

PHYSICO-CHEMICAL THERMODYNAMICS OF MATERIAL SYSTEMS: A REVIEW OF BASIC CONCEPTS AND RESULTS

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1 Introduction

1.1 General Considerations

Thermodynamics developed from the study of heat-engines and the relations between heat and work. However, after some time, it was recognized that the study of the effects of the thermal and mechanical interactions between the system and the surroundings provides valuable information on the equilibrium properties of the material systems, and on the reactions or transformations which occur. Today, thermodynamics might be considered as a discipline which deals with (i) a wide class of macroscopic properties of material systems, (ii) the way in which these properties are influenced by the thermal, mechanical and chemical interactions with other systems, and (iii) the reactions or transformations involved.

One of the key variables in the thermodynamic approach is temperature, and, in a certain sense, thermodynamics may be defined as the science dealing with the forms in which the properties of matter are modified by the changes in temperature. In particular, for material systems, it is interesting to determine the effects of temperature upon the equilibrium properties of a given structure, and to explore the possibility of inducing changes of structure by suitable temperature variations. The question of identifying the most stable structure for given external conditions is usually known as the Phase Stability Problem, which is often considered as a central problem in the study of material systems.

Classical thermodynamics developed without referring to any particular model of the structure of matter. However, the search for a more complete understanding of the equilibrium states and the transitions occurring in material systems, has stimulated the development of a wider thermodynamic approach, which also takes into account the following aspects:

(1) The structure of the system in its various levels, i.e., microstructural, crystalline and electronic.

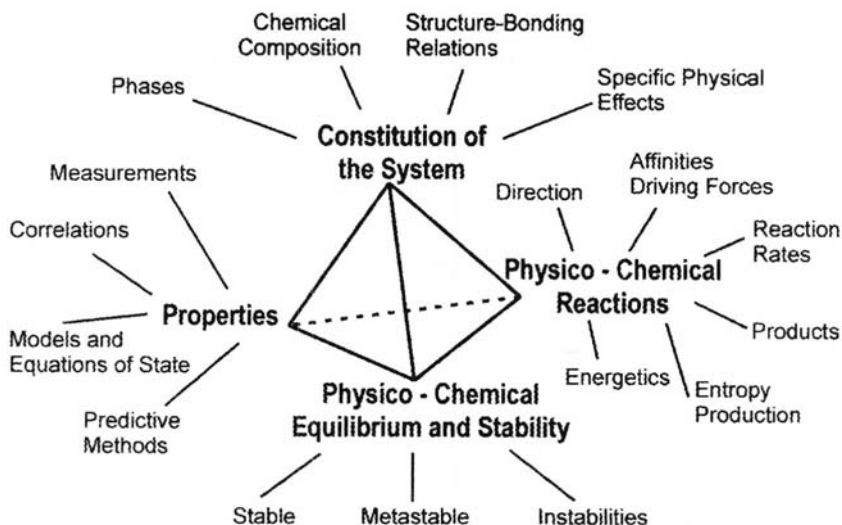


FIGURE 1.

(2) The physical and chemical factors determining phase stability.

(3) The physico-chemical reactions or transformations, their statics, dynamics and products.

Such an approach, which has its conceptual roots in classical and chemical thermodynamics but incorporates concepts, methods and knowledge originated in the physics and chemistry of materials will be referred to as Physico-Chemical Thermodynamics (PhyCheT). Its scope is represented schematically in Fig.1, where a tetrahedron is used to emphasize the connections between the main areas of interest.

1.2 The present notes

The present notes originated in a series of lectures which were conceived as an introduction to some of the key concepts of PhyCheT, viz., energetics, irreversibility, equilibrium, and thermodynamic stability. The various themes covered in the notes were selected and combined according to the following objectives:

(1) Present a review of the scope, ideas, methods, and some basic results of classical and chemical thermodynamics.

(2) Emphasize the unity of thermodynamics, offering an integrated view of the study of equilibrium and non-equilibrium phenomena.

(3) Provide basis for further reading of the thermodynamic literature.

(4) Stimulate the search for applications of PhyCheT of material systems.

In view of the amount of material, and the limitations of time and space, the presentation of some of the topics was very brief, and it was assumed that the students had previously followed a course on classical thermodynamics, e.g., as a part of their undergraduate studies in physics, chemistry or engineering. Indeed, topics such as the First Law, the heat-engines, and the various statements of the Second Law are well covered in any of the textbooks listed at the end of the present notes. Finally, it should be kept in mind that these notes emerged from the transparencies prepared to serve as an aid in the discussion. This is, of course, different from writing a real textbook !.

1.3 Acknowledgments

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2 Energetics of Closed Systems and Reactions

2.1 The First Law for Closed Systems

Starting from the basic result from Mechanics for the relation between work (W), and the variations of potential (ΔE_{pot}), kinetic (ΔE_{kin}), and mechanical (ΔE_{mec}) energy of conservative systems, i.e.,

$$W = \Delta E_{mec} = \Delta E_{pot} + \Delta E_{kin}$$

the First Law of Thermodynamics introduces two additional terms, viz,

$$W + Q = \Delta E_{pot} + \Delta E_{kin} + \Delta U \quad (1)$$

where “ Q ” is the heat exchanged by the system with its surroundings, and ΔU is the variation in the so-called internal energy of the system.

In the particular case in which there is no change in the macroscopic, observable, potential and kinetic energy of the system, the First Law becomes

$$\underbrace{W + Q}_{\substack{\text{Interaction} \\ \text{between the} \\ \text{system and its} \\ \text{surroundings}}} = \underbrace{\Delta U = U(b) - U(a)}_{\substack{\text{Change in a function} \\ \text{of the state} \\ \text{of} \\ \text{the system.}}} \quad (2)$$

In differential form, the First Law may be written as

$$\delta W + \delta Q = dU \quad (3)$$

where δW and δQ represent infinitesimal amounts of work and heat, respectively.

2.2 The Message of the First Law

Let us consider a closed system Σ interacting with its surroundings through the performance of work (W) and the exchange of heat (Q), as indicated in the following figure.

In this case we have

$$W + Q = \Delta U \quad (4)$$

where W and Q are quantities to be determined from measurements at the boundaries of the system, whereas ΔU is a quantity to be determined by measurements inside the system. More precisely, the First Law establishes that

$$\Delta U = \int_a^b dU = U(b) - U(a) \quad (5)$$

i.e., dU is an exact differential.

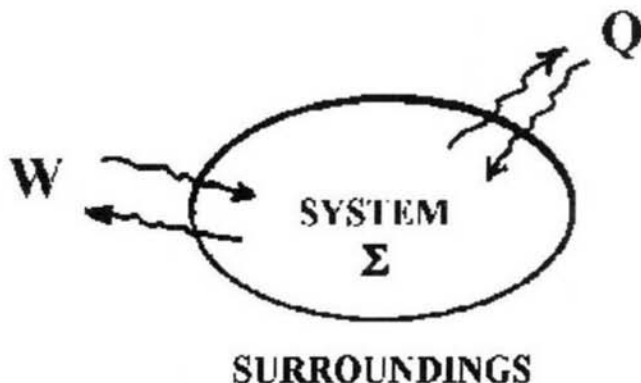


FIGURE 2.

2.3 Consequences and Generalizations

For an isolated system $W = 0$, $Q = 0$, and the First Law becomes

$$W + Q = 0 = \Delta E_{pot} + \Delta E_{kin} + \Delta U \quad (6)$$

which can be written as

$$E_{pot} + E_{kin} + U = \text{constant} \quad (7)$$

This result is usually expressed saying that the total energy is conserved in the isolated system, but there might be changes (“conversions”) from one “form” (e.g. potential or kinetic) to another form (e.g., internal).

In the case of a non-isolated system $W \neq 0$ and $Q \neq 0$, and

$$\underbrace{W + Q}_{\substack{\text{Energy} \\ \text{transferred} \\ \text{to the system} \\ \text{from the surroundings}}} = \underbrace{\Delta (E_{pot} + E_{cin} + U)}_{\substack{\text{Change in a sum of} \\ \text{state functions}}} \quad (8)$$

The result 8 is usually expressed saying that the total energy of the system only changes when there is a transference of energy from the surroundings, in the form of work, heat, or both.

2.4 The Enthalpy Function

Let us now introduce the state function enthalpy, defined as follows

$$H = U + PV \quad (9)$$

The enthalpy difference between two states ("a" and "b") of the system is

$$\Delta H = H(b) - H(a) = U(b) - U(a) + P_b V_b - P_a V_a = \Delta U + P_b V_b - P_a V_a \quad (10)$$

If $P_b = P_a = P$ we have

$$\Delta H = \Delta U + P(V_b - V_a) = \Delta U + P\Delta V \quad (11)$$

which combined with the First Law becomes

$$\Delta H = W + Q + P\Delta V \quad (12)$$

Let us further consider the work (W_{exp}) that the system performs when expanding quasistatically from "a" to "b", viz.,

$$W_{\text{exp}} = - \int_{V_a}^{V_b} P dV \quad (13)$$

If, in addition, the pressure against which the system expands remains constant we have

$$W_{\text{exp}} = -P \int_{V_a}^{V_b} dV = -P\Delta V \quad (14)$$

This result can be introduced in eq. 12, which yields

$$\Delta H = W + Q - W_{\text{exp}} \quad (15)$$

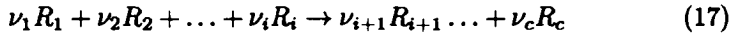
Indeed, if the system and the process are such that $W = W_{\text{exp}}$, we find

$$\Delta H = Q \quad (16)$$

i.e., the enthalpy difference between the final and the initial states represents the heat exchanged by the system with its surroundings.

2.5 Description of Reactions in Closed Homogeneous Systems

Let us consider the following reaction occurring in a closed, single phase system



where ν_i is the stoichiometric coefficient of the reactant "i".

If $m_i(0)$ and $m_i(t)$ are the masses of reactant "i" at $t = 0$ and time "t", respectively, the Law of Definite Proportions yields

$$m_i(t) - m_i(0) = \nu_i M_i \xi \quad (18)$$

where M_i is the molar mass of R_i , and ξ is the extent of reaction coordinate or, simply, the reaction coordinate.

By definition

$\xi = 0(\text{mol})$ represents the initial state

$\xi = 1(\text{mol})$ represents the state when one equivalent of the reaction has occurred

From eq. 18 we obtain

$$\sum_i m_i(t) - \sum_i m_i(0) = \sum_i \nu_i M_i \xi \quad (19)$$

Since the system is closed,

$$\sum_i m_i(t) = \sum_i m_i(0) \quad (20)$$

and eq. 19 yields

$$\sum_i \nu_i M_i = 0 \quad (21)$$

which is often referred to as the stoichiometric equation for the reaction.

By differentiating 18 we obtain

$$dm_i = \nu_i M_i d\xi \quad (22)$$

i.e.,

$$\frac{dm_1}{\nu_1 M_1} = \frac{dm_2}{\nu_2 M_2} = \dots = \frac{dm_c}{\nu_c M_c} = d\xi \quad (23)$$

Alternatively, eq. 18 can be expressed in terms of the number of moles n_i , i.e.,

$$dn_i = \frac{dm_i}{M_i} \quad (24)$$

We obtain

$$n_i(t) - n_i(0) = \nu_i \xi \quad (25)$$

and eq. 23 becomes

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_c}{\nu_c} = d\xi \quad (26)$$

2.6 Rate of a Reaction

Following De Donder, we define the rate of reaction \mathbf{v} , as

$$\mathbf{v} = \frac{d\xi}{dt} \quad (27)$$

i.e.,

$$\mathbf{v} = \frac{1}{\nu_i M_i} \frac{dm_i}{dt} = \frac{1}{\nu_i} \frac{dn_i}{dt}$$

Alternatively, using the number of moles per unit volume, c_i , defined as

$$c_i = \frac{n_i}{V} \quad (28)$$

we obtain

$$\frac{dc_i}{dt} = \frac{1}{V} \left[\nu_i \mathbf{v} - c_i \frac{dV}{dt} \right] \quad (29)$$

If there is no change in the volume of the system we find

$$\frac{dc_i}{dt} = \frac{\nu_i}{V} \mathbf{v}$$

2.7 Simultaneous Reactions

If the system undergoes “ r ” independent reactions we have “ r ” stoichiometric equations, which may be written as

$$\sum_{i=1} \nu_{i,\rho} M_i = 0 \quad (\rho = 1, 2, \dots, r) \quad (30)$$

where ρ is an index which identifies each reaction. In this case, the variation in the extent of the ρ – *th* reaction is given by

$$\frac{d_\rho m_1}{\nu_{1,\rho} M_1} = \frac{d_\rho m_2}{\nu_{2,\rho} M_2} = \dots = \frac{d_\rho m_c}{\nu_{c,\rho} M_c} = d\xi_\rho \quad (31)$$

and

$$\frac{d_\rho n_1}{\nu_{1,\rho}} = \frac{d_\rho n_2}{\nu_{2,\rho}} = \dots = \frac{d_\rho n_c}{\nu_{c,\rho}} = d\xi_\rho \quad (32)$$

The rate of reaction ρ is now

$$\begin{aligned} \mathbf{v}_\rho &= \frac{d_\rho \xi}{dt} = \frac{1}{\nu_{1,\rho} M_1} \frac{d_\rho m_1}{dt} = \dots \\ &= \frac{1}{\nu_{1,\rho}} \frac{d_\rho n_1}{dt} = \dots \end{aligned} \quad (33)$$

The total change in n_i due to the occurrence of the various reactions is

$$dn_i = d_1 n_i + d_2 n_i + \dots = \sum_{\rho=1}^r d_\rho n_i \quad (34)$$

which yields

$$\frac{dn_i}{dt} = \sum_{\rho=1}^r \frac{d_\rho n_i}{dt} = \sum_{\rho=1}^r \nu_{i,\rho} \mathbf{v}_\rho \quad (35)$$

2.8 Energetics of Reactions in Closed Homogeneous Systems

Let us consider a closed homogeneous system Σ exchanging energy with its surroundings in the form of heat and work, as indicated in the following figure. If the surface Ω enclosing the system is subjected to a uniform normal pressure (P) and no other external work is involved we have

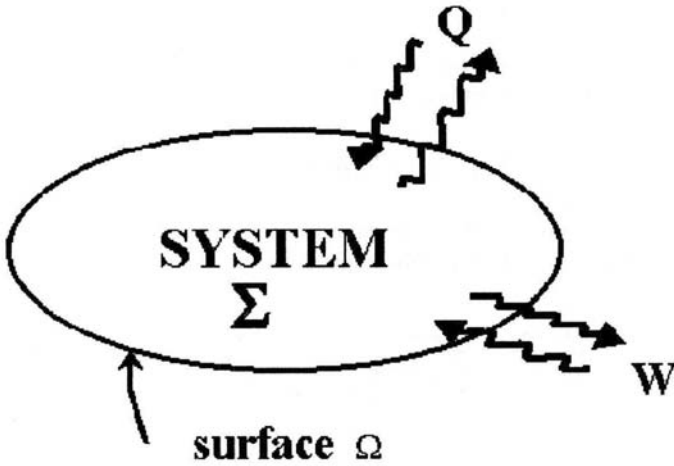


FIGURE 3.

$$\delta Q = dU + PdV \quad (36)$$

Since the internal energy U is a function of the state of the system, it can be expressed in terms of the independent state variables. In particular, at time "t", the state of the system may be determined by adopting the independent variables $T, V, n_1, n_2, \dots, n_c$, i.e., we may assume that

$$U = U(T, V, n_1, n_2, \dots, n_c) \quad (37)$$

In systems in which a single chemical reaction is involved, we can write

$$U = U [T, V, n_1(0), n_2(0) \dots, n_c(0), \xi] \quad (38)$$

and, since the $n_i(0)$ values are given one for all, we have

$$U = U (T, V, \xi) \quad (39)$$

Accordingly,

$$dU = \frac{\partial U}{\partial T}_{V, \xi} dT + \frac{\partial U}{\partial V}_{T, \xi} dV + \frac{\partial U}{\partial \xi}_{T, V} d\xi \quad (40)$$

which combined with the First Law yields

$$\delta Q = \frac{\partial U}{\partial T}_{V,\xi} dT + \left[\frac{\partial U}{\partial V}_{T,\xi} + P \right] dV + \left(\frac{\partial U}{\partial \xi} \right)_{T,V} d\xi \quad (41)$$

This equation for the heat exchanged can be expressed as

$$\delta Q = C_{V,\xi} dT + l_{T,\xi} dV + u_{T,V} d\xi \quad (42)$$

where:

$$C_{V,\xi} = \left(\frac{\partial U}{\partial T} \right)_{V,\xi} \quad (43)$$

is the heat capacity at constant V, ξ ,

$$l_{T,\xi} = \left(\frac{\partial U}{\partial V} \right)_{T,\xi} + P \quad (44)$$

is the heat of unit volume change at constant T, ξ , and

$$u_{T,V} = \left(\frac{\partial U}{\partial \xi} \right)_{T,V} \quad (45)$$

is the heat of reaction at constant T, V .

In a similar way, in terms of the variables T, P, ξ we have

$$dU = \left(\frac{\partial U}{\partial T} \right)_{P,\xi} dT + \left(\frac{\partial U}{\partial P} \right)_{T,\xi} dP + \left(\frac{\partial U}{\partial \xi} \right)_{T,P} d\xi \quad (46)$$

and

$$dV = \left(\frac{\partial V}{\partial T} \right)_{P,\xi} dT + \left(\frac{\partial V}{\partial P} \right)_{T,\xi} dP + \left(\frac{\partial V}{\partial \xi} \right)_{T,P} d\xi \quad (47)$$

By combining eqs. 46 and 47 with the First Law we obtain

$$\delta Q = C_{P,\xi} dT + h_{T,\xi} dP + h_{T,P} d\xi \quad (48)$$

where

$$C_{P,\xi} = \left(\frac{\partial U}{\partial T} \right)_{P,\xi} + P \left(\frac{\partial V}{\partial T} \right)_{P,\xi} = \left(\frac{\partial H}{\partial T} \right)_{P,\xi} \quad (49)$$

is the heat capacity at constant P, ξ ,

$$h_{T,\xi} = \left(\frac{\partial U}{\partial P} \right)_{T,\xi} + P \left(\frac{\partial V}{\partial P} \right)_{T,\xi} = \left(\frac{\partial H}{\partial P} \right)_{T,\xi} - V \quad (50)$$

is the heat of unit pressure change at constant T, ξ , and

$$h_{T,P} = \left(\frac{\partial U}{\partial \xi} \right)_{T,P} + P \left(\frac{\partial V}{\partial \xi} \right)_{T,P} = \left(\frac{\partial H}{\partial \xi} \right)_{T,P} \quad (51)$$

is the heat of reaction at constant T, P .

2.9 Average Heat of a Physico-Chemical Reaction

If a physico-chemical reaction occurs in the closed system Σ (Fig. 3) at constant volume, the heat involved is given by

$$Q_V = \int_a^b (\delta Q)_V = \int_a^b (dU)_V = U(b) - U(a) \quad (52)$$

whereas at constant pressure we have

$$Q_P = \int_a^b (\delta Q)_P = \int_a^b (dH)_P = H(b) - H(a) \quad (53)$$

i.e., in both cases the heat received or released depends only upon the initial and final states.

Let us now consider a reaction which brings the system Σ from the initial state α to the final state β . If we choose ξ as the reaction coordinate, and the conditions under which the reaction takes place are specified, it will be possible to study the evolution of heat (Q) as a function of ξ . In particular, let us introduce the quantity

$$q(\xi) = \frac{\delta Q}{d\xi} \quad (54)$$

In terms of $q(\xi)$, the heat involved in the reaction $\alpha \rightarrow \beta$ will be

$$Q = \int_{\alpha}^{\beta} q(\xi) d\xi \quad (55)$$

whereas the average heat of reaction \bar{q} will be

$$\bar{q} = \frac{Q}{\xi_{\beta} - \xi_{\alpha}} = \frac{\int_{\alpha}^{\beta} q(\xi) d\xi}{\xi_{\beta} - \xi_{\alpha}} \quad (56)$$

If the change $\alpha \rightarrow \beta$ corresponds to one equivalent of reaction, i.e., if

$$\xi_{\beta} - \xi_{\alpha} = 1 \quad (57)$$

eq. 56 becomes

$$\bar{q} = Q = \int_{\xi=0}^{\xi=1} q(\xi) d\xi \quad (58)$$

In particular, if the reaction $\alpha \rightarrow \beta$ occurs at constant T, V , eq. 41 yields

$$\left[\delta Q = \left(\frac{\partial U}{\partial \xi} \right) d\xi \right]_{T,V} \quad (59)$$

and eq. 53 becomes

$$q_{T,V} = \left(\frac{\partial U}{\partial \xi} \right)_{T,V} = u_{T,V} \quad (60)$$

where $u_{T,V}$ was defined in eq. 45. As a consequence,

$$\bar{q}_{T,V} = Q_{T,V} = \int_{\xi=0}^{\xi=1} \left(\frac{\partial U}{\partial \xi} \right)_{T,V} d\xi = U(\beta) - U(\alpha) = \Delta U^{\beta/\alpha} \quad (61)$$

In a similar way, for a reaction occurring at constant T, P , eq. 48 yields

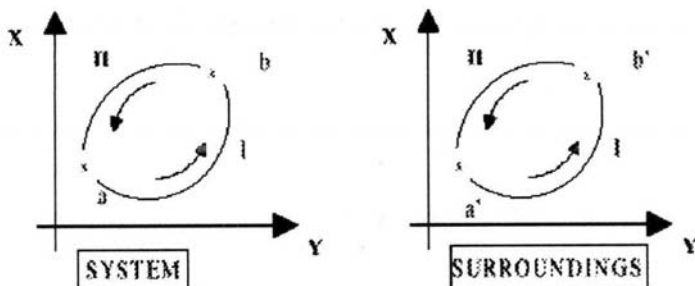


FIGURE 4.

$$q_{T,P} = \left(\frac{\partial H}{\partial \xi} \right)_{T,P} = h_{T,P} \quad (62)$$

and

$$\bar{q}_{T,P} = Q_{T,P} = \int_{\xi=0}^{\xi=1} \left(\frac{\partial U}{\partial \xi} \right)_{T,P} d\xi = H(\beta) - H(\alpha) = \Delta H^{\beta/\alpha} \quad (63)$$

3 Reversible and Irreversible Phenomena. Entropy

3.1 Reversible and Irreversible Processes. The Second Law

A process (I) occurring in a system will be called reversible if there is at least another process (II) which brings the system and its surroundings back to the respective initial states. This is indicated in the following figure.

The experience indicates that reversibility is approached if the process ab (path I) occurs in such way that the system is always close to equilibrium. In that case, the reverse process can be induced by changing infinitesimally the external conditions. In this sense, a reversible process might be described as a succession of equilibrium states. In contrast with this, there are processes in nature which are found to occur spontaneously in one direction, only. This feature of the real world is highlighted by the Second Law of thermodynamics, whose message may be summarized as follows:

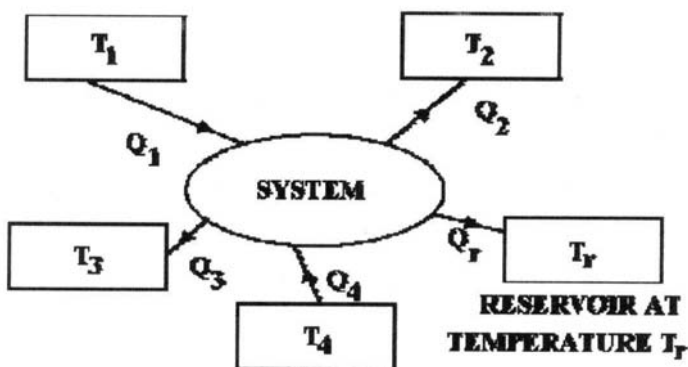


FIGURE 5.

- There are irreversible processes, such as the heat transfer between bodies at different temperatures, or the conversion of mechanical energy into heat.
- The existence of irreversible phenomena can be expressed by statements, such as that of Kelvin-Planck or Clausius, which establish the impossibility of constructing a certain kind of device. Although referring to different phenomena, these statements are logically equivalent.

3.2 The Clausius Theorem

Let α be a closed system that undergoes a cyclic process during which it exchanges heat in quantities Q_1, Q_2, \dots, Q_r , with heat reservoirs at temperatures T_1, T_2, \dots, T_r , respectively, and let the Q_i be positive when heat is transferred to the system and negative when it is transferred to the reservoir, as indicated in the following scheme.

The Clausius theorem establishes that in such case the following relation holds.

$$\sum_r \frac{Q_r}{T_r} \leq 0 \quad (64)$$

where the equality sign corresponds to reversible cycles. Generalized to elemental heat exchanges with a series of heat reservoirs, the Clausius theorem states that

$$\oint \frac{\delta Q}{T_r} \leq 0 \quad (65)$$

The Clausius theorem can be proved once the Kelvin-Planck statement of the Second Law is accepted.

3.3 Application to Reversible Cycles: Entropy Difference between Equilibrium States

For a cyclic process comprising only reversible steps, such as that indicated in the following figure, the Clausius theorem becomes

$$\oint \left(\frac{\delta Q}{T_r} \right)_{rev} = 0 \quad (66)$$

By definition, the system goes through a series of equilibrium states. These states can be described using the thermodynamic variables of the system. In particular the system has a well defined temperature, T_α . Since the heat transfers are reversible, the temperature of the system must be the same as that of the heat reservoirs involved in each transference step, i.e.,

$$T_r = T_\alpha \quad (67)$$

From the series of equilibrium states comprising the reversible cycle we select two, "a" and "b" and write the Clausius theorem

$$\oint \left(\frac{\delta Q}{T_r} \right)_{rev} = \int_{Ia}^b \left(\frac{\delta Q}{T_r} \right)_{rev} + \int_{IIb}^a \left(\frac{\delta Q}{T_r} \right)_{rev} = 0 \quad (68)$$

which yields

$$\int_{I^a}^b \left(\frac{\delta Q}{T_r} \right)_{rev} = - \int_{II^b}^a \left(\frac{\delta Q}{T_r} \right)_{rev} = \int_{II^a}^b \left(\frac{\delta Q}{T_r} \right)_{rev} \quad (69)$$

i.e. the integral of the quantity $\frac{\delta Q}{T_r}$ is independent of the path, as long as the chosen path is reversible.

We next write $T_r = T_\alpha$ and define the entropy difference between "a" and "b"

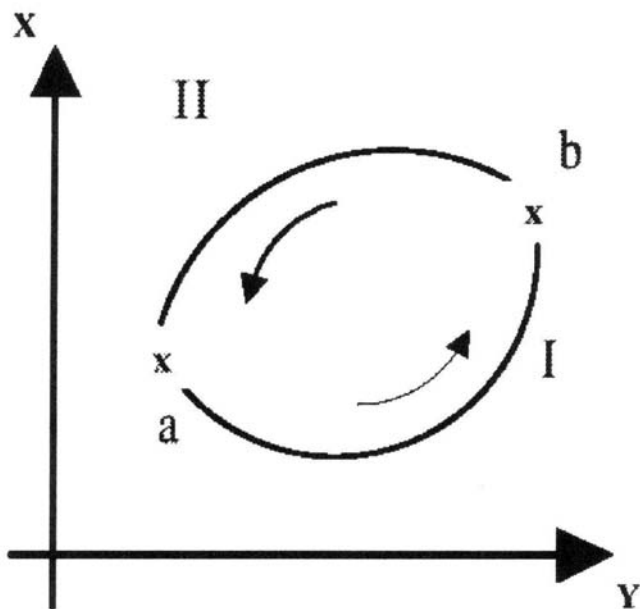


FIGURE 6.

$$\Delta S^\alpha = S^\alpha(b) - S^\alpha(a) = \int_a^b \left(\frac{\delta Q_\alpha}{T_\alpha} \right)_{rev} \quad (70)$$

Since $\frac{\delta Q_\alpha}{T_\alpha}$ is an exact differential we write

$$S^\alpha(b) - S^\alpha(a) = \int_a^b dS^\alpha \quad (71)$$

where

$$dS = \left(\frac{\delta Q_\alpha}{T_\alpha} \right)_{rev} \quad (72)$$

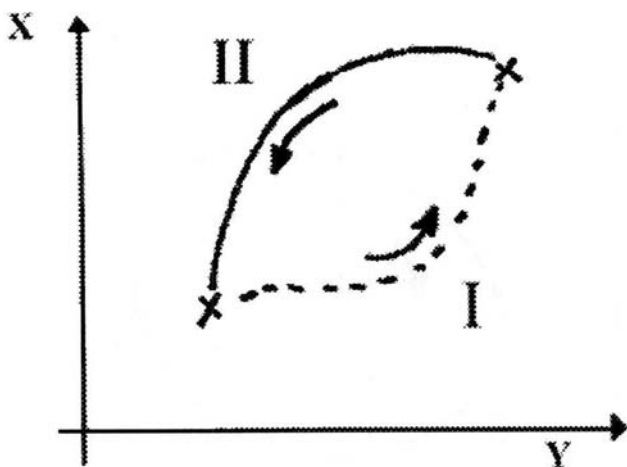


FIGURE 7.

3.4 Application to an Arbitrary Process

Let the system α undergo an arbitrary process "I", which involves a change from the equilibrium state "a" to the equilibrium state "b", and let "II" be a reversible process which brings the system α back to the initial equilibrium state, as indicated in the following scheme. Let T_r be the temperature of the reservoir from which α receives the heat quantity δQ_α .

By applying to the \overline{aba} cyclic process the Clausius theorem, we obtain

$$\oint \frac{\delta Q_\alpha}{T_r} = \int_{Ia}^b \frac{\delta Q_\alpha}{T_r} + \int_{IIb}^a \left(\frac{\delta Q_\alpha}{T_r} \right)_{rev} \leq 0 \quad (73)$$

But, by definition is

$$\left(\frac{\delta Q_\alpha}{T_r} \right)_{rev} = \left(\frac{\delta Q_\alpha}{T_\alpha} \right)_{rev} = dS^\alpha \quad (74)$$

and thus

$$\int_{II^a}^b \left(\frac{\delta Q_\alpha}{T_\alpha} \right)_{rev} = S^\alpha(b) - S^\alpha(a) \geq \int_{I^a}^b \frac{\delta Q_\alpha}{T_r} \quad (75)$$

where T_α is the temperature of the system α in each of the equilibrium states which comprise the reversible step II. It is important to note that in 75 there is no reference to the temperature of the system during process I. Actually, it is not necessary to assume that such temperature can be defined during the arbitrary process.

3.5 Differential forms of the Clausius Theorem: Uncompensated Heat

If eq. 75 is applied to the elemental steps of a process, we have

$$dS^\alpha \geq \frac{\delta Q_\alpha}{T_r} \quad (76)$$

whereas, by definition dS^α is given by eq. 74. Thus it is interesting to introduce the quantity $\delta Q'$ defined as follows

$$\left(\frac{\delta Q_\alpha}{T_r} \right)_{rev} - \frac{\delta Q_\alpha}{T_r} = \frac{\delta Q'}{T_r} \quad (77)$$

Combining eq. 77 with 74 we obtain

$$dS^\alpha = \left(\frac{\delta Q_\alpha}{T_r} \right)_{rev} = \frac{\delta Q_\alpha}{T_r} + \frac{\delta Q'}{T_r} \quad (78)$$

and we conclude from 78 and 76 that

$$\frac{\delta Q'}{T_r} \geq 0 \quad (79)$$

The quantity $\delta Q'$, which is equal to zero if the process is reversible, plays the role of an additional heat given to the system. Therefore $\delta Q'$ will later be referred to as uncompensated heat.

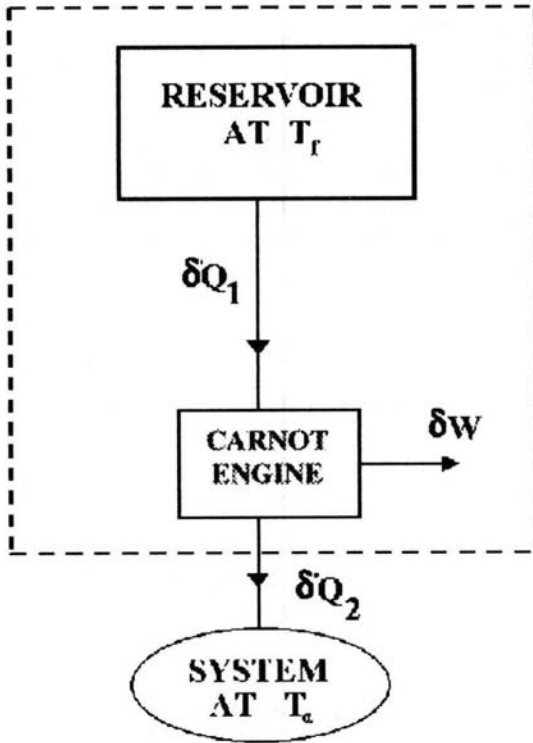


FIGURE 8.

3.6 Processes in a Closed System with a Defined Temperature

Let us now consider the case in which a temperature T_α can be defined in any process of the system α . In such case, the transfer of heat from the reservoir at temperature T_r to the system can be done by using a Carnot engine (CE), as indicated in the following scheme.

Consider, in particular, the case of an elemental heat transfer. For the reversible cycle in the CE the Clausius theorem yields

$$\frac{\delta Q_1}{T_r} + \frac{\delta Q_2}{T_\alpha} = 0 \quad (80)$$

and the First Law requires that

$$\delta Q_1 + \delta Q_2 + \delta W = 0 \quad (81)$$

Furthermore, we take into account that

$$\delta Q_2 = -\delta Q_\alpha \quad (82)$$

and obtain

$$\frac{\delta Q_1}{T_r} = \frac{\delta Q_\alpha}{T_\alpha} \quad (83)$$

Taken together, the heat reservoir at $T = T_r$ and the CE, act as another heat reservoir at $T = T_\alpha$ transferring δQ_α to the system at the same temperature. Applied to this case, eq. 78 becomes

$$dS^\alpha = \frac{\delta Q_\alpha}{T_\alpha} + \frac{\delta Q'_\alpha}{T_\alpha} \quad (84)$$

where the uncompensated heat $\delta Q'_\alpha$ accounts now for the irreversibility of the processes taking place inside the system α at T_α . If the change of state of the system, and therefore dS^α is the same when the CE is used (eq. 84) and without it (eq. 78) we have

$$\frac{\delta Q_\alpha}{T_r} + \frac{\delta Q'}{T_r} = \frac{\delta Q_\alpha}{T_\alpha} + \frac{\delta Q'_\alpha}{T_\alpha} \quad (85)$$

which yields

$$\frac{\delta Q'}{T_r} = \delta Q_\alpha \left(\frac{1}{T_\alpha} - \frac{1}{T_r} \right) + \frac{\delta Q'_\alpha}{T_\alpha} \quad (86)$$

In summary, the uncompensated heat $\delta Q'$ introduced in eq. 77 may be considered as the sum of two contributions: one is due to the transfer of heat from the reservoir at T_r to the system at T_α , and the second is due to the irreversible processes taking place inside the system α . However, in the following we will use the term uncompensated heat only to refer to the term $\delta Q'_\alpha$.

3.7 Results for Heat Reservoirs and Isolated Systems

A heat reservoir is, by definition, a system inside which no irreversible processes occur. Thus for a reservoir $\delta Q'_r = 0$ and eq. 84 yields

$$dS^r = \frac{\delta Q_r}{T_r} \quad (87)$$

Using eq. 87 and making

$$\delta Q_\alpha = -\delta Q_r \quad (88)$$

we obtain from eq. 77

$$\left(\frac{\delta Q_\alpha}{T_r}\right)_{rev} + \frac{\delta Q_r}{T_r} = dS^\alpha + dS^r = \frac{\delta Q'}{T_r} \quad (89)$$

Considering now the system Σ formed by the heat reservoir and the system α , as indicated in the following figure, we note that the sum $dS^\alpha + dS^r$ in eq. 89 represents the increase in entropy in Σ due to irreversible ("irr") processes, since

$$dS_{irr}^\Sigma = dS^\alpha + dS^r = \frac{\delta Q'}{T_r} \geq 0 \quad (90)$$

Equation 90 indicates that in reversible processes the entropy variations dS^α and dS^r compensate each other, viz;

$$dS_{irr}^\Sigma = dS^\alpha + dS^r = 0 \quad (91)$$

If, on the other hand

$$dS_{irr}^\Sigma = dS^\alpha + dS^r > 0 \quad (92)$$

the processes occurring in Σ are irreversible. Furthermore, since the system α exchanges heat only with the reservoir at T_r , Σ can be considered as an isolated system. In this case, the result 92 reproduces the usual statement of the Second Law which establishes that no process occurring in an isolated system can decrease its entropy.

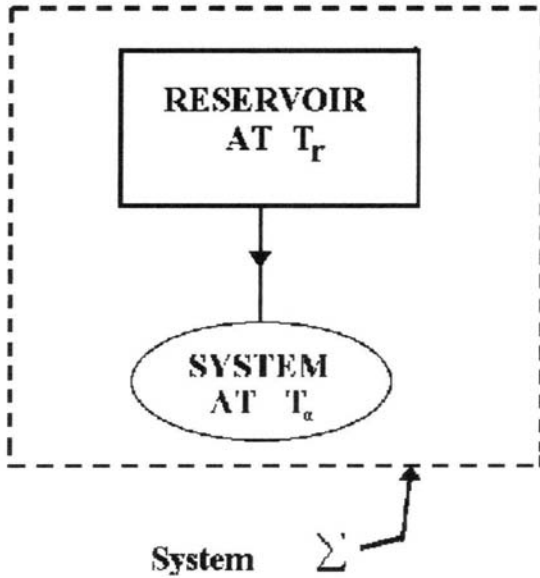


FIGURE 9.

3.8 Contributions to the Entropy Change

The second term on the right side of eq. 84 represents the contribution to dS^α of the irreversible processes taking place inside the system. That contribution will be described by the quantity $d_i S$, defined as follows

$$d_i S^\alpha = \frac{\delta Q'_\alpha}{T_\alpha} \geq 0 \quad (93)$$

The term $d_i S$ will be called Entropy Production. According to the Second Law, this term cannot be negative, and it is equal to zero for reversible processes.

The first term on the right side of eq. 84 represents a contribution to dS^α due to the interaction of the system α with its surroundings. Since α was assumed to be a closed system, such term in eq. 84 describes a thermal interaction. In the most general case, the contribution to the entropy change due to the interaction with the surroundings will be denoted as $d_e S$, and eq. 84 will be written in the form

$$dS^\alpha = d_e S^\alpha + d_i S^\alpha \quad (94)$$

and the term $d_e S^\alpha$ will be referred to as Entropy Flow.

3.9 The Clausius Theorem Expressed as an Equality

In terms of the quantities introduced in the previous section, the entropy equation for a closed system at $T = T_\alpha$ (eq. 84) becomes

$$dS^\alpha = \frac{\delta Q_\alpha}{T_\alpha} + d_i S^\alpha \quad (95)$$

where, according to the Second Law

$$d_i S^\alpha \geq 0 \quad (96)$$

Equation 95 expresses the Clausius theorem as an equality. Since the entropy production cannot be negative, eq. 95 may also be written as

$$dS^\alpha \geq \frac{\delta Q_\alpha}{T_\alpha} \quad (97)$$

which is usually referred to as the Clausius Inequality for a system with a temperature T_α .

4 Affinity, Reaction Rate and Physico-Chemical Equilibrium

4.1 Fundamental Relations

By combining the expression of the First Law for a closed system which can expand against an external pressure, i.e.,

$$dU = \delta Q - PdV \quad (98)$$

with the entropy equation

$$dS = d_e S + d_i S = \frac{\delta Q}{T} + d_i S \quad (99)$$

we obtain

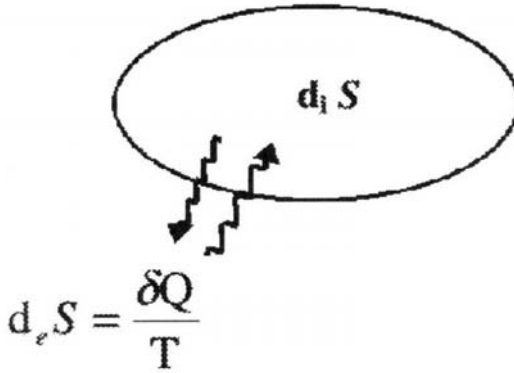


FIGURE 10.

$$d_i S = dS - \frac{dU + PdV}{T} \quad (100)$$

By combining this result with the Second Law, we find the key relations

$$d_i S = dS - \frac{dU + PdV}{T} \geq 0 \quad (101)$$

and

$$Td_i S = TdS - dU - PdV \geq 0 \quad (102)$$

The consequences of these results will now be explored. For processes at constant volume we obtain from eq. 102

$$\left[d_i S = dS - \frac{dU}{T} \right]_V \quad (103)$$

If in addition, the entropy of the system is constant, we have

$$\left[d_i S = -\frac{dU}{T} \geq 0 \right]_{S,V} \quad (104)$$

which implies that in processes taking place at constant S and V

$$(dU)_{S,V} \leq 0 \quad (105)$$

i.e., the internal energy cannot increase. In particular, we obtain

$$(dU)_{S,V} = 0 \text{ for Reversible Processes, and} \quad (106)$$

$$(dU)_{S,V} < 0 \text{ for Irreversible Processes} \quad (107)$$

Analogously, for processes at constant U and V we obtain from eq. 102

$$[d_i S = dS \geq 0]_{U,V} \quad (108)$$

i.e.

$$(dS)_{U,V} \geq 0 \quad (109)$$

Introducing now the enthalpy function

$$H = U + PV$$

we obtain

$$dU + PdV = dH - VdP \quad (110)$$

which combined with eq. 102 yields

$$d_i S = dS - \frac{dH - VdP}{T} \geq 0 \quad (111)$$

For processes at constant pressure we find

$$\left[d_i S = dS - \frac{dH}{T} \geq 0 \right]_P \quad (112)$$

In particular, if the entropy is also constant we obtain

$$(dH)_{P,S} \leq 0 \quad (113)$$

In terms of the Helmholtz energy

$$F = U - TS \quad (114)$$

we may write eq. 102 as follows

$$d_i S = -\frac{1}{T} (dF + SdT + PdV) \geq 0 \quad (115)$$

For processes at constant V eq. 115 reduces to

$$\left[d_i S = -\frac{1}{T} (dF + SdT) \geq 0 \right]_V \quad (116)$$

which reproduces eq.103. Furthermore, at constant T and V we find

$$\left[d_i S = -\frac{1}{T} dF \geq 0 \right]_{T,V} \quad (117)$$

i.e.

$$(dF)_{T,V} \leq 0 \quad (118)$$

Finally, in terms of the Gibbs energy

$$G = U + PV - TS \quad (119)$$

we may write eq. 102 as follows

$$d_i S = -\frac{1}{T} (dG - VdP + SdT) \geq 0 \quad (120)$$

For processes at constant P we obtain from eq. 120

$$\left[d_i S = -\frac{1}{T} (dG + SdT) \geq 0 \right]_P \quad (121)$$

which reproduces eq. 112. Finally, at constant T and P we find

$$\left[d_i S = -\frac{1}{T} (dG) \geq 0 \right]_{T,P} \quad (122)$$

i.e.

$$(dG)_{T,P} \leq 0$$

4.2 Affinity: Definition and Relations

Let us consider a closed system in which there is

- (a) Mechanical Equilibrium
- (b) Thermal Equilibrium
- (c) Diffusion Equilibrium within each phase, so that the production of entropy can be due to Chemical Reactions or Transport of Matter between the various phases, only.

In particular, let us now consider the case in which the production of entropy arises only from chemical reactions and phase changes, i.e., processes that can be described in terms of a reaction coordinate ξ . If only one such process occurs, let $d\xi$ the change in the reaction coordinate, $\delta Q'$ the uncompensated heat and $d_i S$ the entropy production corresponding to the same interval dt . In these conditions, we shall introduce a relation between entropy production and the progress of the reaction, which is often referred to as De Donder's fundamental hypothesis, viz.,

$$\delta Q' = T d_i S = A d\xi \geq 0 \quad (123)$$

The quantity A in eq. 123 will be called the affinity of the reaction. By combining eq. 123 with 102 we obtain

$$T d_i S = T dS - dU - P dV = A d\xi \quad (124)$$

from which we derive, at constant S, V

$$T \left(\frac{\partial_i S}{\partial \xi} \right)_{S,V} = - \left(\frac{\partial U}{\partial \xi} \right)_{S,V} = A$$

Furthermore, we obtain,

$$T \left(\frac{\partial_i S}{\partial \xi} \right)_{S,U} = -P \left(\frac{\partial V}{\partial \xi} \right)_{S,U} = A \quad (125)$$

and

$$T \left(\frac{\partial_i S}{\partial \xi} \right)_{U,V} = T \left(\frac{\partial S}{\partial \xi} \right)_{U,V} = A \quad (126)$$

In a similar way, by combining eq. 123 with eqs. 111, 115 and 120 we obtain, respectively,

$$Td_i S = TdS - dH + VdP = Ad\xi \quad (127)$$

$$Td_i S = -dF - SdT - PdV = Ad\xi \quad (128)$$

$$Td_i S = -dG + VdP - SdT = Ad\xi \quad (129)$$

from which we derive the key relations

$$T \left(\frac{\partial_i S}{\partial \xi} \right)_{P,S} = - \left(\frac{\partial H}{\partial \xi} \right)_{P,S} = A \quad (130)$$

$$T \left(\frac{\partial_i S}{\partial \xi} \right)_{T,V} = - \left(\frac{\partial F}{\partial \xi} \right)_{T,V} = A \quad (131)$$

$$T \left(\frac{\partial_i S}{\partial \xi} \right)_{T,P} = - \left(\frac{\partial G}{\partial \xi} \right)_{T,P} = A \quad (132)$$

4.3 Entropy Production Rate

Let us consider the entropy production occurred during the time interval “ dt ”. By definition,

$$Td_i S = TdS - \delta Q \quad (133)$$

so that

$$T \frac{d_i S}{dt} = T \frac{dS}{dt} - \frac{\delta Q}{dt} \quad (134)$$

Adopting now as state variables T, P and ξ we may write

$$dS = \left(\frac{\partial S}{\partial T} \right)_{P,\xi} dT + \left(\frac{\partial S}{\partial P} \right)_{T,\xi} dP + \left(\frac{\partial S}{\partial \xi} \right)_{T,P} d\xi \quad (135)$$

and also, from a previous chapter,

$$\delta Q = C_{P,\xi} dT + h_{T,\xi} dP + h_{T,P} d\xi \quad (136)$$

By inserting eqs. 135 and 136 into eq. 134 we obtain

$$\begin{aligned} T \frac{d_i S}{dt} = & \left[T \left(\frac{\partial S}{\partial T} \right)_{P,\xi} - C_{P,\xi} \right] \frac{dT}{dt} + \left[T \left(\frac{\partial S}{\partial P} \right)_{T,\xi} - h_{T,\xi} \right] \frac{dP}{dt} \\ & + \left[T \left(\frac{\partial S}{\partial \xi} \right)_{T,P} - h_{T,P} \right] \frac{d\xi}{dt} \end{aligned} \quad (137)$$

Since $\frac{dT}{dt}$ and $\frac{dP}{dt}$ can be varied at will, one could, in principle, choose their values so that $d_i S < 0$. In order to avoid this, we must have

$$T \left(\frac{\partial S}{\partial T} \right)_{P,\xi} - C_{P,\xi} = 0 \text{ i.e., } \left(\frac{\partial S}{\partial T} \right)_{P,\xi} = \frac{C_{P,\xi}}{T} \quad (138)$$

and

$$T \left(\frac{\partial S}{\partial P} \right)_{T,\xi} - h_{T,\xi} = 0 \text{ i.e., } \left(\frac{\partial S}{\partial P} \right)_{T,\xi} = \frac{h_{T,\xi}}{T} \quad (139)$$

Introducing these results in eq. 137 we obtain

$$T \frac{d_i S}{dt} = \left[T \left(\frac{\partial S}{\partial \xi} \right)_{T,P} - \left(\frac{\partial H}{\partial \xi} \right)_{T,P} \right] = - \left(\frac{\partial G}{\partial \xi} \right)_{T,P} \cdot \frac{d\xi}{dt} \quad (140)$$

Taking now into account eqs. 132 and De Donder's relation we obtain

$$T \frac{d_i S}{dt} = A \frac{d\xi}{dt} = A \cdot \mathbf{v} \quad (141)$$

which leads to

$$P_{[S]} = \frac{d_i S}{dt} = \frac{A}{T} \mathbf{v} \quad (142)$$

where the quantity $P_{[S]}$ is the entropy production rate. According to the Second Law is

$$P_{[S]} \geq 0 \quad (143)$$

Equation 142 indicates that the entropy production rate can be expressed as the product of two quantities, viz., the affinity of the reaction and the reaction rate.

4.4 Affinity, Reaction Rate and Equilibrium

De Donder's eq. 142 implies that

$$A \cdot \mathbf{v} \geq 0 \quad (144)$$

which is satisfied in the following cases

$$\text{if } A > 0 \Rightarrow \mathbf{v} \geq 0 \quad (145)$$

$$\text{if } A < 0 \Rightarrow \mathbf{v} \leq 0 \quad (146)$$

and

$$\text{if } A = 0 \Rightarrow \mathbf{v} = 0 \quad (147)$$

because $A = 0$ (i.e. $P_{[S]} = 0$) with $\mathbf{v} \neq 0$ would be against the Second Law. From these results we conclude that the affinity is always of the same sign as the reaction rate, and that if the affinity is zero, the reaction rate is zero, i.e. the system is in equilibrium.

Considering the converse, we may have either

$$\mathbf{v} \neq 0 \Rightarrow \frac{d_i S}{dt} > 0 \Rightarrow A \cdot \mathbf{v} > 0 \quad (148)$$

which is satisfied either by

$$A < 0 \text{ and } \mathbf{v} < 0, \text{ or} \quad (149)$$

$$A > 0 \text{ and } \mathbf{v} > 0 \quad (150)$$

or, alternatively, we may have

$$\mathbf{v} = 0 \Rightarrow \frac{d_i S}{dt} = 0 \Rightarrow A \cdot \mathbf{v} = 0 \quad (151)$$

which may be satisfied either by

$$\mathbf{v} = 0 \text{ and } A = 0 \text{ i.e., true equilibrium, or} \quad (152)$$

$$\mathbf{v} = 0 \text{ and } A \neq 0 \text{ i.e., metastable equilibrium} \quad (153)$$

In summary, neglecting the case of metastable equilibrium we find that $A = 0$ is the necessary and sufficient condition of equilibrium of a physico-chemical reaction.

4.5 Simultaneous Reactions. Thermodynamic Coupling

In the case of several simultaneous reactions, De Donder's relation 123 becomes

$$\delta Q' = T d_i S = \sum_{\rho=1}^r A_{\rho} d\xi_{\rho} \geq 0 \quad (154)$$

where A_{ρ} is the affinity of the ρ -th reaction and ξ_{ρ} is the corresponding reaction coordinate. From 154 we obtain

$$T \frac{d_i S}{dt} = \sum_{\rho=1}^r A_{\rho} \frac{d\xi_{\rho}}{dt} = \sum_{\rho=1}^r A_{\rho} \mathbf{v}_{\rho} \geq 0 \quad (155)$$

and the entropy production rate

$$P_{[S]} = \frac{d_i S}{dt} = \sum_{\rho=1}^r \frac{A_{\rho}}{T} \mathbf{v}_{\rho} \geq 0 \quad (156)$$

Consider now the case of two coupled reactions, i.e.,

$$T \frac{d_i S}{dt} = A_1 \mathbf{v}_1 + A_2 \mathbf{v}_2 \geq 0 \quad (157)$$

Evidently, in this case it is possible to have

$$\begin{array}{ccc} A_1 \mathbf{v}_1 < 0 & \text{together with} & A_2 \mathbf{v}_2 > 0 \\ \text{(The "coupled" reaction)} & & \text{(The "coupling" reaction)} \end{array}$$

if these rates and affinities satisfy the condition

$$\mathbf{v}_2 \geq -\frac{A_1}{A_2} \mathbf{v}_1 \quad (158)$$

This mechanism, called thermodynamic coupling, allows the coupled reaction to proceed in a direction opposite to that indicated by its affinity. This is possible if there exist other coupling reactions which proceed at sufficiently high rates.

5 Thermodynamics of a Phase: Fundamental Equations and the Chemical Potential

5.1 Fundamental Equations and Maxwell Relations

By combining the expressions for $d_i S$ of the previous chapter with De Donder's formula, we obtain, respectively, the fundamental equations

$$dU = TdS - PdV - Ad\xi \quad (159)$$

$$dH = TdS + VdP - Ad\xi \quad (160)$$

$$dF = -SdT - PdV - Ad\xi \quad (161)$$

$$dG = -SdT + VdP - Ad\xi \quad (162)$$

Equations 159 to 161 imply that

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,\xi} = \left(\frac{\partial H}{\partial S}\right)_{P,\xi} \quad (163)$$

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,\xi} = -\left(\frac{\partial F}{\partial V}\right)_{T,\xi} \quad (164)$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,\xi} = \left(\frac{\partial G}{\partial P}\right)_{T,\xi} \quad (165)$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\xi} = -\left(\frac{\partial G}{\partial T}\right)_{P,\xi} \quad (166)$$

In addition, by considering the second derivatives of U , we obtain from eq. 159

$$\left(\frac{\partial T}{\partial V}\right)_{S,\xi} = -\left(\frac{\partial P}{\partial S}\right)_{V,\xi} \quad (167)$$

$$\left(\frac{\partial T}{\partial \xi}\right)_{V,S} = -\left(\frac{\partial A}{\partial S}\right)_{V,\xi} \quad (168)$$

$$\left(\frac{\partial P}{\partial \xi}\right)_{V,S} = \left(\frac{\partial A}{\partial V}\right)_{S,\xi} \quad (169)$$

In a similar way, we obtain from eq. 160

$$\left(\frac{\partial V}{\partial S}\right)_{P,\xi} = \left(\frac{\partial T}{\partial P}\right)_{S,\xi} \quad (170)$$

$$\left(\frac{\partial V}{\partial \xi}\right)_{P,S} = -\left(\frac{\partial A}{\partial P}\right)_{S,\xi} \quad (171)$$

$$\left(\frac{\partial T}{\partial \xi}\right)_{P,S} = -\left(\frac{\partial A}{\partial S}\right)_{P,\xi} \quad (172)$$

Furthermore, from eq. 161 we get

$$\left(\frac{\partial S}{\partial V}\right)_{T,\xi} = \left(\frac{\partial P}{\partial T}\right)_{V,\xi} \quad (173)$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,V} = \left(\frac{\partial A}{\partial T}\right)_{V,\xi} \quad (174)$$

$$\left(\frac{\partial P}{\partial \xi}\right)_{T,V} = \left(\frac{\partial A}{\partial V}\right)_{T,\xi} \quad (175)$$

Finally, from eq. 162 we obtain

$$\left(\frac{\partial S}{\partial P}\right)_{T,\xi} = -\left(\frac{\partial V}{\partial T}\right)_{P,\xi} \quad (176)$$

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,P} = \left(\frac{\partial A}{\partial T}\right)_{P,\xi} \quad (177)$$

$$\left(\frac{\partial V}{\partial \xi}\right)_{T,P} = -\left(\frac{\partial A}{\partial P}\right)_{T,\xi} \quad (178)$$

The results 167 to 178 are usually referred to as Maxwell relations. For a closed phase in which “ r ” simultaneous reactions take place, we can generalize eqs. 159 to 162, as follows

$$dU = TdS - PdV - \sum_{\rho=1}^r A_{\rho}d\xi_{\rho} \quad (179)$$

$$dH = TdS + VdP - \sum_{\rho=1}^r A_{\rho}d\xi_{\rho} \quad (180)$$

$$dF = -SdT - PdV - \sum_{\rho=1}^r A_{\rho}d\xi_{\rho} \quad (181)$$

$$dG = -SdT + VdP - \sum_{\rho=1}^r A_{\rho}d\xi_{\rho} \quad (182)$$

When equilibrium conditions have been attained, i.e., when $A_{\rho} = 0$ ($\rho = 1, 2, \dots, r$), eqs. 179 to 182 become,

$$dU = TdS - PdV \quad (183)$$

$$dH = TdS + VdP \quad (184)$$

$$dF = -SdT - PdV \quad (185)$$

$$dG = -SdT + VdP \quad (186)$$

5.2 Properties of an Open Phase

For closed systems, the First Law establishes the existence of the internal energy function U . We shall now assume that the function U exists even if the number of moles of the various components varies in an arbitrary manner, and we shall write

$$U = U(T, V, n_1, n_2, \dots, n_c) \quad (187)$$

We may also write

$$S = S(T, V, n_1, n_2, \dots, n_c) \quad (188)$$

Choosing now $S, V, n_1, n_2, \dots, n_c$ as independent variables, we may write the total differential of U (eq. 187) as follows

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S, n_i} dV + \sum_{i=1}^c \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} dn_i \quad (189)$$

However, when $n_i = \text{constant}$, the composition of the closed system is fixed, and by comparing with eqs. 163 and 164 we obtain

$$\left(\frac{\partial U}{\partial S}\right)_{V, n_i} = \left(\frac{\partial U}{\partial S}\right)_{V, \xi} = T \quad (190)$$

and

$$\left(\frac{\partial U}{\partial V}\right)_{S, n_i} = \left(\frac{\partial U}{\partial V}\right)_{S, \xi} = -P \quad (191)$$

Hence

$$dU = TdS - PdV + \sum_{i=1}^c \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_j} dn_i \quad (192)$$

Proceeding in a similar way we find

$$dH = TdS + VdP + \sum_{i=1}^c \left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j} dn_i \quad (193)$$

$$dF = -SdT - PdV + \sum_{i=1}^c \left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j} dn_i \quad (194)$$

$$dG = -SdT + VdP + \sum_{i=1}^c \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} dn_i \quad (195)$$

5.3 The Chemical Potential

Since by definition

$$H = U + PV$$

we may write

$$dH = dU + PdV + VdP \quad (196)$$

By inserting eqs. 192 and 193 in 196 we obtain

$$\begin{aligned} TdS + VdP + \sum_{i=1}^c \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} dn_i &= TdS - PdV \\ &+ \sum_{i=1}^c \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} dn_i + PdV + VdP \end{aligned} \quad (197)$$

i.e.,

$$\sum_{i=1}^c \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} dn_i = \sum_{i=1}^c \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} dn_i \quad (198)$$

By doing the same with the other functions, and remembering that the variations dn_i are arbitrary, we conclude that

$$\left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} = \left(\frac{\partial H}{\partial n_i} \right)_{S,P,n_j} = \left(\frac{\partial F}{\partial n_i} \right)_{T,V,n_j} = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} = \mu_i \quad (199)$$

The quantity determined by eq. 199 will be called the Chemical Potential of component "i", μ_i . In terms of μ_i , eqs. 192 to 195 may be written as follows

$$dU = TdS - PdV + \sum_{i=1}^c \mu_i dn_i \quad (200)$$

$$dH = TdS + VdP + \sum_{i=1}^c \mu_i dn_i \quad (201)$$

$$dF = -SdT - PdV + \sum_{i=1}^c \mu_i dn_i \quad (202)$$

$$dG = -SdT + VdP + \sum_{i=1}^c \mu_i dn_i \quad (203)$$

Equations 200 to 203 are usually known as the Gibbs equations.

5.4 Integration of the Gibbs Equations

By applying to the function $U = U(S, V, n_1, \dots, n_c)$ the Euler theorem for homogeneous functions of first degree we obtain

$$U = \left(\frac{\partial U}{\partial S} \right)_{V, n_j} S + \left(\frac{\partial U}{\partial V} \right)_{S, n_j} V + \sum_{i=1}^c \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} n_i \quad (204)$$

which combined with eqs. 164, 165 and 199 yields

$$U = TS - PV + \sum_{i=1}^c \mu_i n_i \quad (205)$$

$$H = U + PV = TS + \sum_{i=1}^c \mu_i n_i \quad (206)$$

$$F = U - TS = -PV + \sum_{i=1}^c \mu_i n_i \quad (207)$$

$$G = U + PV - TS = \sum_{i=1}^c \mu_i n_i \quad (208)$$

5.5 The Gibbs - Duhem Equation

By differentiating eq. 208 we obtain

$$dG = \sum_{i=1}^c n_i d\mu_i + \sum_{i=1}^c \mu_i dn_i \quad (209)$$

which compared with 203 yields

$$\sum_{i=1}^c n_i d\mu_i + SdT - VdP = 0 \quad (210)$$

This equation, which establishes a relation between variations in the potentials T, P and μ_i , is usually known as the Gibbs-Duhem equation. For variations at constant T, P , eq. 210 reduces to

$$\sum_{i=1}^c n_i d\mu_i = 0 \quad (211)$$

5.6 Identities and Maxwell Relations for Chemical Potentials

For composition changes at constant T, P we have

$$(d\mu_i)_{T,P} = \sum_{j=1}^c \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,P,n_k} dn_j = \sum_{j=1}^c \mu_{ij} dn_j \quad (212)$$

where we have introduced the quantity

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,P,n_k} \quad (213)$$

The Gibbs-Duhem equation can now be transformed by using eq. 213. We obtain

$$\sum_{i=1}^c n_i d\mu_i = \sum_{i=1}^c n_i \sum_{j=1}^c \mu_{ij} dn_j = \sum_{i=1}^c \left[\sum_{j=1}^c n_i \mu_{ij} \right] dn_j = 0 \quad (214)$$

Since the dn_j are arbitrary, eq. 214 implies that

$$\sum_{j=1}^c n_i \mu_{ij} = 0 \quad (i = 1, 2, \dots, c) \quad (215)$$

Furthermore, the Maxwell relation

$$\mu_{ij} = \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T,P,n_k} = \left(\frac{\partial \mu_j}{\partial n_i} \right)_{T,P,n_k} = \mu_{ji} \quad (216)$$

leads to

$$\sum_{j=1}^c n_i \mu_{ij} = \sum_{j=1}^c n_i \mu_{ji} = 0 \quad (217)$$

Finally, from eq. 215, i.e.,

$$\sum_{i=1}^c n_i \mu_{ij} = n_i \mu_{ii} + \sum_{j \neq i} n_j \mu_{ij} = 0 \quad (218)$$

we obtain

$$\mu_{ii} = -\frac{1}{n_i} \sum_{j \neq i} n_j \mu_{ij} \quad (219)$$

6 Thermodynamics of Affinity

6.1 The Total Differential of the Affinity

From the relation

$$A = A(T, P, \xi) \quad (220)$$

we obtain

$$d\left(\frac{A}{T}\right) = \left[\frac{\partial(A/T)}{\partial T}\right]_{P,\xi} dT + \frac{1}{T} \left(\frac{\partial A}{\partial P}\right)_{T,\xi} dP + \frac{1}{T} \left(\frac{\partial A}{\partial \xi}\right)_{T,P} d\xi \quad (221)$$

Furthermore, from a previous chapter we have

$$\frac{A}{T} = \left[\frac{\partial S}{\partial \xi}\right]_{T,P} - \frac{1}{T} \left(\frac{\partial H}{\partial \xi}\right)_{T,P} \quad (222)$$

which leads to

$$\left[\frac{\partial(A/T)}{\partial T}\right]_{P,\xi} = \frac{1}{T^2} \left(\frac{\partial H}{\partial \xi}\right)_{T,P} \quad (223)$$

In addition, let us introduce the quantity $a_{T,P}$ defined by

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = - \left[\frac{\partial}{\partial \xi} \left(\frac{\partial G}{\partial \xi}\right)\right]_{T,P} = - \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P} = a_{T,P} \quad (224)$$

By inserting in eq. 221, the results 223 and 224, as well as the following identity,

$$d\left(\frac{A}{T}\right) = \frac{dA}{T} - \frac{A}{T^2}dT \quad (225)$$

we obtain

$$\frac{dA}{T} = \frac{A+(\partial H/\partial\xi)_{T,P}}{T^2}dT - \frac{1}{T}\left(\frac{\partial V}{\partial\xi}\right)_{T,P}dP + a_{T,P}d\xi \quad (226)$$

which may be expressed as

$$dA = \frac{A+h_{T,P}}{T}dT - v_{T,P}dP + a_{T,P}d\xi \quad (227)$$

where

$$v_{T,P} = \left(\frac{\partial V}{\partial\xi}\right)_{T,P} \quad (228)$$

6.2 Affinity as an Independent Variable

In certain cases it is convenient to consider A as an independent variable, so that

$$\xi = \xi(T, P, A) \quad (229)$$

An expression for the total differential $d\xi$ can be obtained from eq. 227. If $a_{T,P} \neq 0$ we find

$$d\xi = -\frac{A+h_{T,P}}{a_{T,P}}dT + \frac{v_{T,P}}{a_{T,P}}dP - \frac{dA}{a_{T,P}} \quad (230)$$

Equation 230 implies that

$$\left(\frac{\partial\xi}{\partial T}\right)_{P,A} = -\frac{A+h_{T,P}}{a_{T,P}T} \quad (231)$$

$$\left(\frac{\partial\xi}{\partial P}\right)_{T,A} = \frac{v_{T,P}}{a_{T,P}} \quad (232)$$

and

$$\left(\frac{\partial \xi}{\partial A}\right)_{T,P} = \frac{1}{a_{T,P}} \quad (233)$$

Starting, instead, from

$$\xi = (T, V, \xi) \quad (234)$$

we obtain

$$d\xi = -\frac{A + u_{T,V}}{a_{T,V} T} dT - \frac{p_{T,V}}{a_{T,V}} dV + \frac{1}{a_{T,V}} dA \quad (235)$$

where

$$a_{T,V} = \left(\frac{\partial A}{\partial \xi}\right)_{T,V} = -\left[\frac{\partial}{\partial \xi} \left(\frac{\partial F}{\partial \xi}\right)\right]_{T,V} = -\left(\frac{\partial^2 F}{\partial \xi^2}\right)_{T,V} \quad (236)$$

$u_{T,V}$ is defined in the chapter on Energetics, and

$$p_{T,V} = \left(\frac{\partial P}{\partial \xi}\right)_{T,V} \quad (237)$$

Finally, it can be shown that

$$a_{T,P} = a_{T,V} + v_{T,P} p_{T,V} \quad (238)$$

6.3 Average Affinity of a Physico-Chemical Reaction

From De Donder's relation we obtain for the uncompensated heat Q' of the reaction $\alpha \rightarrow \beta$

$$Q' = \int_{\alpha}^{\beta} \delta Q' = \int_{\alpha}^{\beta} A(\xi) d\xi \quad (239)$$

The average affinity for the reaction $\alpha \rightarrow \beta$ is defined as follows

$$\bar{A} = \frac{\int_{\xi_{\alpha}}^{\xi_{\beta}} A(\xi) d\xi}{\xi_{\beta} - \xi_{\alpha}} = \frac{Q'}{\xi_{\beta} - \xi_{\alpha}} \quad (240)$$

If $\xi_\beta - \xi_\alpha = 1$ we obtain

$$\bar{A} = Q' \quad (241)$$

i.e., the average affinity corresponds to the uncompensated heat of the reaction $\alpha \rightarrow \beta$.

If the reaction occurs at constant T, V

$$\delta Q' = A d\xi = - \left(\frac{\partial F}{\partial \xi} \right)_{T,V} d\xi \quad (242)$$

and integrating from $\xi = 0$ to $\xi = 1$ we obtain

$$\bar{A}_{T,V} = \int_{\xi=0}^{\xi=1} - \left(\frac{\partial F}{\partial \xi} \right)_{T,V} d\xi = - [F_{(\beta)} - F_{(\alpha)}] \quad (243)$$

i.e.,

$$\bar{A}_{T,V} = Q' = -\Delta F^{\beta/\alpha} \quad (244)$$

Finally, if the reaction occurs at constant T, P we have

$$\bar{A}_{T,P} = \int_{\xi=0}^{\xi=1} - \left(\frac{\partial G}{\partial \xi} \right)_{T,P} d\xi = - [G_{(\beta)} - G_{(\alpha)}] \quad (245)$$

i.e.,

$$\bar{A}_{T,P} = Q' = -\Delta G^{\beta/\alpha} \quad (246)$$

6.4 Relation Between Affinity and the Chemical Potentials in a Phase

Let us now consider the case of a phase, whose composition can change as a consequence of a single reaction occurring at given T and P , involving c' out of c components, and let ξ be the reaction coordinate. In this case,

$$dn_i = \nu_i d\xi \quad (i = 1, 2, \dots, c') \quad (247)$$

As a consequence of the composition changes, there will be a variation in the Gibbs energy of the system, i.e.,

$$G = G(T, P, \xi) \quad (248)$$

which at constant T and P will be given by

$$(dG)_{T,P} = \left(\frac{\partial G}{\partial \xi} \right)_{T,P} d\xi = -Ad\xi \quad (249)$$

Alternatively, we may write

$$(dG)_{T,P} = \sum_{i=1}^{c'} \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_j} dn_i \quad (250)$$

Taking now into account the definition of chemical potential and eq. 247, we may express eq. 250 in the following form

$$(dG)_{T,P} = \left(\sum_{i=1}^{c'} \mu_i \nu_i \right) d\xi \quad (251)$$

Finally, by comparing eqs. 249 and 251 we conclude that

$$A = - \sum_{i=1}^{c'} \nu_i \mu_i \quad (252)$$

This result can be easily generalized to the case of “ r ” reactions occurring in a single phase. We obtain for the affinity of the ρ – *th* reaction which involves c' components

$$A_\rho = - \sum_{i=1}^{c'} \nu_{i,\rho} \mu_i \quad (253)$$

6.5 Variation of the Affinity with the Extent of the Reaction

Starting from the definition

$$A = - \left(\frac{\partial G}{\partial \xi} \right)_{T,P}$$

we obtain

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = -\left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P} \quad (254)$$

In order to evaluate the derivative in eq. 254 we derivate eq. 252 with respect to ξ , i.e.,

$$\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = -\sum_{i=1}^{c'} \nu_i \left(\frac{\partial \mu_i}{\partial \xi}\right)_{T,P} = -\sum_{i=1}^{c'} \nu_i \sum_{j=1}^{c'} \left(\frac{\partial \mu_i}{\partial n_j}\right)_{T,P} \frac{dn_j}{d\xi} \quad (255)$$

i.e.,

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c'} \sum_{j=1}^{c'} \nu_i \nu_j \mu_{ij} \quad (256)$$

Equation 256 can be written as

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = \nu_i^2 \mu_{ii} + \sum_{i=1}^{c'} \sum_{j \neq i}^{c'} \nu_i \nu_j \mu_{ij} \quad (257)$$

Using now the expression for μ_{ii} obtained at the end of the previous chapter, we write eq. 257 as follows

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = -\sum_{i=1}^{c'} \frac{\nu_i^2}{n_i} \sum_{j \neq i}^{c'} \mu_{ij} n_j + \sum_{i=1}^{c'} \nu_i \sum_{j \neq i}^{c'} \nu_j \mu_{ij} \quad (258)$$

i.e.,

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c'} \sum_{j \neq i}^{c'} \nu_i \left[\frac{\nu_j n_i - \nu_i n_j}{n_i} \right] \mu_{ij} \quad (259)$$

Since we obtain zero terms when $i = j$, we can write eq. 259 as follows

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c'} \sum_{j=1}^{c'} \nu_i \left[\frac{\nu_j n_i - \nu_i n_j}{n_i} \right] \mu_{ij} \quad (260)$$

Furthermore, the sum is not altered by interchanging i and j ,

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = \sum_{j=1}^{c'} \sum_{i=1}^{c'} \nu_j \left[\frac{\nu_i n_j - \nu_j n_i}{n_j} \right] \mu_{ji} \quad (261)$$

Finally, adding eqs. 260 and 261 and multiplying by $\frac{1}{2}$ we obtain

$$-\left(\frac{\partial A}{\partial \xi}\right)_{T,P} = \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T,P} = \left(\frac{-1}{2}\right) \sum_{i=1}^{c'} \sum_{j=1}^{c'} n_i n_j \left(\frac{\nu_i}{n_i} - \frac{\nu_j}{n_j}\right)^2 \mu_{ij} \quad (262)$$

In the case of several simultaneous reactions, we have

$$A_\rho = -\left(\frac{\partial G}{\partial \xi_\rho}\right)_{T,P} = -\sum_{i=1}^{c'} \nu_{i,\rho} \mu_i \quad (\rho = 1, 2, \dots, r) \quad (263)$$

and

$$\left(\frac{\partial A_\rho}{\partial \xi_{\rho'}}\right)_{T,P} = -\left[\frac{\partial^2 G}{\partial \xi_\rho \partial \xi_{\rho'}}\right]_{T,P} = -\sum_{i=1}^c \nu_{i,\rho} \left(\frac{\partial \mu_i}{\partial \xi_{\rho'}}\right)_{T,P} \quad (264)$$

The final result is, in this case

$$\left[\frac{\partial^2 G}{\partial \xi_\rho \partial \xi_{\rho'}}\right]_{T,P} = \left(\frac{-1}{2}\right) \sum_{i=1}^{c'} \sum_{j=1}^{c'} n_i n_j \left[\left(\frac{\nu_{i,\rho}}{n_i} - \frac{\nu_{j,\rho}}{n_j}\right) \left(\frac{\nu_{i,\rho'}}{n_i} - \frac{\nu_{j,\rho'}}{n_j}\right) \right] \mu_{ij} \quad (265)$$

7 Physico-Chemical Equilibrium and Reactions in Heterogeneous Systems

7.1 Heterogeneous Systems in Thermal and Mechanical Equilibrium

Let us consider a system Σ with " f " phases. Since the thermodynamic functions U, H, F and G are all extensive, we may express them as sums of the contributions of each phase, viz.,

$$U^\Sigma = \sum_{\alpha=1}^f U^\alpha \quad (266)$$

$$H^\Sigma = \sum_{\alpha=1}^f H^\alpha \quad (267)$$

$$F^\Sigma = \sum_{\alpha=1}^f F^\alpha \quad (268)$$

$$G^\Sigma = \sum_{\alpha=1}^f G^\alpha \quad (269)$$

From eq. 266 we obtain for a change in energy,

$$dU^\Sigma = \sum_{\alpha=1}^f dU^\alpha \quad (270)$$

Where dU^α can be expressed using the Gibbs equation as

$$dU^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_{i=1}^c \left(\frac{\partial U^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} dn_i^\alpha \quad (271)$$

Suppose that the system Σ is in thermal and mechanical equilibrium, i.e.,

$$T^\alpha = T^\beta = T^\gamma = \dots = T^\Sigma \quad (272)$$

$$P^\alpha = P^\beta = P^\gamma = \dots = P^\Sigma \quad (273)$$

In such case, eq. 271 can be introduced in eq. 270, which gives

$$dU^\Sigma = T^\Sigma \sum_{\alpha=1}^f dS^\alpha - P^\Sigma \sum_{\alpha=1}^f dV^\alpha + \sum_{\alpha=1}^f \sum_{i=1}^c \left(\frac{\partial U^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} dn_i^\alpha \quad (274)$$

Furthermore

$$dS^\Sigma = \sum_{\alpha=1}^f dS^\alpha \quad (275)$$

$$dV^\Sigma = \sum_{\alpha=1}^f dV^\alpha \quad (276)$$

and from eq. 266 we find

$$\left(\frac{\partial U^\Sigma}{\partial n_i^\beta} \right)_{S^\Sigma, V^\Sigma, n_j^\beta} = \left(\frac{\partial U^\beta}{\partial n_i^\beta} \right)_{S^\beta, V^\beta, n_j^\beta} \quad (277)$$

By inserting 275 to 277 into 274 we obtain

$$dU^\Sigma = T^\Sigma dS^\Sigma - P^\Sigma dV^\Sigma + \sum_{\alpha=1}^f \sum_{i=1}^c \left(\frac{\partial U^\Sigma}{\partial n_i^\alpha} \right)_{S^\Sigma, V^\Sigma, n_j^\alpha} dn_i^\alpha \quad (278)$$

Finally, by introducing the notation

$$\mu_i^\alpha = \left(\frac{\partial U^\Sigma}{\partial n_i^\alpha} \right)_{S^\Sigma, V^\Sigma, n_j^\alpha} = \left(\frac{\partial U^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} \quad (279)$$

we can give 278 the following form

$$dU^\Sigma = T^\Sigma dS^\Sigma - P^\Sigma dV^\Sigma + \sum_{\alpha=1}^f \sum_{i=1}^c \mu_i^\alpha dn_i^\alpha \quad (280)$$

In a similar way we may derive the relations

$$dH^\Sigma = T^\Sigma dS^\Sigma + P^\Sigma dV^\Sigma + \sum_{\alpha=1}^f \sum_{i=1}^c \mu_i^\alpha dn_i^\alpha \quad (281)$$

$$dF^\Sigma = -S^\Sigma dT^\Sigma - P^\Sigma dV^\Sigma + \sum_{\alpha=1}^f \sum_{i=1}^c \mu_i^\alpha dn_i^\alpha \quad (282)$$

$$dG^\Sigma = -S^\Sigma dT^\Sigma + V^\Sigma dP^\Sigma + \sum_{\alpha=1}^f \sum_{i=1}^c \mu_i^\alpha dn_i^\alpha \quad (283)$$

Where

$$\begin{aligned}\mu_i^\alpha &= \left(\frac{\partial U^\Sigma}{\partial n_i^\alpha} \right)_{S^\Sigma, V^\Sigma, n_j^\alpha} = \left(\frac{\partial H^\Sigma}{\partial n_i^\alpha} \right)_{S^\Sigma, P^\Sigma, n_j^\alpha} = \\ &= \left(\frac{\partial F^\Sigma}{\partial n_i^\alpha} \right)_{T^\Sigma, V^\Sigma, n_j^\alpha} = \left(\frac{\partial G^\Sigma}{\partial n_i^\alpha} \right)_{T^\Sigma, P^\Sigma, n_j^\alpha}\end{aligned}\quad (284)$$

7.2 Affinity of Reactions in Heterogeneous Systems

Let us consider a single reaction occurring in the system Σ , which involves c' out of c components. In this case we have

$$dn_i^\alpha = \nu_i^\alpha d\xi \quad (285)$$

and eq. 283 becomes for changes at constant T and P

$$(dG^\Sigma)_{T,P} = \left[\sum_{\alpha=1}^f \sum_{i=1}^{c'} \nu_i^\alpha \mu_i^\alpha \right] d\xi \quad (286)$$

which can be given the form

$$(dG^\Sigma)_{T,P} = -Ad\xi \quad (287)$$

if the affinity of the reaction in the heterogeneous system is given by

$$A = - \sum_{\alpha=1}^f \sum_{i=1}^{c'} \nu_i^\alpha \mu_i^\alpha \quad (288)$$

Equation 288 can be easily generalized to the case in which “ r ” simultaneous reactions occur in Σ . We obtain

$$A_\rho = - \sum_{\alpha=1}^f \sum_{i=1}^{c'} \nu_{i,\rho}^\alpha \mu_i^\alpha \quad (\rho = 1, 2, \dots, r) \quad (289)$$

7.3 The Equilibrium Condition. Examples

By combining the general equilibrium condition, obtained in a previous chapter with eq. 288 we obtain

$$A = - \sum_{\alpha=1}^f \sum_{i=1}^{c'} \nu_i^\alpha \mu_i^\alpha = 0 \quad (290)$$

which in the case “ r ” reactions occurring in the system becomes

$$A_\rho = - \sum_{\alpha=1}^f \sum_{i=1}^{c'} \nu_{i,\rho}^\alpha \mu_i^\alpha = 0 \quad (\rho = 1, 2, \dots, r) \quad (291)$$

Two applications of the equilibrium conditions 290 and 291 will be presented. As a first example, consider the passage of component “ i ” from the phase “ I ” to the phase “ II ”. In this case, the stoichiometric coefficients are

$$\nu_i^I = -1 \quad \text{and} \quad \nu_i^{II} = +1 \quad (292)$$

Thus the equilibrium condition 290 yields

$$\sum_{\alpha=I}^{II} \nu_i^\alpha \mu_i^\alpha = -\mu_i^I + \mu_i^{II} = 0 \quad (293)$$

i.e.

$$\mu_i^I = \mu_i^{II} \quad (294)$$

The equilibrium condition implies in this case that all components capable of passing from one phase to the other have the same chemical potential.

As a second example, consider the following heterogeneous reaction



The stoichiometric coefficients are, in this case,

$$\nu_{CaCO_3}^\alpha = -1, \quad \nu_{CaO}^\beta = +1, \quad \nu_{CO_2}^g = +1 \quad (296)$$

and the affinity of reaction 295 is

$$A = - \left[(-1)\mu_{CaCO_3}^\alpha + \mu_{CaO}^\beta + \mu_{CO_2}^g \right] \quad (297)$$

Hence, the equilibrium condition becomes

$$\mu_{CaCO_3}^\alpha = \mu_{CaO}^\beta + \mu_{CO_2}^g \quad (298)$$

7.4 Entropy Production from the Gibbs Equation

In the previous chapter, equations were derived for the uncompensated heat involved in the over-all change from the original equilibrium state at T, P to the final equilibrium state at T, P , without assuming equilibrium conditions during the course of the reaction, which might actually take place in a very violent and irregular manner, once it has started. Consider now the case in which the reaction does take place in such a way that we can regard the system at each stage as substantially in a state of metaestable equilibrium at a definite temperature and pressure. As an example, we shall deal with an homogeneous chemical reaction occurring at a rate so slough that we can regard the reacting mixture at each instant as practically equivalent to a non-reacting mixture of definite composition, pressure and temperature. In this case the entropy of the system may be treated using the Gibbs equation

$$dU = TdS - PdV + \sum_i \mu_i dn_i \quad (299)$$

where

$$dn_i = \nu_i d\xi \quad (300)$$

and ξ is the variable describing the progress of the reaction. The variation in entropy caused by a differential change $d\xi$ is

$$dS = \frac{dU}{T} + \frac{P}{T}dV - \sum_i \frac{\nu_i \mu_i}{T} d\xi \quad (301)$$

By applying the First Law to the present, closed phase, we may write

$$dU = \delta Q - PdV \quad (302)$$

which inserted into eq. 301 yields

$$dS = \frac{\delta Q}{T} - \frac{1}{T} \sum_i \nu_i \mu_i d\xi \quad (303)$$

A comparison between this result and the entropy equation

$$dS = d_e S + d_i S$$

indicates that

$$d_e S = \frac{\delta Q}{T} \quad (304)$$

and

$$d_i S = - \frac{\sum_i \nu_i \mu_i}{T} d\xi \quad (305)$$

Equation 305 may be given the same form as De Donder's formula, i.e.,

$$d_i S = \frac{A}{T} d\xi \quad (306)$$

where the affinity A is

$$A = - \sum_i \nu_i \mu_i \quad (307)$$

In addition, from eq. 306 we obtain the entropy production rate for this reaction, viz.,

$$P_{[S]} = \frac{d_i S}{dt} = \frac{A}{T} \frac{d\xi}{dt} \quad (308)$$

In summary, by applying the Gibbs equation, it has been possible to derive the key relations involved in De Donder's formula.

7.5 Entropy Production for Reactions in an Open Phase

Let us now consider a phase " α " which exchanges matter and energy with the surroundings, and let us further assume that a chemical reaction occurs in α , as indicated in the figure.

The first law for this system will be written in the form

$$dU^\alpha = d\Phi^\alpha - P^\alpha dV^\alpha \quad (309)$$

where $d\Phi^\alpha$ accounts for the net energy input, due to exchanges of (matter + heat). In addition, the change in the number of moles of component " i " will be expressed as the sum of two contributions

$$dn_i^\alpha = d_e n_i^\alpha + d_i n_i^\alpha \quad (310)$$

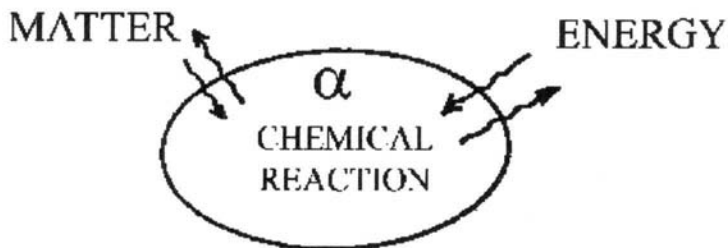


FIGURE 11.

where $d_e n_i^\alpha$ accounts for the interaction with the surroundings, and $d_i n_i^\alpha$ accounts for the composition changes due to the internal chemical reaction. Moreover, we have

$$dn_i^\alpha = \nu_i^\alpha d\xi^\alpha \quad (311)$$

where ξ^α is the coordinate measuring the progress of the reaction in α . Suppose that the Gibbs equation is applicable to each step of this process. In such case, combination of eqs. 299 with eqs. 309 to 311 yields

$$dS^\alpha = \frac{d\Phi^\alpha - P^\alpha dV^\alpha}{T^\alpha} + \frac{P^\alpha}{T^\alpha} dV^\alpha - \sum_i \frac{\mu_i^\alpha d_e n_i^\alpha}{T^\alpha} - \sum_i \frac{\nu_i^\alpha \mu_i^\alpha d\xi^\alpha}{T^\alpha} \quad (312)$$

which can be expressed in the form

$$dS^\alpha = d_e S^\alpha + d_i S^\alpha$$

if

$$d_e S^\alpha = \frac{d\Phi^\alpha}{T^\alpha} - \sum_i \left(\frac{\mu_i^\alpha}{T^\alpha} \right) d_e n_i^\alpha \quad (313)$$

and

$$d_i S^\alpha = - \sum_i \left(\frac{\nu_i^\alpha \mu_i^\alpha}{T^\alpha} \right) d\xi^\alpha \quad (314)$$

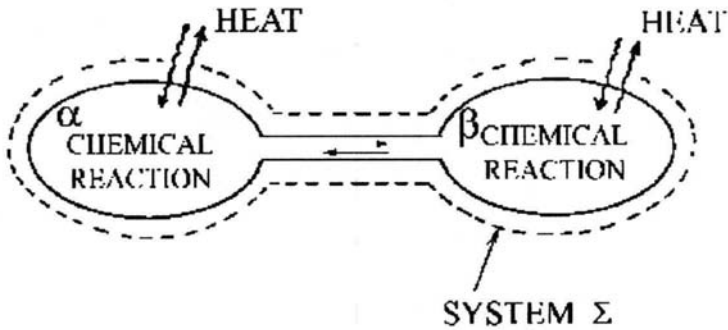


FIGURE 12.

7.6 Entropy Production for Reactions in an Heterogeneous System

Let us now consider a closed system Σ comprising two open phases α and β , in each of which a chemical reaction occurs, as indicated in the following figure.

In this case, the energy input to Σ can be expressed as the sum of two terms,

$$d\Phi^\Sigma = d\Phi^\alpha + d\Phi^\beta \quad (315)$$

Furthermore, each term in eq. 315 can be described as the sum of two contributions, viz.,

$$d\Phi^\alpha = d_e\Phi^\alpha + d_\beta\Phi^\alpha \quad (316)$$

and

$$d\Phi^\beta = d_e\Phi^\beta + d_\alpha\Phi^\beta \quad (317)$$

where $d_e\Phi^\alpha$ and $d_e\Phi^\beta$ account for the interaction with the surroundings, and $d_\beta\Phi^\alpha$ and $d_\alpha\Phi^\beta$ account for the energy exchange between the phases. Since the system Σ behaves as a closed system with respect to the surroundings,

$$d_e\Phi^\alpha = \delta_e Q_\alpha \quad (318)$$

$$d_e\Phi^\beta = \delta_e Q_\beta \quad (319)$$

where $\delta_e Q_\alpha$ and $\delta_e Q_\beta$ represent the heats exchanged with the surroundings. By introducing the results 316 to 319 in 315 we obtain

$$d\Phi^\Sigma = \delta_e Q_\alpha + \delta_e Q_\beta + d_\beta\Phi^\alpha + d_\alpha\Phi^\beta \quad (320)$$

Since Σ is a closed system, we also have

$$d\Phi^\Sigma = \delta Q_\Sigma = \delta_e Q_\alpha + \delta_e Q_\beta \quad (321)$$

and by combining eqs. 320 and 321 we obtain

$$d_\beta\Phi^\alpha + d_\alpha\Phi^\beta = 0 \quad (322)$$

i.e.,

$$-d_\beta\Phi^\alpha = d_\alpha\Phi^\beta \quad (323)$$

Analogously, the quantities dn_i^α and dn_i^β will be expressed as

$$dn_i^\alpha = d_\beta n_i^\alpha + d_i n_i^\alpha \quad (324)$$

and

$$dn_i^\beta = d_\alpha n_i^\beta + d_i n_i^\beta \quad (325)$$

with

$$d_\beta n_i^\alpha + d_\alpha n_i^\beta = 0 \quad (326)$$

i.e.,

$$-d_\beta n_i^\alpha = d_\alpha n_i^\beta \quad (327)$$

Expressing the entropy change in Σ as

$$dS^\Sigma = dS^\alpha + dS^\beta \quad (328)$$

and describing dS^α and dS^β in terms of the Gibbs equation, while taking into account the results of the previous section, as well as the entropy relation

$$dS^\Sigma = d_e S^\Sigma + d_i S^\Sigma$$

we obtain

$$d_e S^\Sigma = \frac{\delta_e Q_\alpha}{T^\alpha} + \frac{\delta_e Q_\beta}{T^\beta} \quad (329)$$

and

$$d_i S^\Sigma = \left(\frac{1}{T^\beta} - \frac{1}{T^\alpha} \right) d_\alpha \Phi^\beta - \sum_i \left(\frac{\mu_i^\beta}{T^\beta} - \frac{\mu_i^\alpha}{T^\alpha} \right) d_\alpha n_i^\beta + \frac{A^\alpha}{T^\alpha} d\xi^\alpha + \frac{A^\beta}{T^\beta} d\xi^\beta \quad (330)$$

where ξ^α and ξ^β are the coordinates measuring the progress of the reactions occurring in α and in β , respectively. Finally, we obtain the entropy production rate in Σ , as follows

$$P_{[S]}^\Sigma = \frac{d_i S^\Sigma}{dt} = \left(\frac{1}{T^\beta} - \frac{1}{T^\alpha} \right) \left(\frac{d_\alpha \Phi^\beta}{dt} \right) - \sum_i \left(\frac{\mu_i^\beta}{T_i^\beta} - \frac{\mu_i^\alpha}{T_i^\alpha} \right) \frac{d_\alpha n_i^\beta}{dt} + \left(\frac{A^\alpha}{T^\alpha} \right) \left(\frac{d\xi^\alpha}{dt} \right) + \left(\frac{A^\beta}{T^\beta} \right) \left(\frac{d\xi^\beta}{dt} \right) \quad (331)$$

8 Thermodynamic Stability of Physico-Chemical Systems.

8.1 Entropy Production Accompanying a Perturbation

Let us consider a system in a state "a" described by the variables x, y and ξ . Suppose now that the system undergoes a change of state $a \rightarrow a'$. The uncompensated heat associated to the transformation is

$$Q'_{aa'} = \int_a^{a'} \delta Q' = \int_a^{a'} T d_i S = \int_a^{a'} A d\xi \quad (332)$$

For a specified process we may regard "x" and "y" as functions completely determined by ξ , and write

$$Q_{aa'} = \int_a^{a'} A(\xi) d\xi \quad (333)$$

Let us assume that the function $A(\xi)$ may be expressed as a Taylor series in the interval ξ_a , to $\xi_{a'}$, i.e., that

$$A(\xi) = A_a + \left(\frac{dA}{d\xi}\right)_a (\xi_{a'} - \xi_a) + \frac{1}{2} \left(\frac{d^2A}{d\xi^2}\right)_a (\xi_{a'} - \xi_a)^2 + \dots \quad (334)$$

where

$$A_a = A(\xi_a)$$

and

$$\left(\frac{dA}{d\xi}\right) = \left(\frac{\partial A}{\partial \xi}\right)_{x,y} + \left(\frac{\partial A}{\partial x}\right)_{y,\xi} \left(\frac{dx}{d\xi}\right) + \left(\frac{\partial A}{\partial y}\right)_{x,\xi} \left(\frac{dy}{d\xi}\right) \quad (335)$$

and similarly for the higher-order differential coefficients. Introducing the quantity

$$\Delta\xi = \xi_{a'} - \xi_a \quad (336)$$

we may write eq. 334 in the form

$$A(\xi) = A_a + \left(\frac{dA}{d\xi}\right)_a \Delta\xi + \left(\frac{1}{2}\right) \left(\frac{d^2A}{d\xi^2}\right)_a (\Delta\xi)^2 + \dots \quad (337)$$

By inserting 337 into eq. 333 and integrating, we obtain

$$Q_{aa'} = A_a \Delta\xi + \frac{1}{2} \left(\frac{dA}{d\xi}\right)_a (\Delta\xi)^2 + \frac{1}{6} \left(\frac{d^2A}{d\xi^2}\right)_a (\Delta\xi)^3 + \dots \quad (338)$$

If we now consider a very small change, which corresponds to the case $\Delta\xi = \delta\xi$, we can limit ourselves to the lowest order terms in 338, i.e.,

$$Q'_{aa'} = A_a \delta\xi \quad \text{if } A_a \neq 0 \quad (339)$$

and

$$Q'_{aa'} = \frac{1}{2} \left(\frac{dA}{d\xi} \right)_a (\delta\xi)^2 \text{ if } A_a = 0 \text{ but } \left(\frac{dA}{d\xi} \right)_a \neq 0 \quad (340)$$

If “ a ” is an equilibrium state, the transformation aa' is usually referred to as a perturbation of the system. In this case we have

$$A_a = 0 \quad (341)$$

and the uncompensated heat becomes

$$Q'_{aa'} = \frac{1}{2} \left(\frac{dA}{d\xi} \right)_a (\delta\xi)^2 \quad (342)$$

Finally, in most cases considered in the following, “ x ” and “ y ” remain constant during the perturbation. In this case the total derivative in eq.342 becomes a partial one, as follows from eq. 335, i.e.,

$$Q'_{aa'} = \frac{1}{2} \left[\left(\frac{\partial A}{\partial \xi} \right)_{x,y} \right]_a (\delta\xi)^2 \quad (343)$$

8.2 Criterion of Stability

Suppose that we have a system in equilibrium at the state a , which is perturbed to a neighbouring state a' . The initial state is said to be stable with respect to the perturbation aa' if the entropy production accompanying the perturbation is negative, i.e., if

$$Q'_{aa'} < 0 \quad (344)$$

In treating perturbations from equilibrium, the parameter ξ may describe, i.a., the appearance of a small amount of a new phase in a existing phase, a perturbation of a chemical equilibrium, the appearance of a slight heterogeneity in a phase which is initially uniform, or a perturbation of the internal configuration of the phase.

8.3 Unilateral Perturbations

In the following we shall distinguish unilateral perturbations (i.e., those in which $\delta\xi$ can have only one sign) from bilateral perturbations, (i.e those in

which $\delta\xi$ can have both signs). Let us now consider an unilateral perturbations, in which, for instance,

$$\delta\xi > 0 \quad (345)$$

only. Because of the nature of ξ , the rate of reaction $d\xi/dt$ must be either positive or zero. In order to establish the equilibrium conditions it is necessary to find those in which the reaction rate is zero at the state "a". De Donder's relation for a possible process

$$T \cdot P_{[S]} = T \frac{d_i S}{dt} = A \frac{d\xi}{dt} \geq 0 \quad (346)$$

implies that the system with $d\xi/dt \geq 0$ will be in equilibrium if

$$A \leq 0 \quad (347)$$

which is less restrictive than the condition $A = 0$ previously obtained for bilateral perturbations. In order to discuss the stability of the equilibrium state "a" we must consider two cases. In the first place, if

$$A_a = 0 \quad (348)$$

eq. 344 yields

$$Q'_{aa'} = \left(\frac{1}{2}\right) \left[\left(\frac{\partial A}{\partial \xi} \right) \right]_a (\delta\xi)^2 < 0 \quad (349)$$

i.e.,

$$\left(\frac{\partial A}{\partial \xi} \right)_a < 0 \quad (350)$$

as the stability condition of the equilibrium state "a". Secondly, when

$$A_a < 0 \quad (351)$$

eq. 339 yields

$$Q'_{aa'} = A_a \delta\xi \quad (352)$$

with $\delta\xi > 0$, which evidently satisfies eq. 344.

8.4 Examples and Geometrical Interpretations

Let us consider the particular case of perturbations at constant T and P . In this case we express A using the Gibbs energy, i.e.,

$$A = - \left(\frac{\partial G}{\partial \xi} \right)_{T,P} \quad (353)$$

and eq. 338 yields, to second order

$$Q'_{aa'} = - \left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right]_a \delta \xi - \left(\frac{1}{2} \right) \left[\left(\frac{\partial^2 G}{\partial \xi^2} \right)_{T,P} \right]_a (\delta \xi)^2 \quad (354)$$

By applying this result to bilateral perturbations we obtain the equilibrium condition at state "a"

$$A_a = 0 \text{ i.e., } \left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right]_a = 0 \quad (355)$$

and the stability condition

$$Q'_{aa'} < 0 \text{ i.e., } \left[\left(\frac{\partial^2 G}{\partial \xi^2} \right)_{T,P} \right]_a > 0 \quad (356)$$

Equations 355 and 356 imply that there is a minimum in the G vs. ξ function of the system, as indicated in the following figure.

Let us now apply eq. 354 to unilateral perturbations, assuming that, in particular, $\delta \xi > 0$, only. The most general equilibrium condition at state "a" may be written as

$$A_a \leq 0 \quad \text{i.e.,} \quad \left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right]_a \geq 0 \quad (357)$$

whereas the stability condition, i.e., $Q'_{aa'} < 0$ yields, when $A_a \neq 0$,

$$\left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right]_a \geq 0 \text{ and } \left[\left(\frac{\partial^2 G}{\partial \xi^2} \right)_{T,P} \right]_a > 0 \quad (358)$$

as illustrated in the following figure.

Alternatively, if $A_a = 0$, we have

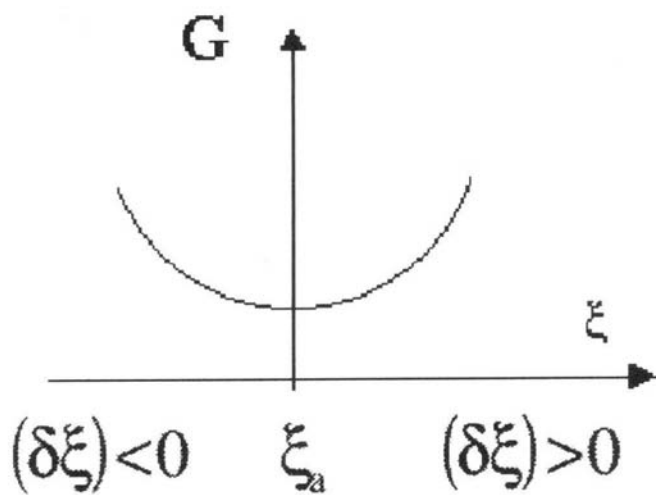


FIGURE 13.

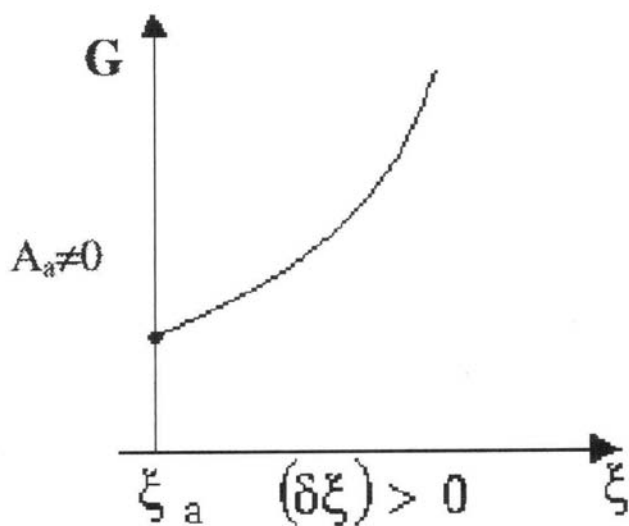


FIGURE 14.

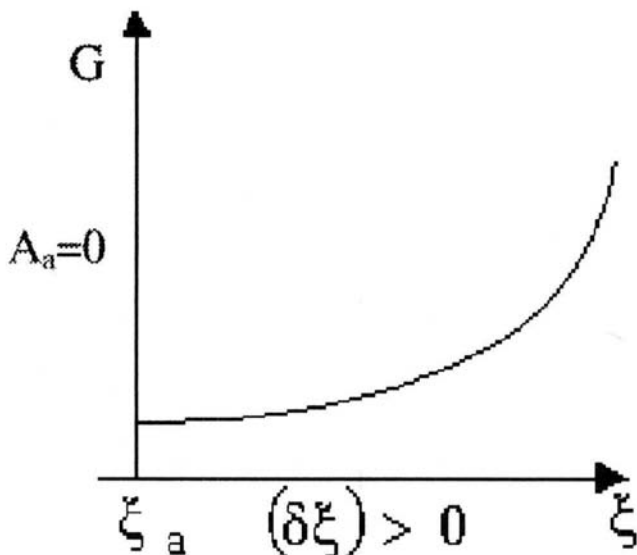


FIGURE 15.

$$\left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right]_a > 0 \quad (359)$$

as indicated in the following scheme.

8.5 Stability of Phases: Definitions

In the following, we shall apply the perturbation method to study the stability of phases. In this case, the unperturbed system consists of a single phase α , whereas the perturbed system comprises α plus a small amount of a new phase, β . In order to treat this problem, we must specify the nature of the new phase. In general, the intensive properties of the new phase differ from those of the original phase either infinitesimally, or by a finite amount. In principle, various possibilities should be considered:

(a) The initial phase is stable with respect to all other phases, whether

infinitesimally different from it or not. In this case we say that the phase is stable.

- (b) The initial phase is stable with respect to all phases infinitesimally different from it, but there is at least one other phase with respect to which it is not stable. In this case we say that the phase is metaestable.
- (c) The initial phase is unstable with respect to phases infinitesimally different from it.

If the phase is unstable, it will disappear and give rise to one or more neighbouring phases. This process will be repeated until we arrive at a phase which is stable with respect to adjacent phases. A phase stable with respect to all other phases, whether adjacent or not, cannot give rise spontaneously to a new phase in macroscopic amounts.

Due to molecular fluctuations, small amounts of phases infinitesimally different from the initial phase will be formed continuously, i.e., by means of such fluctuations the system will be transformed into a perturbed state. If the initial phase is not stable with respect to the perturbed state, the phase will disappear.

In the case of metastable phases, the system may remain indefinitely in equilibrium without the appearance of a new phase. On the other hand, if nuclei of a new, more stable phase are introduced, the system might change over into this phase.

Both stable and metastable phases are often described as "stable", since they have certain properties in common which distinguish them from unstable phases.

8.6 Unilateral Perturbations in a Phase of a Unary System

A phase consisting of a single component must satisfy certain conditions if it is to be stable with respect to adjacent phases. In order to determine those conditions we shall study the entropy change accompanying the formation of a new phase infinitesimally different, at constant V and U . The following notation will be used:

The initial state will be denoted using a single prime, whereas the new phase will be double primed. Furthermore, let the number of moles in the system be n , and assume that both the energy U , and the volume V of the system are fixed. In this case, the unperturbed state (a) may be characterized as

$$n'_a = n ; n''_a = 0 \quad (360)$$

and the perturbed state (a') as

$$n'_{a'} = n - \delta\xi ; n''_{a'} = \delta\xi \quad (361)$$

where $\delta\xi$ represents the amount of the new phase. If V_m and U_m are the molar volume and the molar energy of the system in the initial state, the properties of the newly formed phase will differ infinitesimally from them, i.e.,

$$V''_m = V'_m + \delta''V_m \quad (362)$$

$$U''_m = U'_m + \delta''U_m \quad (363)$$

The volume of the unperturbed state is

$$V_a = nV_m \quad (364)$$

while after the perturbation we have

$$V_{a'} = (n - \delta\xi)(V_m + \delta'V_m) + \delta\xi(V_m + \delta''V_m) \quad (365)$$

Since the volume of the system remains constant, we have

$$V_a = V_{a'} \quad (366)$$

By applying this condition to eqs. 364 to 365 we obtain

$$0 = (n - \delta\xi)\delta'V_m + \delta\xi\delta''V_m \quad (367)$$

Similarly, since the energy remains constant,

$$U_a = U_{a'} \quad (368)$$

and we obtain

$$0 = (n - \delta\xi)\delta'U_m + \delta\xi\delta''U_m \quad (369)$$

Let us now express the molar entropy of each phase in terms of V_m and U_m . For the unperturbed state we have

$$S_a = nS_m(V_m, U_m) \quad (370)$$

After the perturbation, we approximate the molar entropy of the original phase by a Taylor series:

$$\begin{aligned} S'_m &= S_m + \left(\frac{\partial S_m}{\partial V_m}\right)_{U_m} \delta'V_m + \left(\frac{\partial S_m}{\partial U_m}\right)_{V_m} \delta'U_m + \\ &+ \frac{1}{2} \left\{ \left(\frac{\partial^2 S_m}{\partial V_m^2}\right)_{U_m} (\delta'V_m)^2 + 2 \left(\frac{\partial^2 S_m}{\partial V_m \partial U_m}\right) (\delta'V_m) (\delta'U_m) \right. \\ &\left. + \left(\frac{\partial^2 S_m}{\partial U_m^2}\right)_{V_m} (\delta'U_m)^2 \right\} + \dots \end{aligned} \quad (371)$$

and similarly for the molar entropy of the new phase:

$$\begin{aligned} S''_m &= S_m + \left(\frac{\partial S_m}{\partial V_m}\right)_{U_m} \delta''V_m + \left(\frac{\partial S_m}{\partial U_m}\right)_{V_m} \delta''U_m + \\ &+ \frac{1}{2} \left\{ \left(\frac{\partial^2 S_m}{\partial V_m^2}\right)_{U_m} (\delta''V_m)^2 + 2 \left(\frac{\partial^2 S_m}{\partial V_m \partial U_m}\right) (\delta''V_m) (\delta''U_m) + \right. \\ &\left. + \left(\frac{\partial^2 S_m}{\partial U_m^2}\right)_{V_m} (\delta''U_m)^2 \right\} + \dots \end{aligned} \quad (372)$$

The total entropy after the perturbation is given by

$$S_{a'} = (n - \delta\xi) S'_m + \delta\xi S''_m \quad (373)$$

and the increase in entropy resulting from the perturbation, by

$$\delta S = (n - \delta\xi) S'_m + \delta\xi S''_m - nS_m \quad (374)$$

By introducing eqs. 371 and 372 in 374 and expressing $\delta'V_m$ and $\delta'U_m$ in terms of $\delta''V_m$ (eq. 367) and $\delta''U_m$ (eq. 369), respectively, we obtain

$$\begin{aligned} \delta S &= \frac{1}{2} \frac{n\delta\xi}{n - \delta\xi} \left\{ \left(\frac{\partial^2 S_m}{\partial V_m^2}\right)_{U_m} (\delta''V_m)^2 \right. \\ &\left. + 2 \left(\frac{\partial^2 S_m}{\partial V_m \partial U_m}\right) (\delta''V_m) (\delta''U_m) + \left(\frac{\partial^2 S_m}{\partial U_m^2}\right)_{V_m} (\delta''U_m)^2 \right\} \end{aligned} \quad (375)$$

Finally, by dividing by $\delta\xi$, allowing $\delta\xi$ to tend to zero, and multiplying by T , we find that the affinity at the initial state, i.e.,

$$A_\alpha = T \left[\left(\frac{\partial S}{\partial \xi} \right)_{U,V} \right]_\alpha = T \left[\left(\frac{\partial_i S}{\partial \xi} \right)_{U,V} \right]_\alpha \quad (376)$$

is given by the following expression

$$A_\alpha = \frac{T}{2} \cdot \left\{ \left(\frac{\partial^2 S_m}{\partial V_m^2} \right)_{U_m} (\delta'' V_m)^2 + 2 \left(\frac{\partial^2 S_m}{\partial V_m \partial S_m} \right) (\delta'' V_m) (\delta'' U_m) + \right. \\ \left. + \left(\frac{\partial^2 S_m}{\partial U_m^2} \right)_{V_m} (\delta'' U_m)^2 \right\} \quad (377)$$

8.7 Thermal and Mechanical Stability of a Phase

Since the perturbation considered in the previous section is unilateral with $\delta\xi > 0$, the stability condition

$$Q'_{aa'} = A_\alpha \delta\xi + \dots < 0$$

becomes

$$A_\alpha < 0 \quad (378)$$

which applied to eq. 377 yields

$$\left(\frac{\partial^2 S_m}{\partial V_m^2} \right)_{U_m} (\delta'' V_m)^2 + 2 \left(\frac{\partial^2 S_m}{\partial V_m \partial S_m} \right) (\delta'' V_m) (\delta'' U_m) + \left(\frac{\partial^2 S_m}{\partial U_m^2} \right)_{V_m} (\delta'' U_m)^2 < 0 \quad (379)$$

The conditions under which this quadratic form is negative for all values of $\delta'' V_m$ and $\delta'' U_m$ are

$$\left(\frac{\partial^2 S_m}{\partial U_m^2} \right)_{V_m} < 0 \quad (380)$$

and

$$\left(\frac{\partial^2 S_m}{\partial V_m^2} \right)_{U_m} \left(\frac{\partial^2 S_m}{\partial U_m^2} \right)_{V_m} > \left(\frac{\partial^2 S_m}{\partial V_m \partial U_m} \right)^2 \quad (381)$$

The consequences of these results will now be explored. From the fundamental equation

$$dS_m = \frac{1}{T}dU_m + \frac{P}{T}dV_m \quad (382)$$

we obtain

$$\left(\frac{\partial S_m}{\partial U_m}\right)_{V_m} = \frac{1}{T} \quad (383)$$

and

$$\left(\frac{\partial^2 S_m}{\partial U_m^2}\right)_{V_m} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial U_m}\right)_{V_m} = -\frac{1}{T^2 C_V} \quad (384)$$

where C_V is the molar heat capacity at constant volume. Using eq. 384 we express the first stability condition as follows

$$\left(\frac{\partial^2 S_m}{\partial U_m^2}\right)_{V_m} = -\frac{1}{T^2 C_V} < 0 \quad (385)$$

which leads to

$$C_V > 0 \quad (386)$$

i.e., C_V must be positive. This is the condition of thermal stability of the phase. Furthermore, from the total differential of dS_m we obtain

$$\left(\frac{\partial^2 S_m}{\partial V_m^2}\right)_{U_m} = \frac{1}{T} \left(\frac{\partial P}{\partial V_m}\right)_T - \frac{C_V}{T^2} \left(\frac{\partial T}{\partial V_m}\right)_{U_m} \quad (387)$$

and

$$\frac{\partial^2 S_m}{\partial V_m \partial U_m} = -\frac{1}{T^2} \left(\frac{\partial T}{\partial V_m}\right)_{U_m} \quad (388)$$

By inserting the expressions for the second derivatives of the molar entropy into eq. 381 we find

$$\left(\frac{\partial P}{\partial V_m}\right)_T < 0 \quad (389)$$

This condition can be given a very useful form by introducing the isothermal bulk modulus of the phase, B_T , which is defined as follows

$$B_T = -V_m \left(\frac{\partial P}{\partial V_m} \right)_T \quad (390)$$

We obtain

$$B_T > 0 \quad (391)$$

i.e., the isothermal bulk modulus must be positive. This is the condition of mechanical stability of the phase.

8.8 Stability with Respect to Bilateral Perturbations

Let us now consider the equilibrium and stability conditions when the perturbations are such that $\delta\xi$ may be either positive or negative. For an equilibrium state "a" we have

$$A_a = 0 \quad (392)$$

and the stability condition

$$Q'_{aa'} = \left(\frac{1}{2} \right) \left(\frac{\partial A}{\partial \xi} \right)_a (\delta\xi)^2 < 0 \quad (393)$$

yields

$$\left(\frac{\partial A}{\partial \xi} \right)_a < 0 \quad (394)$$

In terms of the thermodynamic functions U, H, F and G we write eqs. 392 and 394, respectively, as

$$A_a = - \left[\left(\frac{\partial U}{\partial \xi} \right)_{S,V} \right]_a = 0 \text{ and } \left[\left(\frac{\partial^2 U}{\partial \xi^2} \right)_{S,V} \right]_a > 0 \quad (395)$$

$$A_a = - \left[\left(\frac{\partial H}{\partial \xi} \right)_{S,P} \right]_a = 0 \text{ and } \left[\left(\frac{\partial^2 H}{\partial \xi^2} \right)_{S,P} \right]_a > 0 \quad (396)$$

$$A_{\alpha} = - \left[\left(\frac{\partial F}{\partial \xi} \right)_{T,V} \right]_{\alpha} = 0 \text{ and } \left[\left(\frac{\partial^2 F}{\partial \xi^2} \right)_{T,V} \right]_{\alpha} > 0 \quad (397)$$

$$A_{\alpha} = - \left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right]_{\alpha} = 0 \text{ and } \left[\left(\frac{\partial^2 G}{\partial \xi^2} \right)_{T,P} \right]_{\alpha} > 0 \quad (398)$$

Geometrically, eqs. 395 to 398 imply that the functions U vs. ξ , H vs. ξ , F vs. ξ and G vs. ξ show a minimum at the unperturbed, equilibrium state "a".

8.9 Stability with Respect to Diffusion in a Binary System

Let us now study a perturbation which consists in the appearance of an heterogeneity in the composition of a binary mixture, which is initially uniform. In particular, consider a binary system $A - B$ which is homogeneous, and characterized by the variables T, P and the mole fraction x_A . Let us focus on two elements of volume " α " and " β ", respectively, as indicated in the following figure. The reaction which is described by ξ , corresponds now to the passage of 1 mole of A atoms from α to β , together with the passage of an arbitrary number (ν) of moles of B from β to α .

In this case we have

$$\frac{dn_A^{\alpha}}{-1} = \frac{dn_A^{\beta}}{+1} = \frac{dn_B^{\alpha}}{+\nu} = \frac{dn_B^{\beta}}{-\nu} = d\xi \quad (399)$$

and the corresponding affinity is

$$A = (\mu_A^{\alpha} - \mu_A^{\beta}) + \nu (\mu_B^{\beta} - \mu_B^{\alpha}) \quad (400)$$

Since the system is in equilibrium, $A_{\alpha} = 0$, and the chemical potentials have the same value independently of the choice of α and β . Furthermore, by derivating eq. 401 at constant T , and P we obtain

$$\left(\frac{\partial A}{\partial \xi} \right)_{T,P} = \left(\frac{\partial \mu_A^{\alpha}}{\partial x_A^{\alpha}} - \nu \frac{\partial \mu_B^{\alpha}}{\partial x_A^{\alpha}} \right) \left(\frac{\partial x_A^{\alpha}}{\partial \xi} \right) - \left(\frac{\partial \mu_A^{\beta}}{\partial x_A^{\beta}} - \nu \frac{\partial \mu_B^{\beta}}{\partial x_A^{\beta}} \right) \left(\frac{\partial x_A^{\beta}}{\partial \xi} \right) \quad (401)$$

Moreover, by definition, we have

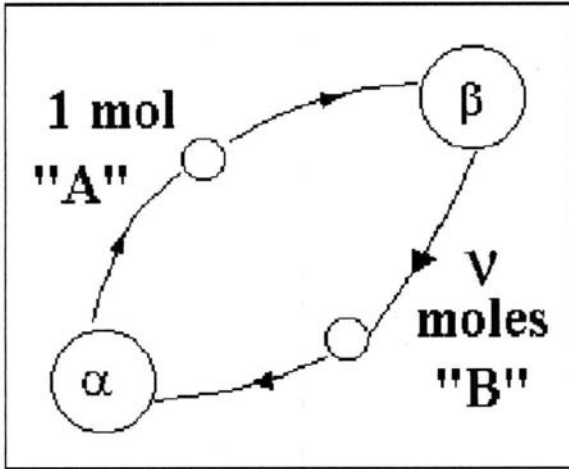


FIGURE 16.

$$x_A^\alpha = \frac{n_A^\alpha}{n_A^\alpha + n_B^\alpha} = \frac{n_A^\alpha(0) - \xi}{n_A^\alpha(0) + n_B^\alpha(0) + (\nu - 1)\xi} \quad (402)$$

and

$$x_A^\beta = \frac{n_A^\beta}{n_A^\beta + n_B^\beta} = \frac{n_A^\beta(0) + \xi}{n_A^\beta(0) + n_B^\beta(0) - (\nu - 1)\xi} \quad (403)$$

where $n_A^\alpha(0)$, $n_B^\alpha(0)$, $n_A^\beta(0)$, $n_B^\beta(0)$ refer to the number of moles of A and B in each of the elements of volume α and β , before the perturbation.

From eqs. 402 and 403 we obtain

$$\left(\frac{\partial x_A^\alpha}{\partial \xi}\right) = -\frac{1}{n^\alpha} [1 + x_A^\alpha (\nu - 1)] \quad (404)$$

and

$$\left(\frac{\partial x_A^\beta}{\partial \xi}\right) = \frac{1}{n^\beta} [1 + x_A^\beta (\nu - 1)] \quad (405)$$

where

$$n^\alpha = n_A^\alpha + n_B^\alpha \quad (406)$$

and

$$n^\beta = n_A^\beta + n_B^\beta \quad (407)$$

The derivatives of the chemical potentials which appear in eq. 401 may be expressed in terms of the molar Gibbs energy, G_m . From the identity

$$G_m^\alpha = x_A^\alpha \mu_A^\alpha + x_B^\alpha \mu_B^\alpha \quad (408)$$

we obtain,

$$\left(\frac{\partial G_m^\alpha}{\partial x_A^\alpha} \right) = \mu_A^\alpha - \mu_B^\alpha \quad (409)$$

and

$$\frac{\partial^2 G_m^\alpha}{(\partial x_A^\alpha)^2} = \frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} - \frac{\partial \mu_B^\alpha}{\partial x_A^\alpha} \quad (410)$$

In addition, the Gibbs-Duhem relation

$$x_A^\alpha \left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) + x_B^\alpha \left(\frac{\partial \mu_B^\alpha}{\partial x_A^\alpha} \right) = 0 \quad (411)$$

yields

$$\left(\frac{\partial \mu_B^\alpha}{\partial x_A^\alpha} \right) = -\frac{x_A^\alpha}{x_B^\alpha} \left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) \quad (412)$$

and the second derivative of the molar Gibbs energy may be written as follows

$$\frac{\partial^2 G_m^\alpha}{(\partial x_A^\alpha)^2} = \left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) + \frac{x_A^\alpha}{x_B^\alpha} \left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) = \frac{1}{x_B^\alpha} \left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) \quad (413)$$

Analogously, we find

$$\frac{\partial^2 G_m^\beta}{(\partial x_A^\beta)^2} = \frac{1}{x_B^\beta} \left(\frac{\partial \mu_A^\beta}{\partial x_A^\beta} \right) \quad (414)$$

as well as

$$\left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) = x_B^\alpha \frac{\partial^2 G_m^\alpha}{(\partial x_A^\alpha)^2} \quad (415)$$

$$\left(\frac{\partial \mu_B^\alpha}{\partial x_A^\alpha} \right) = -\frac{x_A^\alpha}{x_B^\alpha} \left(\frac{\partial \mu_A^\alpha}{\partial x_A^\alpha} \right) = -x_A^\alpha \frac{\partial^2 G_m^\alpha}{(\partial x_A^\alpha)^2} \quad (416)$$

$$\left(\frac{\partial \mu_A^\beta}{\partial x_A^\beta} \right) = x_B^\beta \frac{\partial^2 G_m^\beta}{(\partial x_A^\beta)^2} \quad (417)$$

$$\left(\frac{\partial \mu_B^\beta}{\partial x_A^\beta} \right) = -\frac{x_A^\beta}{x_B^\beta} \left(\frac{\partial \mu_A^\beta}{\partial x_A^\beta} \right) = -x_A^\beta \frac{\partial^2 G_m^\beta}{(\partial x_A^\beta)^2} \quad (418)$$

By combining these results with eq. 401, we obtain

$$\left(\frac{\partial A}{\partial \xi} \right)_{T,P} = -\frac{[1 + x_A^\alpha (\nu - 1)]^2}{n^\alpha} \frac{\partial^2 G_m^\alpha}{(\partial x_A^\alpha)^2} - \frac{[1 + x_A^\beta (\nu - 1)]^2}{n^\beta} \frac{\partial^2 G_m^\beta}{(\partial x_A^\beta)^2} \quad (419)$$

Since the system is homogeneous at the unperturbed state "a", there is no need to keep the indices α and β . After this change we find

$$\left[\left(\frac{\partial A}{\partial \xi} \right)_{T,P} \right]_a = -\frac{2[1 + x_A (\nu - 1)]^2}{n} \left(\frac{\partial^2 G_m}{\partial x_A^2} \right) < 0 \quad (420)$$

As the number ν in the present treatment may be chosen arbitrarily, this condition ensures stability with respect to any diffusion process. From this equation we obtain the stability condition

$$\left(\frac{\partial^2 G_m}{\partial x_A^2} \right)_{T,P} > 0 \quad (421)$$

in terms of the molar Gibbs energy, and

$$\left(\frac{\partial \mu_A^\alpha}{\partial x_A}\right)_{T,P} > 0 \quad (422)$$

as well as

$$\left(\frac{\partial \mu_B^\alpha}{\partial x_A}\right)_{T,P} < 0 \quad (423)$$

in terms of the chemical potentials of the components.

References

1. Beattie, J.A. and Oppenheim, I. *Principles of Thermodynamics* (Elsevier Scientific, Amsterdam, 1979).
2. Callen, H.B. *Thermodynamics and an Introduction to Thermostatistics* (John Wiley, New York, 1985).
3. de Groot, S.R. and Mazur, P.M., *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1963).
4. Denbigh, K.G. *The Thermodynamics of the Steady State* (Methuen Co.Ltd., London, 1958).
5. Denbigh, K.G. *The Principles of Chemical Equilibrium* (Cambridge University Press, UK, 1966).
6. Fitts, D. *Nonequilibrium Thermodynamics* (McGraw Hill, New York, 1962).
7. Glansdorff, P. and Prigogine, I. *Structure, Stabilité et Fluctuations* (Masson, Paris, 1971).
8. Guggenheim, E.A. *Thermodynamics. An Advanced Treatment for Chemists and Physicists* (North-Holland, Amsterdam, 1985).
9. Hillert, M. *Phase Equilibria, Phase Diagrams and Phase Transformations* (Cambridge University Press, Cambridge, UK, 1998).
10. Kirkwood, J.G. and Oppenheim, I. *Chemical Thermodynamics* (McGraw Hill, New York, 1961).
11. Lewis, G.N. and Randall, M. *Thermodynamics and the Free Energy of Chemical Substances* (McGraw-Hill, New York, 1923).
12. Pippard, A.B. *The Elements of Classical Thermodynamics* (Cambridge University Press, Cambridge, UK, 1966).
13. Planck, M. *Treatise on Thermodynamics* (Dover Pub.Inc., 1926).

14. Prigogine, I. *Introduction to Thermodynamics of Irreversible Processes* (Interscience, New York, 1961).
15. Prigogine, I. and Defay, R. *Chemical Thermodynamics* (Longmans, London, 1954).
16. Prigogine, I. *Introduction to Thermodynamics of Irreversible Processes* (Interscience, New York, 1961).
17. Slater, J.C. *Introduction to Chemical Physics* (McGraw Hill, New York, 1939).