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What is a Chemical Equilibrium State?[*]

We review the chemical equilibrium equations, and conclude that both their derivation and their meaning are problematic. We find that these equations can be established for a suitably defined simple system without chemical reactions. [DOI: 10.1115/1.4026384]

1 Introduction

In authoritative discussions [1–3] of chemical equilibrium among r constituents of a system A, the condition of equilibrium in the presence of one chemical reaction mechanism is presumably shown to be

$$\sum_{i=1}^{r} \nu_i \mu_i(U, V, n_1, n_2, \ldots, n_r) = 0 \tag{1}$$

where ν_i, for $i = 1, 2, \ldots, r$ is the i-th stoichiometric coefficient of the chemical reaction mechanism

$$\sum_{i=1}^{r} \nu_i A_i = 0 \tag{2}$$

A_i denotes the i-th constituent, μ_i the chemical potential of the i-th constituent, U the internal energy, V the volume, $n_1, n_2, \ldots, n_r$ are the amounts of constituents given by the relations

$$n_i = n_{ia} + \nu_i \epsilon \quad \text{for } i = 1, 2, \ldots, r \tag{3}$$

and n_{ia}, for $i = 1, 2, \ldots, r$, is the amount of the i-th constituent for which the value of the reaction coordinate ϵ is equal to zero.

For given values of $U, V, n_{1a}, n_{2a}, \ldots, n_{ra}, \nu_1, \nu_2, \ldots, \nu_r$, Condition 1 yields the value ϵ_0 for which the system is in a chemical equilibrium or stable equilibrium state. Thus, at the chemical equilibrium state the amounts of constituents are given by the relations

$$n_{io} = n_{ia} + \nu_i \epsilon_o \quad \text{for } i = 1, 2, \ldots, r \tag{4}$$

and the corresponding mole fractions or compositions by the relations

$$y_{io} = \frac{n_{ia} + \nu_i \epsilon_o}{n_a + \nu \epsilon_o} \quad \text{for } i = 1, 2, \ldots, r$$

where $n_a = \sum_{i=1}^{r} n_{ia}$ and $\nu = \sum_{i=1}^{r} \nu_i$

In the discussions just cited [1–3] it is also stated that Condition 1 results from the requirement that, for an isolated system, the value of the sum $\sum_{i=1}^{r} \mu_i(U, V, \boldsymbol{n}) dn_i$ at the chemical equilibrium state must be zero for any variations of the amounts of constituents compatible with the stoichiometry of the reaction mechanism.

Even though experience shows that Condition 1 leads to results consistent with observations, its derivation and meaning are problematic. According to the second law [4]. an isolated system with one or more chemical reactions, and given values of $U, V, n_{1a}, n_{2a}, \ldots, n_{ra}$ admits one and only one stable equilibrium state. To that state corresponds a unique composition. Any composition that deviates from that of the stable equilibrium state corresponds to a state that is not stable equilibrium and, therefore, chemical potentials cannot be defined. So, what functions $\mu_i(U, V, n_1, n_2, \ldots, n_r)$ should be used in Condition 1 in order to find ϵ_0 and the chemical equilibrium state?

We investigate this question and find a satisfactory answer for any system A that is simple. For such a system, the chemical potentials appearing in Condition 1 are those of a surrogate simple system B consisting of the same constituents as A but experiencing no chemical reactions [5].

In this paper, we summarize our findings. In Section 2 we discuss the definition of a simple system. In Section 3 we derive Condition 1 and show which chemical potentials are involved. In Section 4 we express Condition 1 in terms of temperature, pressure and mole fractions rather than energy, volume, and amounts of constituents, and in Section 5 we present our conclusions.

2 Simple Systems

We define a system as simple [6] if it has volume as the only parameter, and if it satisfies the following two additional requirements:

(a) If in any of its stable equilibrium states it is partitioned into a set of contiguous subsystems in mutual stable equilibrium, the system is such that the effects of the partitions are negligible; and
(b) In any of its stable equilibrium states, the instantaneous switching on or off of one or more internal reaction mechanisms, such as a chemical reaction, causes negligible instantaneous changes in the values of the energy, the entropy, the volume, and the amounts of constituents.

In general, either the introduction of partitions, or the instantaneous switching on or off of chemical reaction mechanisms, or both have definite effects on the system. For example, using the tools of quantum theory [7,8], we can show that the switching on of a reaction mechanism requires the switching on of an additional term in the Hamiltonian of the system which affects the functional form of the fundamental relation for stable equilibrium states. Again, using the tools of quantum theory, we can show that the switching off of a reaction mechanism requires the "destruction" of correlations among constituents and, in general, results in a reduction of the value of the entropy. Nevertheless, we can also show that these effects become less and less important, and negligible for all practical purposes, when the value of the amount of each constituent is larger than a small number. Hence, the definition of a simple system is applicable only to systems with large values of amounts of constituents.

3 Chemical Equilibrium States of a Simple System

In this section, we derive a necessary condition for a simple system with one chemical reaction mechanism to be in a stable equilibrium state.

We consider a simple system A with r constituents and a chemical reaction, given values U of the energy, and V of the volume,

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and values $n_1, n_2, \dots, n_r$ of the amounts of constituents that are obtained from given values $n_{1a}, n_{2a}, \dots, n_{ra}$, as a result of the reaction mechanism. Such a system admits a very large number of states. But the second law requires that among all these states one and only one be stable equilibrium—the chemical equilibrium state. At this state, the values of the amounts of constituents. $n_{1o}, n_{2o}, \dots, n_{ro}$ and the corresponding value of the reaction coordinate, ϵ_o, satisfy Equations 4.

The values $U, V, n_a = \{n_{1a}, n_{2a}, \dots n_{ra}\}$ and the stoichiometric coefficients $\nu = \{\nu_1, \nu_2, \dots, \nu_r\}$ determine uniquely the values of all the properties and quantities that characterize the chemical equilibrium state, including the values of the entropy, S, the reaction coordinate ϵ_o, and each n_{io}. We write the dependences of the latter quantities in the forms

$$S = S(U, V, \boldsymbol{n}_a; \boldsymbol{\nu}) \tag{6}$$

$$\epsilon_o = \epsilon_o(U, V, \boldsymbol{n}_a; \boldsymbol{\nu}) \tag{7}$$

$$n_{io} = n_{io}(U, V, \boldsymbol{n}_a; \boldsymbol{\nu}) \quad \text{for } i = 1, 2, \dots, r \tag{8}$$

In general, we cannot find the explicit functional forms of Equations 6–8. For simple systems, however, we can express chemical equilibrium properties in terms of stable equilibrium properties of a multiconstituent system in which the chemical reaction mechanism is inhibited—switched off. To see how this is done, we proceed as follows [5].

First, we consider a simple system B consisting of the same r types of constituents as system A but with the chemical reaction mechanism inhibited—switched off. Of course, A and B are different systems because they are subject to different internal forces and constraints. We assume that B is in a stable equilibrium state with values U of the energy, V of the volume, and $\boldsymbol{n} = \{n_1, n_2, \dots, n_r\}$ of the amounts of constituents of its r constituents. We denote the entropy at that stable equilibrium state by the fundamental relation

$$S_{\text{off}} = S_{\text{off}}(U, V, \boldsymbol{n}) \tag{9}$$

where we use the subscript "off" to emphasize that the reaction mechanism is switched off.

Next, we assume that the chemical reaction mechanism is instantly switched on, that is, the reaction defined by the stoichiometric coefficients $\boldsymbol{\nu}$ is no longer inhibited. As a result, we obtain again system A.

By virtue of the definition of a simple system, switching on of the chemical reaction mechanism causes negligible instantaneous changes in the values of entropy, energy, volume, and amounts of constituents. Accordingly, immediately after switching on the reaction mechanism the state of system A has the same values of $S, U, V, n_1, n_2, \dots, n_r$ as the corresponding values of the stable equilibrium state of B. In general, however, this state of A is not stable equilibrium. For example, if B is a quiescent mixture of gasoline vapor and air at room temperature and we activate the combustion mechanism by a minute spark, we instantly produce a nonequilibrium state of a system A in which the reaction is no longer inhibited—the burning of the gasoline is proceeding—even though the instantaneous perturbations of the values of $S, U, V, n_1, n_2, \dots, n_r$ introduced by the spark are entirely negligible.

Among all the states of A that may be obtained from B in the manner just cited, we consider the subset that has given values U of the energy and V of the volume, and amounts of constituents that are compatible with given values $n_{1a}, n_{2a}, \dots, n_{ra}$ in the sense that the values of the amounts of constituents satisfy the stoichiometric relations

$$n_i = n_{ia} + \nu_i \epsilon \quad \text{for } i = 1, 2, \dots, r \tag{10}$$

We denote the resulting state by A_ϵ. Among all the states A_ϵ, the one with the highest entropy is the unique chemical equilibrium state with energy U, volume V, and amounts of constituents compatible with $\boldsymbol{n}_a$. We denote it by A_{ϵ_o}.

To prove that indeed A_{ϵ_o} is a chemical equilibrium state, we assume the contrary and reach a contradiction. We assume that A_o is the chemical equilibrium state corresponding to the values $U, V, \boldsymbol{n}_a, \boldsymbol{\nu}$ and that it differs from A_{ϵ_o}. Then, $S_{\epsilon_o} < S_o$ because A_o has the highest entropy. Now, starting from A_o we switch off the chemical reaction mechanism. Because system A is simple, and A_o is a stable equilibrium state, the resulting state B_0 of surrogate system B has the same values U, V, and $\boldsymbol{n}_0$ as A_o and, in particular, its entropy is S_o.

If state B_0 were stable equilibrium, then upon switching the chemical reaction mechanism back on, we would return to state A_0, and conclude that it belongs to the family of states A_ϵ and, hence, coincides with A_{ϵ_o}. If instead state B_0 were not stable equilibrium, then the stable equilibrium state of B with values U, V, $\boldsymbol{n}_0$ would have entropy $S > S_0$, and switching on the reaction beginning from this state would yield a state in the family of the states A_ϵ that has entropy $S > S_o > S_{\epsilon_o}$. The conclusion that $S > S_{\epsilon_o}$ contradicts our stipulation that A_{ϵ_o} has the highest entropy and, therefore, is invalid. So, A_{ϵ_o} must be a chemical equilibrium state.

As a result of these observations, we see that we can express the entropy S_ϵ of a state A_ϵ in terms of the entropy $S_{\text{off}}(U, V, \boldsymbol{n})$ of the state of the surrogate system to which A_ϵ corresponds. Moreover, we can determine the chemical-equilibrium entropy $S(U, V, \boldsymbol{n}_a; \boldsymbol{\nu})$ (Equation 6) by a suitable maximization of the function $S_{\text{off}}(U, V, \boldsymbol{n})$.

To pursue this maximization, first we write the entropy S_ϵ of a state A_ϵ in the form

$$S_\epsilon = S_{\text{off}}(U, V, \boldsymbol{n}_a + \epsilon \boldsymbol{\nu}) \tag{11}$$

where in the fundamental relation $S_{\text{off}} = S_{\text{off}}(U, V, \boldsymbol{n})$ we substitute the short hand notation $\boldsymbol{n}_a + \epsilon \boldsymbol{\nu}$ for the set of Equations 10. Then we note that in order for A_{ϵ_o} to be the state of highest entropy among all the states, A_ϵ with given $U, V, \boldsymbol{n}_a$, and $\boldsymbol{\nu}$ the values ϵ_o must be such that

$$\left(\frac{\partial S_\epsilon}{\partial \epsilon}\right)_{U, V, \boldsymbol{n}_a, \boldsymbol{\nu}} = 0 \tag{12}$$

where the subscripts $\boldsymbol{n}_a$ and $\boldsymbol{\nu}$ denote, respectively, that each of the amounts n_{ia}, and each of the stoichiometric coefficients ν_i are kept fixed. Using Equation 11 in Equation 12, we find

$$\begin{aligned} \left(\frac{\partial S_\epsilon}{\partial \epsilon}\right)_{U, V, \boldsymbol{n}_a, \boldsymbol{\nu}} &= \sum_{i=1}^{r} \left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{U, V, \boldsymbol{n}} \left(\frac{\partial n_i}{\partial \epsilon}\right)_{\boldsymbol{n}_a, \boldsymbol{\nu}} \\ &= -\sum_{i=1}^{r} \frac{\mu_{i,\text{off}}}{T_{\text{off}}} \nu_i = 0 \end{aligned} \tag{13}$$

where $\mu_{i,\text{off}}$ is the chemical potential of constituent i, and T_{off} the temperature of the stable equilibrium state of the surrogate system B that corresponds to $A_{\epsilon o}$ and in writing the second of Equations 13 we use the relation $(\partial S/\partial n_i)_{U, V, \boldsymbol{n}} = -\mu_i/T$ and Equations 10. For finite values of T_{off} we see from Equations 13 that a necessary condition that relates $U, V, \boldsymbol{n}_a, \boldsymbol{\nu}$ and ϵ_o at chemical equilibrium is

$$\sum_{i=1}^{r} \nu_i \, \mu_{i,\text{off}}(U, V, \boldsymbol{n}_a + \epsilon_o \boldsymbol{\nu}) = 0 \tag{14}$$

In Section 4. we show that $\mu_{i,\text{off}}(U, V, \boldsymbol{n}_a + \epsilon_o \boldsymbol{\nu})$ for $i = 1, 2, \dots, r$, is also equal to the corresponding chemical potential of the chemical equilibrium state of system A. Thus, Equation 14 coincides with Equation 1, that is the *chemical equilibrium equation.*

For states other than chemical equilibrium, the expression $\sum_{i=1}^{r} \nu_i \mu_{i,\text{off}}$ is well defined but different from zero. Its negative has been called by de Donder the *affinity of the reaction.* It is noteworthy that this affinity cannot be expressed in terms of chemical potentials of system A because no such potentials can be defined for states of A that are not chemical equilibrium.

For each given set of values $U, V, \boldsymbol{n}_a$, and $\boldsymbol{\nu}$, Equation 14 is a necessary condition for chemical equilibrium. It may be solved to yield Equations 6–8 and, therefore, all properties of the chemical equilbrium state. It confirms the statement made earlier to the effect that properties of chemical equilibrium may be expressed in terms of properties of a multiconstituent surrogate system with all chemical reaction mechanisms switched off.

For the extremum corresponding to Condition 12 to be a maximum, it is also necessary that the second differential of S_ϵ with respect to the reaction coordinate ϵ be negative. This turns out to be true because the fundamental relation of surrogate system B (Equation 9) is concave with respect to all the variables n_i for $i = 1, 2, \ldots, r$. To show that indeed the second differential of S_ϵ is negative, we use Equation 11 and find that

$$\begin{aligned}(d^2S_\epsilon)U, V, \boldsymbol{n}_a, \boldsymbol{v} &= \frac{1}{2!}\left(\frac{\partial^2 S_\epsilon}{\partial \epsilon^2}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{v}}(d\epsilon)^2\\ &= \frac{1}{2!}\sum_{j=1}^{r}\sum_{k=1}^{r}\left(\frac{\partial^2 S_{\text{off}}}{\partial n_j \partial n_k}\right)_{U,V,\boldsymbol{n}}\nu_j\nu_k(d\epsilon)^2\\ &= \frac{1}{2!}\sum_{j=1}^{r}\sum_{k=1}^{r}\left(\frac{\partial^2 S_{\text{off}}}{\partial n_j \partial n_k}\right)_{U,V,\boldsymbol{n}}\nu_j\, d\epsilon\, \nu_k\, d\epsilon\\ &= \frac{1}{2!}\sum_{j=1}^{r}\sum_{k=1}^{r}\left(\frac{\partial^2 S_{\text{off}}}{\partial n_j \partial n_k}\right)_{U,V,\boldsymbol{n}} dn_j\, dn_k < 0 \qquad (15)\end{aligned}$$

where we use $dn_i = \nu_i\, d\epsilon$ for $i = 1, 2, \ldots, r$. The inequality is always satisfied because the fundamental relation of the surrogate system B is concave with respect to every n_i, for $i = 1, 2, \ldots, r$. [9]

Generalizations of the preceding results to many chemical reaction mechanisms are discussed in Ref. 5.

4 The Chemical Equilibrium Equation in Terms of Temperature and Pressure

Rather than using energy, volume, and amounts of constituents as independent variables, we can more conveniently express the chemical equilibrium equation in terms of temperature, pressure, and mole fractions. To this end, we assert that the stable equilibrium state of the surrogate system B obtained by switching off the reaction mechanism at a chemical equilibrium state of a system A has not only the same values of energy, entropy, volume, and amounts of constituents as the chemical equilibrium state, but also the same values of temperature, pressure, and chemical potentials.

To prove this assertion, first we recall the definitions of temperature, pressure, and chemical potential of a constituent for a simple system with a chemical reaction mechanism, namely, $T = 1/(\partial S/\partial U)_{V,\boldsymbol{n}_a,\boldsymbol{v}}, p = (\partial S/\partial V)_{U,\boldsymbol{n}_a,\boldsymbol{v}}/(\partial S/\partial U)_{V,\boldsymbol{n}_a,\boldsymbol{v}}$ and $\mu_i = -(\partial S/\partial n_{ia})_{U,V,\boldsymbol{n}_a,\boldsymbol{v}}/(\partial S/\partial U)_{V,\boldsymbol{n}_a,\boldsymbol{v}}$ for $i = 1, 2, \ldots r$, where the fundamental relation for the chemical equilibrium states is $S = S(U, V, \boldsymbol{n}_a; \boldsymbol{v})$ (Equation 6).

Next, using Equation 7 in Equation 11, we find

$$S = S_{\text{off}}(U, V, \boldsymbol{n}_a + \epsilon_o(U, V, \boldsymbol{n}_a; \boldsymbol{v})\boldsymbol{v}) \qquad (16)$$

Thus, for the inverse temperature of a chemical equilibrium state we have

$$\begin{aligned}\frac{1}{T(U, V, \boldsymbol{n}_a; \boldsymbol{v})} &= \left(\frac{\partial S}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{v}}\\ &= \left(\frac{\partial S_{\text{off}}}{\partial U}\right)_{V,\boldsymbol{n}} + \sum_{i=1}^{r}\left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{U,V,\boldsymbol{n}}\nu_i\left(\frac{\partial \epsilon_o}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{v}}\\ &= \left(\frac{\partial S_{\text{off}}}{\partial U}\right)_{V,\boldsymbol{n}}\left[1 - \left(\frac{\partial \epsilon_o}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{v}}\sum_{i=1}^{r}\nu_i\mu_{i,\text{off}}\right]\\ &= \left(\frac{\partial S_{\text{off}}}{\partial U}\right)_{V,\boldsymbol{n}} = \frac{1}{T_{\text{off}}(U, V, \boldsymbol{n}_a + \epsilon_o(U, V, \boldsymbol{n}_a; \boldsymbol{v})\boldsymbol{v})} \qquad (17)\end{aligned}$$

where in writing the second and the third of Equations 17 we use Equation 16 and the definition of chemical potentials, respectively, and in writing the fourth of Equations 17 we use the chemical equilibrium equation (Equation 14). So, the temperature of a chemical equilibrium state equals the temperature of the corresponding state of the surrogate system B.

For the pressure of the chemical equilibrium state we find

$$\begin{aligned}p(U, V, \boldsymbol{n}_a; \boldsymbol{v}) &= \left(\frac{\partial S}{\partial V}\right)_{U,\boldsymbol{n}_a,\boldsymbol{v}}\Big/\left(\frac{\partial S}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{v}}\\ &= T_{\text{off}}\left[\left(\frac{\partial S_{\text{off}}}{\partial V}\right)_{U,\boldsymbol{n}} + \sum_{i=1}^{r}\left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{U,V,\boldsymbol{n}}\nu_i\left(\frac{\partial \epsilon_o}{\partial V}\right)_{U,\boldsymbol{n}_a,\boldsymbol{v}}\right]\\ &= T_{\text{off}}\left(\frac{\partial S_{\text{off}}}{\partial V}\right)_{U,\boldsymbol{n}} - \left(\frac{\partial \epsilon_o}{\partial V}\right)_{U,\boldsymbol{n}_a,\boldsymbol{v}}\sum_{i=1}^{r}\nu_i\mu_{i,\text{off}}\\ &= T_{\text{off}}\left(\frac{\partial S_{\text{off}}}{\partial V}\right)_{U,\boldsymbol{n}} = p_{\text{off}}(U, V, \boldsymbol{n}_a + \epsilon_o(U, V, \boldsymbol{n}_a; \boldsymbol{v})\boldsymbol{v}) \qquad (18)\end{aligned}$$

where in writing the fourth of Equations IS we use Equation 14. So, the pressure of a chemical equilibrium state equals the pressure of the corresponding state of the surrogate system B.

For each chemical potential of the chemical equilibrium state we find

$$\begin{aligned}\mu_i(U, V, \boldsymbol{n}_a; \boldsymbol{v}) &= -\left(\frac{\partial S}{\partial n_{ia}}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{v}}\Big/\left(\frac{\partial S}{\partial U}\right)_{V,\boldsymbol{n}_a,\boldsymbol{v}}\\ &= -T_{\text{off}}\left[\left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{U,V,\boldsymbol{n}} + \sum_{k=1}^{r}\left(\frac{\partial S_{\text{off}}}{\partial n_k}\right)_{U,V,\boldsymbol{n}}\right.\\ &\qquad\left.\times\, \nu_k\left(\frac{\partial \epsilon_o}{\partial n_{ia}}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{v}}\right]\\ &= -T_{\text{off}}\left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{U,V,\boldsymbol{n}} + \left(\frac{\partial \epsilon_0}{\partial n_{ia}}\right)_{U,V,\boldsymbol{n}_a,\boldsymbol{v}}\sum_{k=1}^{r}\nu_k\mu_{k,\text{off}}\\ &= -T_{\text{off}}\left(\frac{\partial S_{\text{off}}}{\partial n_i}\right)_{U,V,\boldsymbol{n}}\\ &= \mu_{i,\text{off}}(U, V, \boldsymbol{n}_a + \epsilon_o(U, V, \boldsymbol{n}_a; \boldsymbol{v})\boldsymbol{v}) \qquad (19)\end{aligned}$$

where in writing the fourth of Equations 19 we use Equation 14. So, the chemical potential of the i-th constituent of a chemical equilibrium state of system A equals the chemical potential of the i-th constituent of the corresponding state of the surrogate system B.

It is worth emphasizing that the identity of values of temperature, pressure, and chemical potentials of a chemical equilibrium state with the values of the respective properties of a stable equilibrium state of the surrogate system obtains only at chemical equilibrium because only then the chemical equilibrium equation (Equation 14) is satisfied. Away from chemical equilibrium states, temperature, pressure, and chemical potentials are not defined for system A because all such states are not stable equilibrium.

Finally, we note that Equations 17–19 indicate that, geometrically, the surfaces represented by the functions $S = S(U, V, \boldsymbol{n}_a; \boldsymbol{v})$ and $S_{\text{off}} = S_{\text{off}}(U, V, \boldsymbol{n}_a + \epsilon\boldsymbol{v})$ have a contact of first degree for each given set of values of $U, V, \boldsymbol{n}_a$ and $\boldsymbol{v}$ at $\epsilon = \epsilon_o(U, V, \boldsymbol{n}_a; \boldsymbol{v})$, namely, at each chemical equilibrium state.

We recall that each chemical potential of a multiconstituent system, in which the chemical reaction mechanism is switched off, may be expressed in the form $\mu_i = \mu_i(T, p, y_1, y_2, \ldots, y_r)$. Using the stoichiometric relations, we write the mole fractions in the form of Equations 5, and the chemical equilibrium equation in the form

$$\sum_{i=1}^{r}\nu_i\mu_i\left(T, p, \frac{n_{1a} + \nu_1\epsilon_o}{n_a + \nu\epsilon_o}, \ldots, \frac{n_{ra} + \nu_r\epsilon_o}{n_a + \nu\epsilon_o}\right) = 0 \qquad (20)$$

Equation 20 represents the chemical equilibrium equation as a function of T, p, and the mole fractions of the chemical

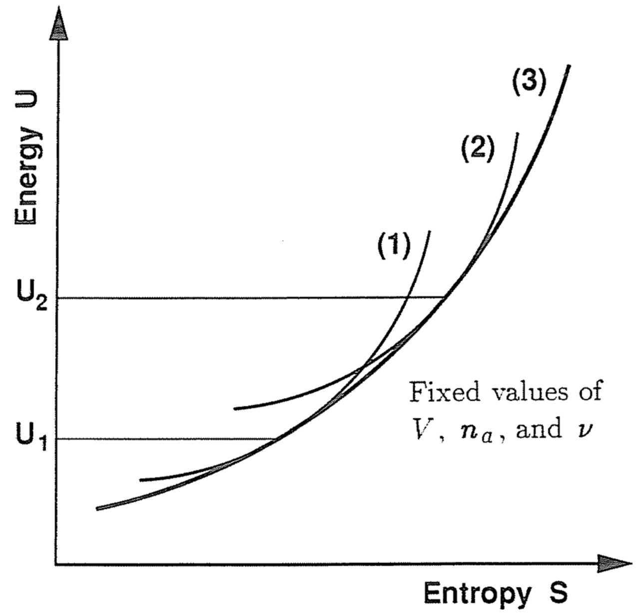

Fig. 1 Energy versus entropy diagram of the states of simple system A with given values of V, n_a and ν. Curve (1) represents the states $A_{\epsilon 1}$ and coincides with the curve of the stable equilibrium states of surrogate system B for the given value V of the volume and fixed values $n_1 = n_a + \epsilon_1 \nu$ of the amounts of constituents, that is, a fixed ϵ_1. Curve (2) represents the states $A_{\epsilon 2}$ and coincides with the curve of the stable equilibrium states of surrogate system B for the given value V of the volume and fixed values no $n_2 = n_a + \epsilon_2 \nu$ of the amounts of constituents, that is, a fixed ϵ_2. Curve (3) represents the chemical equilibrium states of system A for the given values of V, n_a, and ν.

equilibrium state. The chemical potentials are those of surrogate system B. For given values of $T, p, \boldsymbol{n}_a$ and $\boldsymbol{\nu}$, we can solve this equation for the unknown ϵ_o and, hence, determine the chemical equilibrium composition, $y_{1o}, y_{2o}, \ldots, y_{ro}$, and the values of the amounts of constituents $n_{1o}, n_{2o}, \ldots, n_{ro}$.

Conversely, if the values of $T, p, y_1, y_2, \ldots, y_r$ are given but do not satisfy Equation 20, we conclude that the state is not chemical equilibrium but a state A_ϵ that can be described using the stable-equilibrium properties of the surrogate system, although A is either a nonequilibrium or a nonstable equilibrium state. Then, of course, the values of T and p refer to the state of the surrogate system B.

The results can be summarized pictorially with the help of the energy versus entropy graphs introduced in Ref. 10. For given values of V, $\boldsymbol{n}_a$, and $\boldsymbol{\nu}$ three projections of states are superimposed on the single U versus S diagram shown in Figure 1: (1) the projection of the states of system A; (2) the projection of the states of the surrogate system B with values $\boldsymbol{n}_1 = \boldsymbol{n}_a + \epsilon_1 \boldsymbol{\nu}$, and (3) the projection of the states of the surrogate system B with values $\boldsymbol{n}_2 = \boldsymbol{n}_a + \epsilon_2 \boldsymbol{\nu}$ where ϵ_1 and ϵ_2 are two different values of the reaction coordinates ϵ. The curves that represent the stable equilibrium states of the surrogate system B corresponding to the two sets of values $\boldsymbol{n}_1 = \boldsymbol{n}_a + \epsilon_1 \boldsymbol{\nu}$ and $\boldsymbol{n}_2 = \boldsymbol{n}_a + \epsilon_2 \boldsymbol{\nu}$ also represent the loci of all the states $A_{\epsilon 1}$ and $A_{\epsilon 2}$ of system A.

The value ϵ_1 is chosen so that $\epsilon_1 = \epsilon_0(U_1, V, \boldsymbol{n}_a; \boldsymbol{\nu})$ and, therefore, at the energy U_1 the locus of states $A_{\epsilon 1}$ is tangent to the curve of the chemical equilibrium states of A. Similarly, the value ϵ_2 is such that $\epsilon_2 = \epsilon_o(U_2, V, \boldsymbol{n}_a; \boldsymbol{\nu})$ and, therefore, at the energy U_2 the locus of states $A_{\epsilon 2}$ is tangent to the curve of the chemical equilibrium states of A. We see that the curve of the chemical equilibrium states is the envelope of the loci of states A_ϵ for all possible values of ϵ. We also see that for $U \neq U_1$ the states $A_{\epsilon 1}$ represent states of system A that are not stable equilibrium. In general, they are either nonequilibrium or nonstable equilibrium states, and yet can be described using the stable-equilibrium properties of the surrogate system.

Finally, for given values of temperature T, pressure p, stoichiometric coefficients $\boldsymbol{\nu}$, and values of the amounts of constituents $\boldsymbol{n}$ compatible with given values $\boldsymbol{n}_a$ according to Equations 10, we show that the lowest value of the Gibbs free energy of the surrogate system B obtains at the state of B that corresponds to the chemical equilibrium state of A.

For the surrogate simple system B, the Gibbs free energy $G_{\text{off}} = G_{\text{off}}(T, p, n_1, n_2, \ldots, n_r)$. If the amounts of constituents are compatible with $\boldsymbol{n}_a$ and the chemical reaction mechanism, we may rewrite G_{off} in the form

$$G_{\text{off}} = G_{\text{off}}(T, p, \boldsymbol{n}_a + \epsilon \boldsymbol{\nu}) \tag{21}$$

For given T, p and $\boldsymbol{n}_a$, an extreme value of G_{off} obtains when

$$\begin{aligned} \left(\frac{\partial G_{\text{off}}}{\partial \epsilon}\right)_{T,p,\boldsymbol{n}_a,\boldsymbol{\nu}} &= \sum_{i=1}^{r} \left(\frac{\partial G_{\text{off}}}{\partial n_i}\right)_{T,p,\boldsymbol{n}} \left(\frac{\partial n_i}{\partial \epsilon}\right)_{\boldsymbol{n}_a,\boldsymbol{\nu}} \\ &= \sum_{i=1}^{r} \mu_{i,\text{off}} \nu_i = 0 \end{aligned} \tag{22}$$

where we use the equation $(\partial G / \partial n_i)_{T,p,\boldsymbol{n}} = \mu_i$ for $i = 1, 2, \ldots, r$. These conditions are satisfied when the chemical potentials satisfy the chemical equilibrium equation (Equation 14), that is, when the stable equilibrium state of the surrogate system corresponds to the chemical equilibrium state of A.

All these results are readily extended to systems with many chemical reaction mechanisms [5].

Conclusions

If a phenomenon involving chemical reactions can be modeled as occurring in a simple system, a host of practical and powerful results obtain. The prerequisites for such modeling are that the system consist of relatively large values of the amounts of constituents, and that volume is the only parameter [11].

In particular, the study of the stable or chemical equilibrium states is greatly simplified by using the stable-equilibrium-state relations valid for systems without chemical reactions. In addition, a large family of nonequilibrium states—the family A_ϵ discussed in Section 3—can also be characterized in terms of relations valid for simple systems without chemical reactions. This characterization is the starting point of the theory of chemical kinetics.

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[11] All the results can be readily extended also to systems with other parameters in addition to volume, such as, for example, the location in a uniform gravity field, and the intensity of a uniform electrostatic or magnetostatic field.