Wang, Solid-state cooling by elastocaloric polymer with uniform chain-lengths Nature Commun. **13**, 9 (2022), an adiabatic temperature change of -15.3 K and an isothermal entropy change of 145 J $\mathrm{kg}^{-1}\mathrm{K}^{-1}$ are obtained from poly(styrene-b-ethylene-co-butylene-b-styrene) near room temperature.

[401] However, recent findings suggest that the situation is not so simple. It seems that the reason

change L with a stretching force F is expressed as $\omega = FdL$. Thus, the thermodynamic space of the rubber band is spanned by E and L, and the Gibbs relation is given by

$$dE = TdS + FdL. \tag{21.1}$$

The facts (1)-(4) in **21.2** are expressed as:

$$(1,2) \qquad \left(\frac{\partial T}{\partial L}\right)_S > 0. \tag{21.2}$$

$$(3) \qquad \left(\frac{\partial L}{\partial T}\right)_F < 0. \tag{21.3}$$

$$(4) \qquad \left(\frac{\partial F}{\partial T}\right)_L > 0. \tag{21.4}$$

For an adiabatic and reversible quasistatic process the entropy of the system remains constant, so $S =$ const. in (21.2) means the adiabatic condition.

21.4 Mutual relations of empirical facts (1)-(4)

Are the empirical observations (1)-(4) in **21.3** independent? The most straightforward method for examining the relationships among these partial derivatives is to express them in terms of Jacobians (→**20.7**).

$$(1,2) \qquad \left(\frac{\partial T}{\partial L}\right)_S = \frac{\partial(T,S)}{\partial(L,S)} > 0. \tag{21.5}$$

$$(3) \qquad \left(\frac{\partial L}{\partial T}\right)_F = \frac{\partial(L,F)}{\partial(T,F)} < 0. \tag{21.6}$$

$$(4) \qquad \left(\frac{\partial F}{\partial T}\right)_L = \frac{\partial(F,L)}{\partial(T,L)} > 0. \tag{21.7}$$

Very often the presence of S in the formula is a 'practical' nuisance; among T, F, L, S, S is the hardest to measure. To eliminate S we can use a Maxwell's relation (→**20.10**)

$$\frac{\partial(T,S)}{\partial(L,F)} = 1 \tag{21.8}$$

---

the overall volume remains constant is due to the presence of a phase that moves when external forces are applied: Z. Wanga et al., "3D observations provide striking findings in rubber elasticity," Proc. Natl. Acad. Sci., **121**, e2404205121 (2024). Here, let us use the conventional picture that may have averaged out such inhomogeneity.

or specific heats (→**14.6**). Let us first use the chain rule (20.38) and Maxwell's relation:

$$\frac{\partial(T,S)}{\partial(L,S)} = \frac{\partial(T,S)\qquad\quad}{\qquad\quad\partial(L,S)} = \frac{\partial(T,S)}{\partial(L,F)}\frac{\partial(L,F)}{\partial(L,S)} = \frac{\partial(L,F)}{\partial(L,S)}. \tag{21.9}$$

S is still present, but its temperature dependence may be related to the heat capacity and is easy to measure (→**14.6**):

$$\frac{\partial(L,F)}{\partial(L,S)} = \frac{\partial(L,F)\qquad\quad}{\qquad\quad\partial(L,S)} = \frac{\partial(L,F)}{\partial(L,T)}\frac{\partial(L,T)}{\partial(L,S)} = \left(\frac{\partial F}{\partial T}\right)_L \frac{T}{C_L}. \tag{21.10}$$

Here, C_L is the heat capacity of the rubber band under constant length. Thus, we arrive at

$$\left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial F}{\partial T}\right)_L \frac{T}{C_L}. \tag{21.11}$$

Since $C_L > 0$, and the positivity of the left-hand side was easy to observe (empirical fact (1) of **21.2**), this equation means (4).

(3) and (4) appear like two sides of a coin. To understand the relation, let us start with a single fact (say, (3)) and split its Jacobian expression as:

$$\left(\frac{\partial L}{\partial T}\right)_F = \frac{\partial(L,F)}{\partial(T,F)} = \frac{\partial(L,F)\qquad\quad}{\qquad\quad\partial(T,F)}, \tag{21.12}$$

and then start thinking. Since (4) has the factor (T,L), let us introduce this: using the rule for the sign **20.12** (i), we get

$$\left(\frac{\partial L}{\partial T}\right)_F = \frac{\partial(L,F)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(T,F)} = -\left(\frac{\partial F}{\partial T}\right)_L \left(\frac{\partial L}{\partial F}\right)_T \tag{21.13}$$

If we increase F, length L should increase, so the second partial derivative should be positive (this is an example of Le Chatelier's principle.→**22.8**). Therefore, (4) implies (3). That is, if we know (1) the rest may be obtained by thermodynamics.

In this unit, that $C_L > 0$ and that $(\partial F/\partial L)_T > 0$ are taken for granted; if these signs were opposite, horrible things would happen. For example, if the heat capacity were negative, the injecting heat into such a system would reduce its temperature, making it easier to absorb more heat. This would create something like a heat black hole. These signs are determined by the fundamental constraint resulting from the stability of the world, which we will discuss in the next section.

21.5 How does entropy change?

What happens to the entropy of a rubber band when it is stretched under a constant temperature? Equivalently, what is the sign of the following partial derivative? According to our experimental result

$$\left(\frac{\partial S}{\partial L}\right)_T = \frac{\partial(S,T)}{\partial(L,T)} = \frac{\partial(S,T)}{\partial(F,L)}\frac{\partial(F,L)}{\partial(L,T)} = -\frac{\partial(F,L)}{\partial(T,L)} = -\left(\frac{\partial F}{\partial T}\right)_L < 0. \tag{21.14}$$

That is, as long as the temperature is constant, entropy decreases as the band is stretched.

Entropy is not so easy to reduce adiabatically; the above inequality tells us that a rubber band resists being stretched due to the entropy decrease. Such elasticity is called the *entropic elasticity*; The experimental fact (4) that increasing temperature 'strengthens' the rubber band is its characteristic.[402]

According to **17.16**, entropy is related to the amount of knowledge we need to describe a macro state in a detailed fashion. Following this point of view, (21.14) implies that stretching makes the description of polymers making the rubber band simpler. Its exaggerated illustration is Fig. 21.3. That is, if stretched, the chains are more constrained and the shapes become simpler.

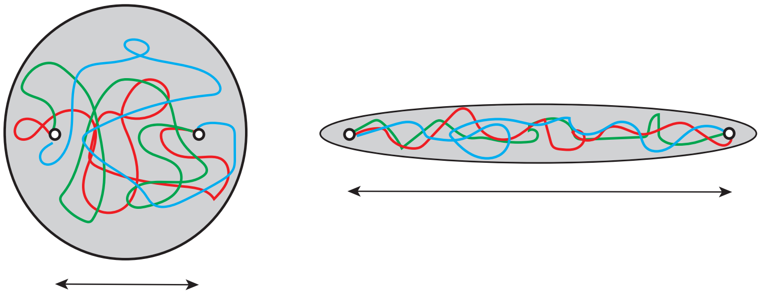

Figure 21.3: If stretched, the range where the chains can wiggle is restricted. Three different conformations are illustrated. The gray zone indicates the rough range where the chains can wiggle.

Then, what happens to the entropy if the rubber band length is kept constant, while increasing the stretching force? If we rely on the intuitive picture Fig. 21.3, the stretching force cannot be increased (or the spring constant cannot be increased)

---

[402] ⟪**Energetic elasticity**⟫ The concept in contrast to entropic elasticity is *energetic elasticity*. This is due to the increase of energy by stretching and we encounter often with ordinary metal springs. Under a constant temperature, its E must increase with L. The ideal rubber band **21.6** is significantly different from this behavior.

unless somehow entropy must be increased. Can we show this? That is,

$$\left(\frac{\partial S}{\partial F}\right)_L > 0 \ ? \tag{21.15}$$

We always follow the same strategy:

$$\left(\frac{\partial S}{\partial F}\right)_L = \frac{\partial(S,L)}{\partial(F,L)} = \frac{\partial(S,L)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(F,L)} = \frac{C_L}{T} \Bigg/ \left(\frac{\partial F}{\partial T}\right)_L > 0 \tag{21.16}$$

The inequality is due to (4) of **21.3**.

21.6 Ideal rubber band

Up to this point no internal energy of the rubber band has been paid any special attention. The actual rubber band becomes brittle if the temperature is too low, and melt if it is too high, indicating internal energy is crucial. However, around room temperature, E does not significantly depend on L. This is just as the ideal gas internal energy does not depend on volume (work coordinate). Therefore, the rubber band whose E does not depend on L is called an *ideal rubber band*. Just as the entropy of the ideal gas (see the fundamental equation of the ideal gas (11.35)) can be written as a sum of the part dependent on E and that dependent on V, the entropy of the ideal rubber band can be written as the sum of the E-dependent part and the L-dependent part:

$$S(E,L) = S_e(E) + S_c(L). \tag{21.17}$$

Here, S_e is the energy depending portion and is independent of the stretching of the rubber band. S_c is the portion dependent on the stretching. The temperature T is determined by the derivative of S_e. If the band is adiabatically stretched, S_c decreases, but since the total entropy is constant, $S_e(E)$ must increase. This is consistent with the work the experimenter has done for stretching.

21.7 The principle of adiabatic cooling

If we allow a strongly stretched rubber band to relax at room temperature (adiabatic relaxation), the rubber band cools down as we have already experienced (**21.1** (2)): since

$$\left(\frac{\partial T}{\partial L}\right)_S > 0, \tag{21.18}$$

if we reduce L under constant S, T must decrease. This is the principle of *adiabatic cooling* (see Fig. 21.4).

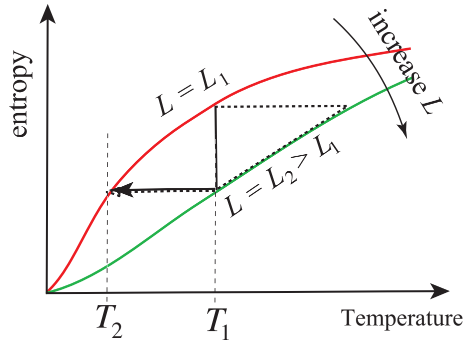

Figure 21.4: Initially, the system temperature is T_1. Under constant temperature, we increase L: $L_1 \to L_2$. This reduces the system entropy. Next, we return L to the original length adiabatically and reversibly. The entropy remains constant, so the system temperature goes down to T_2. The dotted curve denotes the process that occurs when the rubber band is stretched rapidly (i.e., adiabatically).

Unfortunately, we cannot use a rubber band to reduce the system temperature sufficiently, because (21.17) does not hold at low temperatures and the band becomes brittle. In actual low temperature physics experiments, dilute paramagnetic systems are used (→**21.8**).

21.8 Dilute paramagnets or ideal magnets: adiabatic demagnetization

The thermodynamic space of a magnet is spanned by the internal energy and magnetization M. Therefore, its Gibbs relation is given by (→**B.2**)

$$dE = TdS + BdM. \tag{21.19}$$

Here, for an ideal paramagnetic material, just as the ideal gas and idea rubber band, the following fundamental equation holds:

$$S = S_e(E) + S_c(M). \tag{21.20}$$

If an external magnetic field B is imposed, the magnetization aligns to the magnetic field direction. Therefore, there is a very good analogy to the stretching of a rubber band with a stretching force. That is,

$$\left(\frac{\partial T}{\partial B}\right)_S > 0 \tag{21.21}$$

holds. Therefore, if B is adiabatically reduced (*adiabatic demagnetization*), the system temperature goes down. The principle is understandable by replacing L with M in Fig. 21.4.

22 Thermodynamic inequalities due to convexity

Here, we discuss the topic traditionally called the stability of equilibrium states of a system in general.[403] The key point is: the so-called (or the traditionally understood as) the stability criterion is nothing but the convexity of internal energy; there is no equilibrium state that is not stable for any simple systems.

22.1 General remark on thermodynamic stability analysis

Generally speaking, the stability analysis of a state is to apply perturbations to the original state and then study whether the perturbed states can return to the original state. In thermodynamics, the initial state is an equilibrium state, and the perturbation results are also equilibrium states. If they are distinct from the unperturbed state, the perturbation effects never disappear, because any equilibrium state, left alone, will stay in its equilibrium state. Therefore, the meaningful perturbations in thermodynamics are only thermodynamic variations (→**12.10**). It is self-evident that any equilibrium state of a simple system is stable under any thermodynamic variation. Its mathematical core is convex analysis. Thus, we are interested in the consequences of the convexity of internal energy (→**13.9**).

For compound systems the consequences of relaxing internal constraints are the topics of the principle of increasing entropy, and other variational principles (→**12.5**, **13.10**, **18.4**, **19.7**), so we will not repeat the topic.

22.2 Thermodynamic variational inequality for an isolated system[404]

For an isolated system, if it is a simple system, then the convexity of $-S$ implies that for any thermodynamic variation (→**12.10**)

$$\Delta S \leq 0. \tag{22.1}$$

If the system is a compound system, and allowed thermodynamics variations never alters the internal constraints, then we have the same inequality as above. However, if thermodynamic variation does not respect the internal constraints, there may be some variation satisfying

$$\Delta S > 0. \tag{22.2}$$

---

[403] The stability of chemical equilibria specifically will be discussed in Section 24.

[404] This is, basically, a repetition of **12.6**.

This implies that for the compound system under study, a certain relaxing of its internal constraints may spontaneously alter its equillibrium state. Therefore, (22.2) is called the *evolution criterion* for the equilibrium system when internal constraints are relaxed.

Traditionally, (22.1) is called the stability condition of the equilibrium system, but it is nothing but Jensen's inequality for a convex function $-S$. Thus, (22.2) never happens to equilibrium states (if internal constraints are respected).

22.3 Thermodynamic variational inequality for a non-isolated system

To study the effects of thermodynamic variations applied to a non-isolated system, we use the usual trick to regard the system S to be a part of a very large isolated system (Fig. 22.1), whose part other than the system itself is called the *reservoir*.[405] Then, for the total big isolated system, (22.1) tells us

$$\Delta S + \Delta S_{\rm res} \le 0, \tag{22.3}$$

where Δ denotes a thermodynamic variation whose partition respects the system/reservoir distinction. As noted at the end of **22.2** this is due to the convexity of the (negative) total entropy.

In the reservoir the values of the conjugate variables of the thermodynamic coordinates are kept constant and identical to those of the system before thermodynamic variations. The extensive quantities may be exchanged freely between the system and its surrounding bath. Let us assume that the system obtains extensive quantities ΔE, ΔV, $\Delta \boldsymbol{X}$, $\Delta \boldsymbol{N}$, etc., from the reservoir by the variation.[406]

For the reservoir portion, all the intensive quantities are constant, and we obtain

$$\Delta S_{\rm res} = -\frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \sum \frac{x_e}{T_e}\Delta X + \sum \frac{\mu_e}{T_e}\Delta N, \tag{22.4}$$

---

[405] If you argue that assuming such a big system called a reservoir is theoretically dubious, you must prepare increasing sequence of reservoirs to construct your theory. Alternatively, we may utilize special materials that can maintain conjugate variables of the operational coordinates (see, for example, **8.8**).

[406] Here, we have assumed that all the thermodynamic coordinates may be freely exchanged, but we can certainly consider more restricted cases such as only internal energy and volume may be exchanged. To obtain the formulas for such cases, simply suppress coordinates not exchanged between the system and the bath from the following formulas, in particular from (22.5).

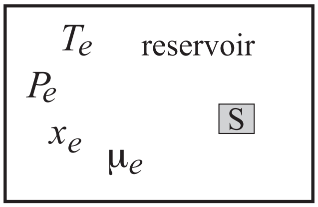

Figure 22.1: The system S is a small part of a very large isolated system. The intensive quantities T_e, P_e, etc., are kept constant. Their conjugate extensive quantities (S, V, etc.) may be assumed to be exchanged freely between the system and its surrounding portion of the total system called the reservoir.

where X and N denote various work coordinates (other than V) and materials coordinates, respectively. We assume chemostats are separately prepared for each chemical.

The entropy of the total system is $\Delta S + \Delta S_{\text{res}}$, so the inequality (22.3) implies

$$\Delta S - \frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \sum \frac{x_e}{T_e}\Delta X + \sum \frac{\mu_e}{T_e}\Delta N \leq 0. \tag{22.5}$$

This is the result of convexity.

Remark In (22.5) ΔN is the exchange between the system and the surrounding reservoir, irrespective of the existence of chemical reactions in the system. If chemical reactions occur in the system, we only need $\Delta\tilde{\boldsymbol{N}} \neq \Delta\boldsymbol{N}$ if we describe the change in terms of chemical composition variables (recall **4.8**). However, since ΔE, ΔX, etc., are not generally zero, there is no guarantee that $\boldsymbol{\mu}_e \cdot \Delta\tilde{\boldsymbol{N}} = \boldsymbol{\mu}_e \cdot \Delta\boldsymbol{N}$ holds.

22.4 Inequality for small thermodynamic variations

If the thermodynamic variation Δ is not large[407] for the reservoir, it may be written in terms of small thermodynamic variation δ as

$$\Delta S_{\text{res}} = -\frac{1}{T_e}\delta E - \frac{P_e}{T_e}\delta V + \frac{x_e}{T_e}\delta X + \sum \frac{\mu_e}{T_e}\delta N. \tag{22.6}$$

The variation of the system entropy ΔS may be (Taylor) expanded in terms of the small thermodynamic variation δ as:[408]

$$\Delta S = \delta S + \delta^2 S + \cdots. \tag{22.7}$$

---

[407] As noted already, if thermodynamic densities for the system do not change appreciably, we may say the perturbation is small.

[408] Notice that, since the reservoir is huge compared with the system itself, the first order approximation for the reservoir is much more accurate than that for the system; for example, the constancy of the first derivatives is much less accurate for the system than for the reservoir, requiring higher order terms.

The first order term may be computed in terms of the derivatives in the original equilibrium state, so we may write

$$\delta S = \frac{1}{T_e}\delta E + \frac{P_e}{T_e}\delta V - \frac{x_e}{T_e}\delta X - \sum \frac{\mu_e}{T_e}\delta N. \tag{22.8}$$

This formula and (22.6) imply that for small thermodynamic perturbations applied to the equilibrium state (22.3) can always be expressed as

$$\delta^2 S \le 0 \tag{22.9}$$

irrespective of the environment of the system.

Note that this may be obtained immediately from the concavity of entropy for small thermodynamic variations.[409] It is universal, but only for small thermodynamic perturbations.

22.5 Inequality for small thermodynamic variations for internal energy

(22.5) may be rewritten as

$$\Delta E - T_e\Delta S + P_e\Delta V - x_e\Delta X - \mu_e\Delta N \ge 0. \tag{22.10}$$

If we Taylor expand ΔE just as we did for ΔS in **22.4**, with the same logic we can obtain a universal local stability criterion

$$\delta^2 E \ge 0 \tag{22.11}$$

which is equivalent to (22.9). Notice that this inequality can also be obtained immediately from the convexity of E (→**13.10**).[410]

22.6 A positive definite quadratic form given by the Hessian of $\boldsymbol{E}$

If we write all the standard variables of E: S, $\boldsymbol{X}$, and $\boldsymbol{N}$ as $\boldsymbol{Y} = \{Y_i\}$, (22.11) can be written as a nonnegative definite quadratic form of δY_i:

$$\delta^2 E = \sum_{i,j} \frac{\partial^2 E}{\partial Y_i \partial Y_j}\delta Y_i \delta Y_j \ge 0. \tag{22.12}$$

---

[409] If there are non-additive work coordinates, such a universal result cannot be asserted.

[410] However, just as the case of the entropy inequality (22.9), if there are non-additive work coordinates, the stability against their variation cannot be obtained this way.

For example,

$$(\delta S, \delta V, \delta N)\begin{pmatrix} \left(\frac{\partial T}{\partial S}\right)_{V,N} & \left(\frac{\partial T}{\partial V}\right)_{S,N} & \left(\frac{\partial T}{\partial N}\right)_{S,V} \\ -\left(\frac{\partial P}{\partial S}\right)_{V,N} & -\left(\frac{\partial P}{\partial V}\right)_{S,N} & -\left(\frac{\partial P}{\partial N}\right)_{S,V} \\ \left(\frac{\partial \mu}{\partial S}\right)_{V,N} & \left(\frac{\partial \mu}{\partial V}\right)_{S,N} & \left(\frac{\partial \mu}{\partial N}\right)_{S,V} \end{pmatrix}\begin{pmatrix} \delta S \\ \delta V \\ \delta N \end{pmatrix} \geq 0. \tag{22.13}$$

22.7 A nonnegative definite condition for the quadratic form

Let $A = \mathrm{matr}(A_{ij})$ be a $n \times n$ symmetric square matrix. A necessary and sufficient condition for the quadratic form

$$\sum A_{ij}x_ix_j \tag{22.14}$$

to be nonnegative definite is that all of its principal minors are nonnegative:

$$\det(A_{kl}) \geq 0, \tag{22.15}$$

where $\mathrm{matr}(A_{kl})$ is with k and l chosen in the same order from a subset $U \subset \{1, 2, \cdots, n\}$.

22.8 Le Chatelier's principle

Since the Hessian of E is nonnegative definite, as seen from **22.7**, all the diagonal elements are nonnegative:

$$\left(\frac{\partial^2 E}{\partial Y_i^2}\right)_{Y_i^c} \geq 0. \tag{22.16}$$

That is, writing the conjugate intensive quantity of Y_i as y_i

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{Y_i^c} \geq 0. \tag{22.17}$$

This is called *Le Chatelier's principle.*

Since the sign of the inverse determinant is also the same, we get

$$\left(\frac{\partial Y_i}{\partial y_i}\right)_{Y_i^c} \geq 0., \tag{22.18}$$

but notice that this is not $(\partial Y_i/\partial y_i)_{y_i^c} \geq 0$. For example, $C_V > 0$ may be obtained from (22.18), but this does not immediately imply $C_P > 0$.[411]

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[411] (22.18) tells us that $(\partial S/\partial T)_V = C_V/T > 0$, but we have not yet discussed the sign of $(\partial S/\partial T)_P$.

22.9 More general Le Chatelier's principle

The heat capacity should be positive irrespective of the conditions. This implies that

$$\left(\frac{\partial S}{\partial T}\right)_{\boldsymbol{Z}} \geq 0, \tag{22.19}$$

where $\boldsymbol{Z}$ is the set of variables chosen one variable from each conjugate pair other than (S,T). We can demonstrate this inequality, starting from the case for all Z being extensive variables inductively[412] (→**22.10**, **22.11**). However, the cleverest way is to go back to $\delta^2 E \geq 0$. This may be expressed (→**9.10**(iii)) as

$$\delta^2 E = \delta T \delta S - \delta P \delta V + \delta x \delta X + \sum \delta\mu\delta N \geq 0, \tag{22.20}$$

so changing independent variables corresponds to choosing δx or δX from each pair $(\delta x, \delta X)$. Then, (22.19) should be obvious.

Imagine what could happen, if the inequality in Le Chatelier's principle were flipped.

22.10 Stability condition under all the conjugate intensity variables are fixed

To begin with we demonstrate the following inequality. Here, the suffixes y_i^c for the partial derivative implies that all the conjugate intensive variables other than y_i are fixed:

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{y_i^c} \geq 0, \quad \left(\frac{\partial Y_i}{\partial y_i}\right)_{y_i^c} \geq 0 \tag{22.21}$$

Indeed (note that in the following Jacobians (y_i, y_i^c) does not mean two variables but general n variable formulas)

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_{y_i^c} = \frac{\partial(y_i, y_i^c)}{\partial(Y_i, y_i^c)} = \frac{\partial(y_i, y_i^c)}{\partial(Y_i, Y_i^c)}\frac{\partial(Y_i, Y_i^c)}{\partial(Y_i, y_i^c)}, \tag{22.22}$$

but the left factor in the rightmost formula is the Hessian matrix of E itself, so it is positive. The right factor must compute partial derivatives regarding $\{Y_i, y_i^c\}$ as independent variables, so $\partial Y_i/\partial y_k = 0$. Consequently, the first column becomes $(1, 0, \cdots)^t$. Thus, this factor is equal to the determinant of $(n-1)\times(n-1)$ which is the principle minor of the original Hessian matrix except for the first raw and column. Thus, it is positive (→**22.6**)

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[412] However, this approach is so cumbersome that, except for calculation practice, you should not follow it.

22.11 Exchange of upper- and down-stairs of general $n \times n$ Hessian

More generally, $(\partial y/\partial Y)_{\mathrm{cond}}$ is nonnegative under any condition ('cond' $= z = \{z_1, \cdots, z_n\}$ (z_i^c implies to remove z_i); Here, $z_j = y_j$ or Y_j) and Z is the conjugate of z. We have

$$\left(\frac{\partial y_i}{\partial Y_i}\right)_z = \frac{\partial(y_i, z_i^c)}{\partial(Y_i, z_i^c)} = \frac{\partial(y_i, z_i^c)}{\partial(Y_i, Z_i^c)} \frac{\partial(Y_i, Z_i^c)}{\partial(Y_i, z_i^c)}. \tag{22.23}$$

The first factor in the right most term is the Hessian of E itself, so it is nonnegative. The second factor requires to calculate the partial derivatives regarding $\{Y_i, z_i^c\}$ as independent variables. Since $\partial Y_i/\partial z_k = 0$, we must demonstrate

$$\frac{\partial(z)}{\partial(Z)} \geq 0 \tag{22.24}$$

for the $(n-1) \times (n-1)$ principal minor constructed by removing the first raw and colum from $\partial(Y_i, Z_i^c)/\partial(Y_i, z_i^c)$. To show this we can step by step exchange the variable in the numerator with the corresponding conjugate in the denominator and show this procedure does not change the sign of the Jakobian.

The first step is as follows ($z = y$ or Y is the starting point). We have

$$\frac{\partial(x, z)}{\partial(X, Z)} = \frac{\partial(x, z)}{\partial(X, z)} \frac{\partial(X, z)}{\partial(x, Z)} \frac{\partial(x, Z)}{\partial(X, Z)} = \left(\frac{\partial x}{\partial X}\right)_z \left(\frac{\partial x}{\partial X}\right)_Z \frac{\partial(X, z)}{\partial(x, Z)}, \tag{22.25}$$

As we have seen in (22.17) and (22.21) the two partial derivatives in the right-most formula is nonnegative, we see the $n \times n$ determinant obtained by exchanging x and X is nonnegative. The resultant $n \times n$ matrix is nonnegative definite, its diagonal elements are nonnegative. Thus, we may repeat the same argument as above for the case with one pair exchanged between numerator and denominator. That is, inequalities similar to (22.17) and (22.21) holds for one pair of conjugate variables exchanged between numerator and denominator. We can repeat this argument, so we may exchange as many conjugate variables between numerator and denominator.

22.12 Le Chatelier-Braun's principle

We know $C_P > C_V$ for the ideal gas due to Mayer's relation (→**14.8**), but actually this is an example of the universal inequality:

$$\left(\frac{\partial X}{\partial x}\right)_y \geq \left(\frac{\partial X}{\partial x}\right)_Y. \tag{22.26}$$

This can be demonstrated as follows.

$$\left(\frac{\partial X}{\partial x}\right)_y = \frac{\partial(X, y)}{\partial(x, y)} = \frac{\partial(X, y)}{\partial(x, Y)} \frac{\partial(x, Y)}{\partial(x, y)} \tag{22.27}$$

$$= \left[\left(\frac{\partial X}{\partial x}\right)_Y \left(\frac{\partial y}{\partial Y}\right)_x - \left(\frac{\partial X}{\partial Y}\right)_x \left(\frac{\partial y}{\partial x}\right)_Y\right] \left(\frac{\partial Y}{\partial y}\right)_x \tag{22.28}$$

$$= \left(\frac{\partial X}{\partial x}\right)_Y - \left(\frac{\partial X}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_Y. \tag{22.29}$$

(22.29) implies, thanks to

$$\left(\frac{\partial X}{\partial y}\right)_x = \frac{\partial(X,x)}{\partial(y,x)} = \frac{\partial(X,x)}{\partial(y,Y)}\frac{\partial(y,Y)}{\partial(x,Y)}\frac{\partial(x,Y)}{\partial(y,x)} = -\left(\frac{\partial y}{\partial x}\right)_Y\left(\frac{\partial Y}{\partial y}\right)_x, \tag{22.30}$$

$$\left(\frac{\partial X}{\partial x}\right)_y = \left(\frac{\partial X}{\partial x}\right)_Y + \left(\frac{\partial Y}{\partial y}\right)_x\left(\frac{\partial y}{\partial x}\right)_Y^2. \tag{22.31}$$

Since the second term on the right-hand side is nonnegative,

$$\left(\frac{\partial X}{\partial x}\right)_y \geq \left(\frac{\partial X}{\partial x}\right)_Y. \tag{22.32}$$

For example, for $X = S$

$$C_P \geq C_V. \tag{22.33}$$

Or for $X = V$, $x = -P$ so we have an inequality about the compressibility:

$$\kappa_T \geq \kappa_S. \tag{22.34}$$

What if Le Chatelier-Braun's principle does not hold? As can be seen from (22.31) then the Le Chatelier's principle for the conjugate pair appearing in the conditions (that is, for y and Y) is violated. That is, Le Chatelier-Braun's principle does not give any constraints substantially different from Le Chatelier's principle.

22.13 Constraints on the changes due to phase transitions

If a phase transition occurs, E need not be twice differentiable. Consequently, we cannot use (22.17). Note that Le Chatelier's principle is a direct consequence of the convexity of E. Even without sufficient differentiability, convexity still imposes strong constraints on the changes of quantities around the phase transition. For example, if we compare the low temperature phase and the high temperature phase, the latter is expected to be with larger entropy. Such a relation can be concluded from the gradient inequality (D.21); Let (x, X) be the conjugate pair. Then, if other variables are kept constant, we have

$$\Delta x \Delta X \geq 0. \tag{22.35}$$

Therefore, for example, we get

$$\Delta T \Delta S \geq 0, \tag{22.36}$$

which supports the above expectation. We can also obtain the following natural inequality:

$$\Delta P \Delta V \leq 0. \tag{22.37}$$

23 Phase equilibrium and phase transition

23.1 Phases and phase diagrams: outline

A substance may exhibit qualitatively different properties under various conditions (say, under different (T, P)). Roughly speaking, if we observe such a situation, we say the substance is in different phases (→**23.2** more precisely). Liquid water, ice and vapor are different phases of water. "Qualitatively different properties" mean, for example, "pushing one end of the system moves the other end" (the existence of a long-range order), or "compressing does not visibly shrink the system" (coherence) (see the table below).

	long-range order	coherence
solid phase	YES	YES
liquid phase	NO	YES
gas phase	NO	NO

Understanding a substance begins with knowing its various phases and their characteristic features. Thus, to begin with, we wish to make a sort of a map of the thermodynamic space (or at least the space spanned by some thermodynamic variables such as T and P) indicating the phase of the substance at each point on the map. This map is called the *phase diagram* (see, for example, Fig. 23.1).

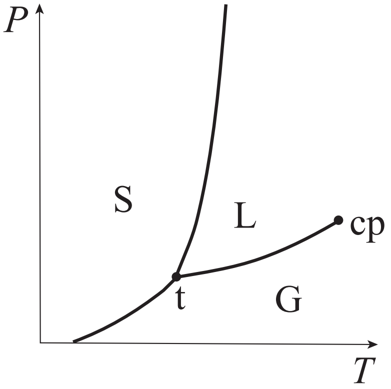

Figure 23.1: A representative phase diagram of an ordinary fluid

Fig. 23.1 A representative phase diagram of an ordinary fluid. S: solid phase; L: liquid phase; G: gas phase; t: triple point; cp: critical point. The curves indicate the phase boundaries, where phase transitions occur. The boundary between L and G ends at cp, so even if 'fluid phase' (= non-solid phase) may be defined globally, liquid phase or gas phase cannot be globally defined.

23.2 What is a phase?

Defining "phase" precisely is not a trivial task. Near a phase boundary coexisting phases may be clearly distinguished, but the region where a particular phase occupies may not be clearly defined as already pointed out for the gas and liquid phases of an ordinary fluid in Fig. 23.1. Furthermore, even if a clear boundary exists in the phase diagram we see, the diagram might be a low-dimensional section of a more complete high-dimensional phase diagram, in which some of the phase boundaries might disappear along the axis perpendicular to the diagram shown to us. Therefore, when we use the word 'phase' precisely, we should do so with respect to the phase diagram shown to us and locally, meaning that in a local region of the given phase diagram. In the local region under consideration, "The two phases are distinct, only if they can change into each other across the phase boundary where phase transitions occur."

23.3 What is a phase transition?

For a given system, its equilibrium state is uniquely mapped to a point in its thermodynamic space (→**5.2**). Even if the system has the coexistence of several phases, its state is still uniquely mapped to a point in its thermodynamic space.

To illustrate this, let us draw the phase diagram of an ordinary fluid in its thermodynamic space (Fig. 23.2).

Fig. 23.2 A schematic phase diagram of an ordinary fluid in its thermodynamic space

The white dots are critical point (in both diagrams). The black small square (left) and the dark gray triangle (right) indicate the triple point. The pale gray regions represent the two-phase coexistence regions. The primary purpose of this figure is to illustrate that the coexistence lines and triple point in the usual phase diagram (left inset) are unfolded into regions corresponding to various ratios of coexisting phases; we can actually know the coexistence ratio of various phases from the diagram.

For example, take the solid-gas coexisting region S + G. The black dot 's' on the solid-phase boundary indicates a pure solid phase with a definite (E, V) coordinates, and the black dot 'g' on the gas-phase boundary indicates a particular gas phase with a definite (E, V) (The figure also contains another pair s' and g' to exhibit another solid-gas coexisting relationship).

The white square on the line connecting s and g can express a particular ratio of these two coexisting phases. If the white square is located at the point with the line segment length ratio

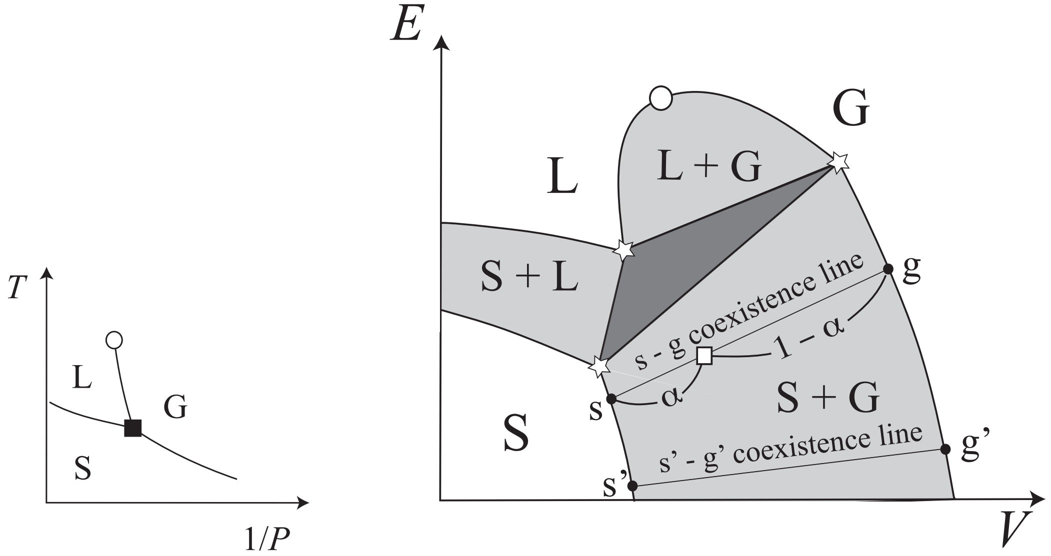

Figure 23.2: Phase diagram in the thermodynamic space. The white dot is a critical point, the black dot and the dark triangular region indicate a triple point (= three-phase coexisting states). The gray regions are two-phase coexisting states. It is a conceptual illustration, but the key point is that coexistence lines and a triple point in the usual phase diagram (left inset) are unfolded into regions corresponding to various ratio of coexisting phases.

$\alpha : (1-\alpha)$, then the coexistence state consists of sold phase 's' and gas phase 'g' in the ratio $(1-\alpha) : \alpha$; This is known as the *lever rule*. Similar lines can be drawn in the solid-liquid coexistence state. Thus, the coexistence region is a ruled surface in the thermodynamic space.

The position of any point in the dark gray representing three-phase coexistence phase expressed in the barycentric coordinates of three white stars, uniquely indicating the states of the coexisting three phases.

In this 2-dimensional phase diagram thermodynamic variables are, especially internal energy is, twice differentiable with respect to S and V in the areas corresponding to individual phases. This smoothness is reduced at the phase boundaries; while E never loses continuous differentiability, its derivatives are generally not differentiable. It is important to note that a change in smoothness of E is necessary for qualitative changes to occur. However, if multiple phases coexist (as in the light or dark gray regions in Fig. 23.2), then E is again smooth.

Therefore, a mathematically clearcut characterization of a phase transition may be some loss of smoothness of E as a function of S and operational coordinates $\boldsymbol{Y}$.[413]

---

[413] One could say that a phase transition occurs, if a certain complete thermodynamic function (→**18.13**) becomes less differentiable than in the bulk phases. Statistical mechanically one could

Accordingly, the (local) definition of phase in **23.2** is mathematically clear.

23.4 First order and second order phase transitions

Phase transitions are often classified into two categories: the first order phase transitions and the rest, called continuous or second order phase transitions. In first-order phase transitions at least one thermodynamic density (→**5.5**) changes discontinuously as a function of the conjugate thermodynamic field (→**5.5**), but for second order phase transitions there is no jump in thermodynamic densities. Gas-liquid phase transitions are usually first order, but under critical pressure, they become second-order.

In many interesting examples, phase transitions occur between ordered and not so ordered phases; we could say transitions occur between low entropy phases and high energy phases. For example folding of proteins usually occur between high energy random-coil states and low entropy folded states.

Intuitively, a first order phase transition occurs, if the stability of an ordered phase is lost catastrophically. In other words, if slight reduction of order induces its further reduction, a first-order phase transition occurs. Consequently, it is impossible to observe an equilibrium state with appreciably reduced order.

In contrast, for a second order phase transition, the above mentioned positive feedback loop of order reduction does not exist. Therefore, it is possible to observe equilibrium states with reduced order. An equilibrium state with reduced order may be intuitively analogized with an oscillator with a reduced spring constant, whose fluctuations become enhanced. Even if fluctuations become large, the ordered state endures them. Since the existence of a sort of order and its disappearance are characteristic features of phase transitions, second order phase transitions become theoretically very interesting.

23.5 Phase coexistence: the case of two phases

Let us assume that an isolated system (without chemical reactions) is described by the thermodynamic coordinates (E, X), and phase I and phase II coexist under the condition to exchange E and X. We follow the argument in **??**. We must maximize the system entropy $S = S_{\rm I} + S_{\rm II}$ under the exchange of E and V (→**12.6**). Gibbs'

---

say that phase transition occurs if a certain complete thermodynamic function loses holomorphy. However, experimentally, 'holomorphy' seems impossible to demonstrate, let alone analyticity.

relation reads

$$dS = \frac{1}{T}dE - \frac{x}{T}dX - \frac{\mu}{T}dN, \tag{23.1}$$

so, if δ denotes virtual variations (actually changes realized by fluctuations), the equilibrium condition becomes[414]

$$\delta S = \frac{1}{T_{\mathrm{I}}}\delta E_{\mathrm{I}} - \frac{x_{\mathrm{I}}}{T_{\mathrm{I}}}\delta X_{\mathrm{I}} - \frac{\mu_{\mathrm{I}}}{T_{\mathrm{I}}}\delta N_{\mathrm{I}} + \frac{1}{T_{\mathrm{II}}}\delta E_{\mathrm{II}} - \frac{x_{\mathrm{II}}}{T_{\mathrm{II}}}\delta X_{\mathrm{II}} - \frac{\mu_{\mathrm{II}}}{T_{\mathrm{II}}}\delta N_{\mathrm{II}} = 0. \tag{23.2}$$

Since $\delta E_{\mathrm{I}} + \delta E_{\mathrm{II}} = 0$, $\delta X_{\mathrm{I}} + \delta X_{\mathrm{II}} = 0$, $\delta N_{\mathrm{I}} + \delta N_{\mathrm{II}} = 0$, (23.2) becomes

$$\delta S = \left(\frac{1}{T_{\mathrm{I}}} - \frac{1}{T_{\mathrm{II}}}\right)\delta E_{\mathrm{I}} - \left(\frac{x_{\mathrm{I}}}{T_{\mathrm{I}}} - \frac{x_{\mathrm{II}}}{T_{\mathrm{II}}}\right)\delta X_{\mathrm{I}} - \left(\frac{\mu_{\mathrm{I}}}{T_{\mathrm{I}}} - \frac{\mu_{\mathrm{II}}}{T_{\mathrm{II}}}\right)\delta N_{\mathrm{I}}, \tag{23.3}$$

so, generally, the following equalities are required:

$$T_{\mathrm{I}} = T_{\mathrm{II}},\ x_{\mathrm{I}} = x_{\mathrm{II}},\ \mu_{\mathrm{I}} = \mu_{\mathrm{II}}. \tag{23.4}$$

The most common cases are with $X = V$ and $x = -P$, so the condition for the chemical potentials is

$$\mu_{\mathrm{I}}(T,P) = \mu_{\mathrm{II}}(T,P), \tag{23.5}$$

which determines the phase coexisting curves in the TP phase diagram.[415]

This relation may be obtained from the principle of Gibbs energy minimization under constant TP condition. From (23.5) we already derived Clapeyron-Clausius's equation (→**19.11**).

The Gibbs energy of the system is given by

$$G = N_{\mathrm{I}}\mu_{\mathrm{I}} + N_{\mathrm{II}}\mu_{\mathrm{II}}. \tag{23.6}$$

Therefore, the state can change without changing G (only N_{I} and N_{II} vary; note $N_{\mathrm{I}} + N_{\mathrm{II}} =$ constant). Consequently, the TP phase coexisting line becomes an area in the thermodynamic space as we have seen in Fig. 23.2.

---

[414] Here, we assume the max entropy is realized at an entropy extremal.

[415] Precisely speaking, E, V and N, and not T and P, are the thermodynamic variables in the current situation of an isolated system. Thus, T, P and μ are functions of E, V and N. Therefore, to obtain (23.5), we must write E_n, V_n and N_n ($n =$ I or II) in terms of T and P, and then convert $\mu(E,V,N)$ to a function of T and P. As stated just below, the result can be obtained directly with the aid of the variational principle for G (→**19.7**).

23.6 The direction of changes due to phase transitions

We have already seen in **22.13** that being in equilibrium implies for any conjugate pair (x, X) there is a constraint:

$$\Delta x \Delta X \geq 0. \tag{23.7}$$

Since this is not usually discussed in elementary textbooks, let us repeat it with examples.

If the changes are not zero, then $\Delta P \Delta V < 0$ or

$$(P_{\rm II} - P_{\rm I})(V_{\rm II} - V_{\rm I}) < 0. \tag{23.8}$$

This requires that the low pressure phase must have larger volume/material quantity (say, molar volume). If we take freezing of water around 1 atm as an example, ice has a larger molar volume than liquid water. This is consistent with the fact that we can melt ice at a constant temperature by applying pressure.

$\Delta T \Delta S \geq 0$ implies that if there is a system that can solidify upon increasing its temperature, the entropy of the solid phase must be larger than that of the fluid phase. There is such an example in ^{3}He (the *Pomeranchuk effect* Fig. 23.3).

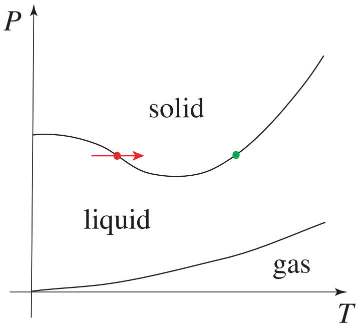

Figure 23.3: The Pomeranchuk effect

Fig. 23.3 The Pomeranchuk effect: if we raise temperature at the red spot, the liquid phase solidifies. Therefore, the solid phase must have a larger entropy than the liquid phase. In this case, the reason why the solid phase has a larger entropy is that the nuclear spins are not ordered in the solid phase. The spins exhibit a antiferromagnetic order below 10^{-3} K. At the green spot, the solid phase has a smaller entropy than the liquid phase just as the ordinary systems.

23.7 Thermodynamic phases when symmetry breaks spontaneously

Suppose a magnet becomes a ferromagnet. Then, its non-zero magnetization can point many directions. Ideally, all the directions have the same energy, so it is just as the case of the shape unrelated to the system energy. That is, the direction of the magnetization vector $\boldsymbol{M}$ is an example of macroobservables that need not[416] be distinguished thermodynamically.

Of course, in practice, the magnetization directions are important, but that is not relevant energetically.[417]

23.8 Phase equilibrium of a pure substance

Suppose ϕ phases (I, II, $\cdots, \phi$) coexist. Let μ_{X} be the chemical potential of phase x. Then, the following $\phi - 1$ equations must be satisfied:

$$\mu_{\mathrm{I}}(T, P) = \mu_{\mathrm{II}}(T, P) = \cdots = \mu_{\phi}(T, P). \tag{23.9}$$

Assume that there is no special functional relations among the chemical potentials of the phases. Then, (23.9) gives $\phi - 1$ independent conditions. For these equations to have solutions T and P there should be at most two independent equalities. Thus, for a pure substance, at most three phases ($\phi = 3$) can coexist.

If three phases coexist, then the T and P are unique (locally in the phase diagram, →**23.10** (2)). This point is called the *triple point*. Until 2019 the Kelvin temperature was defined by fixing the triple point of pure water to be $T = 273.16$ K.[418]

23.9 Gibbs' phase rule

Let us consider a system consisting of c chemical species that are regarded independent (→**4.4**; it is assumed that there is no chemical reaction.[419]).

If ϕ phases coexist, the phase equilibrium conditions are:

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[416] It may be better to say 'cannot'.

[417] If there is an external magnetic field $\boldsymbol{B}$, then $\boldsymbol{M}$ is energetically relevant. However, in this case, in equilibrium, there is only one particular $\boldsymbol{M}$ fixed. In any case, we need not consider the coexistence of continuously many phases.

[418] The unit kelvin 'K' is now (since 2019 or at the 26th General Conference on Weights and Measures in late 2018) defined with a value of the Boltzmann constant to be fixed as $k_B = 1.380649 \times 10^{-23}$ J·K^{-1}. The unit J·K^{-1} = kg·m^2·s^{-2}·K^{-1}, where the kilogram, meter and second are defined in terms of the Planck constant, the speed of light, and the duration of the caesium-133 ground-state hyperfine transition.

[419] When there is a chemical reaction, one relationship between chemical component coordinates is established, so c decreases by 1 for each independent chemical reaction. In other words, if there are r independent extents of chemical reaction (→**25.8**), then a replacement of $c \to c - r$ is necessary in the discussion here. As a consequence, (23.11) becomes $f = c - r + 2 - \phi$.

(1) T and P are common to all the phases
(2) For each of the c independent chemicals the chemical potential is identical for all the phases. Thus, as we have seen in (23.9), each chemical must satisfy $\phi - 1$ equations ($j = 1, \cdots, c$):

$$\mu^j_{\mathrm{I}}(T, P, x^1_{\mathrm{I}}, x^2_{\mathrm{I}}, \cdots x^{c-1}_{\mathrm{I}}) = \mu^j_{\mathrm{II}}(T, P, x^1_{\mathrm{II}}, x^2_{\mathrm{II}}, \cdots x^{c-1}_{\mathrm{II}}) = \cdots = \mu^j_{\phi}(T, P, x^1_{\phi}, x^2_{\phi}, \cdots x^{c-1}_{\phi}). \tag{23.10}$$

Consequently, the number of equalities that must be satisfied is $(\phi - 1) \times c$.[420]

To determine the composition of each phase, its $c-1$ mole fractions $(x^1, x^2, \cdots, x^{c-1})$ must be known.[421] The compositions are different from phase to phase, so we must determine $\phi \times (c - 1)$ mole fractions $x^1_{\mathrm{x}}, x^2_{\mathrm{x}}, \cdots x^{c-1}_{\mathrm{x}}$ ($\mathrm{x} = 1, \cdots, \phi$, if we distinguish phases with suffixes). Therefore, to determine the state of the system, we must determine $2 + \phi(c - 1)$ variables, T, P and x^j_{x} ($j = 1, \cdots, c - 1$, $\mathrm{x} = 1, \cdots, \phi$). Therefore, in the generic case the number of variables remaining undetermined is $f = 2 + \phi(c - 1) - c(\phi - 1) = c + 2 - \phi$. That is, even with the coexisting condition constraints, still (T, P) can move in the region of dimension f in the phase space:

$$f = c + 2 - \phi. \tag{23.11}$$

This f is called the (degree of) *thermodynamic freedom*, and the formula is called *Gibbs' phase rule.*

For a pure substance $c = 1$ gives $f = 3 - \phi$. Thus, if two phases coexist, $f = 1$, that is, the coexisting states make a 1 dimensional shape on the T, P diagram (i.e., coexisting curve). If three phase coexist, then $f = 0$, meaning the coexisting phase makes a zero-dimensional shape (i.e., triple point).

23.10 Remarks on phase coexistence

(1) As can be seen from the derivation of the phase rule, the coexistence is discussed under the condition of genericity; there are no 'accidental' relations among functions. Therefore, mixtures or even pure chemicals can violate the phase rule, i.e., substances for which f is larger than that dictated by the phase rule (23.11) can be realized.[422]

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[420] If there are special (or accidental) relationships, the number of equations that must be satisfied will be reduced to fewer than $(\phi - 1) \times c$.

[421] The mole fraction x_i of chemical i is defined by $x_i = \tilde{N}_i / \sum_{j=1}^c \tilde{N}_j$. In this case, no chemical reaction is assumed to occur, so we can also define x_i in terms of materials coordinates as $x_i = N_i / \sum_{j=1}^c N_j$.

[422] This is because, if there are accidental functional relationships between chemical potentials,

(2) Does the phase rule hold globally for the phase diagram? No. For example, a problem such as the number of crossing points between two curves in the plane cannot be answered by a crude argument utilized in the derivation of the phase rule. Therefore, we cannot answer how many triple points a given substance has. Two triple points could exist very close with each other; we would not be surprised, if they would merge.
(3) Then, when the phase rule predict the coexistence, can the coexistence actually occur? For the phases that thermodynamics can distinguish, the coexistence would happen. However, if the phases are due to a spontaneous symmetry breaking, can they coexist? This depends on the stability of the interface, for example, and is not a concern of thermodynamics (→**23.7**).
(4) Then, are actually coexisting phases equilibrium phases and is the coexistence true equilibrium? This is not a simple question. Liquid-liquid phase separations in a cell or the resultant intracellular membraneless organelles need not be in equilibrium. Or, the folded states of proteins should be considered as distinct phases from the random states, and the transitions between them are first-order like.[423] However, nonequilibrium cases should not be rare; biologically meaningful states can be nonequilibrium states with the true equilibrium state rarely attained, or even the true equilibrium state could be harmful for organisms. Think of prions.

23.11 Legendre-Fenchel transformation with phase transitions

18.12 tells us that the Helmholtz energy can be obtained by a Legendre-Fenchel transformation of the internal energy as

$$-A(T) = \max_S |_{\boldsymbol{Y}}[TS - E(S, \boldsymbol{Y})] = \sup_S |_{\boldsymbol{Y}}[TS - E(S, \boldsymbol{Y})]. \tag{23.12}$$

That is, we have seen

$$-A = E^*. \tag{23.13}$$

This allows the inverse transformation; the convexity of E allows

$$(-A)^* = E^{**} = E. \tag{23.14}$$

---

the actual number of independent constraints will be reduced from $c \times (\phi - 1)$. Therefore, according to the previous argument, no matter how hard one tries, the thermodynamic degrees of freedom cannot be reduced below f as given in (23.11). In general, the phase rule is $f \geq c + 2 - \phi$. Indeed, an example of a pure substance with a quadruple point is provided by K. Akahane, J. Russo, and H. Tanaka, A possible four-phase coexistence in a single-component system, ature Commun. **7**, 12599 (2017).

[423] This is a fact pointed out first by N. Gō.

Thus, the Helmholtz energy A is a complete thermodynamic function (→**18.13**).

However, is temperature T not a proper thermodynamic coordinate (→**3.8**)? Still do we not lose any information that the internal energy has when it is transformed to the Helmholtz energy? This is a reasonable question. The answer is: E as a function is completely reconstructed from A, but the original value of S cannot be recovered. That is, there is indeed lost information due to using non-fundamental thermodynamic variables.

Let us assume that the original state has entropy S with temperature T. As we have seen in the thermodynamic phase diagram Fig. 23.2 with a given T various S can associate. By the transformation $E \to -A$ all the state with the same temperature are mapped to a single point, so naturally, the actual original entropy value is lost. Still, the range of the values of entropy associated with a given T is perfectly recovered (see Fig. 23.4).[424]

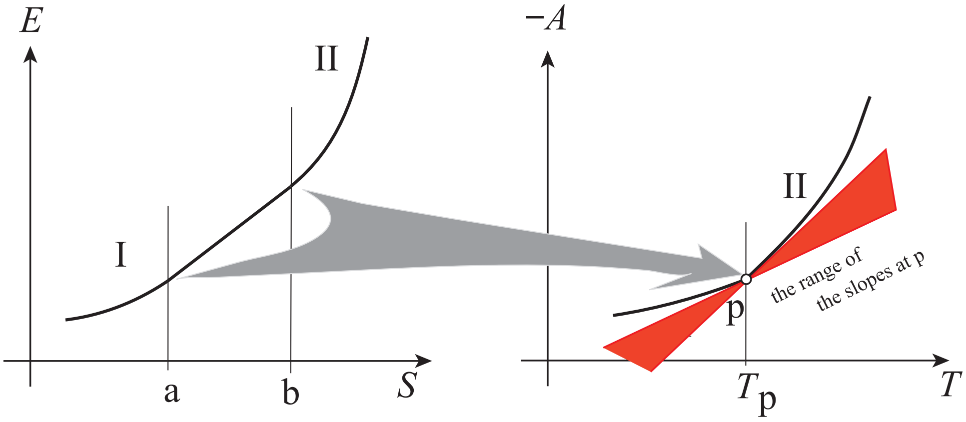

Figure 23.4: Between a and b entropy changes but the temperature is constant. Then, the graph of E is with a constant slope between a and b. This portion is mapped by the Legendre-Fenchel transformation to a point p with the temperature given by the slope (and A becomes non-differentiable). However, the range of the slope of the lines tangent to $-A$ at p (i.e., the red fan) is not lost from the graph of A and can be restored. Needless to say, we cannot tell from which point the arrow started. This is the reason why T is not a fundamental thermodynamic variable.

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[424] Convex analytically, we say it is determined as the *subdifferential* (→**D.3**) of A with respect to T.

24 The third law of thermodynamics

24.1 Determination of the Gibbs energy: motivation for the third law

From the late 19th to the early 20th century, an important question of chemical physics/chemistry was to determine the free-energy change ΔG of a chemical reaction[425] in terms of the reaction heat ΔH. The 'Thomsen-Berthelot principle'[426] was interpreted as $\Delta G = \Delta H$ in the thermal theory of affinity.[427]

According to this theory no endothermic process can proceed spontaneously as pointed out by Helmholtz (1882). Deriving the Gibbs-Helmholtz equation (19.7), he showed that generally $\Delta G \neq \Delta H$:

$$\Delta H = \Delta G - T\left(\frac{\partial \Delta G}{\partial T}\right)_P . \tag{24.1}$$

Integrating the Gibbs-Helmholtz equation (19.7) in the form: $\Delta H/T^2 = -(\partial(\Delta G/T)/\partial T)_P$, we obtain

$$\Delta G = -T\int_{T_0}^{T} \frac{\Delta H}{T^2} dT + \frac{\Delta G(T_0)}{T_0} T. \tag{24.2}$$

That there was no way to determine $\Delta G(T_0)/T_0$ from the reaction heat ΔH was the central difficulty of chemical thermodynamics according to Nernst.[428]

24.2 Nernst's proposal

Nernst asserted that ΔG and ΔH are not generally equal, but at sufficiently low temperatures they are very close. Therefore, close to $T = 0$, the equality must be

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[425] Or, the affinity $-\Delta G$ of a chemical reaction.

[426] Julius Thomsen (1826-1909), `https://en.wikipedia.org/wiki/Hans_Peter_Jrgen_Julius_Thomsen`; Marcellin Berthelot (1827-1907) `https://en.wikipedia.org/wiki/Marcellin_Berthelot`. This principle claims: all chemical changes are accompanied by the production of heat and processes which actually occur will be ones in which the most heat is produced (wikipedia).

[427] The thermal theory of affinity postulated that the heat evolved in a chemical reaction was the true measure of its affinity.

[428] Walther Nernst (1864-1941) `https://en.wikipedia.org/wiki/Walther_Nernst`. See K. Mendelssohn, *The world of Walther Nernst: the rise and fall of German Science 1864-1941* (ebook form from Plunket Lake Press, 2015; the original 1973).

very accurate, and Nernst proposed that in the $T \to 0$ limit

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P - \left(\frac{\partial \Delta H}{\partial T}\right)_P \to 0 \tag{24.3}$$

to remove all the difficulties.[429]

His assertion can be explained as follows: (24.2) is rewritten as

$$\begin{aligned}\Delta G &= T\int_{T_0}^{T}\left(\frac{\partial 1/T}{\partial T}\right)_P \Delta H dT + \frac{\Delta G(T_0)}{T_0}T & (24.4)\\ &= T\left(\frac{\Delta H(T)}{T} - \frac{\Delta H(T_0)}{T_0}\right) - T\int_{T_0}^{T}\frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P dT + \frac{\Delta G(T_0)}{T_0}T & (24.5)\\ &= \Delta H - T\int_{T_0}^{T}\frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P dT + \frac{\Delta G(T_0) - \Delta H(T_0)}{T_0}T. & (24.6)\end{aligned}$$

Note that L'Hospital's theorem implies that

$$\lim_{T\to 0}\frac{\Delta G - \Delta H}{T} = 0 \tag{24.7}$$

is equivalent to Nernst's proposal (24.3). Thus, according to his proposal, we get from (24.6), taking the $T_0 \to 0$ limit,

$$\Delta G = \Delta H - T\int_0^T \frac{1}{T}\left(\frac{\partial \Delta H}{\partial T}\right)_P dT. \tag{24.8}$$

Thus, the 'central difficulty of chemical thermodynamics according to Nernst' (→**24.1**) is resolved.

24.3 Consequences of Nernst's assertion: The third law of thermodynamics

(24.1) and (24.7) imply

$$\lim_{T\to 0}\left(\frac{\partial \Delta G}{\partial T}\right)_P = 0. \tag{24.9}$$

---

[429] Unfortunately in the $T_0 \to 0$ limit, the last term in (24.2) may not be finite, but ignoring this fact, Nernst 'demonstrated' this assertion. Here, a corrected demonstration will be given instead of the original dubious version. A dubious demonstration can be found on p292 of Yamamoto's book (volume 3) quoted at the beginning of Appendix A.

That is,

$$\lim_{T\to 0} \Delta S = 0. \tag{24.10}$$

This implies that the integral in the formal expression (24.8) must be finite and well defined. Thus, the reaction heat completely determines the free energy change (affinity) due to a reaction.

(24.10) means that for the totality of equilibrium states of the systems that can be transformed with reversible processes (including the changes of the materialistic 'stages' as discussed in **4.7**), their entropy densities at $T = 0$ are identical. In other words, all the reversible changes at $T = 0$ occur without any entropy change. This statement (24.10), or the formulas on which this statement is based, such as (24.3) or (24.7), are called *the third law of thermodynamics* or *Nernst's principle*.[430]

24.4 Reversible sectors of equilibrium states

Nernst's principle tells us that we can choose a common origin of entropy for any system mutually related by reversible processes. We may call such a set of systems a *reversible sector*.

The distinction between different sectors may become serious when we consider chemical reactions. For example, since we cannot synthesize any ^{13}C organic compounds from ^{12}C compounds, the systems consisting of these chemicals make two distinct reversible sectors. Thus, the origin of entropy for each sector may be different.

In organic chemistry, the compounds in different sectors may participate in chemical reactions. ^{12}C compounds and ^{13}C compounds can react to make 'mixed' chemicals. A natural question is: even if such 'intersector processes' can occur, can we still arbitrarily choose the entropy origins? Yes, we can, because there is no process in the usual thermodynamics that connect the ^{12}C world and the ^{13}C world reversibly. Therefore, there is no empirical means to check any entropy difference between these two worlds. Thus, we are free to choose the origin of different reversible sectors (if

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[430] ⟪**Nernst's joke on the three principles**⟫ Kurt Mendelssohn writes, "When lecturing on 'his' heat theorem, Nernst was careful to point to an interesting numerical phenomenon concerning the discovery of the three fundamental laws of thermodynamics. The first one had three authors, Mayer, Joule and Helmholtz; the second had two, Carnot and Clausius; whereas the third was the work of one man only, Nernst. This showed conclusively that thermodynamics was now complete since the authorship of a hypothetical fourth law would have to be zero." (*The world of Walther Nernst: the rise and fall of German Science 1864-1941* (ebook form from Plunket Lake Press, 2015; the original 1973) Chapter 4. Note that Thomson is not mentioned.

something is not observable, you can conveniently assume anything you wish about it[431]).

24.5 Nernst-Planck's theorem

24.3 tells us that the value of the entropy in the $T \to 0$ limit can be anything as long as it is bounded from below. We know empirically that there is no such divergence (i.e., $S \to -\infty$ does not happen).

Planck recognized that this means that the entropy origin for each reversible sector can be set 0. Thus,

$$\lim_{T \to 0} S = 0 \tag{24.11}$$

is called the *Nernst-Planck theorem*.

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[431] In more detail: what we can obtain is the 'cost' to bring A and B from some starting points to AB. The costs to bring A and B to their starting points depend on their conventions. Thus, the total costs of making AB depends on all the costs A and B inherit, but as long as these inherited costs are consistently given in their own worlds, no inconsistency shows up.

25 Chemical reactions and chemical equilibria: Outline

This section provides an overview of the basic concepts of chemical thermodynamics that are typically covered in standard thermodynamics textbooks. It should be noted that any mathematically incorrect or flawed explanations and discussions in traditional thermodynamics have been rectified (→**25.27** for a summary of the grave problems).[432]

25.1 The expression of material constitution of a system: summary

Even in a closed system, the amount of chemicals can change (→**4.4**), depending on the system internal energy and work coordinates $(E, \boldsymbol{X})$ (the ordinary thermodynamic coordinates) (→**4.4**). Chemical changes can cause various complications as discussed in **4.4**-**4.11**, but it was rather long ago (→Section 4), so here let us review the problems.

The key point is that "the operations the experimenter can perform" and "the observations the experimenter can make" on the chemical constitution of the system must be distinguished and must be expressed in terms of different variables, because the latter are dependent on $(E, \boldsymbol{X})$ (see Fig. 25.1).

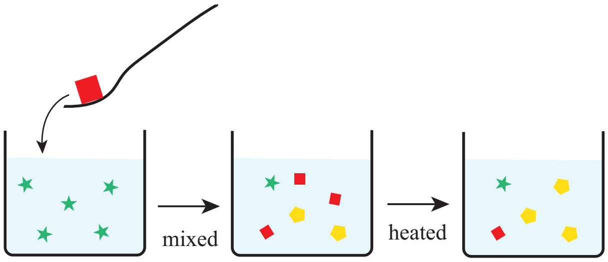

Figure 25.1: Cartoon explanation of materials coordinates and chemical composition coordinates. What you add may react with the existing chemicals. Even if you do not add chemicals anymore, if you, e.g., heat the system, its chemical compositions change.

The mole numbers of chemicals that the experimenter can add to or remove from the system independently (→**4.7**) are called the materials coordinates. For example, the totality $\boldsymbol{N}$ of the moles of the chemicals used to construct the system to

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[432] Perhaps, some explanations may be added as footnotes.

study may be adoptedn as the materials coordinates of the state of the system; this materials coordinates will dictate the materials constitution as long as the system is closed, even if chemical reactions occur. Needless to say, the materials coordinates must be updated every time new chemicals are added or removed (for the detail see **25.6**)

According to the principle II of chemistry in **4.3**, when the materials coordinates of the system are $\boldsymbol{N}$, for each ordinary thermodynamic coordinate value set $(E, \boldsymbol{X})$ the chemical composition variables $\tilde{\boldsymbol{N}}$ of the system, that is, the amounts (moles) of chemicals currently present in the system, are uniquely determined—the reaction map (→**4.11**) $R : \tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$ determines the equilibrium chemical composition $\tilde{\boldsymbol{N}}$ based on $E, \boldsymbol{X}$ and $\boldsymbol{N}$.

See **4.8** for the detailed distinction between the materials coordinates and the chemical composition variables, which we will collectively call 'chemical variables'. The next unit illustrates chemical variables of a system with a simple reaction.

25.2 Materials coordinates, a simple illustration

As an example, let us use the chemical reaction $(*)$ in **4.4**, i.e.,

$$\mathrm{A} + \mathrm{B} \longleftrightarrow \mathrm{C}.$$

For simplicity, the system has a unit volume ($1\ l$) that is kept constant, so that the molarities and the moles of the chemicals are numerically identical.[433] Let us assume the following equilibrium condition with the equilibrium constant K:[434]

$$[\mathrm{C}]/[\mathrm{A}][\mathrm{B}] = K = 1, \tag{25.1}$$

where [X] denotes the molarity[435] of chemical X.

(1) Suppose we prepare a system with 2 moles each of A and B. In this case the materials coordinates of the system may be chosen, for example, as $(N_{\mathrm{A}}, N_{\mathrm{B}}, N_{\mathrm{C}}) = (2, 2, 0)$. The equilibrium composition may be computed as follows: When the above reaction reaches an equilibrium, x moles each of A and B are consumed and x moles of C is formed, so (25.1) implies $x/(2-x)^2 = 1$, which implies $x = 1$ in equilibrium. Hence, the actual chemical composition variables of the system may be written as $(\tilde{N}_{\mathrm{A}}, \tilde{N}_{\mathrm{B}}, \tilde{N}_{\mathrm{C}}) = (1, 1, 1)$.

When a new equilibrium is attained, it is sensible to say that the materials coordinates that are needed to make the system in this state is identical to the present chemical compositions. Therefore, although this is not mathematically mandatory,[436] since the system is closed, it

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[433] In many cases for liquid systems, there is a 'solvent' that does not participate in the reactions. We ignore the solvent in this example.

[434] Such conditions will be derived thermodynamically (→**25.23**).

[435] In these lecture notes, we use mol/l as its unit.

[436] There are infinitely many possible choices of materials coordinates that give identical chemical compositions (→**25.5**) for a given state of a given system.

is generally convenient to update the materials coordinates to $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (1,1,1)$; we can actually build the system by combining the chemicals whose amounts are described by the materials coordinate $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (1,1,1)$ initially instead of $(2,2,0)$ (see a practical choice summarized in **25.6**).

(2) For the system in (1) if, for example, we change its internal energy E (or its temperature) while the system is still closed, let us assume that the equilibrium constant K in (25.1) (→**25.23**) is modified to be $K = 3$. Then, the equilibrium composition is given by $(\tilde{N}_\mathrm{A}, \tilde{N}_\mathrm{B}, \tilde{N}_\mathrm{C}) = (2/3, 2/3, 4/3)$. Needless to say, its materials coordinates can still be chosen as $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (1,1,1)$ as before. However, it may be sensible to update the materials coordinates to be $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (2/3, 2/3, 4/3)$, because the chemical compositions are the directly observable quantity of the state.

(3) To prepare the system under consideration we only need to prepare the system according to one of the many equivalent materials coordinate expressions (→**25.5**) of the system. For example, we can prepare the same system with 2 moles of C only. Thus, the materials coordinates of the system can be $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (0,0,2)$, but in the state with $K = 1$ (25.1) implies $(2-x)/x^2 = 1$, where x is the moles of C decomposed. This implies $x = 1$. That is, the system chemical composition is, just as in (1), $(\tilde{N}_\mathrm{A}, \tilde{N}_\mathrm{B}, \tilde{N}_\mathrm{C}) = (1,1,1)$. Therefore, even in this case after equilibration, it may be sensible to choose the materials coordinates as in (1): $(N_\mathrm{A}, N_\mathrm{B}, N_\mathrm{C}) = (1,1,1)$.

(4) These are cases in which reactions occur spontaneously in a single closed system, but we could prepare the system as in (1) by combining two half-volume systems. Suppose we prepare a system with volume 1/2 containing only 2 moles of A (its materials coordinates are $(2,0,0)$ and so are its chemical compositions) and a system with volume 1/2 containing only 2 moles of B (its materials coordinates are $(0,2,0)$ and so are its chemical compositions). Combining these two systems, we make a system of volume 1 with the materials coordinates given by $(2,0,0) + (0,2,0) = (2,2,0)$. Recall that materials coordinates $\boldsymbol{N}$ are additive in contradistinction to chemical compositions $\tilde{\boldsymbol{N}}$. After this procedure is over, the system will reach its new equilibrium (e.g., with $K = 1$) as discussed in (1), so it may be sensible to choose the materials coordinates after equilibration to be $(1,1,1)$ in this case as well.

(5) Let us add 2 moles of C to the system prepared in (1). The materials coordinates of the system become $(1,1,1) + (0,0,2) = (1,1,3)$.[437] If $K = 1$, assuming that y moles of C is decomposed before reaching a chemical equilibrium, $(3-y)/(1+y)^2 = 1$, so $y = (-3+\sqrt{17})/2$ and the equilibrium chemical compositions are $((\sqrt{17}-1)/2, (\sqrt{17}-1)/2, (9-\sqrt{17})/2)$, so this should be chosen as the materials coordinates for the system.

25.3 Independent chemical ingredients

There are two interpretations of the independence of chemicals for a given system (→**25.1**). One is the operational independence (can we add separately?) and the

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[437] This choice is recommended as sensible; $(2,2,0) + (0,0,2) = (2,2,2)$ is perfectly fine, but not recommended. If we choose the materials coordinates to be $(2,2,2)$, assuming that x moles of A is consumed before reaching chemical equilibrium, $(2+x)/(2-x)^2 = 1$, so $x = (5-\sqrt{17})/2$, that is, the resultant chemical compositions are $((\sqrt{17}-1)/2, (\sqrt{17}-1)/2, (9-\sqrt{17})/2)$.

other the observational independence (can we distinguish and quantify separately in situ?). Maybe there is one more independence: the independence of changes of compositions in a closed system, but this independence is complicated at best and is hard to use (→**4.7**).

The materials coordinates are introduced to describe the operational independence, but the intrinsically accompanying chemicals make operational introduction of really pure substance into the system practically impossible. For example, to introduce a certain amount of water inevitably introduces certain amount of OH^-, H_3O^+, etc. Under constant T and P the amount of these accompanying compounds are uniquely fixed (due to the chemical equilibrium conditions). Therefore, even though in this case there are (at least) three chemicals, the equilibrium condition $2H_2O \longleftrightarrow H_3O^+ + OH^-$ and electroneutrality tell us only one of them is independently and operationally changed. Thus, usually, water is regarded as the independent chemical.[438]

As is clear, the number of independent chemical components is less than that of the independent materials coordinates due to chemical equilibrium relations. The following has already been stated clearly in **4.7** (ii), but is repeated just below because of its importance.

If we ignore accompanying chemicals, all the materials coordinates are independent. How about the chemical composition? According to the elementary chemistry principle II (→**4.3**), for a closed system, the chemical composition variables are not thermodynamically independent variables at all; they are dictated by the ordinary thermodynamic coordinates E and $\boldsymbol{X}$.

25.4 Is there any way not to introduce two kinds of chemical variables?

We have introduced the materials coordinates and chemical composition variables, because the variation of the ordinary thermodynamic coordinates $(E, \boldsymbol{X})$ can vary chemical constituents, even if we do not perform any experimental manipulation of chemicals. That is, 'chemical coordinates' is dependent on $(E, \boldsymbol{X})$ mathematically. Therefore, for example, the expression such as (in this unit, '$\boldsymbol{N}$' with quotation marks is interpreted as in the conventional thermodynamics; not the materials coordinates,

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[438] However, the amounts of accompanying compounds change when the system state changes, since they are determined by chemical equilibria. In most cases, this effect is ignored. However, in terms of materials coordinates, we have nothing to worry. See **25.11**.

but generic chemical coordinates)

$$\left(\frac{\partial E}{\partial S}\right)_{\boldsymbol{X},\text{`}\boldsymbol{N}\text{'}} \tag{25.2}$$

turns out to be extremely delicate (at best; generally, meaningless if we follow the conventional choice '$\boldsymbol{N}$' $= \tilde{\boldsymbol{N}}$).

To avoid such a difficulty, the standard chemical thermodynamics, if honest, explicitly assumes that '$\boldsymbol{N}$' may be kept constant in any equilibrium state (that is, any chemical reaction may be frozen at will (→**4.2**) without spoiling the thermodynamic equilibrium of the system under study. Indeed, this assumption decouples '$\boldsymbol{N}$' and the ordinary thermodynamic coordinates; $(E, \boldsymbol{X}, \tilde{\boldsymbol{N}})$ becomes a set of genuine independent mathematical variables under this assumption.

Since the second law is stated without chemical variables in existing chemical thermodynamics textbooks, we must understand that the convexity (of, e.g., $-S$ or E) holds only without chemical reactions (or under the assumption that the chemical compositions are fixed).

When we wish to discuss chemical reactions thermodynamically, we wish to apply the thermodynamic variational principle (→**12.10**) to chemistry. However, with the above convention, it is impossible to show the concavity of entropy as a function of $(E, \boldsymbol{X}, \tilde{\boldsymbol{N}})$. Thus, the principle of increasing entropy cannot be formulated with these variables. The Gibbs energy may not be used to formulate the variational principle in terms of the usual expression of the amounts of chemicals.

To formulate chemical thermodynamics mathematically consistently, we need convex analysis without halting chemical reactions, so we need the materials coordinates $\boldsymbol{N}$, but to describe the current chemical constituents of the system we need the chemical composition variables $\tilde{\boldsymbol{N}}$.

25.5 Mathematical expression of the materials coordinates and the representative elements[439]

When the ordinary thermodynamic coordinates of the system are given, its materials coordinates $\boldsymbol{N}$ determines the chemical composition variables $\tilde{\boldsymbol{N}}$ in terms of the reaction map (→**4.11**) as $\tilde{\boldsymbol{N}} = R_{E,\boldsymbol{X}}(\boldsymbol{N})$. There are infinitely many choices of materials coordinates that give the identical $\tilde{\boldsymbol{N}}$ as we have seen in **25.2**. That is, if we introduce the equivalence relation $\approx$ among materials coordinates as

$$\boldsymbol{N} \approx \boldsymbol{N}' \iff R_{E,\boldsymbol{X}}(\boldsymbol{N}) = R_{E,\boldsymbol{X}}(\boldsymbol{N}'), \tag{25.3}$$

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[439] based on T. Tsujishita's input.

mathematically the materials coordinates should be the equivalence class of the range of the materials coordinates ${\mathbb{R}^+}^D$ due to $\approx$, where D is the dimension of the materials coordinate space, i.e., the number of operationally independently modifiable chemicals. That is, the element of ${\mathbb{R}^+}^D/\approx$ corresponds to a distinct set of materials coordinates.

If a chemical reaction 'b' is stoichiometric, we can algebraically express it as (→**25.8**, especially (25.7))

$$\sum \nu_i^b \mathrm{C}_i = 0. \tag{25.4}$$

Therefore, irrespective of $(E, \boldsymbol{X})$, if we use the reaction coordinate ξ^b for reaction b, the equivalence relation $\boldsymbol{N} \approx \boldsymbol{N}'$ is equivalent to the existence of $\Delta\xi^b$ satisfying

$$N_i - N_i' = \sum_b \nu_i^b \Delta\xi^b. \tag{25.5}$$

If the reactions are not stoichiometric, then not only the so-called stoichiometric coefficients may depend on $(E, \boldsymbol{X})$, but existing chemicals themselves also depend on $(E, \boldsymbol{X})$. Consequently, we cannot simply rewrite the equivalence class determined by $R_{E,\boldsymbol{X}}$ in terms of chemical reaction formulas as (25.5).

Practically it is convenient to choose an appropriate member in an element of ${\mathbb{R}^+}^D/\approx$ as the representative as explained in **25.6** (or as illustrated in **25.2**).

25.6 Practical choice of the chemical variables $\boldsymbol{N}$ and $\tilde{\boldsymbol{N}}$

In conventional chemical thermodynamics textbooks, there is a requirement that chemical constituents (typically corresponding to our chemical composition variables $\tilde{\boldsymbol{N}}$) can be freely frozen during any process. Subsequently, once the desired change (e.g., of the ordinary thermodynamic coordinates) is completed, chemical reactions are permitted to progress in order to attain the true chemical equilibrium. To adhere as closely as possible to this *ad hoc* convention our basic 'policy' is, in short:

> When conventional textbooks require reaction freezing, interpret chemical coordinates '$\boldsymbol{N}$' as materials coordinates $\boldsymbol{N}$. Otherwise, interpret '$\boldsymbol{N}$' as chemical composition coordinates $\tilde{\boldsymbol{N}}$.

In more detail (see examples already discussed in **25.2**):

(I) For a closed system, if some process (changing the ordinary thermodynamic coordinates or joining systems) is considered, all the 'chemical coordinates' must be $\boldsymbol{N}$ (so that they are additive independent variables).

(II) For a closed system after all the processes in (I) are completed, compute its equilibrium chemical compositions $\tilde{\boldsymbol{N}}^*$ (as illustrated in **25.2** (1)). Then, update its material coordinates to agree with $\tilde{\boldsymbol{N}}^*$.

(III) When chemicals are added (by $\Delta\boldsymbol{N}$), the materials coordinates are revised as

$\boldsymbol{N} \to \boldsymbol{N} + \Delta\boldsymbol{N}$. Then, update the materials coordinates by obtaining the new chemical compositions as in (II).

25.7 The algebraic expression of chemical reactions

If chemicals A, B, C, $\cdots$ react to produce chemicals Z, Y, X, $\cdots$, the corresponding chemical changes or chemical reaction is represented by

$$a\ \mathrm{A} + b\ \mathrm{B} + c\ \mathrm{C} + \cdots \longrightarrow z\ \mathrm{Z} + y\ \mathrm{Y} + x\ \mathrm{X} + \cdots. \tag{$*$}$$

Here, lower case letters are positive integers (usually) and are called stoichiometric coefficients.[440] Notice, however, that the above expression need not express the actually occurring reactions, but can be a summary of various reactions in parallel or a summary of a sequence of several reactions. Needless to say, the chemical reaction in a system need not be a single reaction.

In the above expression, the left-hand side is called the *original* or *reactant system* and the right-hand side is called the *product system*.

In thermodynamics it is convenient to write the above formula algebraically as

$$\sum_i \nu_i \mathrm{C}_i = 0. \tag{25.6}$$

Here, ν_i is called the *generalized stoichiometric coefficient* for chemical C_i (e.g., $-b$ for B, x for X in ($*$)). The sign convention is: It is negative for the reactant (or the original) system and positive for the product system.

Many reactions can occur simultaneously in the system, so each reaction is distinguished with a superfix b, and (25.6) is more generally expressed as

$$\sum_i \nu_i^b \mathrm{C}_i = 0. \tag{25.7}$$

25.8 The extent of chemical reaction

Suppose in (25.6) the reaction proceeds to the right in a closed system and the moles of chemical C_i (moles as the chemical composition variables in the system) changes by $\delta\tilde{N}_i$. This quantity and ν_i are proportional for all i and has the same sign. Therefore, we introduce the *extent of chemical reaction* ξ through the following

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[440] Such expressions are enough for the usual chemistry and biochemistry, but for, e.g., geochemistry, many so-called nonstoichiometric compounds show up, so the coefficients need not be integers.

differential form:

$$d\xi = \frac{d\tilde{N}_i}{\nu_i}. \tag{25.8}$$

If there are many chemical reactions in the system, the extent of the chemical reaction for each reaction will be distinguished with a superscript as ξ^b, and we get

$$d\tilde{N}_i = \sum_b \nu_i^b d\xi^b. \tag{25.9}$$

Here, the reactions need not be 'independent.'[441]

25.9 What process does the chemical reaction formula express?

It is not entirely clear what (25.6) or (∗) of **25.7** actually represent as physical processes. If it only describes the chemical equilibrium relation, then the chemical potentials of the chemicals appearing on the both sides are determined by the equilibrium mixture. However, for example, according to Kirkwood-Oppenheim's *Chemical Thermodynamics* the reaction consists of the following three stages:

(a) Pure reactants are mixed under given T, P.

(b) Chemical reactions are allowed to proceed.

(c) Pure products are separated from the product mixture.

According to Kirkwood and Oppenheim a reaction implies the totality of (a) - (c). Kirkwood and Oppenheim state that for gas phase reactions (b) overwhelms, but in liquids mixing heats cannot be ignored, so corrections are required.

25.10 van't Hoff's equilibrium box

An apparatus to observe a chemical equilibrium maintained by reaction (∗) of **25.7** (that is, the stage (b) of **25.9**) is proposed by van't Hoff (*van't Hoff's reaction box*). From the cylinders containing pure chemicals A, B, $\cdots$, Y, Z with selectively permeable membranes corresponding to them is constructed an apparatus illustrated in Fig. 25.2. Here, each piston is regulated to change each chemical i by $-\nu_i d\xi$ according to (25.8).

The mixture in the big box, that is kept at conant T and P in the present case, is an equilibrium mixture, so the reactions proceed reversibly and quasistatically (→**25.17**).

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[441] The independence of reactions is just the linear independence of the chemical reactions expressed as (25.6) regarding C_i to be the basis vectors of a vector space.

Figure 25.2: Van't Hoff's reaction box

With this device it is in principle possible to realize (a)-(c) in **25.9**. The point is that the device allows us to observe or determine the chemical potential change $\Delta\mu_i$ for chemical i in the equilibrium mixture and that in its standard state in terms of the work we do with the piston; in principle, we take a chemical in its standard state and adjust its temperature equal to that of the reaction box, and then change P so that its chemical potential is identical to that in in the box. Therefore, in principle, equilibrium thermodynamic experiments can be performed for any chemical reaction. That is, (a), (b) and (c) in **25.9** can be realized reversibly and quasistatically.
Remark To perform equilibrium thermodynamic experiments some textbooks propose the use of 'negative catalysts' to slow down reactions. A catalyst is a compound whose presence of negligible amount can change the reaction rates. This idea works to accelerate a reaction that hardly proceeds spontaneously. Here, however, we must kill the reactions that easily proceed spontaneously, so any effective negative catalyst must stoichiometrically block reacting chemicals. This is hardly realizable without changing the reaction mixture; to behead all at once, you need a lot of swards. Thus, negative catalysts should not be relied on as a means to regulate the reaction speed in thermodynamics.[442],[443]

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[442] Even when a positive catalyst makes impossible reactions proceed, the realized reactions may proceed very often irreversibly (like a gas leak from a pinhole). Thus, even if the reaction is slow, we cannot apply thermodynamics.

[443] W. Pauli's last paper is about avoiding negative catalysts, which he says too arbitrary, for $I_2 \longleftrightarrow 2I$ with the aid of an external magnetic field: Zur Thermodynamik dissoziierter Gleichgewichtsgemische in äusseren Kraftfeldern [On the thermodynamics of equilibrium mixtures of dissociated in external force fields], Z. angew. Math. Phys., **9b**, 490 (1958).

25.11 The case of inseparable equilibrium mixture

This unit is basically a repetition of **16.5** restated in the present context.

In **25.10** it is assumed that chemicals in the cylinders are pure chemicals. Unfortunately, not all the chemicals may be isolated as pure chemicals, but best at only as equilibrium mixtures. The cases of intrinsically accompanying compounds are examples (→**4.7**), but they are benign cases. A famous example often mentioned in the textbooks is

$$N_2O_4 \longleftrightarrow 2\ NO_2.$$

In this example, neither chemical can be isolated. Thus, we cannot even approximately use van't Hoff's reaction box with pure ingredients. However, we do not need such a special example. How can we handle the following reaction with the reaction box:

$$A + B \longleftrightarrow C\ ?$$

In this case it is generally impossible to have pure C in the cylinder in equilibrium. If C does not decompose into A and B spontaneously, then we may avoid this difficulty. However, if the decomposition reaction can proceed at a non-negligible rate,[444] as an experimentalist who wishes to add a particular amount of C to the system, she would take a mixture of A, B and C in equilibrium with the stoichiometry consistent with the pure C. The cylinder containing this mixture is attached to the reaction box with a selective membrane for C. We do not care about what happens at this membrane; it may allow only C or allow A+B to pass through stoichiometrically consistent to C. This detail does not matter because we express the amount of C added to the system quantitatively in terms of a materials coordinate for C, which may not necessarily agree with the actual amount of C. This is an advantage of the materials coordinates over the chemical component variables.

In conclusion, if a chemical cannot be isolated due to reactions, we add a stoichiometric amount of chemicals to the cylinder attached to the reaction box, consistent with the chemical.

25.12 Gibbs energy change due to chemical reactions

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[444] The usual approach in such cases is to use a negative catalyst (poison). However, as already seen in Remark of **25.10**, this is hardly admissible, since a stoichiometric poison to keep all C at once is needed, so the composition is not at all pure C.

In the reaction (25.6) if the extent of reaction changes by $\delta\xi$, the free energy change due to this reaction is written as

$$\delta G = \sum \mu_i \delta \tilde{N}_i = \delta\xi \left(\sum \nu_i \mu_i \right). \tag{25.10}$$

From this we see that the Gibbs energy change ΔG for a unit amount of this reaction (usually, 1 mole change for a chemical with $|\nu_i| = 1$) is given by[445]

$$\Delta G = \sum \nu_i \mu_i. \tag{25.11}$$

To obtain this change we must measure the chemical potential. We can measure only $\Delta\mu_i$ appearing in **25.10**, which may be written as

$$\Delta\mu_i = \mu_i^* - \mu_i^{\ominus} \tag{25.12}$$

where * implies the state in the van't Hoff equilibrium mixture, and $^{\ominus}$ implies the standard state. Since the mixture is in chemical equilibrium (minimizing G: $\Delta G = 0$, →**19.9**),

$$\sum_i \nu_i \mu_i^* = 0. \tag{25.13}$$

Consequently, in terms of the measurable chemical potentials, we obtain

$$\sum_i \nu_i \Delta\mu_i = \sum_i \nu_i \mu_i^{\ominus} \equiv \Delta G^{\ominus}, \tag{25.14}$$

where $\Delta G^{\ominus}$ is the difference between the reactant and product systems in the standard states. This quantity may characterize the reaction. See the units culminating in **25.21** for how to obtain $\Delta G^{\ominus}$.

25.13 Reaction free energy (Gibbs energy)

Following **25.12**, we can measure the free energy (Gibbs energy) change due to a chemical reaction converting a collection of reactants with specified states into a collection of products with specified states. Here, 'specified states' means that the chemical potentials for all the pure chemicals of the reactant and product sets are

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[445] Thermodynamics deals only with equilibrium states, so one can consider only chemical equilibrium. The reader might wonder how a non-zero $\delta\xi$ is possible in a given equilibrium state. To be precise, this is the result of a thermodynamic variation (→**12.10**) here.

given as $\{\mu_i\}$. Then, the free energy change due to the reaction is given, just as (25.14), by

$$\Delta G = \sum \nu_i \mu_i. \tag{25.15}$$

Notice that this is the Gibbs energy change due to a quasistatic and reversible reaction.

Whether a reaction is thermodynamically permissible or not can be seen from the stability of the system. If T, P are constant, and if there is no other work than volume work (i.e., the usual case), according to the free energy minimization principle (→**19.7**) if $\Delta G > 0$ the reaction does not proceed (however, see **25.14**). If $\Delta G < 0$, thermodynamics does not object the advancement of the reaction to the right (that is, from the original or reactant system to the product system). However, whether the reaction actually happens or not is a separate issue (see **12.6**).

Remark Notice that the usual thermodynamics textbooks do not explicitly state the second law applicable to chemical reactions, and since the chemical components are used to describe the amounts of chemicals, it is hardly possible to justify the free energy minimization principle for chemical reactions in the existing textbooks.

25.14 Combinations making impossible possible

The essence of application of thermodynamics is to make a possible process through combining/coupling thermodynamically impossible processes and possible processes. For chemical reactions a reaction with $\Delta G \ll 0$ and one with $\Delta G > 0$ may be coupled to advance the reaction with $\Delta G > 0$. Many biochemical reactions are such examples of this, and the wonders of biology are often realized by such couplings.[446]

As mentioned several times before, even if thermodynamics tells us that some reaction is 'very likely to occur (e.g., due to large negative ΔG),' the relevant rate processes have nothing to do with thermodynamics. Consequently, to realize such a reaction requires a great deal of ingenuity, trial and error or evolution processes.

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[446] The origin of life itself is thought to be such an example. For example, just as we have demonstrated, a geochemically natural process coupled with reduction of carbon dioxide, which was impossible on the Hadean Earth, enables production of organic compounds [N. Kitadai et al., Metals likely promoted protometabolism in early ocean alkaline hydrothermal systems, Sci Adv 5 7848 (2020); Thioester synthesis through geoelectrochemical CO_2 fixation on Ni sulfide, Commun. Chem. **4**, 37 (2021)]. As seen in these papers, even electrochemical coupling, that should be far easier than the usual organic reaction coupling, requires special electrodes for the stage of chemical reactions. That is, even energetically possible coupling is hard to realize.

25.15 The expression of chemical potentials

The chemical potential of chemical i with the partial pressure P_i in an ideal gas mixture is given by

$$\mu_i = \mu_i^\ominus + RT \log P_i. \tag{25.16}$$

Here, $\mu_i^\ominus$ is its chemical potential in the standard state (→**17.9**, **17.10**). For a general real gas, *fugacity* f is defined to preserve the shape of the formula (25.16) as much as possible to write

$$\mu_i = \mu_i^\ominus + RT \log f_i. \tag{25.17}$$

Needless to say, the fugacity must be determined empirically.

For an ideal liquid mixture the chemical potential of its component i with the molar fraction x_i is given by[447]

$$\mu_i = \mu_i^\ominus + RT \log x_i. \tag{25.18}$$

If the mixture is not ideal, the *activity* a_i is defined to replace the molar fraction to maintain the functional form of (25.18) as

$$\mu_i = \mu_i^\ominus + RT \log a_i. \tag{25.19}$$

Again the activity a_i must be empirically obtained.

Important Remark as to the use of chemical potentials

Mathematically, a chemical potential μ is a function of T, P and $\boldsymbol{N}$ (in this section). However, there are many choices for $\boldsymbol{N}$. When its expressions as (25.16)-(25.19) are used, the amount of chemicals are all in terms of $\tilde{\boldsymbol{N}}$ (precisely speaking, $\boldsymbol{N}$ chosen to be numerically identical to $\tilde{\boldsymbol{N}}$), the actual amount extant in the system at present. See, for example, an example of actual calculations in **25.26**.

25.16 Chemical substances with zero concentration

For the reaction A+B $\longrightarrow$ C, if the concentration of C is zero or very close to zero, its chemical potential would be well approximated by the ideal solution formula (→**19.12**), so its chemical potential has an extremely large negative value. This suggests that the generalized work we can obtain (→**19.6**) from such a reaction could be very large; think of a potential energy difference in the ordinary mechanics. However, this never occurs in practice. Why not?

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[447] There are different choices for the standard state (→**25.18**), here, the pure state (i.e., $x_i = 1$) is chosen as the standard state.

This highlights the distinction between the ordinary work coordinates and the chemical components. In contrast to most work coordinates, the change of chemical components tend to deviate considerably from equilibrium as soon as the changing rate becomes non-zero. For the case of zero concentration chemicals, if we can wait sufficiently (i.e., if we can slow down the process sufficiently) considerably large amount of generalized work could be produced.

25.17 Chemical reactions have equilibrium states: thermodynamic understanding

As shown in (25.11), when P and T are held constant, the chemical equilibrium condition in a closed system is (as already noted in **25.12**)

$$\sum \nu_i \mu_i = 0. \tag{25.20}$$

The sum on the left-hand side can be made as large as possible by reducing the concentrations of some chemicals in the reactant system. Instead, we can make the sum as small as possible by reducing the concentrations of some chemicals in the product system. The sum changes continuously, so we can always find a condition to satisfy the equilibrium condition (25.20). That is, for any reaction there is a chemical equilibrium. This means that thermodynamics and the elementary chemistry is consistent (→**4.3** II).

25.18 Prescription of standards

To use chemical potentials we need the quantities with $^\ominus$ such as $H^\ominus$ and $S^\ominus$, that is, the thermodynamic quantities for various chemicals in their standard states.

The standard enthalpy (of combustion, reaction, etc.) $H^\ominus$ is prescribed by stating that the standard enthalpy of formation is

$$\Delta H_{\rm f}^\ominus = 0 \tag{25.21}$$

for every element in the stable state (at $T = 298.15$ K). Likewise, the standard entropy of formation is prescribed as

$$\Delta S_{\rm f}^\ominus = 0 \tag{25.22}$$

for every element in the stable state in the $T \to 0$ K limit (→**24.5**). Then,

$$G^\ominus = H^\ominus - TS^\ominus. \tag{25.23}$$

$H(T) - H^{\ominus}$ or $S(T) - S^{\ominus}$ can be calorimetrically determined (→**25.19**, **25.20**), where $X^{\ominus}$ are obtained from the standard X of formation.

The standard values are tabulated, so we must know how tables are constructed.

25.19 How to determine the standard enthalpies of formation[448]

For $H^{\ominus}$, first choose reactions for which H can be directly measured. From their ΔH the standard change $\Delta H^{\ominus}$ can be obtained. To this end we use Hess's law and Kirchhoff's relations (Fig. 25.3).

Since H is a state function, ΔH for successive processes at the same T is additive

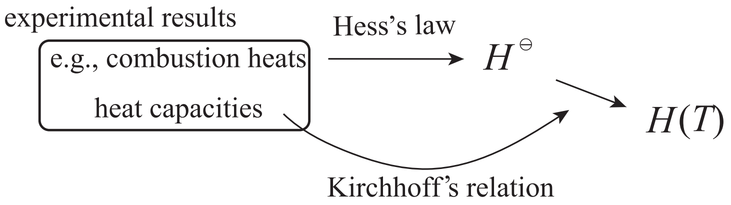

Figure 25.3: How to obtain the standard enthalpy from measurable quantities: summary

(*Hess's law*). For example, the following reaction heats are measurable:

$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \to \mathrm{CO_2(g)} \qquad -\Delta H = 393.5\ \mathrm{kJ}, \tag{25.24}$$

$$\mathrm{CO(g)} + (1/2)\mathrm{O_2(g)} \to \mathrm{CO_2(g)} \qquad -\Delta H = 283.0\ \mathrm{kJ}. \tag{25.25}$$

Subtracting the second formula from the first one, we can obtain

$$\mathrm{C(graphite)} + (1/2)\mathrm{O_2(g)} \to \mathrm{CO(g)} \qquad -\Delta H = 110.5\ \mathrm{kJ}. \tag{25.26}$$

Enthalpies of formation can be obtained from enthalpies of combustion like the above reactions (although there is a danger of cancellation of significant digits). For example, from the following combustion reactions

$$\mathrm{CH_4(g)} + 2\mathrm{O_2(g)} \to \mathrm{CO_2(g)} + 2\mathrm{H_2O(l)} \qquad -\Delta H = 890.3\ \mathrm{kJ}, \tag{25.27}$$

$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \to \mathrm{CO_2(g)} \qquad -\Delta H = 393.5\ \mathrm{kJ}, \tag{25.28}$$

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \to \mathrm{H_2O(l)} \qquad -\Delta H = 571.6\ \mathrm{kJ}, \tag{25.29}$$

we obtain

$$\mathrm{C(graphite)} + \mathrm{H_2(g)} \to \mathrm{CH_4(g)} \qquad -\Delta H = 74.8\ \mathrm{kJ}. \tag{25.30}$$

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[448] The examples are taken from Guggenheim p242.

If we can convert this value to the one at 298.15 K, we can obtain the standard enthalpy of formation $\Delta H_{\mathrm{f}}^{\ominus}$ of methane.

Thus, we need the values of ΔH at different temperatures. For a reaction $\sum \nu_i \mathrm{C}_i = 0$, we have

$$\Delta H(T) - \Delta H(T') = \sum_i \nu_i H_i(T) - \sum_i \nu_i H_i(T') = \sum_i \nu_i [H_i(T) - H_i(T')], \quad (25.31)$$

where $H_i(T)$ is the enthalpy of chemical i at temperature T. Therefore,

$$\frac{d\Delta H}{dT} = \sum_i \nu_i \frac{dH_i}{dT} + \sum_i \nu_i C_i, \quad (25.32)$$

where C_i is the specific heat of chemical i that is measurable. This is called *Kirchhoff's relation*. Integrating this relation, we can obtain $\Delta H(298.15)$.

25.20 How to determine the standard entropies

To obtain the standard entropy $S^{\ominus}$, we need

$$S^{\ominus}(\mathrm{crystal}, T \to 0) = R \log \sigma, \quad (25.33)$$

and consequently we write

$$S^{\ominus}(298.15\ \mathrm{K}) = \{S^{\ominus}(298.15\ \mathrm{K}) - S^{\ominus}(\mathrm{crystal}, T \to 0)\} + R \log \sigma. \quad (25.34)$$

We must know the value of σ. There are three cases:
(1) For a few simple substances (about 30 species) the caloric entropy, which is the value in the curly brackets in (25.34) and the spectroscopic entropy (the actual value) agree, so $\sigma = 1$.
(2) For some simple substances such as CO, N_2O, NO, H_2O σ is measured. For example, for the substance mentioned here, in this order, $\sigma = 2$, $\sigma = 2$, $\sqrt{2}$ and $3/2$. These values can be understood in terms of crystal metastability.
(3) For all other substances σ is not experimentally determined; they are assumed to be $\sigma = 1$ (recall the third law, e.g., **24.5**).

To calculate the difference in { } in (25.34), we must take all the phase transitions into account.

25.21 The standard Gibbs energy of formation for compounds

From the standard enthalpy $\Delta H_{\mathrm{f}}^{\ominus}$ and entropy $\Delta S_{\mathrm{f}}^{\ominus}$ of formation we can compute the standard Gibbs energy of formation as

$$\Delta G_{\mathrm{f}}^{\ominus} = \Delta H_{\mathrm{f}}^{\ominus} - 298.15\Delta S_{\mathrm{f}}^{\ominus} \tag{25.35}$$

It is the value at 25 °C under 1 atm.

In biochemistry, the biochemical standard Gibbs energy $\Delta G^{\ominus\prime}$ is used. It is similarly defined as $\Delta G_{\mathrm{f}}^{\ominus}$, but the chemicals are in a dilute aqueous solution at pH 7 in which the activities of water and H^+ are both defined as unity.[449]

25.22 How to obtain chemical composition variables from materials coordinates

The chemical equilibrium condition is

$$\sum_i \nu_i \mu_i(T, P, \boldsymbol{N}) = 0. \tag{25.36}$$

If the equilibrium chemical composition is $\tilde{\boldsymbol{N}}^e$, then we can choose the materials coordinates as $\boldsymbol{N} = \tilde{\boldsymbol{N}}^e$:

$$\sum_i \nu_i \mu_i(T, P, \tilde{\boldsymbol{N}}^e) = 0. \tag{25.37}$$

However, generally, we do not know $\tilde{\boldsymbol{N}}^e$ for a given $\boldsymbol{N}$ when the system is closed (or prepared). Therefore, we must be able to obtain $\tilde{\boldsymbol{N}}^e$ from $\boldsymbol{N}$ and (25.36). Notice that there must be the extent of reaction ξ such that

$$\tilde{\boldsymbol{N}}^e = \boldsymbol{N} + \boldsymbol{\nu}\xi, \tag{25.38}$$

where $\boldsymbol{\nu} = (\nu_1, \nu_2, \cdots)$ (→**25.5**).[450] Since μ_i are expressed in terms of $\tilde{\boldsymbol{N}}^e$, we must find ξ such that

$$\sum_i \nu_i \mu_i \left(T, P, \boldsymbol{N} + \boldsymbol{\nu}\xi\right) = 0. \tag{25.39}$$

Here, $\boldsymbol{N}$ is the system materials coordinates (e.g., the amount of chemicals actually used for the construction of the system). Due to the convexity of G with respect to $\boldsymbol{N}$, (25.39) has a unique solution for ξ.[451] Thus, we can obtain $\tilde{\boldsymbol{N}}^e$ from (25.38).

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[449] See, e.g., Chapter 3 of Voet, Donald; Voet, Judith G. *Biochemistry*, 4th Edition (Wiley).

[450] We will not consider non-stoichiometric compounds (→**4.3**) for simplicity.

[451] Precisely speaking, the extremal set need not be a point, but must be a convex set. This means that the resultant equilibrium states can continuously change. Such an example must be extremely rare, if known at all.

25.23 Equilibrium condition for a chemical reaction: the law of mass action

The equilibrium condition[452] for the reaction (25.6) is given by

$$0 = \sum \nu_i \mu_i = \sum_i \nu_i \left[\mu_i^{\ominus} + RT \log a_i\right]. \tag{25.40}$$

This formula can be rewritten as

$$-\Delta G^{\ominus} \equiv -\sum_i \nu_i \mu_i^{\ominus}(T, P) = RT \log \left(\prod_i a_i^{\nu_i}\right). \tag{25.41}$$

The middle expression in the above does not depend on the system composition, so we may define the *chemical equilibrium constant* dependent only on T and P as

$$K(T, P) = e^{-\Delta G^{\ominus}/RT} = \frac{\cdots a_p^{\nu_p} \cdots}{\cdots a_r^{-\nu_r} \cdots}. \tag{25.42}$$

Here, the chemicals appearing the numerator of the right-hand side are all chemical in the original/reactant system and those on the denominator are chemicals of the product system. (25.42) is called the *law of mass action*. All the exponents are positive.

A large K implies that the reaction shifts to the product system (to the right). The following expression is intuitive and useful:

$$-\Delta G^{\ominus} = RT \log K. \tag{25.43}$$

As seen from this $-\Delta G^{\ominus}$ is chemically very useful (see electromotive force in electrochemistry **26.24**), so, generally, $-\Delta G$ due to chemical reactions is called chemical *affinity*.

It is claimed that "the equilibrium constants can be computed, in principle, statistical-mechanically," but, except for the reactions among ideal gas species, the computation of needed chemical potentials is almost impossible, so especially for interesting reactions theoretical calculations are useless.

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[452] We assume that the system is closed. In some cases we may use chemostats, but then we must pay extra care not to realize nonequilibrium steady states. It is therefore wise to impose closedness conditions.

25.24 Changes in equilibrium condition: Le Chatelier's principle

If we differentiate the chemical equilibrium constant with T, we can get the standard reaction heat, i.e., the enthalpy change $\Delta H^\ominus$ due to the reaction. Due to the Gibbs-Helmholtz relation (or its Gibbs energy version (19.7)) we have

$$\left(\frac{\partial \log K}{\partial T}\right)_{P,\boldsymbol{N}} = \frac{\Delta H^\ominus}{RT^2}. \tag{25.44}$$

$\Delta H^\ominus$ is the enthalpy change in the standard state. The formula is called *van't Hoff's formula*.

Similarly, we can obtain

$$\left(\frac{\partial \log K}{\partial P}\right)_{T,\boldsymbol{N}} = -\frac{\Delta V^\ominus}{RT}. \tag{25.45}$$

Here, $\Delta V^\ominus$ is the volume change due to the reaction in the standard state. Notice that Δ in chemical reactions always denote (sum for the product system) − (sum for the original/reactant system).

(25.44) implies that if the reaction is exothermic, i.e., if $\Delta H^\ominus < 0$, then the equilibrium can be shifted to the direction producing less heat by increasing the system temperature (that is, K is reduced, so the rightward advance of the reaction becomes harder). This is an example of Le Chatelier's principle (→**22.8**) that the response of the system occurs in the direction to reduce the effect of external perturbations. (25.45) is also such an example. Needless to say, they show that our ambient world is stable.

25.25 Le Chatelier's principle in terms of extent of reaction

Let us study how the extent of reaction ξ changes if, for example, T is changed under chemical equilibrium condition. There are two key points:

(1) the original (unperturbed) equilibrium chemical composition may be described in terms of materials coordinates whose values agree with the corresponding equilibrium chemical composition $\tilde{\boldsymbol{N}}^e$.

(2) the chemical composition change due to chemical reaction in the closed system may also be realized without reaction but by the (algebraic) addition of chemicals

$\delta \boldsymbol{N} = \{\nu_i d\xi\}$ from outside.[453]

The chemical equilibrium condition is given by $\sum \nu_i \mu_i = 0$ (→**19.9**). Therefore, after changing T and P, we must have

$$\sum_i \nu_i \mu_i(T + \delta T, P + \delta P, \xi + \delta\xi) = 0. \tag{25.46}$$

Noting that

$$\left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,P} = \sum_j \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,N_j^c} \left(\frac{\partial N_j}{\partial \xi}\right)_{T,P} = \sum_j \nu_j \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P,N_j^c}, \tag{25.47}$$

we can Taylor expand (25.46) as

$$\sum_i \nu_i \left(-s_i \delta T + v_i \delta P + \sum_j \nu_j \mu_{i,j} d\xi\right) = 0, \tag{25.48}$$

where partial derivatives are given by

$$-s_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,\boldsymbol{N}}, \quad \mu_{i,j} = \left(\frac{\partial \mu_i}{\partial N_j}\right)_{T,P.N_j^c}. \tag{25.49}$$

Therefore, we have

$$\sum_i \nu_i(-s_i)\delta T + \sum_i \nu_i v_i \delta P + \sum_{i,j} \nu_i \nu_j \mu_{i,j} \delta\xi = 0, \tag{25.50}$$

From this, $\Delta S = \sum \nu_i s_i$ is the entropy change for the unit chemical reaction extent, so, for example, under constant P we get

$$\left(\frac{\partial \xi}{\partial T}\right)_P = \frac{\Delta S}{\sum \nu_i \nu_i \mu_{i,j}}. \tag{25.51}$$

Since $\mu_{i,j}$ is positive definite due to the convexity of G as a function of $\boldsymbol{N}$, and $\Delta S = Q/T$ for an imported heat Q, an exothermic reaction ($Q < 0$ or $\Delta S < 0$) moves 'backward' when the temperature is increased. This may be a better expression of le Chatelier's principle (25.44).

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[453] Needless to say, there is no net import of materials. That is, if we wish, we may describe the system without changing the materials coordinates after the change $\delta \boldsymbol{N} = \{\nu_i d\xi\}$.

25.26 Shift of chemical equilibrium due to added chemicals

For a closed system, the equilibrium shift is possible only by changing T, P or ordinary thermodynamic coordinates other than E and V. This can be understood through appropriate generalization of **25.25**.

Now, let us assume that the system is not closed, and materials coordinates are changed by $\delta\boldsymbol{N}$ under constant T and P. The equilibrium condition must be

$$\sum_i \nu_i \mu_i(T, P, \tilde{\boldsymbol{N}}^e + \delta\boldsymbol{N}) = 0. \tag{25.52}$$

Here, the partial derivative is evaluated at $\boldsymbol{N} = \tilde{\boldsymbol{N}}^e$; we assume that the system is in equilibrium before perturbation, so its materials coordinates may be chosen as $\boldsymbol{N} = \tilde{\boldsymbol{N}}^e$. The resultant equilibrium state can be obtained as discussed in **25.22**. The point is that all the chemical potentials are expressed in terms of the values of chemical composition $\tilde{\boldsymbol{N}}$. The key point is that the variables we use are materials coordinates $\boldsymbol{N}$, but their values are given by the current chemical composition (→Important Remark in **25.15**):

$$\sum_i \nu_i \mu_i \left(T, P, \tilde{\boldsymbol{N}}^e + \delta\boldsymbol{N} + \boldsymbol{\nu}\delta\xi\right) = 0. \tag{25.53}$$

In terms of components, we can rewrite this, after expansion, as

$$\sum_{ij} \nu_i \mu_{i,j}(\delta N_j + \nu_j \delta\xi) = 0. \tag{25.54}$$

For example, if we change only N_1, we get

$$\sum_i \nu_i \mu_{i,1} \delta N_1 = -\sum_{ij} \nu_i \nu_j \mu_{i,j} \delta\xi. \tag{25.55}$$

That is,

$$\left(\frac{\partial \xi}{\partial N_1}\right)_{T,P,N_1^c} = -\frac{\sum_i \nu_i \mu_{i,1}}{\sum_{ij} \nu_i \nu_j \mu_{i,j}}. \tag{25.56}$$

Here, the partial derivative is evaluated at $\boldsymbol{N} = \tilde{\boldsymbol{N}}^e$ under constant T and P while allowing all the chemical composition (chemical composition variables) to vary.[454]

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[454] Notice that all the materials coordinates other than N_1 are kept constant.

Since the system is stable, the denominator is positive. Maxwell's relation implies $\mu_{i,1} = \mu_{1,i}$, so the above formula implies[455]

$$\left(\frac{\partial \xi}{\partial N_1}\right)_{T,P,N_1^c} = -\frac{1}{\sum_{ij} \nu_i \nu_j \mu_{i,j}} \left(\frac{\partial \mu_1}{\partial \xi}\right)_{T,P}. \tag{25.57}$$

Therefore,

$$\left(\frac{\partial \xi}{\partial N_1}\right)_{T,P,N_1^c} \left(\frac{\partial \mu_1}{\partial \xi}\right)_{T,P} < 0 \tag{25.58}$$

That is, if its chemical potential is reduced when the reaction proceed to the right (toward the production side), then adding the chemical promotes the reaction. Usually, adding N_1 increases its chemical potential, so the reaction opposes this tendency. However, this is not always the case, dependent on the condition as noted just below.

When such an inequality as (25.58) is applied (more generally, when we consider le-Chatelier-principle-related relations are used), do not forget the conditions under which the relations are derived. Thus, for (25.58) do not forget that T and P are fixed.[456]

Consider the following gaseous reaction to form ammonia:

$$N_2 + 3\ H_2 \longrightarrow 2\ NH_3$$

To use (25.58), the system is under constant T and P. We wish to add nitrogen into the system and study which way the equilibrium of the above reaction shifts. Needless to say, the reaction does not occur appreciably without appropriate catalysts, so we assume an effective catalyst is always available. Assuming gases and the gas mixture are ideal, so the chemical potential of the components may be written as

$$\mu = \mu^{\ominus} + RT \log(Px), \tag{25.59}$$

where x is the mole fraction of the chemical. Therefore, the chemical potential for chemical $*$ reads in terms of mole numbers of the components N_* as

$$\mu_* = \mu_*^{\ominus} + RT \log \frac{PN_*}{N_{N_2} + N_{H_2} + N_{NH_3}} \tag{25.60}$$

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[455] Note that

$$\sum_i \nu_i \left(\frac{\partial}{\partial N_i} \mu_1\right)_{T,P,N_i^c} = \left(\frac{\partial \mu_1}{\partial \xi}\right)_{T,P}$$

[456] A good expository article may be found in Y. Yoshimura's homepage `http://khem2022.starfree.jp/index.htm`: "There is a counterexample for Le Chatelier's principle?". This site was introduced to the author by Prof. Y. Tanimura. The following example here is discussed by Yoshimura, but may be found in Chapter 17 of Prigogine and Defay, *Thermodynamique Chimique* (1944).

Therefore, the chemical potential of the nitrogen gas when the reaction proceeds by ξ as

$$\mu_{\mathrm{N}_2} = \mu^{\ominus}_{\mathrm{N}_2} + RT\log\left[P\frac{N_{\mathrm{N}_2}-\xi}{(N_{\mathrm{N}_2}-\xi)+(N_{\mathrm{H}_2}-3\xi)+(N_{\mathrm{NH}_3}+2\xi)}\right] \tag{25.61}$$

$$= \mu^{\ominus}_{\mathrm{N}_2} + RT\log\left[P\frac{N_{\mathrm{N}_2}-\xi}{N_{\mathrm{N}_2}+N_{\mathrm{H}_2}+N_{\mathrm{NH}_3}-2\xi}\right]. \tag{25.62}$$

Therefore, the derivative evaluated at $\xi = 0$ is given by

$$\left(\frac{\partial\mu_{\mathrm{N}_2}}{\partial\xi}\right)_{T,P} = RT\left[\frac{2}{N_{\mathrm{N}_2}+N_{\mathrm{H}_2}+N_{\mathrm{NH}_3}} - \frac{1}{N_{\mathrm{N}_2}}\right] = RT\frac{N_{\mathrm{N}_2}-N_{\mathrm{H}_2}-N_{\mathrm{NH}_3}}{(N_{\mathrm{N}_2}+N_{\mathrm{H}_2}+N_{\mathrm{NH}_3})N_{\mathrm{N}_2}} \tag{25.63}$$

It is immediately clear that the derivative can change its sign depending on the amount of nitrogen in the system.

If nitrogen is not sufficiently abundant, (25.63) is negative, so adding nitrogen increases ξ according to (25.58), shifting the reaction to the product side as expected naively. On the other hand, if nitrogen is abundant, then (25.63) is positive, so, apparently a naive understanding of le Chatelier's principle is violated. This is simply due to dilution effect due to excessive nitrogen.

25.27 The extant chemical thermodynamics is logically bankrupt

(1) To describe chemical reactions, we need extensive variables expressing the chemical constituents of the equilibrium system. They are regarded as kinds of work coordinates with respect to the second principle. That is, no compensation in the Clausius sense (→**A.11**) is required for the interconversion of chemical energy and mechanical energy as the founders of thermodynamics assumed according to the mechanical Weltanschauung represented by Helmholtz (→**A.17**). However, this is not a demonstration; we need clear empirical demonstration of this fact, but most textbooks cite no relevant facts.

(2) The fundamental reason for the thermodynamic variational principle is the principle of increasing entropy (→**12.5**), but to derive this we need the second law. However, since the chemical composition variables $\tilde{\boldsymbol{N}}$ (which are the traditional variables) are not independent from the ordinary work coordinates, Planck's principle (→**8.5**) cannot be formulated fully. Thus, it is highly questionable that we can demonstrate the existence of entropy. Perhaps, its existence might be demonstrated, but the principle of increasing entropy cannot be demonstrated. Thus, the entropy maximization principle (→**12.6**) cannot be formulated when chemical reactions occur.

(3) Since the chemical compositions $\tilde{\boldsymbol{N}}$ are not additive, for any reaction its extent of chemical reaction ξ is not an additive extensive variable.
(4) Thus, $-S$ does not satisfy Jensen's inequality if chemical reactions can happen, so S is not generally concave; the internal energy is not convex. Consequently, the internal energy minimization principle (→**13.10**) cannot be demonstrated, when chemical reactions can happen.
(5) More generally, convex analysis is not applicable to internal energy, if there are chemical reactions. Thus, it is questionable that Gibbs energy can be defined that satisfies the variational principle applicable to chemical equilibria.
(6) Therefore, the chemical equilibrium cannot be thermodynamically formulated by the free energy minimization principle.

26 Electrochemistry: Outline

26.1 Electrochemistry is of principle importance

Despite its importance of principle nature (→**A.16**, **4.3**, **17.3**) thermodynamics textbooks for physicists discussing electrochemistry seriously seem rare.[457] However, electrochemistry is the key for chemical reactions to be discussed thermodynamically (→**26.7**). Therefore, starting from its rudiments, elementary electrochemistry is summarized in this section.

As we have seen in **A.16** Faraday, Joule and other founders of thermodynamics already knew the Daniell cell (→**26.34**) and *electrolytes* (→**26.2**), substances that allow electric conduction upon making aqueous solutions.

26.2 Electrolytes and electrolytic dissociation

Faraday thought that the particles called 'ions' that carry electricity through electrolyte solutions were formed upon imposing an electric field, but Arrhenius[458] pro-

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[457] Note that there are no textbooks squarely emphasizing the fundamental importance of electrochemistry.

Consequently, for example, many textbooks either do not discuss electric cells at all or only provide a brief overview. As a result, Faraday's constant often goes unmentioned. From this perspective, Tasaki's book is a rare exception, while Callen's and Landsberg's books make no mention of electrochemistry.

Textbooks on thermodynamics that neglect electrochemistry suffer from a similar logical flaw as those that omit explanations of the Mayer-Joule principle (→**7.14**) or Joule's experiments. We require empirical justification for treating chemical variables (e.g., materials coordinates) in the same way as ordinary work coordinates, in order to fully integrate chemical thermodynamics within the broader field of thermodynamics. There appear to be no better empirical facts for this integration than those found in electrochemical processes.

[458] Svante Arrehenius (1859-1927) `https://en.wikipedia.org/wiki/Svante_Arrhenius`. "Arrhenius put forth 56 theses in his 1884 dissertation, most of which would still be accepted today unchanged or with minor modifications. The most important idea in the dissertation was his explanation of the fact that solid crystalline salts disassociate into paired charged particles when dissolved, for which he would win the 1903 Nobel Prize in Chemistry. Arrhenius's explanation was that in forming a solution, the salt disassociates into charged particles that Michael Faraday had given the name ions (after a suggestion by William Whewell (1794-1866); See Laura J. Snyder, *The Philosophical Breakfast Club: Four Remarkable Friends Who Transformed Science and Changed the World* (Crown, 2012)) many years earlier. Faraday's belief had been that ions were produced in the process of electrolysis, that is, an external direct current source of electricity was necessary to form ions. Arrhenius proposed that, even in the absence of an electric current, aqueous solutions of salts contained ions. He thus proposed that chemical reactions in solution were reactions between

posed in 1884 his theory of electrolyte dissociation: even in the absence of an electric current, aqueous solutions of salts contained ions.

In 1887 visiting van't Hoff in Amsterdam, Arrhenius realized that the coefficient i in van't Hoff's formula for the osmotic pressure (→**19.15**):[459]

$$\pi = icRT \tag{26.1}$$

is affected by dissociation, where c is the molarity of the solute.

Thus, in the electrolyte solution, electrolytic dissociation does occur, forming ions. However, not all the electrolytes dissociate into independent ions completely in the (e.g., aqueous) solutions. The electrolytes dissociating completely into ions are called *strong electrolytes*. Otherwise, they are called *weak electrolytes* (→**26.21**).

26.3 Faraday's law of electrolysis

In the Daniell cell (→**26.34**), zinc ions are generated from the zinc electrode as the zinc metal ionizes, leaving electrons within the metal. On the copper electrode, copper metal is deposited through the neutralization of copper cations, which involves the removal of electrons from the electrode. Consequently, in this electric cell, the zinc electrode generates electrons, becoming the negative electrode, while the copper electrode acts as a sink for electrons, becoming the positive electrode.

Fortunately, the reaction in this cell is reversible.[460] By applying a sufficiently large positive voltage to the copper electrode relative to the zinc electrode, we can drive the reaction in the opposite direction, causing zinc to be deposited on the zinc electrode. As we have previously observed in **A.16**, this allows Faraday and others

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ions.

The dissertation did not impress the professors at Uppsala, but Arrhenius sent it to a number of scientists in Europe who were developing the new science of physical chemistry, such as Clausius, Ostwald, and van't Hoff. They were far more impressed, and Ostwald even came to Uppsala to persuade Arrhenius to join his research team. Arrhenius declined, however, as he preferred to stay in Sweden-Norway for a while (his father was very ill and would die in 1885) and had received an appointment at Uppsala.

[459] However, according to Wikipedia van't Hoff (`https://en.wikipedia.org/wiki/Jacobus_Henricus_van_%27t_Hoff`) "He worked on Svante Arrhenius's theory of the dissociation of electrolytes and in 1889 provided physical justification for the Arrhenius equation".

[460] ⟪**Irreversible cells**⟫ There are so-called reversible and irreversible cells. However, the distinction is not thermodynamic, but pragmatic. All the cell reactions themselves are reversible in the sense that the backward reactions are also realizable, in principle. However, in practice, for example, inside a cell a metal may be oxidized into a noncrystal form that cannot easily be reduced into a continuous metal phase again.

to quantify the amount of electricity involved in a process by weighing the formed zinc metal.

The empirical work in this field culminated in *Faraday's Law of Electrolysis*:[461]
Faraday's First Law of Electrolysis: During electrolysis, the change $\Delta\xi$ in the extent of chemical reaction (→**25.8**) under the influence of electrical energy is directly proportional to the amount of electricity Q passed through the electrolyte.
Faraday's Second Law of Electrolysis: The amount of electricity Q is directly proportional to the mole number of ions deposited at the electrodes.

In a formula, if we measure $\Delta\xi$ in moles and Q in C (coulombs), then

$$\Delta\xi = \frac{Q}{F}, \tag{26.2}$$

where F is *Faraday's constant* ($= e \times N_A = 96485.3321$ C/mol; here, e is the elementary charge $1.60217663 \times 10^{-19}$ C, N_A is Avogadro's constat $6.02214076 \times 10^{23}$ mol^{-1}).

26.4 Electrochemical reactions to realize redox reactions

We have stated three principles of chemistry in **4.3**. Among them, (III) tells us that not only simple electrolytic reactions, as discussed in **26.3**, but also any chemical reaction can be realized as a redox reaction, in principle.

Recall that the gain of electrons is called *reduction*, and the loss of electrons is called *oxidation*. Therefore, any reaction can be realized, in principle, electrochemically through the exchange of electrons and reactions involving ions, because breaking a covalent bond can, in theory, produce ions.

For example, consider A + B $\longrightarrow$ C + D in which A is oxidized and B is reduced, resulting in C + D. We can explicitly represent this reaction as X-C + B $\longrightarrow$ X-B+ C, where A is actually X-C and D is actually X-B in detail (see Fig. 26.1). Here, one electron is removed from $^{\mathrm{e}}$X-C and transferred to B. In an ordinary synthesis perhaps its mechanism is as follows: in an intermediate complex $^{\mathrm{e}}$AB one electron localized on $^{\mathrm{e}}$X is extracted by B and this extraction severs X-C bond to transfer X to $^{\mathrm{e}}$B to make $^{\mathrm{e}}$B-X (= $^{\mathrm{e}}$D).

As a typical electrochemical reaction, perhaps this reaction might proceed with

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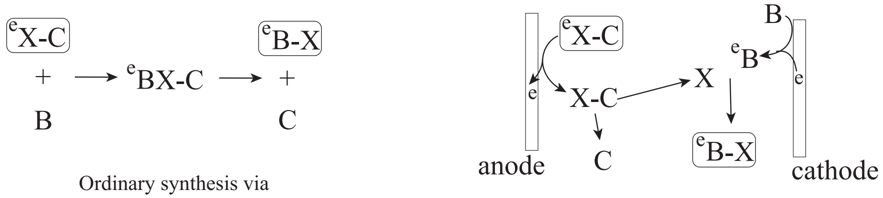
[461] The following statements are essentially the technical rewording of the statements found in US high school textbooks.



Ordinary synthesis via intermediate complex

Electrosynthesis

Figure 26.1: Ordinary synthesis vs electrosynthesis. 'e' denotes one electron. In ordinary synthesis, perhaps in the intermediate complex one electron is transferred from ^{e}X-C to B, leading to the destabilization of X-C and the subsequent ejection of C. In electrosynthesis, on the other hand, the anode (→**26.5**) removes one electron from ^{e}X-C, which is adsorbed onto the anode. This process results in the destabilization of X-C, leading to its decomposition. The resulting (usually positively charged) X moves toward the cathode (→**26.5**). At the cathode, B gains one electron, allowing it to react with X and eventually forming ^{e}B-X.

the following mechanism: the anode (→**26.5**) removes one electron from ^{e}X-C, which is adsorbed onto the anode. This process results in the destabilization of X-C, leading to its decomposition. The resulting (usually positively charged) X moves toward the cathode (→**26.5**). At the cathode, B gains one electron to become ^{e}B, allowing it to react with X and eventually forming ^{e}B-X.

A similar concrete example: $^{e}A \to A$, then $A + B \longrightarrow D$, ending up with ^{e}D, is given in Fig. 26.2.[462]

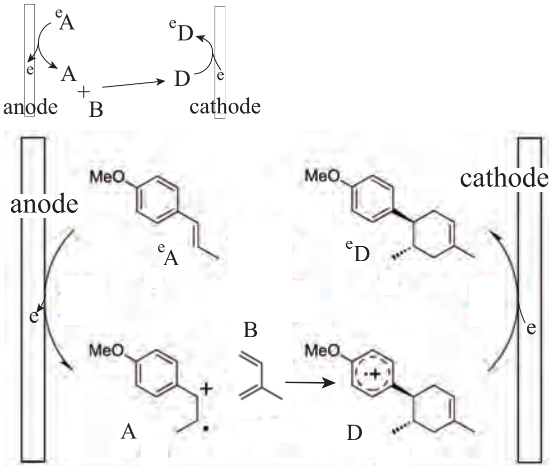


Figure 26.2: Example of electrosynthesis $^{e}A + B \longrightarrow {}^{e}D$. Based on Fig. 1 of Y. Imada, Y. Okada and K. Chiba, Investigating radical cation chain processes in the electrocatalytic Diels-Alder reaction, Beilstein J. Org. Chem., **14**, 642 (2018). A: *trans*-anethole, B: isoprene, and D is a Diels-Alder adduct. 1 V potential difference is used.

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[462] In this Diels-Alder example, the non-electrochemical ordinary reaction that is catalyzed by the electrodes also occurs parallelly, so there is no one to one correspondence between the yield of D and the consumed electricity.

26.5 Nomenclature of electrodes

In the electrochemical reaction we need two kinds of electrodes as we have seen in **26.4**. An electrode towards which cations move is referred to as a *cathode* and an electrode to which anions move toward is referred to as an *anode*.

As can be seen from Fig. 26.3, the electrode through which current flows into the system is the anode, and the electrode from which current flows out is the cathode.

For a cell its positive pole (the point from which current flows out) is the cathode. However, in an electrolytic process the pole where current is injected is termed the positive pole, even though it functions as an anode, as illustrated in Fig. 26.3 Right. The definitions of positive and negative poles are determined by the relative voltage of the electrodes, making them fundamentally different concepts from anodes and cathodes.

It is advisable to avoid using of "positive" and "negative" poles in the context of electrochemistry.[463] Use "anode" and "cathode."

26.6 Hydrogen fuel cell vs. electrolysis of water

As an illustration of the crucial relevance of electrochemistry to thermodynamics, let us look at the hydrogen fuel cell and its reverse operation: electrolysis of water (even Helmholtz discussed them →**A.17**).

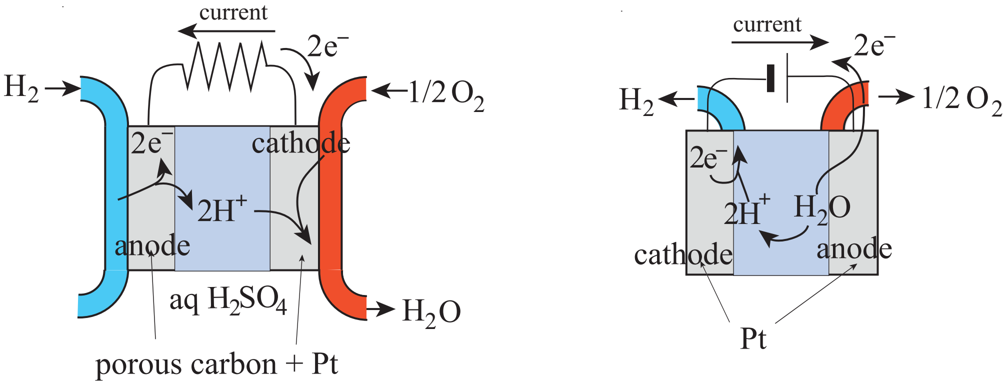

Figure 26.3: Left: A hydrogen fuel cell; Right: electrolysis of water

Fig. 26.3 Left: the hydrogen fuel cell; Right: electrolysis of water

Left: Hydrogen molecules adsorbed on the platinum electrode lose electrons and dissolve into the

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[463] In US high schools, the following mnemonics are taught: "RED CAT: REDuction always occurs at the CAThode." "AN OX: OXidation always occurs at the ANode."

aqueous solution as H_3O^+(depicted as H^+ in the figure). On the other electrode this ion gains an electron to produce a (perhaps) chemically active hydrogen species adsorbed on the platinum surface, which then reacts with oxygen to produce water. Since the equilibrium of the reaction $H_2 + (1/2)\ O_2 \longrightarrow H_2O$ is extremely shifted to the right, electrons can flow through the external circuit from the anode to the cathode (i.e., as long as the current can flow from the cathode to the anode outside the cell) until the chemical equilibrium is reached. This current can perform electrical work, but the process is not quasistatic.
Right: Electrolysis of water. If the current direction in Left is reversed by imposing an external voltage as shown here, the reaction $H_2 + (1/2)\ O_2 \longrightarrow H_2O$ may be reversed. By carefully controlling the external voltage, now the reaction may be realized quasistatically, so $-\Delta G = W$, the work we can obtain from the cell.

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \tag{26.3}$$

is highly skewed toward the product side under normal condition, making it inconceivable to envision an equilibrium gas mixture with a balanced composition of hydrogen, oxygen, and water vapor. If we construct a hydrogen fuel cell as illustrated in Fig. 26.3 Left with a large resistor attached as in the figure, we can reduce the reaction rate to our desired level. However, this is not a reversible quasistatic process; it is just like a gas leak from a pin hole (→**26.7**).

26.7 Thermodynamic significance of electrochemistry revisited

If we apply an external electric potential to reverse the direction of the current in Fig. 26.3 Left as illustrated in Fig. 26.3 Right, when the electric potential exceeds a threshold (in this case given by $|\Delta G|/2F$) we can drive (26.3) backward to the left. This is the electrolysis of water. In this case no current in the direction of the arrow in the Right figure is realized, since no reaction occurs with the electromotive force less than the threshold value (cf. **26.8**, (1) and (2)).

In the fuel cell with a sufficiently large resistor, the reaction rate can be reduced as much as the experimenter wishes. This process is, however slowed down, not a quasistatic process (→**6.4**), because we have not controlled the ΔG (which is $\ll 0$) of the reaction, so the process is analogous to the leak of heat from a good thermos or gas escaping from a pinhole of a high pressure canister; it is not a quasistatic process.

A crucial advantage of electrochemistry is that in Fig. 26.3 Right we can control the external voltage imposed between the electrodes. Thus, at the threshold when the current to the right in the external circuit is 0+, the reaction is indeed quasistatically realized. That is, we can actually achieve the chemical equilibrium under any pressures of hydrogen and oxygen gases, in principle.

Furthermore, the device allows a direct conversion of chemical energy into mechanical (or electrical) energy and vice versa quasistatically and reversibly (if the reaction is reversible as in this case). Thus, as has been stressed throughout this set of notes (see **A.16**, **A.18**, **17.3**) electrochemistry holds fundamental importance in thermodynamics.

26.8 The true picture of electrochemical systems[464]

Since we are studying equilibrium thermodynamics, we do not need to concern ourselves excessively with the specific events occurring at the electrodes. However, to dispel the previously held, entirely incorrect notion that the imposed electric field generates a current that drives ions to the electrodes where reactions take place, we will provide some additional details here.

As depicted in Fig. 26.2 two electrodes are immersed in the system: an anode, towards which negatively charged entities move, and a cathode, towards which positively charged entities migrate.

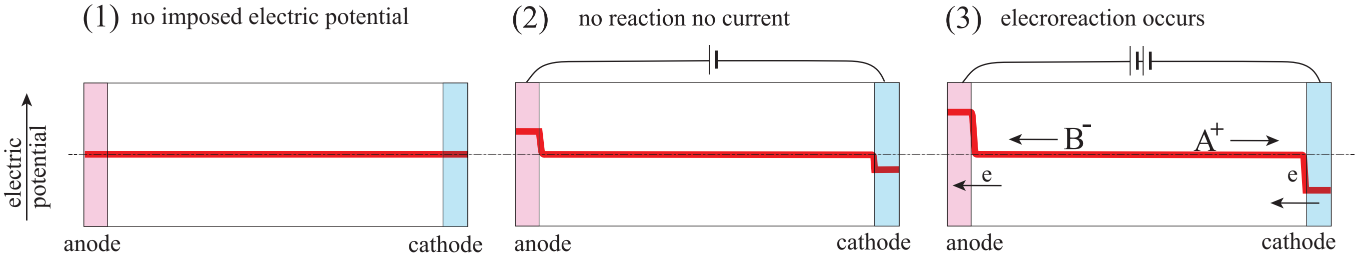

Figure 26.4: An electrochemical reaction cell with various imposed electric potentials: For (1)-(3) see the text. The white portions are filled with electrolyte solutions. The thick lines indicate the electric potential.

The most crucial observation to note is that neither a reaction nor current occurs if the applied electric potential difference between the anode and the cathode is not sufficiently large. This corresponds to (1)-(2) in Fig. 26.4. Essentially, what occurs

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[464] The exposition relies on an excellent textbook: T. Watanabe, K. Kanamura, H. Masuda and M. Watanabe, *Electrochemistry* (Maruzen, 2001).

in the system is the charging of the capacitors formed between the electrodes and the electrolytic solution, where the electric potential undergoes a rapid change as depicted in Fig. 26.4. While the solution contains ions, there is no systematic electric field in the bulk phase, causing the ions not to move and carry a current.

When the applied electric potential exceeds the redox potential (→**26.25**) as shown in (3) of Fig. 26.4, the electrochemical reaction begins to proceed, leading to a current flowing through the system. A gets oxidized near the anode and cations A^+ accumulate there. Similarly, B is reduced near the cathode and anions B^- accumulate there. These excess charges then begin to leave the electrodes, causing ions to move and carry a current, as indicated in (3) of Fig. 26.4. Note that between (2) and (3) at the threshold electric potential, the chemical reaction under examination is in equilibrium, allowing us to proceed with the reaction reversibly and quasi-statically.

Clearly recognize that a current flows through the system only if electrochemical reactions occur at the electrodes, not the other way around.

> Take an example: electrolysis of water. The old (wrong) explanation is that water is always slightly ionized as $H_2O \longrightarrow H^+ + OH^-$. H^+ moves to the cathode to get electrons and generates hydrogen gas: $2\,H^+ + 2\,e^- \longrightarrow H_2$. OH^- moves to the anode to lose electrons to produce oxygen gas: $2\,OH^- \longrightarrow (1/2)\,O_2 + H_2O + 2\,e^-$.
>
> However, in most electrochemical reactions reactants are *not* ions, but neutral molecules. In the present case under a sufficiently large voltage difference the main reactions are:
> At the cathode: $2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^-$,
> At the anode: $2\,H_2O \longrightarrow O_2 + 4\,H^+ + 2\,e^-$.
> Even in dilute solutions of sulfuric acid or sodium hydroxide these are dominant reactions.

In the above discussion, we mentioned the capacitors formed between the electrodes and the electrolytic solution. In reality, these are *electric double layers* with a thickness of approximately 1 nm. Thus, electrons can pass through the gap from the electrodes to the appropriate chemicals capable of accepting or donating electrons. It should be noted that an electric potential difference of approximately 1 V is applied across a gap of about 1 nm, resulting in an extremely strong electric field existing at these interfaces.

26.9 Effects of charge imbalance

Ions carry an electric charge, so their (free) energies must depend on the electric potential of the location of the ions. Furthermore, to utilize electrochemistry, a portion of the system must be maintained at a different electric potential. This means that there must be charge imbalance because of div$\boldsymbol{E} = \rho/\varepsilon$ (see (B.24)), where $\boldsymbol{E}$ is the electric field, ρ the charge density and ε the dielectric constant of the medium where ions are present.

The total charge equivalent to Avogadro's number of elementary charges is referred to as the *Faraday constant*: $F = N_A e = 0.96487 \times 10^5$ C/mol. If there is only 10^{-10} moles of charge imbalance on a 1 mm sphere, its electric potential is ~ 1 MV (in water), if we assume that the electric potential at infinity is 0.

This calculation implies that even a quantity of ions far too small to be detected chemically can produce an electrostatic potential which could be encountered only in high voltage laboratories.

26.10 Electroneutrality

The numerical example in **26.9** implies that even when there are voltage differences, bulk phases can contain extremely small amount of imbalanced charges (if any). That is, with an extremely high precision, bulk phases are charge neutral. Let z_i represent the charge of ionic species i (in terms of *elementary charge* $e = 1.60217663 \times 10^{-19}$ C) and its mole number be N_i. Then, in any bulk phase

$$\sum_i z_i N_i = 0 \tag{26.4}$$

holds extremely accurately.

26.11 Phases of identical composition and chemical potential[465]

As discussed in **26.9**, we can change the electric potential of a phase without modifying its composition to affect chemistry. For example, if the two spheres containing precisely 1 g of Cu differing in electric potential by 200 V. Then, this corresponds to about 2×10^{-14} g excess of Cu ion.

Hence, we are allowed to discuss phases with identical chemical compositions but maintained at different electrical potentials without paying any attention to the contribution of composition changes. The chemical potential must depend on the composition and its electrical state independently. In other words, if we change the electric potential of a closed system by $\Delta\phi$, the chemical potential of chemical i with

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[465] The exposition in this unit is almost solely relies on Guggenheim. In his book the vacuum dielectric constant is used. Thus, in water, the estimated amount of charge should be multiplied by 80. The conclusions are not different.

charge z_i changes by

$$\Delta\mu_i = z_i F \Delta\phi. \tag{26.5}$$

To emphasize this fact, the chemical potential of an ionic species is often referred to as its *electrochemical potential*.[466] It is essential to note, however, that this *is* the true chemical potential under the presence of electric potentials, as per the definition of chemical potentials **17.7**. There is only one chemical potential, even though it is traditionally called the electrochemical potential.

(26.5) implies that the chemical potential can generally be written as

$$\mu_i = \mu_i^{\ominus} + RT \log a_i + z_i F \phi. \tag{26.6}$$

Here, the first two terms correspond to the 'ordinary non-electrochemical' potential, so it is often the case that the (ordinary) chemical potential $\mu_i^{non} = \mu_i^{\ominus} + RT \log a_i$ plus the electric potential dependent term $z_i F\phi$ defines the electrochemical potential. However, as noted above, the true chemical potential, that is, thermodynamically meaningful chemical potential, is the 'so-called' electrochemical potential, which encompasses the entire expression (26.6).

As will be explained in the following, it should be noted that there is no unique way to split μ into μ^{non} and $zF\phi$, because we cannot determine the absolute value of ϕ.[467]

26.12 Chemical potential of electrons

As we have observed in **26.4**, it is convenient to treat electrons as if they were chemical species.

When a metal ionizes into an aqueous solution, electrons are separated (and often remain in the metal phase). When two metals are electrically connected without any current, then there must be an equilibrium in the exchange of electrons between them. Thus, it is convenient to introduce the *chemical potential* μ_e^α *of electrons* in phase α.

If two metals α and β are in contact and in equilibrium (without any electric current), we have the equality

$$\mu_e^\alpha = \mu_e^\beta. \tag{26.7}$$

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[466] This terminology was introduced by J. Guggenheim, "Studies of cells with liquid-liquid junctions. II" J. Phys. Chem., **23**, 842 (1929).

[467] However, the chemical potential difference can be split uniquely into $\Delta\mu^{non}$ and $zF\Delta\phi$.

If two metal pieces A and B both made of the same metal α are at two different electric potentials ϕ^A and ϕ^B, respectively, but if other conditions are identical, then (see Fig. 26.5) (26.5) implies

$$\mu_e^{\alpha A} - \mu_e^{\alpha B} = -F(\phi_A - \phi_B). \tag{26.8}$$

Here, the minus sign on the right-hand side exists because electrons are negatively charged.

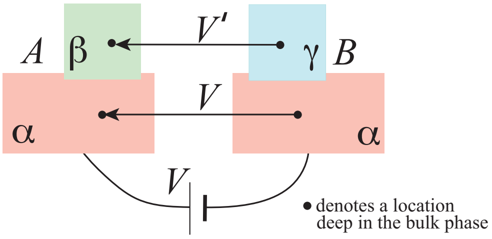

Figure 26.5: Metals in contact and electric potential differences

Fig. 26.5 Metals in contact and electric potential differences
Metals α, β, γ are different metals. Metal pieces made of metal α at A and B are insulated but connected to a battery with a wire made of a single metal (say, α). Metal β is in electrical contact with α at A and Metal γ is in electrical contact with α at B. The Galvani potential difference (→**26.14**) between $A\alpha$ and $B\alpha$ is V, which is equal to their measurable Volta potential difference (→**26.14**). The potential difference V' is the Galvani potential difference between $A\beta$ and $B\gamma$, but it cannot be measured due to the surface potentials χ of metals (→**26.13**).

If a metal piece made of β is in electrical contact with the metal α piece A, and if another metal piece made of γ in electrical contact with the metal α piece B in equilibrium as in Fig. 26.5, then (26.7) implies

$$\mu_e^{\alpha A} - \mu_e^{\alpha B} = \mu_e^{\beta A} - \mu_e^{\gamma B} = -F(\phi_A - \phi_B). \tag{26.9}$$

However, the electrical potential difference between two different metals is *not* measurable directly. The reason for this will become clear with (26.13). Gibbs already wrote in 1899 that the difference of potentials in pieces of metal of the same kind attached to the electrodes are the only measurable potential differences that are purely electromagnetic.

26.13 Chemical potential of electrons reconsidered

Let us reconsider the chemical potential of electrons **26.12** from a fundamental physics point of view.

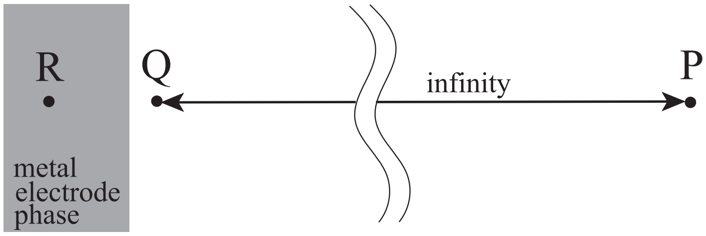

Figure 26.6: Chemical potential of electrons

By definition (see Fig. 26.6), the chemical potential of electrons is the reversible work required to bring 1 mole of electrons from infinity P in the vacuum to the location R that is sufficiently within the electrode metal phase. This process is considered in two steps, P to Q, which is the point where we may ignore the image force, and Q to R. Q may be about 1 μm from the surface.[468] The work needed for the transport of one-mole of electrons P to Q is ($-$ in front of the right-hand side of (26.10) is required, because electrons have negative charges)

$$W_1 = -F\psi^{\mathrm{M}}, \tag{26.10}$$

where ψ^{M} is called the *outer potential* (or *Volta potential*). What Gibbs pointed out (→(26.9)) is that we can directly measure only the difference of the outer potentials.

On the other hand, the work needed to transport one mole of electrons from Q to R includes the electrostatic work to overcome the surface potential χ^{M} that is due to the nonuniformity of the metal (bulk phase) structure and the chemical potential $\mu_e^{non\mathrm{M}}$ attributed to chemical bond formation (e.g., structural rearrangements)

$$W_2 = \mu_e^{non\mathrm{M}} - F\chi^{\mathrm{M}}. \tag{26.11}$$

Therefore, the electrochemical potential of electrons is given by

$$\mu_e^{\mathrm{M}} = \mu_e^{non\mathrm{M}} - F\phi^{\mathrm{M}}, \tag{26.12}$$

where

$$\phi^{\mathrm{M}} = \psi^{\mathrm{M}} + \chi^{\mathrm{M}} \tag{26.13}$$

---

[468] The mirror potential is given by $e/4\pi\varepsilon_0 a = 3.6 \times 10^{-9}/a$ V, where the distance $a \sim 1$ μm gives 4 mV, still sufficiently small.

is called the *inner potential* (or *Galvani potential*) of phase M.

Since we do not know (cannot measure) $\mu_e^{non\mathrm{M}}$, χ^{M} is not measurable, either.[469]

Since $\mu_e^{non\mathrm{M}}$ is not measurable, neither is χ^{M}. Still, $\mu_e^{non\mathrm{M}}$ is the chemical potential of electrons in the metal M when its Galvani potential is 0 relative to the infinity P. Therefore, henceforth we will denote it as $\mu_e^{\mathrm{M}\ominus}$:

$$\mu_e^{\mathrm{M}} = \mu_e^{\mathrm{M}\ominus} - F\phi^{\mathrm{M}}. \tag{26.14}$$

26.14 Volta vs Galvani potential difference: summary

When two phases are compared, the outer potential difference is referred to as the *Volta potential difference* (or the outer potential difference), while the inner potential difference is called the *Galvani potential difference* (Fig. 26.7).

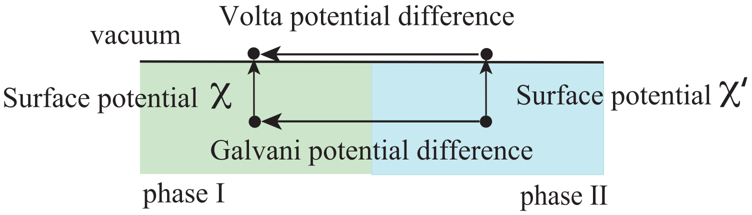

Figure 26.7: Galvani and Volta potential differences; only the latter is directly measurable

We can only measure the potential difference between two points in the same phase due to not measurable surface potentials that depend on material details. Therefore, we can only measure Volta potential difference, and not the Galvani potential difference (→**26.12**).

26.15 Chemical potential of salts

If identical solutions α are in container A and in container B both in contact with a silver wire (phase β) allowing for the exchange of silver ions, then we have (see Fig. 26.8)

Fig. 26.8 The identical solutions α are contained in insulating vessels A and B. If the silver wire β is removed without otherwise touching or disturbing the two solutions (Left to Right), then (26.16) remains valid until one solution is touched by some electrically charged or conducting body.

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[469] Needless to say, model calculations are possible.

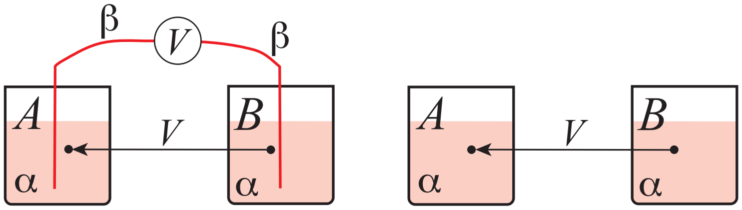

Figure 26.8: Galvani potential difference between identical solutions

$$\mu^{\alpha A}_{\mathrm{Ag}^+} = \mu^{\beta A}_{\mathrm{Ag}^+},\ \mu^{\alpha B}_{\mathrm{Ag}^+} = \mu^{\beta B}_{\mathrm{Ag}^+}. \tag{26.15}$$

Therefore (→**26.11**),

$$\mu^{\alpha A}_{\mathrm{Ag}^+} - \mu^{\alpha B}_{\mathrm{Ag}^+} = \mu^{\beta A}_{\mathrm{Ag}^+} - \mu^{\beta B}_{\mathrm{Ag}^+} = F(\phi_A - \phi_B). \tag{26.16}$$

If the silver ion containing solution α also contains nitrate ions maintaining charge neutrality, we have

$$\mu^{\alpha A}_{\mathrm{NO}_3^-} - \mu^{\alpha B}_{\mathrm{NO}_3^-} = -F(\phi_A - \phi_B). \tag{26.17}$$

Adding (26.16) and (26.17), we obtain

$$\mu^{\alpha A}_{\mathrm{Ag}^+} + \mu^{\alpha A}_{\mathrm{NO}_3^-} = \mu^{\alpha B}_{\mathrm{Ag}^+} + \mu^{\alpha B}_{\mathrm{NO}_3^-}. \tag{26.18}$$

We accordingly speak of the chemical potential of a salt, for example, as

$$\mu_{\mathrm{AgNO}_3} = \mu_{\mathrm{Ag}^+} + \mu_{\mathrm{NO}_3^-}. \tag{26.19}$$

This is independent of the electric potential as it should be.

The reader who is not particularly interested in electrochemistry may skip **26.16** - **26.20**.

26.16 Chemical potential of dilute electrolytes[470]

The chemical formula for electrolyte Y may be expressed as

$$\mathrm{Y} = \mathrm{A}_{\nu_a}\mathrm{B}_{\nu_b}\cdots\mathrm{X}_{\nu_x}\cdots, \tag{26.20}$$

where A, B, $\cdots$ are ionic components and $\nu_a, \nu_b, \cdots$ are stoichiometric coefficients describing the composition of Y. The ionic species X has charge z_x. Thus, charge neutrality of Y reads

$$\sum \nu_x z_x = 0. \tag{26.21}$$

---

[470] The units in smaller fonts rely on Kirkwood-Oppenheim p 189-.

We write the chemical potential of ion X as

$$\mu_x = \mu_x^{\ominus}(T,P) + RT\log\gamma_x m_x, \tag{26.22}$$

where γ_x is the activity coefficient, and m_x is the molarity (mol/liter[471]) of the ion component x in the solution. The reference state $^{\ominus}$ is chosen to be

$$\mu_x^{\ominus} = \lim_{m_k\to 0}(\mu_k - RT\log m_k). \tag{26.23}$$

The chemical potential of electrolyte Y is, according to the general formula corresponding to (26.19), given by

$$\mu_y = \sum_x \nu_x\mu_x = RT\sum_x \nu_x\log\gamma_x m_x + \mu_y^{\ominus}, \tag{26.24}$$

where (cf. (26.19))

$$\mu_y^{\ominus} = \sum_x \nu_x\mu_x^{\ominus}. \tag{26.25}$$

26.17 Logarithmic average expressions

Rearranging (26.24) yields

$$\begin{aligned}\mu_y &= \mu_y^{\ominus} + RT\sum_x \nu_x\log\gamma_x m_x && (26.26)\\ &= \mu_y^{\ominus} + RT\log\left[\prod_x(\gamma_x m_x)^{\nu_x}\right] && (26.27)\\ &= \mu_y^{\ominus} + RT\nu_y\log\left[\prod_x(\gamma_x m_x)^{\nu_x}\right]^{1/\nu_y}, && (26.28)\end{aligned}$$

where

$$\nu_y = \sum_x \nu_x. \tag{26.29}$$

Introducing logarithmic averages

$$\gamma_{\pm}^{y} = \left[\prod_x \gamma_x^{\nu_x}\right]^{1/\nu_y},\quad m_{\pm}^{y} = \left[\prod_x m_x^{\nu_x}\right]^{1/\nu_y}, \tag{26.30}$$

we finally write

$$\mu_y = \mu_y^{\ominus}(T,P) + \nu_y RT\log(\gamma_{\pm}^{y} m_{\pm}^{y}). \tag{26.31}$$

where

$$\mu_y^{\ominus} = \lim_{x_1\to 1}[\mu_y - \nu_y RT\log m_{\pm}^{y}] \tag{26.32}$$

with '1' designating the solvent (water). This limit exists if μ_y/ν_y is the partial free energy of M_y' grams of electrolyte Y, where M_y' is the solution molecular weight of the electrolyte

---

[471] However, the mol/kg called the *mass concentration* may also be used, which is very close to molarity when dilute.

Y with $M_y/M'_y = \nu_y$ (i.e., the equivalent grams).

For a single electrolyte or a mixture of electrolytes without any common ions, M/M' are constant.

Example: for NaCl

$$m_\pm^{\text{NaCl}} = (m_{\text{Cl}^-} m_{\text{Na}^+})^{1/2} = m_{\text{NaCl}} \tag{26.33}$$

$M' = 29$ and $M = 58$, so $\nu = 2$.[472]

26.18 Non-operational nature of log averages

$\gamma_\pm$ in (26.30) is non-operational, since the individual γ_x cannot be measured. (26.31) can be looked upon as providing a definition for $\gamma_\pm^y$ in terms of measurable quantities μ_y, $\mu_y^\ominus$ and calculable $m_\pm^y$. The argument leading to (26.30) is only an aid to understand the involved concepts.

For strong electrolyte $\gamma_\pm$ is a slowly varying function of concentrations, and is close to 1 in the dilute solutions.

26.19 Dilution limit approximation

The dilution limit approximation to (26.31) is often useful:

$$\mu_y = \mu_i^\ominus(T,P) + \nu_y RT \log m_\pm^y. \tag{26.37}$$

All the laws of elementary qualitative analysis may be derived from this formula.

Solubility product rule: Phase α is a solution including Y, and phase β is pure solid Y. The equilibrium condition between the two phases is

$$\mu_y^\alpha = \mu_y^\beta(T,P). \tag{26.38}$$

Setting $\mu_y^\alpha = \mu_y$, we get

$$\mu_y^\ominus(T,P) + RT \log m_\pm^y = \mu_y^\beta(T,P). \tag{26.39}$$

Thus,

$$m_\pm^y = (\prod m_x^{\nu_x})^{1/\nu_y} \tag{26.40}$$

reads

$$\prod m_x^{\nu_x} = \exp\left[\frac{\mu_y^\beta(T,P) - \mu_y^\ominus(T,P)}{RT}\right] = K(T,P). \tag{26.41}$$

---

[472] The logarithmic averages may also be defined for salt mixture solutions. Example: NaCl + BaCl_2.

$$m_\pm^{\text{NaCl}} = (m_{\text{Cl}^-} m_{\text{Na}^+})^{1/2} = [(m_{\text{NaCl}} + 2m_{\text{BaCl}_2}) m_{\text{NaCl}}]^{1/2} \tag{26.34}$$

$$m_\pm^{\text{BaCl}_2} = (m_{\text{Cl}^-}^2 m_{\text{Ba}^{2+}})^{1/3} = [(m_{\text{NaCl}} + 2m_{\text{BaCl}_2})^2 m_{\text{BaCl}_2}]^{1/3} \tag{26.35}$$

Even in this case, if it is assumed that

$$\lim_{x_1 \to 1} \frac{m_{\text{NaCl}}}{m_{\text{BaCl}_2}} = C \neq 0 \tag{26.36}$$

is finite, then (26.32) exists.

This is the *solubility product rule*.

The fact that this approximation gives good results when applied to dilute solutions of, e.g., NaCl is strong evidence for the structural hypothesis that NaCl dissociates into Na^+ and Cl^- ions in solution.[473]

26.20 Weak electrolytes

If an electrolyte does not completely dissociate into its constituent ions, $m_\pm = m$ is not true, so the strong electrolyte formula (26.31) cannot be used; we need a dissociation constant K as

$$\gamma_\pm m_\pm = K(T, P)\gamma. \tag{26.42}$$

If we use the nonelectrolyte expression

$$\mu = \mu^\ominus(T, P) + RT\log(\gamma m), \tag{26.43}$$

then the following limit

$$\lim_{m\to 0}[\mu - RT\log m] \tag{26.44}$$

does not exist. That is, γ in the dilute limit is not 1. Thus, neither the strong-electrolyte nor the nonelectrolyte formulation is applicable to weak electrolytes throughout the entire range of concentration.

The usual approach is to discuss the dissociation as chemical equilibrium:

$$\mu_{AB} = \mu_{A^+} + \mu_{B^-}, \tag{26.45}$$

introducing the degree of ionization α (= extent of chemical reaction).

26.21 Acidity constant

Let HA be an acid (e.g., acetic acid, HAc, where Ac = CH_3COO). For

$$\mathrm{HA} + \mathrm{H_2O} \to \mathrm{A^-} + \mathrm{H_3O^+} \tag{26.46}$$

the equilibrium constant (→**25.23**) in dilute solutions becomes

$$K_{\mathrm{HA}} = \frac{a_{\mathrm{A^-}} a_{\mathrm{H_3O^+}}}{a_{\mathrm{AH}}}, \tag{26.47}$$

where K_{HA} is called the *acidity constant* of HA in water at a given temperature. Here, note that the activity of the solvent (water) is 1. For example, for acetic acid $K_{\mathrm{HAc}} = 1.75 \times 10^{-5}$. The acids that do not dissociate completely in water are called *weak acids* whose K_{HA} is usually much smaller than 1 as acetic acid. For strong acid, K_{HA} can be huge. For example for HI, it is more than 10^9. For HCl it is about 10^8.

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[473] The Debye-Hückel theory gives $\gamma_\pm \sim 1$ for $m < 0.05$ (mol/l).

26.22 Ionization of water

Two molecules of water can react as

$$2H_2O \to OH^- + H_3O^+. \tag{26.48}$$

The equilibrium constant K_W for this reaction reads

$$a_{H_3O^+} a_{OH^-} = K_W, \tag{26.49}$$

where K_W is called the *ionization product* of water. It is about 10^{-14}. This implies $a \approx 10^{-7}$,[474] so a is almost identical to the molarity.

For

$$H_2O + A^- \to OH^- + HA \tag{26.50}$$

we have

$$\frac{a_{OH^-} a_{HA}}{a_{A^-}} = K_W/K_{HA} \tag{26.51}$$

where K_{HA} is the acidity constant (26.47).

If we regard H_3O^+ as HA, and obtain its acidity constant (26.47) in water, we obtain

$$K_{H_3O^+} = \frac{a_{H_2O} a_{H_3O^+}}{a_{H_3O^+}} = a_{H_2O} \approx m_{H_2O} \simeq 55. \tag{26.52}$$

No molecule or ion that is much stronger acid than H_3O^+ can exist in appreciable quantity in water. For example, HCl in water is almost completely changed to H_3O^+ and Cl^-.

Similarly no base stronger than OH^- can exist in appreciable quantity in water. Examples are O^{2-} and ${NH_2}^-$.

26.23 pH

The *pH* of a solution is defined as

$$\text{pH} \ = -\log_{10} a_{H^+}. \tag{26.53}$$

Thus, for pure water pH ≈ 7 according to the ionization product (→**26.22**). Since, as we will see soon, the origin of the reduction potential scale is determined with

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[474] This implies that pH of pure water is 7. See **26.23**.

the aid of the hydrogen electrode which depends on this formula, we cannot purely electrochemically determine the proton activity in the solution.

It is possible to prepare a solution with a known molarity of the hydrogen ions (say, using pure HCl), but there is no direct way to determine its activity coefficient. Therefore, IUPAC Gold Book (Compendium of Chemical Terminology)[475] clearly acknowledges the following:

1. pH cannot be measured independently because calculation of the activity involves the activity coefficient of a single ion. Thus, it can be regarded only as a notional definition.[476] That is, pH is not defined operationally.
2. The establishment of primary pH standards requires the application of the concept of 'primary method of measurement', that assures full traceability of the results of all measurements and their uncertainties. Any limitation in the theory of determination of experimental variables must be included in the estimated uncertainty of the method.

> The primary method for measurement of pH involves the use of a cell without transference (a cell without movement of materials between the electrodes),[477] known as the Harned cell:
>
> $$\mathrm{Pt(s)} \mid \mathrm{H_2(g)} \mid \text{Buffer Solution, } \mathrm{Cl^-(aq)} \mid \mathrm{AgCl(s)} \mid \mathrm{Ag(s)}.$$
>
> The equation for this cell can be rearranged to give:
>
> $$-\log_{10}[a_{\mathrm{H}^+}\gamma_{\mathrm{Cl}^-}] = \frac{E - E^{\ominus}}{(RT\log 10)/F} + \log_{10} m_{\mathrm{Cl}^-}, \tag{26.54}$$
>
> where m_{Cl^-} is the mass concentration of chlorine ion in mol/kg. All the quantities on the right-hand side are measurable. The value of $\gamma(\mathrm{Cl}^-)$ is calculated with the aid of the Debye-Hückel theory (this is called the *Bates-Guggenheim convention*). The procedure explained here may be regarded as the true operational definition of pH.

26.24 Equilibrium electrode potential

The electrode reaction occurs at the boundary of the electrode (metal) phase M and the solution phase S, so the *electrode potential* E is defined as (→**26.13**)

$$E = \phi^{\mathrm{M}} - \phi^{\mathrm{S}}, \tag{26.55}$$

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[475] `https://goldbook.iupac.org/terms/view/P04524`.

[476] However, it is definitely different from p[H$^+$]. See Christopher G. McCarty and Ed Vitz, pH Paradoxes: Demonstrating that it is not true that pH $= -\log[\mathrm{H}^+]$, Journal of Chemical Education **83**, 752 (2006).

[477] In electrochemistry, "transference" generally refers to the movement of ions or charged species through a solution or an electrolyte.

where ϕ^{X} implies the inner (Galvani) potential of phase X. Recall Fig. 26.4. The voltage across the electric double layer is the electrode potential.

If there is only one kind of electrode reaction and if the reaction is in equilibrium, E is called the *equilibrium electrode potential*.

Consider the following reductive reaction (cf **26.4**):

$$\mathrm{O}^{z+} + ne^- \to \mathrm{R}^{(z-n)+}. \tag{26.56}$$

Here O is an oxidized form and R is a reduced form of a chemical. Chemical potentials for O and R ions read as

$$\begin{aligned} \mu_{\mathrm{O}} &= \mu_{\mathrm{O}}^{\ominus} + RT \log a_{\mathrm{O}} + zF\phi^{\mathrm{S}}, & (26.57) \\ \mu_{\mathrm{R}} &= \mu_{\mathrm{R}}^{\ominus} + RT \log a_{\mathrm{R}} + (z-n)F\phi^{\mathrm{S}}. & (26.58) \end{aligned}$$

For the electrons the chemical potential is given by (26.12).

In equilibrium (26.56) implies

$$\mu_{\mathrm{O}} + n\mu_e^{\mathrm{M}} = \mu_{\mathrm{R}}. \tag{26.59}$$

Combining all the explicit expressions, we get

$$\mu_{\mathrm{O}}^{\ominus} + RT \log a_{\mathrm{O}} + zF\phi^{\mathrm{S}} + n(\mu_e^{\mathrm{M}\ominus} - F\phi^{\mathrm{M}}) = \mu_{\mathrm{R}}^{\ominus} + RT \log a_{\mathrm{R}} + (z-n)F\phi^{\mathrm{S}} \tag{26.60}$$

or

$$nF(\phi^{\mathrm{M}} - \phi^{\mathrm{S}}) = \mu_{\mathrm{O}}^{\ominus} + n\mu_e^{\mathrm{M}\ominus} - \mu_{\mathrm{R}}^{\ominus} + RT \log \frac{a_{\mathrm{O}}}{a_{\mathrm{R}}} = -\Delta G, \tag{26.61}$$

where ΔG is the Gibbs energy change due to the reducing reaction (26.56). Therefore,

$$E = \phi^{\mathrm{M}} - \phi^{\mathrm{S}} = -\frac{\mu_{\mathrm{R}}^{\ominus} - \mu_{\mathrm{O}}^{\ominus} - n\mu_e^{\mathrm{M}\ominus}}{nF} + \frac{RT}{nF} \log \frac{a_{\mathrm{O}}}{a_{\mathrm{R}}} = -\frac{\Delta G}{nF}. \tag{26.62}$$

If we set

$$E^{\ominus} = -\frac{\mu_{\mathrm{R}}^{\ominus} - \mu_{\mathrm{O}}^{\ominus} - n\mu_e^{\mathrm{M}\ominus}}{nF} = -\frac{\Delta G^{\ominus}}{nF} \tag{26.63}$$

we have

$$E = E^{\ominus} + \frac{RT}{nF} \log \frac{a_{\mathrm{O}}}{a_{\mathrm{R}}}. \tag{26.64}$$

Here $E^{\ominus}$ is the *standard reduction potential* and the formula is called *Nernst's equation.*[478]

The larger $-\Delta G$ in (26.61), the reaction shifts more toward the product system, so larger reduction potential E implies that the ion is easier to be reduced (i.e., more readily captures electrons).

As seen here and also below RT/F appears often. At the room temperature (298.15 K)

$$\frac{RT}{F} = \frac{k_BT}{e} = \frac{1.380649 \times 10^{-23} \times 298.15}{1.60217663 \times 10^{-19}} = 2.569258 \times 10^{-2}\ \mathrm{V} = 25.7\ \mathrm{mV}. \tag{26.65}$$

A special case of **26.24** is the reduction of metal ion to metal that occurs when the electrode itself is involved as

$$\mathrm{M}^{n+} + ne^- \to \mathrm{M}. \tag{26.66}$$

The equilibrium electrode potential reads (note that the activity of the solid metal is 1)

$$E = E^{\ominus} + \frac{RT}{nF} \log a_{\mathrm{M}^{n+}}. \tag{26.67}$$

A variation is the case that metal ion forms an insoluble salt on the electrode as

$$\mathrm{AgCl} + e^- \to \mathrm{Ag} + \mathrm{Cl}^-. \tag{26.68}$$

Since the activity of a solid is 1, we have

$$E = E^{\ominus} - \frac{RT}{F} \log a_{\mathrm{Cl}^-}. \tag{26.69}$$

26.25 Standard reduction potentials

As can be seen from **26.24**, if we know the standard Gibbs energy of formation $\Delta G_f^{\ominus}$, then we can obtain the standard reduction potential.

For the non-ionic chemical species we have already discussed how to get $\Delta G_f^{\ominus}$ in **25.21**. For ionic chemical species, as indicated in (26.63), $E^{\ominus}$ includes the chemical potential of electrons that is not observed.[479] Therefore, it is impossible to determine

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[478] The reduction potential is often called *redox potential*, but this potential is directly related to the Gibbs energy change due to a reduction reaction, so in these notes, the terminology 'redox potential' will totally be avoided.

[479] Is it measurable? As discussed in **26.13** it depends on the surface potential. We must move an electron from outside the solid phase deep into the solid. This process seems very hard to realize experimentally.

the absolute chemical potential of an ion experimentally.

However, the chemical potential difference of two different ions may be measurable. For example, if we compare NaCl and KCl, we may obtain the difference of the reduction potentials for Na^+ and K^+. Therefore, in practice, we can fix the standard reduction potential of some ion to be 0.

Thus, Nernst proposed to use the reduction of hydrogen ion

$$2H^+{}_{\rm aq} + 2e^- \longrightarrow H_{2\rm gas} \tag{26.70}$$

to determine the origin (= reference point) of the reduction potentials (→**26.26**).

The *standard reduction potential* $E^\ominus_{red}$ is measured under standard conditions: $T = 298.15$ K, a unity activity ($a = 1$) for each ion participating in the reaction, a partial pressure of 1×10^5 Pa[480] for each gas taking part in the reaction, and metals in their pure state.

26.26 Standard hydrogen electrode: SHE

The equilibrium electrode potential E discussed so far pertains to the inner (Galvani) potential of the electrode relative to the liquid phase. It is not directly observable. In practice, we connect the 'standard electrode' and the target electrode, constructing a Galvanic cell (→**26.28**), to measure the relative electrode potential. As the standard electrode, Nernst proposed to use the standard hydrogen electrode (SHE):

$$\text{Pt(platinum black)}\,|\,H_2(P_{H_2} = 10^5 \text{ Pa})\,|\,H^+(a_{H^+} = 1). \tag{26.71}$$

The electrode reaction is given by (26.70). Therefore, the standard reduction potential of the hydrogen ion is given by

$$E_{\rm SHE} = E^\ominus - \frac{RT}{2F}\log\frac{(P_{H_2}/P^\ominus_{H_2})}{a^2_{H^+}} \tag{26.72}$$

with

$$E^\ominus = -\frac{\mu^\ominus_{H_2} - 2\mu^\ominus_{H^+} - 2\mu^{\rm Pt}_e}{2F}. \tag{26.73}$$

Here, the hydrogen gas is in its standard state (at $P^\ominus = 1 \times 10^5$ Pa, $T^\ominus = 298.15$ K). Following (26.67), we find

$$E = E^\ominus - \frac{RT}{2F}\log\frac{1}{a^2_{H^+}} = E^\ominus + \frac{RT}{F}\log a_{H^+}. \tag{26.74}$$

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[480] Now the standard pressure is not 1 atm (1.013 bar = 1013 hPa = 1.013×10^5 Pa), but 1×10^5 Pa.

The convention for the origin of the reduction potential is '$E^\ominus = 0$ for (26.70) at any T' (according to Guggenheim). Since the definition of pH is pH$= -\log_{10} a_{\mathrm{H}^+}$,[481]

$$E = -\frac{RT \log 10}{2F}\ \mathrm{pH}\ \ (= -0.0591\ \mathrm{pH}\ \text{at}\ T = 298.15\,\mathrm{K}). \tag{26.75}$$

In many elementary textbooks, the molarity of H^+ and the activity a_{H^+} are not distinguished, and pH is defined as pH $= -\log_{10}[\mathrm{H}^+]$, so the reduction potential of (26.70) with 1M HCl solution is set to be $E = 0$ V. However, this is not the IUPAC definition. Precisely speaking, $E = 0$ for the aqueous phase with the proton activity 1 (i.e., pH $= 0$) is the standard state. See **26.23**.

With the above definition of the origin of the reduction potential provided above, we can determine the reduction potentials of various substances (ions). The results may be found in a table in `https://en.wikipedia.org/wiki/Standard_electrode_potential_(data_page)`.

To measure reduction potentials the most common method is to construct appropriate electric cells (→**26.28**).

26.27 Formal potential

The formula for the standard reduction potential can be rewritten as

$$\begin{aligned} E &= E^\ominus + \frac{RT}{nF}\log\frac{a_\mathrm{O}}{a_\mathrm{R}} && (26.76)\\ &= E^{\ominus\prime} + \frac{RT}{nF}\log\frac{c_\mathrm{O}}{c_\mathrm{R}} && (26.77)\end{aligned}$$

with

$$E^{\ominus\prime} = E^\ominus + \frac{RT}{nF}\log\frac{\gamma_\mathrm{O}}{\gamma_\mathrm{R}}, \tag{26.78}$$

where $c_\mathrm{O}/c_\mathrm{R}$ is the concentration ratio. $E^{\ominus\prime}$ is called the *formal potential*.

26.28 Cells to realize electrochemical reactions: Galvanic cells

As can be seen from the explicit expression of $E^\ominus$ in (26.63) containing μ_e, it is not measurable. Therefore, reduction and oxidation reactions must be coupled to realize a complete chemical reaction in which no electron chemical potentials explicitly appear. A device designed to realize such a reaction is called a *Galvanic cell*. It is a device to convert chemical energy to work reversibly. Thus, its existence is of

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[481] `https://en.wikipedia.org/wiki/Standard_hydrogen_electrode`.

fundamental importance to thermodynamics as emphasized in these notes.

A *half cell* is a system comprising two parts M and S, in contact, where M conducts electrons, and S ions. An electric cell is a system consisting of two half cells in contact through their ion-conducting portions. A half cell E may be expressed as

$\mathrm{E} = \mathrm{M} \mid \mathrm{S}$.[482]

Then, an electric cell C may be described as

$\mathrm{C} = \mathrm{E}_1$ ▮ $\mathrm{E}_2 = \mathrm{M}_1 \mid \mathrm{S}_1$ ▮ $\mathrm{S}_2 \mid \mathrm{M}_2$.

In the notation above ▮ is used to indicate the contact between two half cells E_1 and E_2, but it is not a standard notation. In the standard notation, when two distinct ion-conducting phases (e.g., different solutions) are in contact, ▮ is denoted as $\|$. Otherwise, ▮ is denoted as $|$. We will use ▮, if we do not wish to distinguish these two cases.

26.29 Positive reaction in the cell: IUPAC convention

The positive direction of the reaction that occurs in the cell C (→**26.28**) is designated as the direction of positive charges to move from 1 to 2 (left to right) in the cell. This positive direction is an IUPAC convention. In many examples the reaction in the half cell may be written as

$\mathrm{M} \to \mathrm{M}^{z+} + z\mathrm{e}$

Then, the reactions in the cell are given by

$$\begin{aligned} \mathrm{M}_1 &\to \mathrm{M}_1{}^{z+} + z\mathrm{e}, \qquad (26.79) \\ \mathrm{M}_2{}^{z+} + z\mathrm{e} &\to \mathrm{M}_2. \qquad (26.80) \end{aligned}$$

Thus, the electromotive force (measured as **26.30**) is given by [the reduction potential of 2] − [the reduction potential of 1] = $E_2 - E_1$. Adding these two reactions, the reaction in the electric cell is given by

$$\mathrm{M}_1 + \mathrm{M}_2{}^{z+} \to \mathrm{M}_1{}^{z+} + \mathrm{M}_2. \qquad (26.81)$$

M_1 is oxidized and M_2 is reduced.

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[482] Note: The standard positive direction of the electrochemical reaction is the reducing direction $\mathrm{M}^+ + \mathrm{e} \longrightarrow \mathrm{M}$, but the natural reaction direction for the half cell $\mathrm{M} \mid \mathrm{S}$ is opposite (oxidating direction).

26.30 Electromotive force of the cell

The *electromotive force* E of cell C in **26.28** is defined operationally by the measurement illustrated in Fig. 26.9. Assuming that the potential of the right electrode 2 is higher than that of the left 1, with the assistance of a galvanometer G in the figure, we search for the voltage E that prevents any current from flowing through the cell. This voltage is defined as the electromotive force of the cell. If we denote the Galvani potential of metal phase i as ϕ_i, then

$$E = \phi_2 - \phi_1. \tag{26.82}$$

In this case, oxidation occurs in the electrode 1 and reduction occurs in the electrode 2. This implies that electrons are supplied by M_2 and subsequently absorbed by M_1. This is consistent with the IUPAC definition of the positive direction of the cell reaction (→**26.29**). In other words, the reaction in this cell reads

$$\mathrm{M}_1 + \mathrm{M}_2^+ \to \mathrm{M}_1^+ + \mathrm{M}_2. \tag{26.83}$$

Note that here, for simplicity, we assume that all the metals ionize into univalent ions, e.g., $\mathrm{M}_1 \to \mathrm{M}_1^+ + \mathrm{e}$.

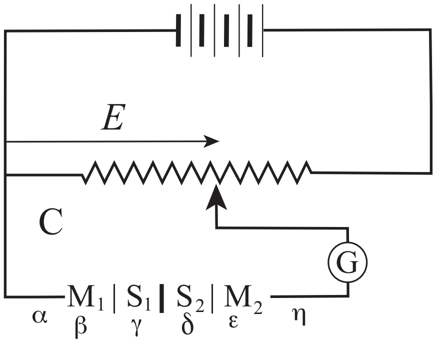

Figure 26.9: Electromotive force of a cell, measurement/definition

Fig. 26.9 The measurement/definition of the electromotive force of cell $\mathrm{C} = \mathrm{M}_1 \mid \mathrm{S}_1 \,\|\, \mathrm{S}_2 \mid \mathrm{M}_2$. G is a galvanometer to ensure the absence of any current while selecting the value of E that cancels out any current through the cell. This value E represents the electromotive force of cell C. As noted in **26.31**, it is essential to use wires made of the same metal, such as copper (cf. **26.31**). Along with **26.31**, the material phases constituting each part of the wires and batteries are assigned as $\alpha, \beta, \cdots, \eta$. In this unit, for simplicity, the equation for the case where $\alpha = \beta =$ metal phase M_1, $\varepsilon = \eta =$ metal phase M_2 is written. Actually, as we will see in the following **26.31**, this is not realistic.

From this we can 'roughly' estimate (see **26.24**) the electromotive force E in cell C as:

$$E_2 - E_1 = E_2^{\ominus} - E_1^{\ominus} + \frac{RT}{F}\left[\log\frac{a_{\mathrm{M}_2^+}}{a_{\mathrm{M}_2}} - \log\frac{a_{\mathrm{M}_1^+}}{a_{\mathrm{M}_1}}\right], \tag{26.84}$$

that is,

$$E = E^{\ominus} + \frac{RT}{F}\log\frac{a_{\mathrm{M}_2^+}}{a_{\mathrm{M}_1^+}}, \tag{26.85}$$

because $a = 1$ for metals (crystals). However, as seen from the analysis in the following unit **26.31**, the electrical effect of the S_1-S_2 mismatch cannot be ignored.

26.31 General electromotive force formula for the Galvani cell

The Galvani potential difference is not directly observable (→**26.14**). Unless M_1 and M_2 are the same metal (electron conductor) (→**26.12**), so the true electromotive force cannot be observed for the cell C in **26.28**.

We know that if two metals are identical we can measure the Galvani potential difference as the Volta potential difference (→**26.14**). To achieve this, we add two terminal metal pieces α and η both made of the same metal T to the cell C as

$$\mathrm{C} = \mathrm{T}(\alpha)\mid \mathrm{M}_1(\beta)\mid \mathrm{S}_1(\gamma)\parallel \mathrm{S}_2(\delta)\mid \mathrm{M}_2(\varepsilon)\mid \mathrm{T}(\eta).$$

Here, Greek letters α-η denote distinct phases.

Let us analyze the electromotive force of the cell C step by step. For simplicity, as in **26.28**, let us assume all the metals ionize into univalent ions, e.g., $\mathrm{M}_1 \to \mathrm{M}_1{}^+ + \mathrm{e}$. In the metal phases in equilibrium we have

$$\mu^{\alpha}_{\mathrm{T}^+} + \mu^{\alpha}_{\mathrm{e}} = \mu^{\alpha}_{\mathrm{T}} = \mu^{\eta}_{\mathrm{T}^+} + \mu^{\eta}_{\mathrm{e}}, \tag{26.86}$$

$$\mu^{\beta}_{\mathrm{M}_1^+} + \mu^{\beta}_{\mathrm{e}} = \mu^{\beta}_{\mathrm{M}_1}, \tag{26.87}$$

$$\mu^{\varepsilon}_{\mathrm{M}_2^+} + \mu^{\varepsilon}_{\mathrm{e}} = \mu^{\varepsilon}_{\mathrm{M}_2}. \tag{26.88}$$

The contact equilibrium conditions are

$$\mu^{\alpha}_{\mathrm{e}} = \mu^{\beta}_{\mathrm{e}}, \tag{26.89}$$

$$\mu^{\beta}_{\mathrm{M}_1^+} = \mu^{\gamma}_{\mathrm{M}_1^+}, \tag{26.90}$$

$$\mu^{\delta}_{\mathrm{M}_2^+} = \mu^{\varepsilon}_{\mathrm{M}_2^+}, \tag{26.91}$$

$$\mu^{\varepsilon}_{\mathrm{e}} = \mu^{\eta}_{\mathrm{e}}. \tag{26.92}$$

From (26.89) and (26.92) we obtain

$$\mu_{\rm e}^{\eta} - \mu_{\rm e}^{\alpha} = \mu_{\rm e}^{\varepsilon} - \mu_{\rm e}^{\beta}. \tag{26.93}$$

Since α and η are made of the same metal, the Galvani potential difference is obtained from the electron chemical potential difference as

$$\mu_{\rm e}^{\eta} - \mu_{\rm e}^{\alpha} = -F(\phi^{\eta} - \phi^{\alpha}). \tag{26.94}$$

Here, $\phi^{\eta} - \phi^{\alpha}$ represents the electromotive force of the cell (recall **26.30**). Notably, this value is independent of the metal T fused to construct the terminals. Therefore, this is determined completely by the two metals M_1, M_2 and the two ion-conducting (solution) phases.

The RHS of (26.93) reads, according to (26.87) and (26.88),

$$\begin{aligned}\mu_{\rm e}^{\varepsilon} - \mu_{\rm e}^{\beta} &= (\mu_{\rm M_2}^{\varepsilon} - \mu_{\rm M_2^+}^{\varepsilon}) - (\mu_{\rm M_1}^{\beta} - \mu_{\rm M_1^+}^{\beta}) = \mu_{\rm M_1^+}^{\beta} + \mu_{\rm M_2}^{\varepsilon} - \mu_{\rm M_1}^{\beta} - \mu_{\rm M_2^+}^{\varepsilon} && (26.95)\\ &= \mu_{\rm M_1^+}^{\gamma} + \mu_{\rm M_2}^{\varepsilon} - \mu_{\rm M_1}^{\beta} - \mu_{\rm M_2^+}^{\delta} && (26.96)\end{aligned}$$

consistent to the guess (26.83). Thus, the electromotive force of this cell is

$$-F(\phi^{\eta} - \phi^{\alpha}) = \mu_{\rm M_1^+}^{\gamma} + \mu_{\rm M_2}^{\varepsilon} - \mu_{\rm M_1}^{\beta} - \mu_{\rm M_2^+}^{\delta}. \tag{26.97}$$

If the counter anion is, say, Cl^-, in terms of the chemical potentials of the salts (→**26.15**) we can write as

$$\begin{aligned}\mu_{\rm M_2^+}^{\delta} &= \mu_{\rm M_2Cl}^{\delta} - \mu_{\rm Cl^-}^{\delta}, && (26.98)\\ \mu_{\rm M_1^+}^{\gamma} &= \mu_{\rm M_1Cl}^{\gamma} - \mu_{\rm Cl^-}^{\gamma}. && (26.99)\end{aligned}$$

Using these, we can rewrite (26.97) as

$$\begin{aligned}-F(\phi^{\eta} - \phi^{\alpha}) &= \mu_{\rm M_1Cl}^{\gamma} - \mu_{\rm Cl^-}^{\gamma} + \mu_{\rm M_2}^{\varepsilon} - \mu_{\rm M_1}^{\beta} - (\mu_{\rm M_2Cl}^{\delta} - \mu_{\rm Cl^-}^{\delta}), && (26.100)\\ &= -\left[\mu_{\rm M_1}^{\beta} - \mu_{\rm M_1Cl}^{\gamma}\right] - \left[\mu_{\rm Cl^-}^{\delta} - \mu_{\rm Cl^-}^{\gamma}\right] + \left[\mu_{\rm M_2}^{\varepsilon} - \mu_{\rm M_2Cl}^{\delta}\right]. && (26.101)\end{aligned}$$

Such a decomposition into M_1 and M_2 electrodes and liquid-liquid junction contributions is not unique, because we can add or subtract certain values from each [ ] while preserving the sum. See **26.37**.

26.32 Cells are with or without liquid-liquid interface

According to our convention an electric cell C has the following expression

$$\mathrm{C} = \mathrm{E}_1 \text{ ❚ } \mathrm{E}_2 = \mathrm{M}_1 \mid \mathrm{S}_1 \text{ ❚ } \mathrm{S}_2 \mid \mathrm{M}_2.$$

Here, ❚ denotes the contact between two half cells, but this need not represent a boundary of two different ion-conducting phases (often liquid phases). Thus, there are two major cases: the cells without liquid-liquid interfaces (→**26.33**) and the cells with liquid-liquid interfaces (→**26.34**). A cell with liquid-liquid interface consists of two liquid compartments (or ion-conductive phases more generally these days) each of which is in contact with an appropriate metal (solid) electrode.

26.33 Electric cells without liquid-liquid interface

A cell without liquid-liquid interface consists of one solution with two appropriate solid electrodes dipped in it. Needless to say, such a cell is simpler than the cells with liquid-liquid interfaces. If n electrons take part in the following reaction

$$a\mathrm{A} + b\mathrm{B} + \cdots \rightarrow z\mathrm{Z} + y\mathrm{Y} + \cdots \tag{26.102}$$

in the following cell without any liquid-liquid interface

$$\mathrm{Pt}(\alpha) \,|\, \mathrm{A}, \mathrm{B}, \cdots \,|\, \mathrm{Z}, \mathrm{Y}, \cdots \,|\, \mathrm{Pt}(\beta), \tag{26.103}$$

its electromotive force E is defined by the potential of the β phase relative to the α phase. That is. E is the potential of the right electrode relative to the left electrode. This is the IUPAC convention for the sign of the electromotive force for the cell (→**26.29**). Thus, (26.62)

$$E = -\Delta G/nF \tag{26.104}$$

is given by

$$E = E^{\ominus} - \frac{RT}{nF} \log \frac{a_{\mathrm{Z}}^{z} a_{\mathrm{Y}}^{y} \cdots}{a_{\mathrm{A}}^{a} a_{\mathrm{B}}^{b} \cdots}. \tag{26.105}$$

Manganese dry battery is an example of Galvanic cell without any liquid-liquid contact:

$$\mathrm{Zn} \,|\, \mathrm{ZnCl_2}, \mathrm{NH_4Cl} \,|\, \mathrm{MnO_2} \,|\, \mathrm{C}. \tag{26.106}$$

At the negative electrode (anode) $\mathrm{Zn} \to \mathrm{Zn}^{2+} + 2\mathrm{e}^-$ occurs, and at the positive electrode $2\mathrm{MnO}_2 + 2\mathrm{H}_2\mathrm{O} + 2\mathrm{e}^- \to 2\mathrm{MnOOH} + 2\mathrm{OH}^-$. In this case in the electrolyte solution the following reaction occurs:[483]

$$\mathrm{Zn}^{2+} + 2\mathrm{NH}_4\mathrm{Cl} + 2\mathrm{OH}^- \to \mathrm{Zn}(\mathrm{NH}_3)_2\mathrm{Cl}_2 + 2\mathrm{H}_2\mathrm{O}. \tag{26.107}$$

The overall reaction is

$$2\mathrm{MnO}_2 + \mathrm{Zn} + 2\mathrm{NH}_4\mathrm{Cl} \to 2\mathrm{MnOOH} + \mathrm{Zn}(\mathrm{NH}_3)_2\mathrm{Cl}_2. \tag{26.108}$$

Notice that the reduction $\mathrm{Mn}^{4+} + \mathrm{e}^- \to \mathrm{Mn}^{3+}$ is used as the positive electrode reaction in this cell.

If the solution is alkaline, then $\mathrm{Mn}^{4+} + 2\mathrm{e}^- \to \mathrm{Mn}^{2+}$ occurs as the positive electrode reaction. The resultant battery is called an alkaline dry battery

$$\mathrm{Zn}\,|\,\mathrm{KOH}\,|\,\mathrm{MnO}_2\,|\,\mathrm{C}, \tag{26.109}$$

where C denotes a carbon rod.

26.34 Electric cells with liquid-liquid junction

Many practical cells have liquid-liquid interface (*liquid junction*) between two distinct solutions. A typical example is the *Daniell cell*

$$\mathrm{Cu}(\alpha)\,|\,\mathrm{Zn}(\beta)\,|\,\mathrm{Zn}^{2+}(\gamma)\,||\,\mathrm{Cu}^{2+}(\delta)\,|\,\mathrm{Cu}(\varepsilon)\,|\,\mathrm{Cu}(\zeta) \tag{26.110}$$

Here, $||$ is the liquid-liquid interface. Although there is an ionic conduction through it, the phases (in the above example, phase γ and δ) on both sides are uniform. The electrode reactions are, in the positive direction (→**26.29**, i.e., the direction in which positive charge moves to the right)

$$\mathrm{Zn} \to \mathrm{Zn}^{2+} + 2\mathrm{e}^-, \tag{26.111}$$

$$\mathrm{Cu}^{2+} + 2\mathrm{e}^- \to \mathrm{Cu}. \tag{26.112}$$

The total reaction is

$$\mathrm{Zn} + \mathrm{Cu}^{2+} \to \mathrm{Zn}^{2+} + \mathrm{Cu}. \tag{26.113}$$

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[483] This is a so-called irreversible cell. The irreversibility is not in the thermodynamic sense, but solely practical/technological or economical.

The (standard) reduction potential of zink is $E^{\ominus} = -0.7628$ V, and for copper, $E^{\ominus} = 0.337$ V. Therefore, the standard electromotive force of the Daniell cell is $0.337 + 0.7628 = 1.0998$ V (note that copper ions are reduced and zinc is oxidized).

If the circuit is open, $E = \phi^{\zeta} - \phi^{\alpha}$, which would be equal to $E_{\mathrm{Cu}} - E_{\mathrm{Zn}}$, if there were no liquid junction. Actually, however, the phases γ and δ in (26.110) are distinct, so across the junction there could be a potential difference:

$$\begin{aligned} \Delta G &= \mu^{\gamma}_{\mathrm{Zn}^{2+}} + \mu^{\zeta}_{\mathrm{Cu}} - \mu^{\beta}_{\mathrm{Zn}} - \mu^{\delta}_{\mathrm{Cu}^{2+}} \qquad (26.114) \\ &= \mu^{\ominus}_{\mathrm{Zn}^{2+}} + \mu^{\ominus}_{\mathrm{Cu}} - \mu^{\ominus}_{\mathrm{Zn}} - \mu^{\ominus}_{\mathrm{Cu}^{2+}} + 2F\phi^{\gamma} + RT\log a^{\gamma}_{\mathrm{Zn}^{2+}} - 2F\phi^{\delta} + RT\log a^{\delta}_{\mathrm{Cu}^{2+}} \\ & \qquad (26.115) \end{aligned}$$

or

$$E = -\frac{\Delta G}{2F} = E^{\ominus} - \frac{RT}{2F}\log\frac{a^{\gamma}_{\mathrm{Zn}^{2+}}}{a^{\delta}_{\mathrm{Cu}^{2+}}} + (\phi^{\delta} - \phi^{\gamma}). \qquad (26.116)$$

The last term is called the *liquid junction potential difference*. It is generally hard to obtain this theoretically; experimentally, this potential difference can practically be removed with the aid of indifferent (or support) electrolyte method (→**26.38**) or by a salt bridge.

26.35 Concentration cells, an overview

Since chemical potentials depend on concentrations, even if the electrodes are the same and the solutions consist of the same chemicals but with different concentrations, the electromotive force of the following cell can be non-zero:

$$\mathrm{C} = \mathrm{M} \mid \mathrm{S}_1 \,\rule{0.15em}{1.2ex}\, \mathrm{S}_2 \mid \mathrm{M},$$

where S_1 and S_2 contain different concentrations (activities) of (say) M ions.

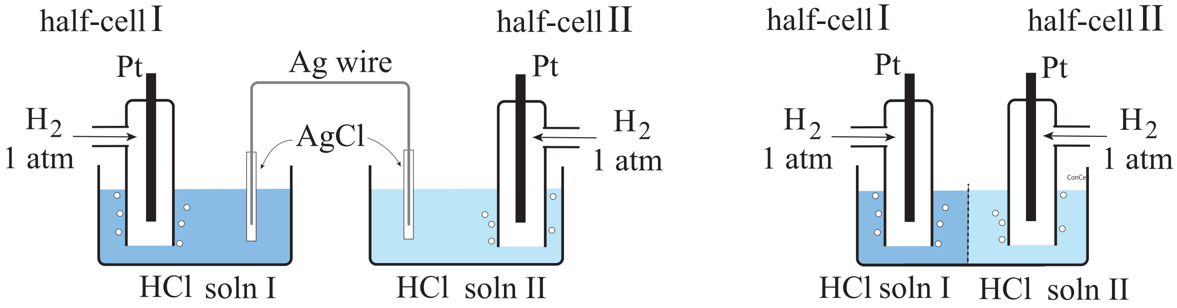

Figure 26.10: Two kinds of concentration cells

Fig. 26.10 Two kinds of concentration cells

Left: A concentration cell without any liquid-liquid junction

Right: A concentration cell with a liquid-liquid junction across a membrane (denoted by a dotted line)

There are two different ways to make such a cell depending on the choice of the connection ▮ between two half-cells.

First of all we can even remove the liquid/liquid contact altogether as illustrated in Fig. 26.10 Left. The second way is to separate the liquid phases with a membrane as illustrated in Fig. 26.10 Right. In this case the left and the right portions have different electric potential, so there is an electric double layer around the membrane to sustain the potential difference called the *membrane potential*.

26.36 Concentration cells without liquid-liquid junctions

This is illustrated in Fig. 26.10 Left. The cell may be expressed as

$$\mathrm{Pt} \mid \mathrm{H_2(I)} \mid \mathrm{HCl(I)} \mid \mathrm{AgCl} \mid \mathrm{Ag\text{-}Ag} \mid \mathrm{AgCl} \mid \mathrm{HCl(II)} \mid \mathrm{H_2(II)} \mid \mathrm{Pt}.$$

Note that the activities of solids are all 1 and the hydrogen gas is in the standard state. The electrode reactions in the positive direction are as follows:

$$\begin{aligned}
&\text{Leftmost Pt electrode: } (1/2)\mathrm{H_2} \longrightarrow \mathrm{H^+(I)} + \mathrm{e^-},\\
&\text{Left Ag electrode: } \mathrm{AgCl} + \mathrm{e^-} \longrightarrow \mathrm{Ag} + \mathrm{Cl^-(I)},\\
&\text{Right Ag electrode: } \mathrm{Ag} + \mathrm{Cl^-(II)} \longrightarrow \mathrm{AgCl} + \mathrm{e^-},\\
&\text{Rightmost Pt electrode: } \mathrm{H^+(II)} + \mathrm{e^-} \longrightarrow (1/2)\mathrm{H_2}\ .
\end{aligned}$$

Thus, the overall cell reaction in the positive direction is given by

$$\mathrm{H^+(II)} + \mathrm{Cl^-(II)} \longrightarrow \mathrm{H^+(I)} + \mathrm{Cl^-(I)}$$

or

$$\mathrm{HCl(II)} \longrightarrow \mathrm{HCl(I)}.$$

Therefore, the electromotive force E of this cell is given by

$$E = \frac{RT}{F} \log \frac{a_{\mathrm{HCl(II)}}}{a_{\mathrm{HCl(I)}}}. \tag{26.117}$$

If we introduce the logarithmic average $a_\pm$ of ionic activities for HCl (→**26.17**), this reads

$$E = \frac{2RT}{F} \log \frac{a_{\pm(\mathrm{II})}}{a_{\pm(\mathrm{I})}}. \tag{26.118}$$

26.37 Concentration cells with liquid-liquid junctions

This is illustrated in Fig. 26.10 Right. The cell may be expressed as

$$\mathrm{Pt} \mid \mathrm{H_2(I)} \mid \mathrm{HCl(I)} \parallel \mathrm{HCl(II)} \mid \mathrm{H_2(II)} \mid \mathrm{Pt}.$$

The electrode reactions in the positive direction are as follows:

Leftmost Pt electrode: $(1/2)\mathrm{H_2} \longrightarrow \mathrm{H^+(I)} + \mathrm{e^-}$,
Rightmost Pt electrode: $\mathrm{H^+(II)} + \mathrm{e^-} \longrightarrow (1/2)\mathrm{H_2}$.

Across the membrane the ion transport reactions can be written as

Transport of $\mathrm{H^+}$: $t_+ \ \mathrm{H^+(I)} \longrightarrow t_+ \ \mathrm{H^+(II)}$,
Transport of $\mathrm{Cl^-}$: $t_- \ \mathrm{Cl^-(II)} \longrightarrow t_- \ \mathrm{Cl^-(I)}$.

Here t_+ is the *transport number* of the cation, and t_- that of the anions. The *transport number* t_i of ion i is the fraction of the total electric current carried in an electrolyte by ion i. Thus, $t_+ + t_- = 1$. The overall transport reaction is given by

$$t_+\mathrm{H^+(I)} + t_-\mathrm{Cl^-(II)} \longrightarrow t_+\mathrm{H^+(II)} + t_-\mathrm{Cl^-(I)}. \tag{26.119}$$

Thus the overall positive reaction is given by

$$\mathrm{H^+(II)} + t_+\mathrm{H^+(I)} + t_-\mathrm{Cl^-(II)} \longrightarrow \mathrm{H^+(I)} + t_+\mathrm{H^+(II)} + t_-\mathrm{Cl^-(I)}$$

If we use $t_+ + t_- = 1$, this reads

$$(t_+ + t_-)\mathrm{H^+(II)} + t_+\mathrm{H^+(I)} + t_-\mathrm{Cl^-(II)} \longrightarrow (t_+ + t_-)\ \mathrm{H^+(I)} + t_+\mathrm{H^+(II)} + t_-\mathrm{Cl^-(I)}$$

That is,

$$t_-\mathrm{H^+(II)} + t_-\mathrm{Cl^-(II)} \longrightarrow t_-\mathrm{H^+(I)} + t_-\mathrm{Cl^-(I)}$$

or $\quad t_-\mathrm{HCl(II)} \longrightarrow t_-\mathrm{HCl(I)}$.

Therefore, the electromotive force of this cell is given by

$$E = \frac{2t_-RT}{F} \log \frac{a_{\pm(\mathrm{II})}}{a_{\pm(\mathrm{I})}}. \tag{26.120}$$

26.38 Membrane potential

According to (26.119) we have

$$t_+\mathrm{H^+(I)} - t_-\mathrm{Cl^-(I)} \longrightarrow t_+\mathrm{H^+(II)} - t_-\mathrm{Cl^-(II)}. \tag{26.121}$$

The electromotive force due to this reaction can be written as

$$E = \frac{2t_- RT}{F} \log \frac{a_{\pm(\mathrm{II})}}{a_{\pm(\mathrm{I})}} - \frac{RT}{F} \log \frac{a_{\mathrm{H}^+(\mathrm{II})}}{a_{\mathrm{H}^+(\mathrm{I})}}. \tag{26.122}$$

If we may assume $a_{\mathrm{H}^+} = a_\pm$, then the above formula may be approximated as

$$E = (t_- - t_+) \frac{RT}{F} \log \frac{a_{\pm(\mathrm{II})}}{a_{\pm(\mathrm{I})}}. \tag{26.123}$$

Thus, the membrane potential depends on transport numbers.

If we add overwhelming amount of a salt MX to the system with a membrane, then the charge balance across a membrane is sustained by the exchange of ions due to MX. Thus, the membrane potential is determined by MX called the *support electrolyte.* If the transport numbers of the cations and anions are close for the support electrolyte (as in the case of KCl), then it can eliminate the membrane potential.

26.39 Effects of solution phase equilibria

Suppose O and R make complexes with ligands L.

$$\begin{tikzcd}
\mathrm{O} \arrow[r, leftrightarrow, "ne^-"] \arrow[d, leftrightarrow, "K_\mathrm{O}"', "\mathrm{L}"] & \mathrm{R} \arrow[d, leftrightarrow, "K_\mathrm{R}"', "\mathrm{L}"] \\
\mathrm{OL} \arrow[r, leftrightarrow, "ne^-"] & \mathrm{RL}
\end{tikzcd} \tag{26.124}$$

Here, K' are dissociation constants such as

$$K_\mathrm{O} = \frac{a_\mathrm{O} a_\mathrm{L}}{a_\mathrm{OL}}, \quad K_\mathrm{R} = \frac{a_\mathrm{R} a_\mathrm{L}}{a_\mathrm{RL}} \tag{26.125}$$

It is customary to write the equilibrium electrode potential as

$$E = E^\ominus_\mathrm{app} + \frac{RT}{nF} \log \frac{a_\mathrm{O} + a_\mathrm{OL}}{a_\mathrm{R} + a_\mathrm{RL}}, \tag{26.126}$$

where

$$E^\ominus_\mathrm{app} = E^\ominus + \frac{RT}{nF} \log \frac{a_\mathrm{L}/K_\mathrm{R} + 1}{a_\mathrm{O}/K_\mathrm{O} + 1} \tag{26.127}$$

Note that if L is regarded as the electrode and the complexes are the results of adsorption, the formula describes the effect of adsorption.

If $a_\mathrm{L} \ll K$, then $E^\ominus_\mathrm{app} = E^\ominus$.

If O does not make appreciable complex with L but R makes a stable complex (that is $1/K_\mathrm{R} \gg 1$), then we consider

$$\mathrm{O} + \mathrm{L} + ne^- \to \mathrm{R} \tag{26.128}$$

so (26.127) reads

$$E^{\ominus}_{\mathrm{app}} = E^{\ominus} + \frac{RT}{nF}\log\frac{a_{\mathrm{L}}}{K_{\mathrm{R}}} \tag{26.129}$$

26.40 Contribution of protons

(26.128) with $\mathrm{L} = \mathrm{H}^+$ is often encountered in organic chemistry:

$$\mathrm{O} + m\mathrm{H}^+ + ne^- \to \mathrm{RH}_m \tag{26.130}$$

In this case (26.129) becomes

$$E^{\ominus}_{\mathrm{app}} = E^{\ominus} + \frac{RT}{nF}\log\frac{a^m_{\mathrm{H}^+}}{K_{\mathrm{R}}} = E^{\ominus} + \frac{mRT}{nF}\log a_{\mathrm{H}^+} + C. \tag{26.131}$$

That is,

$$E^{\ominus}_{\mathrm{app}} = E^{\ominus} - \frac{m}{n}\frac{2.303RT}{F}\mathrm{pH} + C. \tag{26.132}$$

This allows us to determine m/n.

26.41 Determination of entropy change electrochemically[484]

Consider the following cell:

$$\mathrm{Pt}(\alpha)\,|\,\mathrm{Pb}^{(\mathrm{Hg})}\,|\,\text{Salt Soln of }\mathrm{PbI}_2\,|\,\mathrm{PbI}_2\,|\,\mathrm{I}\,|\,\mathrm{Pt}(\beta). \tag{26.133}$$

Here, superfix (Hg) implies an amalgam and I is solid. The reaction is

$$\frac{1}{2}\mathrm{Pb}^{(\mathrm{Hg})} + \mathrm{I} \to \frac{1}{2}\mathrm{PbI}_2. \tag{26.134}$$

For the cell at 25 °C the measured results are

$$E_1 = 893.62\ \mathrm{mV}, \quad \frac{\partial E_1}{\partial T} = -0.042 \pm 0.005\ \mathrm{mV\ K}^{-1}. \tag{26.135}$$

For the following cell

$$\mathrm{Pt}(\alpha)\,|\,\mathrm{Pb}^{(\mathrm{Hg})}\,|\,\mathrm{PbI}_2\,|\,\text{Salt Bridge of KI}\,|\,\mathrm{AgI}\,|\,\mathrm{Ag}\,|\,\mathrm{Pt}(\beta) \tag{26.136}$$

the reaction is

$$\frac{1}{2}\mathrm{Pb}^{(\mathrm{Hg})} + \mathrm{AgI} \to \frac{1}{2}\mathrm{PbI}_2 + \mathrm{Ag}. \tag{26.137}$$

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[484] taken from E. A. Guggenheim, *Thermodyamics* (Fifth revised edition, 1967 North-Holland Publ. Co.) Section 8.13.

For the cell at 25 °C the measured results are

$$E_2 = 207.8 \pm 0.2 \text{ mV}, \ \frac{\partial E_2}{\partial T} = -0.0188 \pm 0.002 \text{ mV K}^{-1}. \tag{26.138}$$

Subtracting (26.137) from (26.134), we obtain the reaction (i.e. 1 minus 2)

$$\mathrm{Ag} + \mathrm{I} \to \mathrm{AgI}. \tag{26.139}$$

Therefore, for this reaction

$$E = E_1 - E_2 = 685.8 \pm 0.2 \text{ mV}, \ \frac{\partial E}{\partial T} = \frac{\partial E_1}{\partial T} - \frac{\partial E_2}{\partial T} = 0.146 \pm 0.004 \text{ mV K}^{-1}. \tag{26.140}$$

E gives $\Delta G = -EF = -66.17$ kJ/mV·mol, where $F = 0.09649$ kJ/mV·mol is used. Its temperature differentiation gives $\Delta S = -\partial \Delta G/\partial T = F \partial E/\partial T = 14.06 \pm 0.4$ J/K·mol. Both values are at 298 K.[485]

Calorimetrically, $S(298 \text{ K}) - S(0)$ are known (in unit J/K·mol) as for AgI: 115 ± 1.2, Ag: 42.5 ± 0.4, I: 58.4. These data give $\Delta S(298 \text{ K}) - \Delta S(0)$ for this reaction to be 14.6 ± 1.2 J/K·mol. From this we can compute $\Delta S(0)$ as -0.5 ± 1.3 J/K·mol. This confirms the third law (→**24.3**).

26.42 Example of a cell based on biochemistry

Electric cells may be constructed not only with the aid of metal ions but also with physiologically crucial chemicals. Here an example using the TCA cycle is illustrated (Fig. 26.11).

Fig. 26.11 Schematic of the complete biofuel cell. Ethanol is oxidized serving as the fuel source at the anode (dark red lettering represents dehydrogenase enzymes, whereas the light red/pink lettering represents other non-energy producing enzymes). Oxygen is reduced to water at the 20% Pt on carbon GDE (= ELAT gas diffusion electrode) cathode. Potentiostat is used to measure open circuit potential and linear sweep polarization curves.[486]

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[485] Thus, we have

$$\Delta H = \Delta G + T\Delta S = -61.95 \text{ kJ/mol} = -14.81 \text{ kcal/mol}.$$

Its calorimetric value is known as −14.97 kcal/mol.

[486] Daria Sokic-Lazic, & Shelley D. Minteer, Citric acid cycle biomimic on a carbon electrode, Bios Bioe 24 839 (2008). The citric acid cycle uses acetyl-CoA as the substrate and undergoes eight en-

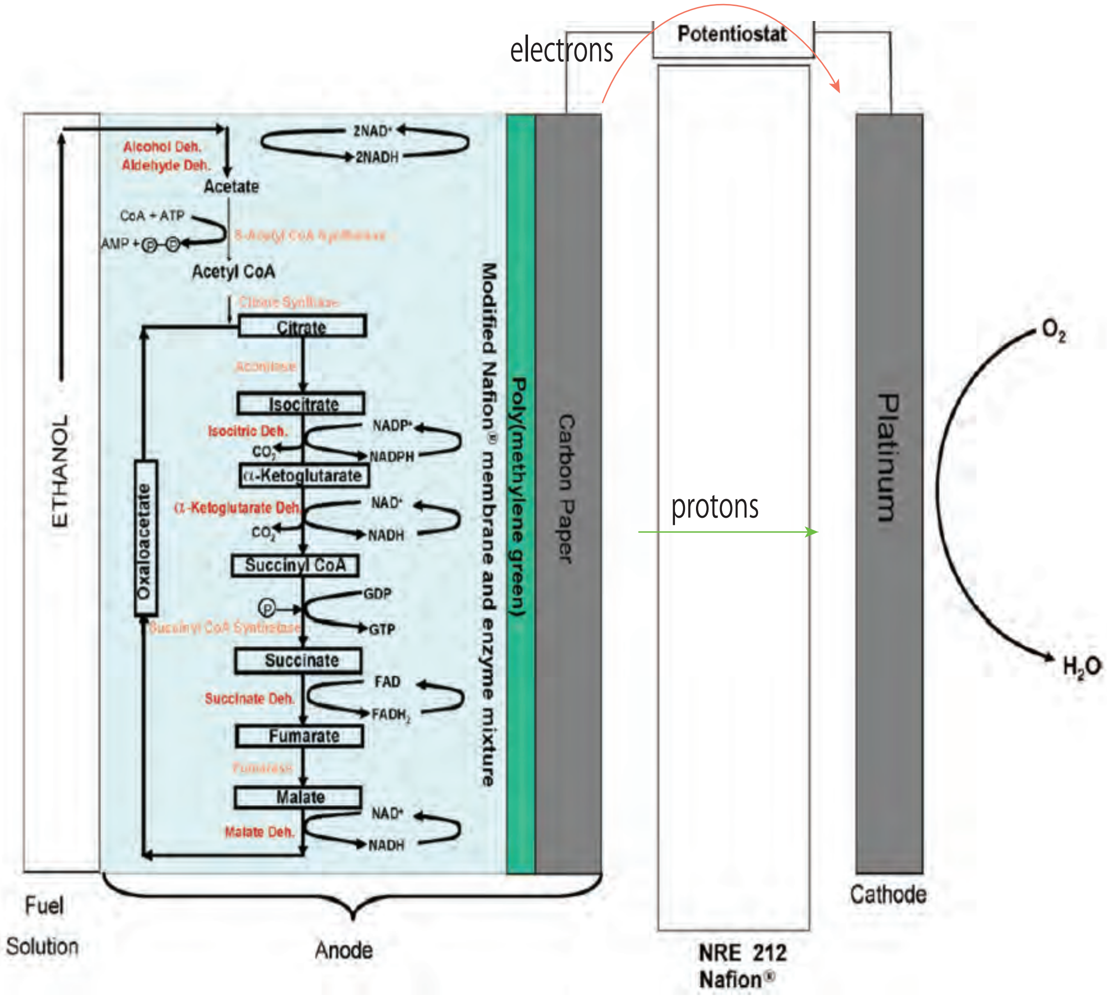

Figure 26.11: Biophysical fuel cell that utilizes ethanol as its fuel. [Fig. 1 of Sokic-Lazic, & Minteer, Bios Bioe 24 839 (2008)]

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zymatic reactions out of which four are electron producing dehydrogenases. The electron producing enzymes of the citric acid cycle are NAD-dependent dehydrogenases except for succinate dehydrogenase (SDH), which is a FAD-dependent dehydrogenase. The redox couples NAD$^+$/NADH and FAD/FADH$_2$ are two electron electrochemical processes and their regeneration can be catalyzed by poly(methylene green).

All the enzymes employed for this biomimic were immobilized in a quaternary ammonium bromide salt modified Nafion membrane layer. Dehydrogenase enzymes along with non-electron producing enzymes and cofactors were immobilized in cascades for the cycle to progress.

Since dehydrogenase enzymes are NAD$^+$-dependent, a polymer-based electrocatalyst (poly(methylene green))was used to regenerate NAD$^+$ and to shuttle electrons from NADH to the electrode.

The starting point for this biomimic was ethanol. ADH, AldDH, and S-acetyl-CoA synthetase

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were incorporated along with all the enzymes and cofactors of the citric acid cycle. The entire ethanol metabolic path can be seen in Fig. 26.11.

Naflon: the brand name used by DuPont for a series of fluorinated sulfonic acid copolymers, the first synthetic ionic polymer. It is resistant to chemical breakdown, making it useful for membranes in proton exchange membrane fuel cells. [Energy Library]

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