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Chemical potential—a quantity in search of recognition

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Abstract
The chemical potential is a quantity for which students hardly have an intuitive feeling in contrast to other intensive quantities like pressure or temperature. Some students may believe that this is not really an insufficiency because the chemical potential seems to be essentially a quantity for chemists. We will try to show that the chemical potential does not merit its reputation as a difficult to understand quantity. Not only is it easy to grasp, it is a particularly intelligible quantity for which even the layman can develop a feeling. Moreover, this quantity is not only important for chemists. It is just as useful for describing physical phenomena and processes, such as phase transitions, the stratification of gases in a gravitational field and electric currents in semi-conductor junctions and nuclear reactions, to mention just a few.

1. Introduction

One of the variables appearing in Gibbs's fundamental equation (Callen 1960, p 32, Falk *et al* 1983) is the chemical potential μ:

$$\mathrm{d}E = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}n + \varphi\,\mathrm{d}Q + \mathbf{v}\,\mathrm{d}\mathbf{p} + \psi\,\mathrm{d}m + \cdots . \tag{1}$$

Each of the terms on the right-hand side of the equation is the product of the differential of an extensive quantity and the energy-conjugated intensive quantity.

The equation tells us that we can change the energy of a system in various ways: by changing its entropy S, its volume V, its amount of substance n, its electric charge Q, its momentum $\mathbf{p}$, its mass m, etc. The intensive quantity determines the magnitude of an energy change related to a change of the corresponding extensive quantity. For example, if we add the entropy dS to a system, the energy increase is large if the temperature is high, and it is small, if the temperature is low.

Our intuitive understanding of most of the intensive variables in equation (1) is rather clear. Everybody has a vivid idea about the temperature T and pressure p. We all know the electric potential φ from high school or from introductory lectures about electromagnetism:

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a potential difference appears as the cause of an electric current. Velocity $\mathbf{v}$ is familiar to every child. A physicist does not have problems with the understanding of the gravitational potential ψ: he knows that we feel its increase whenever we lift a body.

The state of affairs seems to be different for the chemical potential. Most physicists have to deal with it only occasionally. Although it is treated in thermodynamics lectures, it remains rather nondescript. It seems difficult to get an intuitive feeling for the chemical potential[3].

Only in some domains of advanced physics, such as statistical physics (see for instance Reif 1965) or the theory of the chemical bond (Parr *et al* 1978, Politzer and Weinstein 1979, Ganguly 2000) is it commonly used. A thorough analysis of various dissenting definitions of the chemical potential in the framework of statistical physics has recently been given by Kaplan (2005). In the thermodynamic limit, which is our concern in this paper, they all give the same result.

When introduced in lectures on statistical mechanics, the students hardly get a more concrete idea about the part it plays in nature. Moreover, it seems that many physicists do not view this as a shortcoming. Actually, some may not really know what the chemical potential could be useful for and they probably feel that, as the name suggests, it is a quantity reserved for chemists.

Three things will be shown in the following:

- that the chemical potential does not deserve its reputation as a quantity we cannot develop a feeling for;
- that the chemical potential can be introduced and effectively applied without taking a detour via thermodynamics;
- that the chemical potential is not only important for chemists, but is also extraordinarily useful to physicists.

In recent years, dissatisfaction about the virtual non-existence of the chemical potential in physics curricula has been mentioned in, or was the subject of, several articles (Cook and Dickerson 1995, Baierlein 2001).

The proposal of Cook and Dickerson (1995) for understanding the chemical potential is based on the equation

$$\mu = \left(\frac{\partial E}{\partial n}\right)_{S,V..} \tag{2}$$

which follows from equation (1). Baierlein (2001) discusses the question more comprehensively and gives three characterizations of the chemical potential. The third of these is the one given in equation (2). He also mentions that this manner of introducing μ corresponds to introducing the temperature via

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,n..}. \tag{3}$$

There is no doubt that relations (2) and (3) must have their place in lectures on thermodynamics. We believe, however, that neither the first nor the second is appropriate for a first contact with the quantity on the left-hand sides of these equations. Note that similar relations could be used to introduce the other intensive quantities of equation (1), i.e., pressure, electric potential difference, velocity, gravitational potential, and so on. However, we prefer a more direct access whenever possible, so we do not introduce the pressure as

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,n..}$$

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[3] Callen (1960, p 48) writes: '. . . the reader is apt to feel that he has an intuitive response to the concepts of temperatures and pressure, which is lacking, at least to some degree, in the case of the chemical potential'.

or the velocity as

$$v_i = \left(\frac{\partial E}{\partial p_i}\right)_{S,n..} .$$

Instead of explaining the chemical potential by relating it to an energy change, we propose to introduce it by describing its properties. We will explain it in the same manner as one would explain temperature to a person who does not know the concept: temperature measures our feeling of hot and cold. Temperature tells us in which direction heat spontaneously flows, etc.

Introducing the chemical potential in this manner corresponds to Baierlein's first and second characterizations: (1) the chemical potential measures the tendency to diffuse and (2) the chemical potential measures the 'rate of change' (not in time) of a thermo-dynamical function.

Our approach is related to these two characterizations. It differs from them, however, in two respects:

- we subsume both characterizations of the chemical potential under one single property: the tendency of substances to change their location, chemical composition or state of aggregation;
- we will keep out thermodynamic calculus for as long as possible. It may appear as a surprise that a great number of problems requiring the use of the chemical potential for their solutions can be solved at an elementary level. Many problems can be solved without considering entropy, or even energy. Energy comes into play only when energy conversion processes are considered. Entropy is used when we deal with heat balances in a reaction or phase transition.

A thermodynamics course in which the chemical potential was introduced correspondingly was proposed in 1972 (Job 1972, 1981, 1992). Since then, the approach has been successfully applied in thermodynamics lectures at the universities of Hamburg and Karlsruhe, Germany. It was also adopted in Fuchs' (1996) textbook *The Dynamics of Heat*. This paper presents an introduction to this concept.

In section 2, we shall introduce the chemical potential in the same way one would explain the meaning of temperature to somebody who knows nothing of the concept. In section 3 some examples will be discussed. We will already be able to operate quantitatively with the chemical potential before discussing its metrization.

A process often does not run although, according to the chemical potential, it should. The reason for this is that the resistance to the conversion is too high. This situation will be considered in section 4. A linear approximation of temperature and pressure dependence increases the usefulness of the chemical potential tremendously. In section 5, we will show how freezing points, freezing-point depression and many other effects can be calculated with satisfactory precision in this simple approximation. Only then, in section 6, we will discuss the metrization of the chemical potential which allows us to define a measuring procedure. In section 7 we will introduce a general equation which describes the asymptotic behaviour of the chemical potential for low concentrations.

The temperature and pressure coefficients of the chemical potential are the subject of section 8. Phase transitions are driven by chemical potential differences. Nevertheless, in a phase transition the effects of the chemical potential often cannot be noticed. In section 9, we shall discuss the reason for this. In section 10, we will examine the interplay of the chemical, electrical and gravitational potentials and, finally, in section 11, we will briefly show how the chemical potential can be applied to nuclear reactions.

2. An intuitive conception of the chemical potential

Every substance has a tendency to change, i.e.,

- to react with other substances;
- to transform into another state of aggregation;
- to migrate to another place.

Examples of this would be rusting iron, evaporating water, the bleaching of clothes, the crusting of sugar or salt, the weathering of wood or rocks, the petrifying of mud, clay, silt, sand or soil, and the spoiling of foodstuffs or medicines even in an airtight pack. The perishing of chemicals in sealed bottles shows that the cause or driving force for these ubiquitous phenomena is not an interaction between different substances as chemists believed in former times, but it is an intrinsic property of each substance itself[4]. This tendency can be described by a single physical quantity, the chemical potential. The value of the chemical potential always refers to a specific substance. For a given substance, it also depends on temperature, pressure and, if it is a solute, its concentration and the kind of solvent. Moreover, it depends on the phase or state of aggregation of the substance. At the same pressure and temperature, liquid water and ice have different chemical potentials. We might also say: liquid water and ice are different substances.

A chemical reaction, a phase change or a migration take place voluntarily, because the tendency for a change is more pronounced in the initial state than in the final state, i.e., because the chemical potential in the initial state A is greater than in the final state B.

- $\mu_A > \mu_B$: transformation of substance A into substance B, or transport from place A to place B
- $\mu_A = \mu_B$: no transformation, no transport, chemical equilibrium
- $\mu_A < \mu_B$: transformation of substance B into substance A, or transport from place B to place A.

A and B must not necessarily be pure substances. Each of them can be any combination of substances: a mixture, an alloy, a solution or even a set of substances in various distinct environments.

3. Values of the chemical potential

For the time being, we will consider the values of the chemical potential as given. We will take the potential values from a table just as we would do when we are interested in a mass density, in an electric conductivity or in a specific heat capacity[5].

From equation (1), it follows that the unit of chemical potential is Joule per mole. Because of the versatility of the chemical potential, a unit not derived from other units would be preferable. Just as the units of temperature, electric potential and pressure have their own names, we shall attribute a proper name to the unit of chemical potential. Following a proposition of Wiberg (1972) we shall call it Gibbs, in honour of the scientist who first introduced the chemical potential (Gibbs 1961)[6], and abbreviate it by the letter G. Thus we

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[4] In former times, chemists tried to understand a reaction as an interaction, resulting from a relationship between the various substances. Some remnants of these early ideas survive in the language of chemistry. An example of this is the concept affinity.

[5] The chemical potential of a pure substance is equal to its molar Gibbs free energy $g = G/n$. Hence, when looking for the chemical potential, the tables in which g is listed can be used.

[6] Gibbs called his new quantity simply *potential*, or when it was necessary to distinguish it from other potentials, *intrinsic potential*.

have 1 G = 1 J mol^{-1}. A convenient multiple for reactions of the electronic shell is kiloGibbs (kG).

The values usually found in tables refer to standard conditions, i.e. a temperature of 298 K and a pressure of 1.1013 bar. Whenever the state of aggregation is not specified, the values refer to the most stable state at standard conditions. If the substance is dissolved, they correspond to a concentration of 1 kmol m^{-3}.

Chemical tables never contain absolute values of chemical potentials. A number with 11–13 digits would be necessary to give an absolute value. Changes occurring in a normal chemical reaction would manifest only in the last few digits. However, chemical potentials cannot be measured to such a precision. This is why the tables contain only differences: the difference between the potential of the respective substance and the potentials of the elements of which this substance is composed. This is similar to measuring the height of a mountain with respect to sea level instead of, say, the centre of the Earth or of measuring the temperature with respect to the freezing point of water instead of absolute zero.

Indeed, we can freely choose as many zero points as there are chemical elements[7]. Chemists make this choice so that the potential of every element is zero when it is in its most stable modification and under standard conditions (conventional scale). A less arbitrary choice would be to take the elements as isolated atoms at rest (atomic scale).

Several insights about the chemical potential can be gained just by considering such a table. Table 1 is an excerpt of a table of chemical potentials where the substances are listed alphabetically. We first see that the potential of a chemical element is 0 G in its most stable modification or state of aggregation: gaseous argon, solid arsenic, solid gold and solid boron. Moreover, we state that the chemical potential of most substances is negative. This is not a surprise. It means that these substances are stable. They do not decompose spontaneously into the elements they are made up of. Those substances, which have a positive potential are difficult to synthesize and conserve. They are meta-stable at best.

Table 2 contains the potentials of three gaseous dioxides. Among the three elements C, N and Cl, only carbon is combustible, i.e., only carbon reacts voluntarily with oxygen. Nitrogen dioxide and chlorine dioxide cannot be synthesized in this way. On the contrary, they tend to decompose. ClO_2, the oxide with the highest potential, is explosive.

We shall use two examples to show how to predict the direction of a chemical reaction by inserting values taken from a table. Let us begin with

$$\mathrm{Ca(OH)_2 + CO_2 \overset{?}{\rightarrow} CaCO_3 + H_2O}.$$

The following values for normal conditions would be obtained from a table of chemical potentials:

$$\mu_{\mathrm{Ca(OH)_2}} = -897\ \mathrm{kG}$$
$$\mu_{\mathrm{CO_2}} = -394\ \mathrm{kG}$$
$$\mu_{\mathrm{CaCO_3}} = -1129\ \mathrm{kG}$$
$$\mu_{\mathrm{H_2O}} = -237\ \mathrm{kG}.$$

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[7] This fact may, at first sight, appear unexpected. But notice that only potential differences cause observable effects. If we limit ourselves to considering such processes in which the amount n of a substance is conserved, the origin of the chemical potential scale of this substance can be chosen freely. By definition, normal chemistry treats only reactions in which no transformation of one element into another take place. Thus, the amounts of the roughly 100 elements are conserved quantities. Therefore, within chemistry, the same number of zero-points can be arbitrarily fixed. Actually, since chemists treat ions as compounds of atoms or molecules with a positive or negative number of electrons, there is one more conserved ‘substance’, the electrons, and one more arbitrary zero point. Traditionally, it is not the potential of the electrons that is chosen to be zero, but that of the hydrogen ion H^+ under standard conditions.

Table 1. Excerpt of a table of chemical potentials.

Substance	Name, phase	μ (kG)
...	...	...
$Al_6Si_2O_{13}$	mullite, solid	−6441.94
Ar	argon, gaseous	0
Ar	water solution	16.32
As	arsenic, gaseous	261.08
As	grey, metallic, solid	0
$AsCl_3$	gaseous	−248.95
$AsCl_3$	liquid	−259.41
AsF_3	liquid	−909.14
AsI_3	solid	−59.41
As_2O_3	monoclinic, solid	−577.02
As_2O_5	solid	−782.41
As_2S_3	solid	−168.62
As_4O_6	cubic, solid	−1152.52
Au	gold, gaseous	326.36
Au	solid	0
Au_2O_3	solid	163.3
B	boron, gaseous	511.67
B	liquid	19.35
B	solid	0
...	...	...

Table 2. Chemical potentials of three dioxides.

Substance	μ (kG)
CO_2	−394.00
NO_2	52
ClO_2	124

In order to decide whether the reaction proceeds from left to right or from right to left, we have to compare the total potential μ_A of the reactants with the total potential μ_B of the products. We get

$$\mu_A = \mu_{Ca(OH)_2} + \mu_{CO_2} = -1291 \text{ kG}$$
$$\mu_B = \mu_{CaCO_3} + \mu_{H_2O} = -1366 \text{ kG}.$$

Thus, we have $\mu_A > \mu_B$. This result was to be expected since our reaction equation describes nothing else than the setting of mortar which we know proceeds spontaneously.

Here is a second example:

$$CaC_2 + 2H_2O \overset{?}{\rightarrow} Ca(OH)_2 + C_2H_2.$$

The pertinent potentials, as found in a table, are

$$\mu_{CaC_2} = -68 \text{ kG}$$
$$\mu_{H_2O} = -237 \text{ kG}$$
$$\mu_{Ca(OH)_2} = -897 \text{ kG}$$
$$\mu_{C_2H_2} = +209 \text{ kG}.$$

The potentials of the reactants and the products are

$$\mu_A = \mu_{CaC_2} + 2\mu_{H_2O} = -542 \text{ kG}$$
$$\mu_B = \mu_{Ca(OH)_2} + \mu_{C_2H_2} = -688 \text{ kG}.$$

Again, we have $\mu_A > \mu_B$. This is also a well-known reaction. In former times, acetylene, which is produced from calcium carbide and water, was used for welding. The example shows that the potential of water has to be weighted with a factor of 2. This becomes clear when writing the reaction equation in the following way.

$$CaC_2 + H_2O + H_2O \rightarrow Ca(OH)_2 + C_2H_2.$$

Note that one of the products (acetylene) has a positive chemical potential. This means that acetylene can decompose spontaneously into its elements. The reason it does not do so, or only does very slowly, is the high resistance which the reaction has to overcome (see the next section).

The values we have used in the preceding examples were values at standard conditions. Correspondingly, our conclusions about the direction of the reactions are valid only for these conditions. If one had a table with potential values for other temperatures, pressures and concentrations, the same procedure could be applied for other conditions.

4. Resistance of a reaction and catalysts

A difference of chemical potentials is not sufficient for a reaction to proceed. Many substances are stable even though, according to the chemical potentials, they should decompose. An example is acetylene, which was discussed in the preceding section. Another example is benzene whose chemical potential is 125 kG. Similarly, many mixtures of substances do not react although it seems they would if only the values of the chemical potentials mattered. Thus, many of the substances around us, such as wood, metals and plastic materials, should react with the oxygen in the air. The reason why these reactions do not take place is the reaction resistance. The situation is similar to the following one which is familiar to every physicist. Two bodies carry electric charge and have different electric potentials. In spite of the potential difference, it may be that no electric current is flowing. The reason is that the resistance of the connection between the bodies is too high. There are several other analogies of this kind: a body (with a mass) does not move from a high to low gravitational potential because the table on which it is lying represents too high a resistance for the movement of the body. The air in a car tire does not leak out, i.e., it does not follow the pressure difference, since the wall of the tire represents a high resistance for the flow. Entropy only reluctantly follows a temperature gradient if the thermal resistance is high.

Just as we control a flow of electric charge by making the electric resistance high or low by means of a switch, a chemical reaction can be switched on or off by acting upon the chemical resistance.

Several methods can be employed to reduce the reaction resistance. If we consider a reaction with more than one reactant, the first thing to do would be to bring the reactants in contact by pulverizing and mixing them. If this does not help, the next measure would be to increase the temperature. The reaction resistance decreases strongly with the increasing temperature. In this case, attention has to be paid to the fact that chemical potentials are also temperature dependent, although generally much less so than the reaction resistance. A more elegant method to speed up a reaction is to use a catalyst: a further substance is added, whose amount does not change as the reaction proceeds. By adding the catalyst, the reaction is switched on. Removing the catalyst switches the reaction off. This is directly comparable to an electric current which is switched on or off by means of an electric switch.

Table 3. Some chemical potentials together with the temperature and the pressure coefficients.

Substance	μ (kG)	α (G K^{-1})	β (G bar^{-1})
C (graphite)	0.00	5.74	0.541
C (diamond)	2.90	2.38	0.342
H_2O (solid)	−236.59	−44.8	1.973
H_2O (liquid)	−237.18	−69.9	1.807
H_2O (vapour)	−228.59	−188.7	2446

5. Linear approximations

Many familiar phenomena having to do with reactions are based on the fact that the chemical potential depends upon pressure and temperature. Such behaviour is not unusual. Virtually all properties of materials depend on pressure and temperature: elastic modulus, mass density, viscosity, electric conductivity, magnetic susceptibility, specific heat capacity and many others. Usually, the mathematical functions that describe the corresponding dependences are complicated. For practical purposes, however, it is often sufficient to use linear approximations of these functions. This means that we can describe the dependency by a single coefficient. In this way, the temperature coefficient $\mathrm{d}\sigma/\mathrm{d}T$ of the electric conductivity tells us by how much the conductivity changes when the temperature changes by one unit. The pressure coefficient $\mathrm{d}\rho/\mathrm{d}p$ of the mass density tells us by how much the density changes if the pressure changes by one unit and so on.

It is also convenient to approximate the dependency of the chemical potential on temperature and pressure by using linear functions:

$$\mu(T) = \mu(T_0) + \alpha(T - T_0), \tag{4}$$

$$\mu(p) = \mu(p_0) + \beta(p - p_0). \tag{5}$$

Here, α is the temperature coefficient and β is the pressure coefficient of the chemical potential. The first equation allows us to calculate the chemical potential at temperature T, if the potential $\mu(T_0)$ at temperature T_0 is known. With the second equation, we can calculate the chemical potential at pressure p, if the chemical potential at pressure p_0 is known. The values of α and β are listed in tables together with the chemical potential[8]. Table 3 gives some examples. For gases, equation (5) is applicable only in small intervals of pressure. For greater intervals, see section 8.

Again, we consider two examples. First, we ask for the transformation of graphite (index 'gr') into diamond (index 'di'). According to table 3, the potential of graphite at standard conditions is smaller than that of diamond, so the transformation cannot take place. However, due to $\beta_{\mathrm{gr}} > \beta_{\mathrm{di}} > 0$ the chemical potential of graphite increases with growing pressure more rapidly than that of diamond. Therefore, if we raise the pressure, μ_{gr} must eventually become greater than μ_{di}, making the desired reaction possible. Let us call p_0 the normal pressure and p the pressure for which

$$\mu_{\mathrm{gr}}(p) = \mu_{\mathrm{di}}(p). \tag{6}$$

We now express μ_{gr} and μ_{di} in equation (6) by means of equation (5):

$$\mu_{\mathrm{gr}}(p_0) + \beta_{\mathrm{gr}}(p - p_0) = \mu_{\mathrm{di}}(p_0) + \beta_{\mathrm{di}}(p - p_0).$$

[8] In section 8 it will be shown that the temperature coefficient of the chemical potential is equal to the negative molar entropy and that the pressure coefficient is equal to the molar volume.

From this, we get the required increase of pressure:

$$p - p_0 = -\frac{\mu_{\mathrm{di}}(p_0) - \mu_{\mathrm{gr}}(p_0)}{\beta_{\mathrm{di}} - \beta_{\mathrm{gr}}}.$$

With the values from table 3 we get

$$p - p_0 = -\frac{2.9 - 0}{0.342 - 0.541}\ \mathrm{kbar} \approx 15\ \mathrm{kbar}.$$

In our second example, we will apply the same kind of reasoning to the case of temperature and pressure changing simultaneously. Let us consider a block of ice at a temperature of 273 K (0 °C) and a pressure of 1 bar. Under these conditions, its chemical potential is equal to that of liquid water. If a high pressure is now applied, the ice will partly melt, since $\beta_{\mathrm{solid}} > \beta_{\mathrm{liquid}} > 0$. The reason the ice does not completely melt is that upon melting, its temperature decreases. The temperature coefficient α is negative. Thus, the chemical potentials of both the solid and the liquid water increase. Since $0 > \alpha_{\mathrm{solid}} > \alpha_{\mathrm{liquid}}$, the potential of the liquid water increases more than that of the ice. Eventually, the potential change caused by the additional pressure is compensated for and the melting process will stop. Only a further increase of pressure will cause the melting of more ice, until the potential of the liquid and the solid phase are again equal.

The depression of the freezing point can easily be calculated. The condition of equilibrium between the solid and the liquid phase is $\mu_{\mathrm{solid}} = \mu_{\mathrm{liquid}}$. Using equations (4) and (5) we get

$$\mu_{0,\mathrm{solid}} + \beta_{\mathrm{solid}} \cdot \Delta p + \alpha_{\mathrm{solid}} \cdot \Delta T = \mu_{0,\mathrm{liquid}} + \beta_{\mathrm{liquid}} \cdot \Delta p + \alpha_{\mathrm{liquid}} \cdot \Delta T.$$

Since $\mu_{0,\mathrm{solid}}$ and $\mu_{0,\mathrm{liquid}}$ are equal, they cancel from the equation and the only remaining unknown quantity is ΔT. This yields

$$\Delta T = -\frac{\beta_{\mathrm{solid}} - \beta_{\mathrm{liquid}}}{\alpha_{\mathrm{solid}} - \alpha_{\mathrm{liquid}}} \Delta p.$$

For $\Delta p = 100$ bar and α and β taken from table 3, we get a freezing-point depression of $\Delta T = -0.66$ K.

Other phase transitions can be calculated similarly: boiling, freezing, sublimation temperatures, decomposition temperatures, whole state diagrams and more.

6. Measuring the chemical potential

How can we determine the values of chemical potentials? In order to keep the explanations concrete, let us consider a combustion cell. The general significance of the arguments will be seen at the end.

We make the following assumptions:

- the cell works reversibly, i.e., no entropy production takes place within the cell;
- the cell is in a steady state;
- the cell works at ambient temperature.

Figure 1 shows the cell symbolically: a flow of chemical energy is entering the cell from the left and an electric energy flow is leaving it toward the right.

The electrical energy flow is

$$P_{\mathrm{el}} = (\varphi_1 - \varphi_2) \cdot J_Q \tag{7}$$

and the chemical energy flow is

$$P_{\mathrm{chem}} = \Sigma \mu_i \cdot J_{n_i}. \tag{8}$$

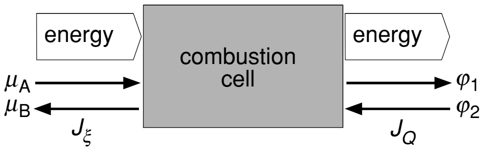

Figure 1. Flow chart of the combustion cell. While substances go from high to low chemical potential, electric charge is lifted from low to high electric potential.

Equation (8) can be rewritten (see the appendix) so that it has the same form as equation (7):

$$P_{\mathrm{chem}} = (\mu_{\mathrm{A}} - \mu_{\mathrm{B}}) \cdot J_\xi.$$

Here, μ_{A} is the total chemical potential of the reactants and μ_{B} is the total potential of the reaction products. $J_\xi = \dot{\xi}$ is the reaction rate[9].

Since the combustion cell works reversibly, the entering chemical energy flow must be equal to the outgoing electrical energy flow:

$$P_{\mathrm{chem}} = P_{\mathrm{el}}$$

or

$$(\mu_{\mathrm{A}} - \mu_{\mathrm{B}}) \cdot J_\xi = (\varphi_1 - \varphi_2) \cdot J_Q. \tag{9}$$

This equation has a suggestive form: the reactants enter the combustion cell at a high chemical potential μ_{A}. They then transform into other substances with a lower chemical potential μ_{B}, thereby lifting the electric charge from the lower electric potential φ_2 to the higher potential φ_1. Thus, the decline or drop of the chemical potential is used to lift, raise or pump the electric charge to a higher electric potential.

Equation (9) gives us the means to measure differences of chemical potentials:

$$\mu_{\mathrm{A}} - \mu_{\mathrm{B}} = \frac{(\varphi_1 - \varphi_2) \cdot J_Q}{J_\xi}.$$

The method is as follows: measure the electric energy flow (or power) $P_{\mathrm{el}} = (\varphi_1 - \varphi_2) \cdot J_Q$ and divide by the reaction rate J_ξ.[10] Actually, the procedure is even simpler. The electric current and the reaction rate are related:

$$J_Q = z \cdot F \cdot J_\xi.$$

Here, z is a small integer, whose value depends on the considered reaction, and F is the Faraday constant. We get

$$\mu_{\mathrm{A}} - \mu_{\mathrm{B}} = z \cdot F \cdot (\varphi_1 - \varphi_2).$$

[9] Similar equations describe other types of energy flow. A thermal energy flow entering a heat engine is described by

$$P_{\mathrm{therm}} = (T_1 - T_2) \cdot J_S,$$

i.e., temperature difference times entropy flow. A gravitational energy flow driving a water wheel can be written as follows

$$P_{\mathrm{grav}} = (\psi_1 - \psi_2) \cdot J_m,$$

i.e., gravitational potential difference times mass flow. A mechanical energy flow transmitted by a drive belt can be expressed by

$$P_{\mathrm{mech}} = (v_1 - v_2) \cdot J_p.$$

Here, v_1 is the velocity of the drive belt, v_2 is the velocity of the reference system (often zero) and $J_p = F$ the momentum flow or force.

[10] In order to keep dissipation negligible, the cell has to be operated in open circuit mode (the load resistance must be high compared with the internal resistance of the cell).

Thus, the chemical potential difference can be calculated directly from the open-circuit voltage of the corresponding electro-chemical cell.

Let us consider the hydrogen–oxygen combustion cell as an example. The net reaction is

$$2H_2 + O_2 \rightarrow 2H_2O.$$

Since the hydrogen is ionized, for every two moles of hydrogen we have four moles of electrons:

$$2H_2 \rightarrow 4H^+ + 4e^-.$$

hence, $z = 4$. The observed electric potential difference is 1.23 V. With $F = 9.65 \times 10^4$ C mol^{-1}, we get

$$\begin{aligned}\mu_A - \mu_B &= 2\mu(H_2) + \mu(O_2) - 2\mu(H_2O) = z \cdot F \cdot (\varphi_2 - \varphi_1)\\ &= 4 \times 9.65 \times 10^4\,\mathrm{C\,mol^{-1}}1.23\ \mathrm{V} = 474.8\ \mathrm{kG}.\end{aligned}$$

Since $2\mu(H_2) = 0$ and $\mu(O_2) = 0$, the chemical potential of water turns out to be

$$\mu(H_2O) = -237\ \mathrm{kG}.$$

In principle, every chemical reaction can be run reversibly and electrochemically. Starting from the chemical elements, whose potential values are arbitrarily chosen to be zero for normal conditions, the potential of any other substance can generally be measured.

Actually, practical measurement of chemical potentials is not necessarily done in this way. When we need a practical way to measure some quantity, we usually do not go back to the definition of this quantity. What we do is to look for a way that is technically simple and inexpensive. For a measurement of the quantity X, any effect that depends on the values of X is applicable. In general, we do not measure a temperature by directly using the thermodynamic definition of temperature (see equation (3)). Instead, we use thermocouples, resistance thermometers or mercury thermometers. The same holds true for the measurement of chemical potentials. Here, the number of possible effects that are appropriate for a measurement is even larger, given the great number of different substances and the great number of phenomena that are related to the chemical potential.

7. The asymptotic behaviour of the chemical potential for low densities

The concepts as well as the mathematical tools that we have used so far are so basic that the information in the preceding sections can easily be taught to high school students (Herrmann 1998, 2000). Only in the following shall we apply some university level mathematical tools.

One important property of the chemical potential has not yet been mentioned. This quantity displays a universal behaviour when the molar density decreases. Indeed, when n/V is sufficiently small, the chemical potential as a function of the amount of substance is

$$\mu(n) - \mu(n_0) = RT \ln\left(\frac{n}{n_0}\right) \qquad \text{for} \quad V, T = \text{constant}. \tag{10}$$

This relation holds for whatever the substance, be it a gas (considered a solute in vacuum), a solute in a liquid or a solute in a solid. It also holds for electromagnetic radiation (photons) and sound (phonons).

Equation (10) can be considered the chemical analogue of the third law. The third law informs us about the behaviour of the temperature for vanishing entropy, i.e.,

$$T \rightarrow 0 \qquad \text{for} \quad S \rightarrow 0,$$

whereas equation (10) tells us what happens with the chemical potential when the amount of substance tends to zero[11] (Job 1973):

$$\mu \to -\infty \qquad \text{for} \quad n \to 0.$$

Numerous other laws can be derived directly from equation (10). Examples are the law of mass action, the perfect-gas law, Raoult's law, Henry's law, Nernst's distribution law, the vapour pressure equation, van t'Hoff's law or Boltzmann's distribution law.

Equation (10) is usually derived from the perfect-gas law. This seems reasonable since it is easy to verify the perfect-gas law experimentally. However, we believe that it is more appropriate from a conceptual point of view to conceive equation (10) as a basic law.

For a substance with $p \propto n$ at $V, T =$ constant, equation (10) can be written in the form

$$\mu(p) - \mu(p_0) = RT \ln\left(\frac{p}{p_0}\right) \qquad \text{for} \quad T = \text{constant}. \tag{11}$$

For a solution of low concentration, equation (11) holds if the osmotic pressure is taken for p. In this case, we can also express the chemical potential by the concentration c:

$$\mu(c) - \mu(c_0) = RT \ln\left(\frac{c}{c_0}\right) \qquad \text{for} \quad T = \text{constant}.$$

8. The temperature and pressure coefficients of the chemical potential

Let us write the temperature and the pressure coefficients as partial derivatives:

$$\alpha = (\partial\mu/\partial T)_{p,n}$$

and

$$\beta = (\partial\mu/\partial p)_{T,n}.$$

Using the appropriate Maxwell relation (Callen 1960, p 117) we get

$$(\partial\mu/\partial T)_{p,n} = -(\partial S/\partial n)_{T,p} = -s$$

and

$$(\partial\mu/\partial p)_{T,n} = (\partial V/\partial n)_{T,p} = v. \tag{12}$$

Here, s is the partial molar entropy and v is the partial molar volume. For a pure substance, we simply have

$$s = S/n \qquad \text{and} \qquad v = V/n.$$

Therefore,

$$\alpha = -s$$

and

$$\beta = v.$$

Expressed in words: the temperature coefficient of the chemical potential is equal to the negative molar entropy and the pressure coefficient is equal to the molar volume. Let us consider two examples that show the usefulness of these statements.

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[11] $T \to 0$ for $S \to 0$ is true only if the entropy exchange between the system and its surroundings is not inhibited, in other words, if thermal equilibrium can be established. The corresponding restriction holds for the chemical analogue of this statement: $\mu \to -\infty$ for $n \to 0$ is true only if the exchange of the amount of substance (particle exchange) is not inhibited, i.e., if chemical equilibrium can be established.

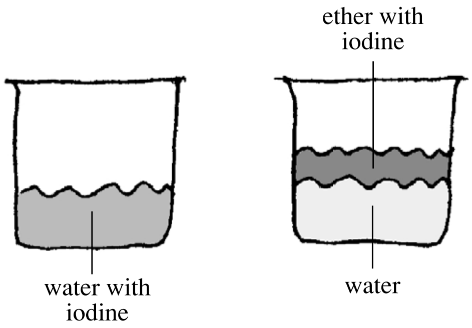

Figure 2. When adding ether, iodine goes from the water to the ether. When chemical equilibrium is reached, the iodine concentration in the ether is higher than that in the water.

We first derive the perfect-gas law from equation (11). The pressure derivative of equation (11) is

$$\left(\frac{\partial\mu}{\partial p}\right)_T = \frac{RT}{p},$$

and with $v = V/n$ we get the perfect-gas law

$$p \cdot V = n \cdot R \cdot T.$$

As a second example, let us determine the pressure dependence of the chemical potential for an incompressible liquid. For such a liquid, the molar volume v is independent of the pressure. From equation (12) we obtain

$$\mu(p) - \mu(p_0) = v \cdot (p - p_0). \tag{13}$$

We see that for a liquid, the chemical potential is proportional to the pressure.

In both equations (11) and (13) the chemical potential grows monotonically with the increasing pressure. That is why it is often possible to consider a pressure difference as the driving force of a flow of a liquid or a gas. In the same way, a concentration gradient or difference is considered as the driving force for the diffusion of a dissolved substance.

In general, however, the correct 'force' is not a respective difference of the pressure or concentration, but a difference of the chemical potential. This is seen whenever transport occurs across the interface between two phases. Consider the experiment of figure 2. Some iodine is dissolved in a beaker with water. The iodine gives the solution a brown colour. Subsequently, some ether is added, which floats above the water. After stirring, the water turns colourless and the ether turns brown. Apparently, the iodine has moved from the water into the ether. This process comes to a halt when the iodine concentration in the ether is substantially higher than in the water. Now, the chemical potential of the iodine in the water is equal to that in the ether, although the iodine concentration in the ether is higher than in the water. Thus, the iodine has moved against a concentration difference.

9. Phase transitions

A phase transition is a special case of a reaction: there is only one reactant and one product:

$$\mathrm{A} \rightarrow \mathrm{B}.$$

This peculiarity is often used as a criterion for a reaction to be called a physical rather than a chemical process. However, for a formal description, it is clearly insignificant. Phase

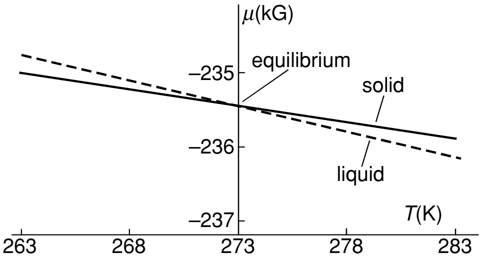

Figure 3. At a pressure of 1 bar, the $\mu(T)$ curves of solid and liquid water intersect at a temperature of 273 K. At this temperature the two phases are in chemical equilibrium.

transitions fit perfectly into the procedure that has been described in the previous sections. We thus have

- $\mu_A > \mu_B$: transition from phase A to phase B
- $\mu_A = \mu_B$: phase equilibrium
- $\mu_A < \mu_B$: transition from phase B to phase A.

Since the chemical potential depends upon pressure and temperature, a change of these two quantities can cause a phase change.

9.1. Phase transition due to change of temperature

The chemical potential decreases when temperature increases. It does so for almost all substances and for all states of aggregation. Of course, the magnitude of change depends on the chemical nature of the substance and on the phase. In particular, the decrease is greater for gases than for liquids, and greater for liquids than for solids. Therefore, it can be expected that the $\mu(T)$ curves of two different phases intersect and indeed they do so. Figure 3 shows the corresponding curves for solid and liquid water at a pressure of 1 bar. They intersect at 273 K. At this temperature, the chemical potential of ice is equal to that of liquid water. Here, both phases can coexist. They are in chemical equilibrium.

Similar observations hold for the transition between the liquid and the gaseous phase.

Since the chemical potential also depends upon pressure, the position of the intersection of the $\mu(T)$ curves depends on pressure as well. In other words: melting and boiling temperatures depend upon pressure.

9.2. Phase transition due to a change of pressure

The chemical potential usually increases when pressure grows. It does so for almost all substances and states of aggregation; see section 8. Again, the change is not the same for the various phases of a substance. Therefore, the $\mu(p)$ curves of two phases of a substance intersect. Figure 4 shows these curves for liquid and for gaseous butane. They intersect at a pressure of approximately 2 bar. At this pressure, the chemical potential of liquid butane is equal to that of gaseous butane. Both phases can coexist. They are in chemical equilibrium. Butane in a lighter is in this state. In the case of chemical equilibrium between the liquid and the gaseous phase, the pressure is called the saturation pressure.

The equilibrium pressure depends upon temperature in the same way that the equilibrium temperature depends on pressure.

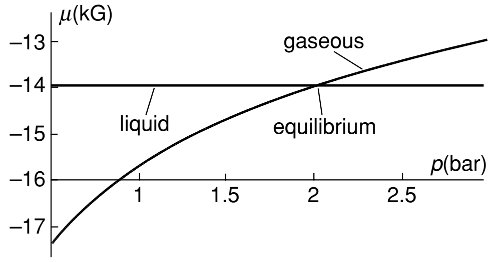

Figure 4. At a temperature of 20 °C, the $\mu(p)$ curves of liquid and gaseous butane intersect at a pressure of 2 bars. At this pressure the two phases are in chemical equilibrium.

9.3. Reaction resistance of phase transitions

The phase transitions most familiar to us, namely the transitions between solid, liquid and gaseous phases, display a peculiarity. They proceed almost unhindered because the reaction resistance is practically zero. As a consequence, it is difficult to build up a potential difference between these phases.

It is similar to trying to build up an electric potential difference between two bodies that are connected via an electric conductor. Even if we deposit additional charge on one of them, no potential difference will be established because the charge rapidly distributes itself in such a way that the potentials of the two bodies remain equal.

For this reason, at a given temperature and pressure, a substance usually exists in a well-defined state of aggregation. Water, for instance, is liquid (at normal pressure) when its temperature is between 0 °C and 100 °C, and gaseous when the temperature is higher. With the necessary precautions, liquid water can actually be brought into a state with a temperature of more than 100 °C, meaning into a state in which its chemical potential is higher than that of water vapour. However, the fact that the phase transition takes place at a higher temperature is so unfamiliar to us that we give it a particular name. We call it delayed boiling. As we have discussed in section 4, such behaviour is absolutely normal for many other reactions.

10. Combined potentials

In the preceding sections, we got to know the chemical potential as the driving force which acts upon the amount of substance n. A gradient of chemical potential can cause a flow of n, a substance current.

Now, n is only one of several extensive quantities which are carried by a substance (or by the particles that constitute the substance). Other such quantities are the mass m, electric charge Q, entropy S and angular momentum L. Whenever one of these quantities—let us call it X—is coupled to the amount of the substance n, then the flow of the substance must not necessarily be driven by a gradient of the chemical potential. It can also be driven by the conjugated intensive quantity of the quantity X. The stronger the coupling, the more efficient is the 'entrainment' or 'drag'. Actually, some of the above-mentioned extensive quantities are rigidly coupled to n, for instance mass and electric charge. As a result, a current J_n of the amount of substance n is necessarily associated with a mass current J_m:

$$J_m = M \cdot J_n.$$

Here, M is the molar mass. If the substance carries electric charge, then J_n is associated with a well-defined electric current J_Q:

$$J_Q = z \cdot F \cdot J_n.$$

Here, F is the Faraday constant, and z is a small integer that indicates how many elementary charges are associated with one charge carrier.

Sometimes, the coupling between n and the entropy S can be considered just as rigid. In this case, we can write

$$J_S = s \cdot J_n.$$

Here s is the molar entropy.

Whenever one of these couplings exists, the effective gradient for a substance flow is not simply that of the chemical potential. The substance flow can also be driven via coupling to the mass, electric charge, or entropy, by a gradient of the gravitational potential, electric potential or temperature, respectively.

If, in addition to the chemical potential, we take the gravitational potential into account, then the pertinent total potential is essentially the sum of the chemical and the gravitational potential. We call

$$\gamma = \mu + M \cdot \psi$$

the gravito-chemical potential. The substance current will be zero if

$$\operatorname{grad} \gamma = 0.$$

Note that we can have a zero net driving force although non-zero gradients of both the gravitational and the chemical potential may exist. An example would be a liquid or a gas in the gravitational field of the earth. The water at the bottom of a container does not flow upwards, although the chemical potential decreases in this direction. And the water at the top does not flow downwards, although the gravitational potential decreases in this direction. Actually, we have two gradients or driving forces that compensate each other. The gradient of the combined potential (the gravito-chemical potential) is zero everywhere. We have gravito-chemical equilibrium.

Similar arguments hold when an electric potential is acting along with the chemical potential. Now the pertinent combined potential is the well-known electro-chemical potential

$$\eta = \mu + z \cdot F \cdot \varphi.$$

The condition of zero current is

$$\operatorname{grad} \eta = 0.$$

A vanishing net driving force is possible even when we have both an electric and a chemical potential gradient. Consider as an example two electric conductors in contact with one another, e.g., copper and silver, or p-doped silicon and n-doped silicon. The chemical potential of the charge carriers is different in each of the two materials. When the two materials are brought in contact, charge carriers displace until an electric potential difference has built up which compensates for the chemical potential difference. In the resulting non-current state, the electro-chemical potential has the same value in both materials, whereas both the electric and the chemical potential display a gradient in the vicinity of the interface (the space-charge layer). The difference of the electric potentials is usually called the contact-potential difference. The electro-chemical potential (multiplied by the elementary charge) is called Fermi energy. The state of constant electro-chemical potential is called electro-chemical equilibrium[12].

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[12] It is sometimes claimed that, in this case, two currents compensate: a current due to a field and a diffusion current. We prefer to say that the driving forces compensate. Indeed, when dealing with two opposite currents, one might expect that each of them causes dissipation which is obviously not the case.

There are even situations where the pertinent driving force is a combination of three potentials. An example of this would be the atmosphere. Since the thermal conductivity is weak and the pertinent geometrical extensions are great, we can admit that the entropy S is firmly coupled to m and n. The resulting driving force is

$$\varepsilon = \mu + M \cdot \psi + s \cdot T.$$

Here, s is the molar entropy. If the atmosphere is well mixed, the combined potential ε is constant, we have a gravito-thermo-chemical equilibrium. The corresponding temperature gradient is called the adiabatic temperature gradient. Dividing ε by c_p, the specific heat capacity at constant pressure, we get what meteorologists call the potential temperature.

11. The chemical potential in nuclear reactions

The general principles developed in sections 1, 2 and 4 also apply to nuclear reactions. However, since in such reactions the numbers of the atoms are not conserved, we are not allowed to choose an arbitrary zero point for the chemical potential. We have to use its absolute zero.

As long as the molar density $c = n/V$ is much smaller than the degeneration density

$$c^*(T) = \frac{2}{N_A}\left(\frac{e_0 RT}{2\pi(\hbar c)^2}\right)^{3/2},$$

the absolute value of the chemical potential is

$$\mu(T, c) = e_0 + RT \ln\left(\frac{c}{c^*}\right).$$

Here, e_0 is the rest energy. Consider a reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C}$. The chemical potential difference that tells us about the direction in which the reaction will proceed is

$$\Delta\mu = (e_{0\mathrm{A}} + e_{0\mathrm{B}} - e_{0\mathrm{C}}) + RT \ln\left(\frac{c_\mathrm{A} \cdot c_\mathrm{B} \cdot c^*_\mathrm{C}}{c^*_\mathrm{A} \cdot c^*_\mathrm{B} \cdot c_\mathrm{C}}\right).$$

For a typical nuclear reaction, the sum $(\mathrm{e}_{0\mathrm{A}} + \mathrm{e}_{0\mathrm{B}} - \mathrm{e}_{0\mathrm{C}})$ is of the order of 1 MeV. At moderate temperatures, the term $RT \ln(\cdots)$ is much smaller than this value. As a consequence, it is sufficient to compare the rest energies of the reactants and the reaction products in order to determine the direction of the reaction. Note that for a nuclear reaction, a temperature of 10 000 000 K can still be considered moderate. Therefore, in dealing with nuclear reactions within the Sun, it is sufficient for many purposes to consider the rest energies.

This method does not work for temperatures as high as those in the nucleus of a red giant star which are two orders of magnitude higher than in the nucleus of the Sun. Consider the process of helium burning as an example:

$$^4\mathrm{He} + {}^4\mathrm{He} \overset{?}{\rightarrow} {}^8\mathrm{Be}. \tag{14}$$

Taking only the rest energies, we would obtain

$$\Delta\mu = -95\ \mathrm{keV},$$

i.e., the reaction runs from beryllium to helium. This means that no beryllium could be synthesized via reaction (14).

At red-giant temperatures, however, the $RT \ln(\cdots)$-term enters into things in such a way that the difference of the chemical potentials becomes positive, meaning the reaction proceeds from helium to beryllium.

To reduce the reaction resistance of a nuclear reaction, the same methods are employed as when dealing with a reaction of the electronic shell. The fusion reaction in a Tokamak-type reactor is possible due to the high temperature. Note that the temperature increase for accelerating a nuclear reaction has to be roughly a million times as great as that which helps to accelerate a normal chemical reaction.

The high fission rate of U-235 in a nuclear fission reactor is due to the presence of neutrons. The neutrons can therefore be considered as a catalyst. Since more neutrons are coming out in the balance, the reaction is what a chemist would call an autocatalytic reaction.

12. Conclusion

The chemical potential is a useful quantity that is indispensable not only to chemistry, but also to physics (contrary to what its name might suggest). It is crucial for the understanding of many processes dealt with in physics. It tells us about the direction in which a phase transition proceeds. The pressure and temperature dependence of a phase transition can be calculated via the chemical potential. It is needed for the description of equilibria in which two driving forces compensate for each other. Examples of this are gravito-chemical or electro-chemical equilibrium. The chemical potential can also be applied to nuclear reactions, for instance, nucleo-synthesis in stars.

Dealing with the chemical potential is no more difficult than dealing with electrical potential or temperature, two quantities that are used in high school. It is easy to obtain an intuitive understanding of the chemical potential as a tendency to change: change of location, of chemical composition or state of aggregation. A difference of chemical potential can be considered a driving force for such changes.

In this paper, we did not mention another area where the chemical potential is of considerable use: it is suitable for describing various states of electromagnetic radiation (Würfel 1982, Herrmann and Würfel 2005). Usually one only considers thermal radiation, i.e., to states in which the chemical potential is zero. However, the usefulness of the chemical potential reveals itself when luminescence radiation is considered.

Appendix

We write the reaction taking place inside the cell in a general form:

$$a'\mathrm{A}' + a''\mathrm{A}'' + \cdots \rightarrow b'\mathrm{B}' + b''\mathrm{B}'' + \cdots .$$

Here, A', A'', ... are the reactants and B', B'', ... are the reaction products. $a', a'', \ldots$ and $b', b'', \ldots$ are the stoichiometric coefficients. The change in the amount of substance of the reactants and the products can all be represented as integer multiples of the *extent of reaction* ξ:

$$n_{\mathrm{A}'} = a' \cdot \xi; \qquad n_{\mathrm{A}''} = a'' \cdot \xi; \ldots; \qquad n_{\mathrm{B}'} = -b' \cdot \xi; \qquad n_{\mathrm{B}''} = -b'' \cdot \xi; \ldots .$$

The substance currents can then be written as

$$J_{n_{\mathrm{A}'}} = a' \cdot J_\xi; \qquad J_{n_{\mathrm{A}''}} = a'' \cdot J_\xi; \ldots; \qquad J_{n_{\mathrm{B}'}} = -b' \cdot J_\xi; \qquad J_{n_{\mathrm{B}''}} = -b'' \cdot J_\xi; \ldots$$

where J_ξ is the reaction rate.

Note that the currents leaving a system carry a minus sign. Equation (8) now becomes

$$P = [(a'\mu_{\mathrm{A}'} + a''\mu_{\mathrm{A}''} + \cdots) - (b'\mu_{\mathrm{B}'} + b''\mu_{\mathrm{B}''} + \cdots)] \cdot J_\xi .$$

Characterizing the combination of reactants by the index A, and the combination of products by B, we can write

$$(a'\mu_{A'} + a''\mu_{A''} + \cdots) = \mu_A \qquad (b'\mu_{B'} + b''\mu_{B''} + \cdots) = \mu_B,$$

where μ_A is the total chemical potential of the reactants and μ_B is the total potential of the products. With this abbreviation, we get

$$P_{\text{chem}} = (\mu_A - \mu_B) \cdot J_\xi.$$

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