Chemical Thermodynamics Revisited[1]

The currently available textbooks on thermodynamics handle chemistry hardly seriously, which start with principles that do not discuss chemistry explicitly. Yet, those who teach chemical thermodynamics remain silent, and fail to mention any serious issues. I will try to summarize as simply as possible what the problems are and outline what we should do.

1 The aim of this short note

I will point out that expositions of (chemical) thermodynamics have serious difficulties and then discuss how to amend them. An amended course (ver. 0.82) is proposed on my homepage.[2]

2 Elementary chemical facts

Fundamental facts about chemistry are imported to thermodynamics from elementary chemistry. The following three principles are particularly notable:
(I) The possibility of reversible separation and mixing of compounds ($\rightarrow$[20]),
(II) The uniqueness of chemical equilibrium ($\rightarrow$[21]), and
(III) The potential for the formation of any compound through redox reactions ($\rightarrow$[22]).

Here, (II) implies the following: if a system is prepared with energy E, volume V and moles $\boldsymbol{N}$ of chemical compounds, then there is a map R (called the reaction map) that uniquely gives the equilibrium chemical composition $\tilde{\boldsymbol{N}}$ of the system as $\tilde{\boldsymbol{N}} = R_{E,V}(\boldsymbol{N})$ ($\rightarrow$[21]).

Difficulties of (chemical) thermodynamics textbooks

3 Basic variables of chemical thermodyamics

The existing courses on (chemical) thermodynamics adopt internal energy E, extensive work coordinates (here, for simplicity, only the volume V), and the number of moles $\tilde{\boldsymbol{N}} = (\tilde{N}_1, \tilde{N}_2, \cdots)$ of chemical compounds present in the system (which we will refer to as chemical composition coordinates) as the fundamental extensive variables

---

(thermodynamic coordinates) used to describe the state.

4 Principles of thermodynamics with chemical reactions, preliminary

When starting to explain thermodynamics, there should at least be some description of the system's materials composition and the energy exchanges involving the materials (the so-called mass action Z). At the very least, the equivalence of the energy represented as mass action Z involved in chemical reactions and the ordinary mechanical work W must be stated as a principle based on empirical facts.[3]

Is there a thermodynamics textbook that meets the requirements mentioned here?

5 Thomson's principle with chemical reactions

The traditional principle that "it is impossible to perform work with a single heat source without leaving any other trace" is correct if chemical work is also included as "work." In other words, after at least describing the Z-W relationship as stated in [4], the conventional form of Thomson's principle can be used as the basis for (chemical) thermodynamics.

Of course, descriptions concerning chemical energy must first be included in the first law.

6 Planck's principle with chemical reactions

Planck's principle or the equivalent is needed to establish entropy with its increasing principle. The principle is expressed as, "In an adiabatic process where work coordinates (such as V) are altered in a cycle, the internal energy does not decrease." The entropy derived from this principle without explicit chemistry is applied without any caution to chemical reactions.

In textbooks that adopt $(E, V, \tilde{\boldsymbol{N}})$ as thermodynamic coordinates (all textbooks), in order to include chemistry, it would be a simple extension of Planck's principle, stating, "In cycles concerning thermodynamic coordinates other than E, the internal energy does not decrease." However, due to the uniqueness of chemical equilibrium (II), in such cycles E generally does not change (see (9) or R in [2]), so the "Planck's principle" described above is almost meaningless.

Even in thermodynamics formulations centered around temperature, it is required

---

[3]First, the quantitative equivalence of chemical and mechanical energies, analogous to the Mayer-Joule equivalence of heat and work, has been considered established electrochemically by Faraday and others. However, this is an ancient story of BC (Before Clausius).

Existing thermodynamics takes it for granted that chemical energy and mechanical energy are equivalent in the sense of the second law as well. This relation should be explicitly stated at the outset of thermodynamics as a principle with supporting empirical facts.

that "temperature increases after an adiabatic cycle," but due to the uniqueness of chemical equilibrium, cycles cannot generally occur if the temperature changes.

The issues pointed out here arise solely due to chemical reactions. However, as indicated below ($\rightarrow$[7], [8]), the chemical composition variables $\tilde{\boldsymbol{N}}$ also have properties that are inconvenient as fundamental variables in thermodynamics.

7 The amounts of existing chemicals $\tilde{\boldsymbol{N}}$ are usually not operational

When chemical reactions occur, the quantities of chemicals added by the experimenter do not remain intact within the system. Instead, the amounts present are always the result of new chemical equilibria.[4] Under the constant E, V condition, we expect

$$d\tilde{\boldsymbol{N}} = R_{E,V}(\boldsymbol{N} + d\boldsymbol{N}) - R_{E,V}(\boldsymbol{N}) = R_{E,V}(\boldsymbol{N} + d\boldsymbol{N}) - \tilde{\boldsymbol{N}}. \tag{1}$$

Note that the experimenter cannot directly control $d\tilde{\boldsymbol{N}}$.

8 The amounts of existing chemicals $\tilde{\boldsymbol{N}}$ are not additive

Even if we combine two equilibrium systems $(E_{\text{I}}, V_{\text{I}}, \tilde{\boldsymbol{N}}_{\text{I}})$ and $(E_{\text{II}}, V_{\text{II}}, \tilde{\boldsymbol{N}}_{\text{II}})$ in a hard adiabatic container, we cannot obtain the state $(E_{\text{I}} + E_{\text{II}}, V_{\text{I}} + V_{\text{II}}, \tilde{\boldsymbol{N}}_{\text{I}} + \tilde{\boldsymbol{N}}_{\text{II}})$. Needless to say, the results for the internal energy and the volume are correct due to their additivity. However, since the equilibrium chemical compositions generally depend on chemical concentrations which are not additive, the chemical composition of the resultant equilibrium system is not $\tilde{\boldsymbol{N}}_{\text{I}} + \tilde{\boldsymbol{N}}_{\text{II}}$. Consequently, even if one could demonstrate the increasing principle of entropy under adiabatic conditions,

$$S(E_{\text{I}} + E_{\text{II}}, V_{\text{I}} + V_{\text{II}}, \tilde{\boldsymbol{N}}_{\text{I}} + \tilde{\boldsymbol{N}}_{\text{II}}) \geq S(E_{\text{I}}, V_{\text{I}}, \tilde{\boldsymbol{N}}_{\text{I}}) + S(E_{\text{II}}, V_{\text{II}}, \tilde{\boldsymbol{N}}_{\text{II}}) \tag{2}$$

cannot be shown generally. That is, $-S$ is not a convex function of the thermodynamic coordinate adopted by the existing textbooks. Therefore, we cannot claim such a basic inequality as $\delta^2 S \geq 0$, so Le Chatelier's principle cannot be demonstrated generally. Furthermore, the convexity of the internal energy does not hold. In short thermodynamic variational principles cannot be formulated.

Revising textbooks

9 What is the difficulty and how to amend it

Describing the materials composition of a system is certainly essential, and the most natural variables for this purpose are the mole numbers $\tilde{\boldsymbol{N}}$ of all compounds currently existing in the system. Therefore, $(E, V, \tilde{\boldsymbol{N}})$ is adopted as the thermodynamic coordinates in all textbooks.[5] However, there are many issues with $\tilde{\boldsymbol{N}}$, such as being non-operational [7] or non-additive [8].

---

[4]Remember that thermodynamics deals only with equilibrium systems.

[5]With allowing the freezing equilibrium without reactions in a small number of serious textbooks as Guggenheim's and Kirkwood-Oppenheim's to make all the variables mathematically independent.

The variables $\boldsymbol{N}$ for the amounts of chemicals introduced by Gibbs ($\rightarrow$[21]), who proposed the chemical potential, are considered operational variables, i.e., quantities that the experimenter can actually add, since his paper did not deal with chemical reactions. This makes $\boldsymbol{N}$ distinct from $\tilde{\boldsymbol{N}}$.

Thus, it should be candidly acknowledged that there are two types of variables for representing the amount of chemical substances in thermodynamics. One is the "chemical composition coordinates" $\tilde{\boldsymbol{N}}$, which represent the quantities actually measured by the experimenter as existing within the system, and the other is the "materials coordinates" $\boldsymbol{N}$, used to describe direct operations such as when experimenters actually add chemicals to the system. The relationship between the two is provided by the reaction map R ($\rightarrow$[2], [21]).

10 Characters of materials coordinates

The materials coordinates $\boldsymbol{N}$, newly named in [9] are coordinates that describe the amount of chemicals that the experimenter can (in principle) handle. The most common interpretation of the materials coordinates $\boldsymbol{N}$, which Gibbs at least implicitly assumed, is the "batch quantity," that is, the number of moles of various compounds that the experimenter uses when setting up a closed system. $d\boldsymbol{N}$ denote the number of moles of various compounds added later by the experimenter.

The materials coordinates $\boldsymbol{N}$ is trivially additive when two systems are combined:

$$(E_{\mathrm{I}}, V_{\mathrm{I}}, \boldsymbol{N}_{\mathrm{I}}) + (E_{\mathrm{II}}, V_{\mathrm{II}}, \boldsymbol{N}_{\mathrm{II}}) = (E_{\mathrm{I}} + E_{\mathrm{II}}, V_{\mathrm{I}} + V_{\mathrm{II}}, \boldsymbol{N}_{\mathrm{I}} + \boldsymbol{N}_{\mathrm{II}}). \tag{3}$$

When the system is not closed, the Gibbs relation is expressed as:

$$dE = TdS - PdV + \sum \mu_i dN_i, \tag{4}$$

where S, V, $N_1, N_2, \ldots$ are mutually independent variables (even without freezing reactions).

11 Mathematically well defined thermodynamic coordinates

The most straightforward conclusion of [10] is that mathematically the thermodynamic coordinates are $(E, V, \boldsymbol{N})$, and cannot be $(E, V, \tilde{\boldsymbol{N}})$.

12 Can we do with materials coordinates alone?

As concluded in [11], theoretically, the materials coordinates $\boldsymbol{N}$ are fundamental coordinates. Fundamentally, the materials coordinates $\boldsymbol{N}$ describes operations on chemical quantities by the experimenter from outside the system. However, as long as chemical reactions occur, the actual amounts of chemicals are $\tilde{\boldsymbol{N}}$ ($\neq \boldsymbol{N}$ generally). This is the nature of chemical reactions.

If one knows the reaction map R ($\rightarrow$[21]), discussions could be settled with only $\boldsymbol{N}$. However, to determine the reaction map, one must use thermodynamics to determine the chemical

equilibrium states, that requires chemical potentials, which are usually expressed in terms of $\tilde{\boldsymbol{N}}$. Therefore, in practical calculations, it is most practical to continue using the chemical composition coordinates, as traditionally done.

13 Why was there any distinction of two chemical coordinates?

It seems natural that there is a difference between the chemical composition coordinate $\tilde{\boldsymbol{N}}$ and the materials coordinates $\boldsymbol{N}$. Their separate use also seems natural. Yet, such distinct variables have never been introduced. Why is that?

To me, the reason seems quite simple. Situations where both coordinates appear simultaneously have been avoided. When adding chemicals, there is no reaction (for example, it is frozen in serious textboks), and when a reaction occurs, the system is closed. Therefore, in the former case, the materials coordinates equal the frozen chemical composition coordinates, and in the latter, only the chemical composition coordinates appear.

However, one must not overlook a critical point: if reactions are always frozen whenever the materials coordinates naturally appear, chemical thermodynamics could not be formulated at all ($\rightarrow$[**4**]).

14 The Second Principles with chemical reactions

Issues were pointed out with the traditional choice of thermodynamic coordinates ([**4**]-[**6**]), but if the coordinates are $(E, V, \boldsymbol{N})$, E and $\boldsymbol{N}$ are always independent variables. According to Planck's principle, it is sufficient to extend the work coordinates to include materials coordinates. From this, in contrast to the false (2), the convexity of $-S$ follows:

$$S(E_{\mathrm{I}} + E_{\mathrm{II}}, V_{\mathrm{I}} + V_{\mathrm{II}}, \boldsymbol{N}_{\mathrm{I}} + \boldsymbol{N}_{\mathrm{II}}) \geq S(E_{\mathrm{I}}, V_{\mathrm{I}}, \boldsymbol{N}_{\mathrm{I}}) + S(E_{\mathrm{II}}, V_{\mathrm{II}}, \boldsymbol{N}_{\mathrm{II}}). \qquad (5)$$

Therefore, we can demonstrate the principle of increasing entropy. Needless to say, the convexity of internal energy also follows.

Under the conventional choice of variables $(E, V, \tilde{\boldsymbol{N}})$, this cannot be demonstrated ($\rightarrow$[**8**]). Therefore, tools of convex analysis are not applicable. For example, since the Legendre(-Fenchel) transformation does not work, the Gibbs energy cannot be properly defined, and of course, the principle of minimum free energy also makes no sense.

Why rewriting needed

I will emphasize once more that, as it stands, it is difficult to assign a mathematical meaning to chemical thermodynamics explained in the existing textbooks.

15 The difficulties of the current chemical thermodynamics

The conventional fundamental variables $\tilde{\boldsymbol{N}}$ are not independent from E and V in a closed system ($\rightarrow$[**21**]). Furthermore, within $\tilde{\boldsymbol{N}} = (\tilde{N}_1, \tilde{N}_2, \cdots)$, the amounts of chemicals are not independent variables due to chemical equilibrium relationships.

This is recognized in (the few) serious thermodynamics textbooks (such as Guggenheim and Kirkwood-Oppenheim), and to avoid this difficulty "frozen equilibrium states" are utilized where the chemical compositions can be frozen without disturbing the equilibrium states 'whenever one likes.' [6]

Depending on how 'whenever one likes' is interpreted, it can even make violating the law of conservation of energy possible. The biggest issue with the "freezing method" is how to apply the principles of thermodynamics under freezing to chemical reactions themselves ($\rightarrow$[4]).

While the following is a very minor issue compared to the above, most textbooks discuss chemical reactions and adopt $(E, V, \tilde{\boldsymbol{N}})$ as the thermodynamics coordinates without mentioning the freezing assumption at all. Therefore, the Gibbs relation is written as:

$$dE = TdS - PdV + \sum_i \mu_i d\tilde{N}_i. \tag{6}$$

Consequently, the absolute temperature is defined as:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,\tilde{\boldsymbol{N}}}. \tag{7}$$

Remember that $\tilde{\boldsymbol{N}} = R_{E,V}(\boldsymbol{N})$. $\tilde{\boldsymbol{N}}$ is a function of E, if V is fixed and if the system is materially closed (fixing $\boldsymbol{N}$). The partial derivative in (7) is mathematically meaningless.[7]

16 Freezing reactions does not rescue chemical thermodynamics

What we understand from [6] and [15] is that chemical reactions are the 'root of all evil.' Then, as mentioned in [15], why not consider the 'frozen equilibrium' as per Guggenheim's approach? If the descriptions of traditional principles such as the Second Law are under frozen conditions, wouldn't that resolve the issue?

However, can a theory constructed using principles that either completely ignore or only address reactions under frozen conditions handle chemical reactions that are not frozen?[8] After determining the equilibrium state achieved in a reaction-frozen

---

[6]Negative catalysts might be introduced to achieve this, but this does not fit well with thermodynamics ($\rightarrow$[18]). Pauli's last published paper proposed an alternative (although specific to certain reactions), disliking overly arbitrary use of negative catalysts.

[7]If $(E, V, \boldsymbol{N})$ are adopted as the thermodynamic coordinates, the definition of absolute temperature becomes proper:

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,\boldsymbol{N}}. \tag{8}$$

[8]In the case of Planck's principle, no chemical work such as done by electrochemistry should be frozen while discussing the internal energy change.

state variationally and then unfreezing it, what principle determines the course of the reaction? Current textbooks unconditionally use the principle of minimum Gibbs energy, but as already seen in [**14**], there are fundamental problems with the Legendre transformation.

17 Chemostats are useless for thermodynamics

The reader might think that using a chemostat to fix the existing amount of compounds $\tilde{\boldsymbol{N}}$ could give meaning to (7). However, in equilibrium thermodynamics, this is generally not possible. Since $(E, V, \tilde{\boldsymbol{N}})$ represents an equilibrium state, and the chemical equilibrium is unique, changing E to E' ($\neq E$) would generally result in $(E', V, \tilde{\boldsymbol{N}})$ not being an equilibrium state. Indeed, while it might be possible to set variables $(E', V, \tilde{\boldsymbol{N}})$ using suitably designed chemostats, what is generally achieved with chemostats is a non-equilibrium steady state, not an equilibrium. Thus, in equilibrium thermodynamics, a chemostat is a potentially dangerous device that can disrupt equilibrium.

As can be seen, while it is always in principle possible to fix conventional work coordinates and internal energy without energetic cost to the experimenter while maintaining the equilibrium state, it is generally not possible to externally fix the amount of chemical substances present in the system while modifying E and V in the equilibrium state.

In other words, let us note the asymmetry in operations: it is possible to add something externally to change the chemical composition while fixing the thermodynamic coordinates not related to chemical composition (in our case, E and V), whereas it is generally not possible to vary E and V while keeping the chemical composition fixed[9]

18 There is no room for catalysts in thermodynamics

A catalyst, in the most general sense, is a substance that alters chemical reaction rates within a system but remains unchanged before and after the reaction. In the conventional sense, it refers to a substance that promotes chemical reactions in the system in such minute amounts that it does not change the composition of the system. A catalyst that accelerates a reaction is called a positive catalyst, while one that inhibits a reaction is called a negative catalyst. However, a small amount of negative catalyst is naturally meaningless; if one wants to stop a reaction that would otherwise proceed on its own, a stoichiometric amount of negative catalyst is needed, which significantly alters the composition of the system. Therefore, the concept of a "small amount of negative catalyst" is in itself contradictory (an oxymoron).

Can positive catalysts be used in thermodynamics? A positive catalyst is a catalyst that enables reactions that are thermodynamically feasible but kinetically slow. Adding a small amount of positive catalyst is akin to punching a small hole in a high-pressure gas cylinder. In other words, the resulting reaction is generally non-quasistatic. Therefore, positive catalysts cannot be used in the development of thermodynamics (except perhaps to maintain an equilibrium state).

19 Is the 'top-down' entropy based thermodynamics without any prob-

---

[9]Chemical thermodynamics prefers the set of variables $(T, P, \tilde{\boldsymbol{N}})$, but in this case, while it is possible to change $\tilde{\boldsymbol{N}}$ by adding chemicals under constant T and P, it would generally not be possible to change T and/or P while keeping $\tilde{\boldsymbol{N}}$ as an equilibrium state.

lem?[10]

As already stated in [**4**]-[**6**], when chemical reactions are present, entropy satisfying the principle of increase cannot be derived from the conventional second law, so the issue of whether or not convex analysis tools are applicable is moot. Thus, discussions in lectures or courses on chemical thermodynamics that derive entropy during the course are flawed.

Fortunately, the 'top-down' approach, which has been familiar to physicists since Guggenheim and was popularized by Callen, assumes entropy and several of its properties, including the principle of increase. However, even Guggenheim, who primarily describes chemical thermodynamics, does not reflect on the fundamental variables as mentioned previously. Therefore, the concavity of entropy (unless reactions are frozen) does not hold. In other words, convex analysis does not function (the variational principle is not applicable to chemistry). In the presence of chemical reactions, it is highly unlikely that the definition of Gibbs energy is mathematically sound.

Elementary chemical facts: auxiliary comments

20 Possibility of reversible mixing/demixiing of chemicals (I)

This discussion pertains to the existence of what is known as a semipermeable membrane. Many physicists, including Fermi, seem to think that such things do not exist and should not be used. This view stems from their lack of understanding of what a "semipermeable membrane" actually is.

When two distinct compounds are present, it is possible to separate them quasi-statically and reversibly, for example, by utilizing phase changes.[11]Techniques like reversible thin-layer chromatography, concentric cylindrical multi-stage distillation columns, or gas chromatography can nearly achieve complete separation. Although it is not feasible to reach the ideal limit in reality, a "semipermeable membrane" or "selective permeable membrane" is an idealized device, much like a lossless transformer in circuit theory, that nearly approaches reality. In other words, a "semipermeable membrane" or "selective permeable membrane" is a "symbol" representing (I) in [**2**].

It should not be forgotten that many textbooks on chemical thermodynamics rely on much more unrealistic concepts (such as negative catalysts →[**18**]) to develop their explanations.

21 What (II) uniqueness of chemical equilibrium implies

For simplicity, let us consider the work coordinate of the system to be only the volume V. This

---

[10]In a serious introductory course on thermodynamics, a top-down approach starting with entropy is improper. It is worth considering the historical fact that Thomson was unable to grasp the concept of entropy, and that the concept was not understood by British physicists until Gibbs's papers became widely known. This should be carefully considered in undergraduate-level courses.

[11]Of course, there could be various problems with unstable compounds, but here we consider the most elementary scenario. Generally, it is sufficient to consider the separation of a compound along with equilibrium mixture containing it.

means that if the system is materially closed, the thermodynamic coordinates that represent its equilibrium state are solely the internal energy E and V. To specify a particular equilibrium state of a closed system, one would normally specify its chemical composition $\tilde{\boldsymbol{N}} = (\tilde{N}_1, \tilde{N}_2, \cdots)$ (where $\tilde{N}_i$ is the molar quantity of compound i in the system) along with E and V. However, in reality, since the system is closed, it is sufficient to specify the amounts of chemical substances $\boldsymbol{N} = (N_1, N_2, \cdots)$ that are prepared when the system is created. The equilibrium state of this system is uniquely determined by $(E, V, \boldsymbol{N})$, which is the meaning of the uniqueness of chemical equilibrium (II). In other words, there exists a map R (called the reaction map) from $(E, V, \boldsymbol{N})$ to the current equilibrium chemical composition $\tilde{\boldsymbol{N}}$:

$$\tilde{\boldsymbol{N}} = R_{E,V}(\boldsymbol{N}). \tag{9}$$

In a closed system, since $\boldsymbol{N}$ are fixed, the mole numbers of chemical substances $\tilde{\boldsymbol{N}}$ present in the systemare not an independent variable thermodynamically. Therefore, the Gibbs relation for a closed system, regardless of its chemical structure or composition, is always:

$$dE = TdS - PdV. \tag{10}$$

Terms like $\sum \mu dN$ do not appear.[12]

22 Possible redox production of chemicals
While (III) in [**2**] is usually not mentioned, it is considered essential for incorporating chemistry into physics as explained in the following.

The relationship between chemical energy, or the energy obtained from chemical reactions, and mechanical energy must be understood in order to handle chemical energy in thermodynamics. Recall that energy was clearly defined in classical mechanics, and that heat was meaningful in physics only when it was connected with mechanical energy. Thanks to Faraday's work, chemical energy has been linked to well-understood physical energy using batteries powered by electrochemistry. To achieve this, it suffices to construct a battery; essentially, it is enough to produce certain compounds through redox reactions. In principle, ions can be produced by breaking covalent bonds, so chemical bonds can be formed through redox reactions. Therefore, "in principle," any compound can be produced as a battery reaction. Thus, chemical energy can be converted into mechanical energy (via electrical energy). The reverse reaction can also "in principle" be realized as an electrolytic reaction.

---

[12]This is properly noted in the Kirkwood-Oppenheim textbook. However, the reason this term does not exist is not due to the usual condition of chemical equilibrium, "summing to zero," but rather simply that each dN_i does not exist ($d\boldsymbol{N} = 0$).