

THE FUNDAMENTALS OF CHEMICAL THERMODYNAMICS

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I. INTRODUCTION

In recent years a general and accurate method of chemical thermodynamics has been developed by De Donder (1) and, independently, by Schottky, Ulich, and Wagner (6, 7). De Donder's exposition of the subject is particularly clear and rigorous. Its main feature is the introduction of a function of the state of the system called the *affinity*, closely related to the chemical potentials of Gibbs. The object of chemical thermodynamics is the study of reactions actually taking place in time and of the corresponding changes in the various properties of the system. Classical thermodynamics, as treated by Gibbs (3) and quite recently by Guggenheim (4), is mainly concerned with the study of equilibria and reversible changes. The term "thermostatistics", suggested and actually used by several authors, very properly applies to this type of thermodynamics. Chemical thermodynamics would then simply be called thermodynamics.

Lewis and Randall (5) treat both parts of the subject, but their formal treatment of chemical thermodynamics can be improved upon. A monograph by van Lerberghe (8) is particularly instructive from this point of view.

As no attention seems to have been paid so far to this method of thermodynamics in the English or American literature, this introduction to the subject is presented as a service to physical chemists.

II. THE FIRST AND THE SECOND LAW OF THERMODYNAMICS; THERMODYNAMIC FUNCTIONS

The first law of thermodynamics is the principle of the conservation of energy. Let us consider an infinitesimally small transformation of a closed system taking place between the time t and the time $t + dt$ (dt is positive). During this transformation the system receives the quantity of heat¹ dQ , undergoes the exterior work dW , and increases its internal

¹ dQ may or may not be an exact differential. It is the principal part of the increment ΔQ when this increment tends toward zero. We have, for a given transformation of the system:

$$\lim \Delta Q = dQ + \frac{d^2Q}{2!} + \frac{d^3Q}{3!} + \dots$$

d^2Q , d^3Q , etc., are neglected.

energy by the amount dU . The conservation of energy requires that:

$$dQ + dW = dU \quad (2.1)$$

We shall only consider systems for which

$$dW = -pdV \quad (2.2)$$

p being the pressure and V the volume of the system. For the sake of simplicity we shall suppose that temperature and pressure are the same throughout the system. Equation 2.1 becomes:

$$dU = dQ - pdV \quad (2.3)$$

The second law of thermodynamics is the so-called principle of the degradation of energy. It can be made to assume a general mathematical form, thanks to the introduction of the function of the state of the system called entropy. Calling S the entropy and T the absolute temperature of the system, we have for reversible transformations taking place between the times t and $t + dt$ ($dt > 0$)

$$TdS - dQ = 0 \quad (2.4)$$

for irreversible transformations:

$$TdS - dQ > 0 \quad (2.5)$$

Hence the difference $TdS - dQ$ is always positive or equal to zero; it can never be negative for a natural process. This quantity was called by Clausius the uncompensated heat of the process. We shall represent it by the symbol dQ' . We have then according to equation 2.5:

$$TdS = dQ + dQ' \quad (2.6)$$

According to equation 2.4 we have for reversible changes:

$$dQ' = 0 \quad (2.7)$$

and according to equation 2.5 for irreversible changes:

$$dQ' > 0 \quad (2.8)$$

The first law (equation 2.3) can then be written for reversible changes:

$$dU = TdS - pdV \quad (2.9)$$

for irreversible changes:

$$dU = TdS - pdV - dQ' \quad (2.10)$$

Let us now introduce the other thermodynamic functions: the heat content

$$H \equiv U + pV \quad (2.11)$$

the maximum work or free energy of Helmholtz

$$A \equiv U - TS \quad (2.12)$$

the thermodynamic potential of Gibbs or free energy of Gibbs

$$F \equiv U - TS + pV \quad (2.13)$$

From relations 2.10, 2.11, 2.12, and 2.13, we obtain

$$dH = TdS + Vdp - dQ' \quad (2.14)$$

$$dA = -SdT - pdV - dQ' \quad (2.15)$$

$$dF = -SdT + Vdp - dQ' \quad (2.16)$$

We are now able to deduce the following conclusions:

- (1) For a natural process taking place at constant entropy and volume

$$dQ' = -dU > 0 \quad (2.17)$$

- (2) For a natural process taking place at constant entropy and pressure

$$dQ' = -dH > 0 \quad (2.18)$$

- (3) For a natural process taking place at constant temperature and volume

$$dQ' = -dA > 0 \quad (2.19)$$

- (4) For a natural process taking place at constant temperature and pressure

$$dQ' = -dF > 0 \quad (2.20)$$

The relations 2.1 to 2.20 apply to all types of physicochemical changes and constitute the basis of chemical thermodynamics.

III. CRITIQUE OF CURRENT CHEMICAL THERMODYNAMICS

The variation in free energy corresponding to one occurrence of a given chemical reaction at constant temperature and pressure is considered to be a measure of the *affinity* of that reaction. This variation of free energy is represented by ΔF . Relation 2.20 becomes

$$\Delta Q' = -\Delta F > 0 \quad (3.1)$$

which shows that the ΔF of a spontaneous reaction is negative. The composition of the system changing gradually from the initial to the final state, F and hence ΔF are functions of p , T , and the composition. In practice, however, one considers the ΔF corresponding to one complete occurrence of the reaction, the initial state being such that only the components on the left-hand side of the chemical reaction are present.

Various devices are used for the experimental determination and the calculation of ΔF . For instance:

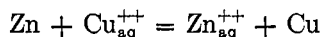
(1) The reaction is made to occur reversibly by means of a separation of the phases of the system and the adjunction of an auxiliary system able to develop a difference of electric potential equal and of opposite sign to that of the chemical system. The complete system is in equilibrium and one writes:

$$\Delta F_{\text{total}} = \Delta F_{\text{reaction}} + NFE = 0 \quad (3.2)$$

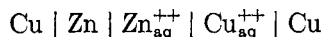
and hence:

$$\Delta F_{\text{reaction}} = -NFE \quad (3.3)$$

(N = number of equivalents involved in one occurrence of the reaction, F = Faraday's constant, and E = electromotive force.) A large number of chemical changes are amenable to this method, but the approximations involved and the limitations of the procedure are usually not fully realized. A moment of thought, however, will easily convince the reader that only for systems containing one reactant per phase does this procedure lead to a good approximation for ΔF . Whenever two or more reactants belong to the same phase and have thus to be separated by means of a membrane or a liquid junction, the measured E.M.F. does not take into account the specific effects of one component upon the thermodynamic properties of the others. The affinity of the reaction



for instance, is deduced from the E.M.F. of a cell of the type:



in which the specific effects resulting from the mixture of the two metallic ions are absent.

(2) The value of ΔF corresponding to a certain mixture of the reactants in which they all possess unit activity is deduced from an equilibrium measurement, at the pressure and temperature desired, by means of the formula

$$\Delta F = -RT \cdot \log K(p, T) \quad (3.4)$$

in which K is the equilibrium constant and R the gas constant.

The composition of the particular mixture corresponding to this ΔF can only be approximated, and there is no way of deducing the value of ΔF for some other composition of the system.

(3) ΔF is often deduced from the relation:

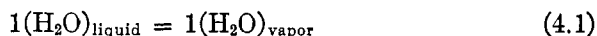
$$\Delta F = \Delta H - T \cdot \Delta S \quad (3.5)$$

in which the three Δ 's correspond to changes taking place at constant temperature. In using actual thermochemical and heat capacity data one has moreover to assume that volume or pressure is constant. Since only the ΔF corresponding to a change at constant temperature and pressure is a measure of the affinity, the ΔH in relation 3.5 is the heat of reaction at constant temperature and pressure and the ΔS is deduced from heat capacities at constant pressure. The dependence of ΔF on composition could only be obtained if the heat of reaction and the entropy were known functions of composition. The present analysis shows the absolute necessity of introducing a "chemical variable" to complete the definition of the state of the system. This chemical variable will be a measure of the degree of advancement of the reaction; in case several independent reactions occur simultaneously there will be as many chemical variables as reactions. The introduction of such variables is the object of the following section, and we shall therefore interrupt at this point our discussion of current chemical thermodynamics.

IV. THE CHEMICAL VARIABLE

The law of definite proportions

Let us first consider a change of state and take as an example the evaporation of liquid water. The phenomenon can be represented by the "reaction":



The system consists of a liquid phase and a vapor phase and is closed. If m_l is the mass of the liquid and m_v is that of the vapor, we have:

$$dm_l = - dm_v \quad (4.2)$$

If evaporation is actually taking place, reaction 4.1 goes from left to right, dm_l is negative, and dm_v is positive. The number of moles of water evaporated is given by:

$$- \frac{dm_l}{M_{\text{H}_2\text{O}}} = \frac{dm_v}{M_{\text{H}_2\text{O}}} = d\xi \quad (4.3)$$

$M_{\text{H}_2\text{O}}$ being the molecular mass of water. ξ is a pure number. It can be considered as the "degree of advancement" of the process.² If we write equation 4.1 as follows:

$$0 = -1(\text{H}_2\text{O})_{\text{liquid}} + 1(\text{H}_2\text{O})_{\text{vapor}} \quad (4.4)$$

we see that the signs of the ratios appearing in equation 4.3 are given by the signs of the coefficients of the chemical symbols in equation 4.4. Let us now take the case of a typical chemical reaction, the formation of ammonia from hydrogen and nitrogen. The chemical reaction is:



or

$$0 = -3\text{H}_2 - 1\text{N}_2 + 2\text{NH}_3$$

The masses of hydrogen and nitrogen are decreasing; that of ammonia is increasing, and by analogy with equation 4.3 we have:

$$\frac{dm_{\text{H}_2}}{-3M_{\text{H}_2}} = \frac{dm_{\text{N}_2}}{-1M_{\text{N}_2}} = \frac{dm_{\text{NH}_3}}{+2M_{\text{NH}_3}} = d\xi \quad (4.6)$$

Equation 4.6 is the mathematical form of the law of definite proportions. ξ is the degree of advancement of the reaction. It gives the number of molar groups formed (2NH_3) or destroyed (3H_2 , 1N_2) during the reaction.

If at the beginning (time zero) the mass of ammonia is zero, we have at time t , when ξ molar groups have been formed:

$$\begin{aligned} m_{\text{NH}_3} &= 2M_{\text{NH}_3} \cdot \xi \\ m_{\text{H}_2} &= m_{\text{H}_2}^0 - 3M_{\text{H}_2} \cdot \xi \\ m_{\text{N}_2} &= m_{\text{N}_2}^0 - M_{\text{N}_2} \cdot \xi \end{aligned} \quad (4.7)$$

$m_{\text{H}_2}^0$ and $m_{\text{N}_2}^0$ are the masses of hydrogen and nitrogen at the time zero. These relations are immediately obtained by integration of the differential equations 4.6.

It is now easy to generalize. In the case of a single reaction we may write

$$\sum_{\gamma''} |\nu_{\gamma''}| \cdot \bar{M}_{\gamma''} = \sum_{\gamma'} \nu_{\gamma'} \bar{M}_{\gamma'} \quad (4.8)$$

$|\nu_{\gamma''}|$ is the absolute value of the coefficient of the chemical symbol $M_{\gamma''}$ of the constituent γ'' whose mass decreases in the process (reaction from left

² In French: *degré d'avancement* (cf. De Donder). In German: *Reaktionslaufzahl* (cf. Schottky).

to right). $\nu_{\gamma'}$ is actually negative. $\nu_{\gamma'}$ is the coefficient of the chemical symbol $\bar{M}_{\gamma'}$ of the constituent γ' whose mass increases in the process. $\nu_{\gamma'}$ is positive. Equation 4.8 can also be written:

$$0 = \sum_{\gamma=1}^{\gamma=c} \nu_{\gamma} \bar{M}_{\gamma} \quad (4.9)$$

in which the summation is extended to all the constituents, whether on the left or the right of equation 4.8. The ν_{γ} 's of the constituents on the left are negative, those of the constituents on the right are positive. By analogy with equations 4.3 and 4.6 we write:

$$\frac{dm_{\gamma}}{\nu_{\gamma} \bar{M}_{\gamma}} = d\xi \quad (4.10)$$

for $\gamma = 1, 2, \dots, c$. The ν_{γ} 's are again taken with their signs.

In the case of a system of φ phases ($a = 1, 2, \dots, \varphi$) in which one reaction takes place, equation 4.10 becomes

$$\sum_a \frac{dm_{\gamma a}}{\nu_{\gamma} \bar{M}_{\gamma}} = d\xi \quad (4.11)$$

In the case of a system of one phase in which r independent reactions take place ($\rho = 1, 2, \dots, r$), equation 4.10 becomes

$$\frac{dm_{\gamma \rho}}{\nu_{\gamma \rho} \bar{M}_{\gamma}} = d\xi_{\rho} \quad (4.12)$$

Finally, in the case of a system of φ phases in which r independent reactions take place, equation 4.10 becomes

$$\sum_a \frac{dm_{\gamma a \rho}}{\nu_{\gamma \rho} \bar{M}_{\gamma}} = d\xi_{\rho} \quad (4.13)$$

By independent reactions we mean reactions such that none can be obtained by means of a linear combination of two or more of the others.

Introducing the numbers of moles

$$dn_{\gamma} = \frac{dm_{\gamma}}{\bar{M}_{\gamma}} \quad (4.14)$$

the general expression 4.13 becomes

$$\sum_a \frac{dn_{\gamma a \rho}}{\nu_{\gamma \rho}} = d\xi_{\rho} \quad (4.15)$$

from which one easily deduces that

$$dn_{\gamma} = \sum_{\rho} \nu_{\gamma\rho} d\xi_{\rho} \quad (4.16)$$

and also that

$$dn_{\gamma} = \sum_{\rho} \sum_a dn_{\gamma a \rho} \quad (4.17)$$

The velocity of the reaction ρ is conveniently defined as follows:

$$\mathbf{v}_{\rho} = \frac{d\xi_{\rho}}{dt} = \frac{1}{\nu_{\gamma}} \cdot \frac{dn_{\gamma}}{dt} \quad (4.18)$$

Let us emphasize that in a closed system in which chemical reactions are taking place the dn_{γ} 's are not independent. They are connected by the law of definite proportions with the degrees of advancement of the independent reactions. These degrees of advancement are independent variables and play in chemical thermodynamics a part entirely analogous to that of pressure and temperature, for instance.

V. DEFINITION OF AFFINITY; FUNDAMENTAL HYPOTHESIS

In this section we shall develop a line of reasoning which could be based upon any one of the four equations 2.10, 2.14, 2.15, and 2.16. Let us, for instance, use equation 2.16:

$$dF = -SdT + Vdp - dQ' \quad (5.1)$$

We easily see that F should be considered as a function of T , p , and composition. Let us assume, for the sake of simplicity, that only one reaction occurs in the system. F is then a function of T , p , and ξ :

$$F = F(p, T, \xi) \quad (5.2)$$

We should have

$$dQ' = a_{p\xi} \cdot dT + a_{T\xi} \cdot dp + a_{pT} \cdot d\xi \quad (5.3)$$

in which $a_{p\xi}$, $a_{T\xi}$, and a_{pT} are also functions of p , T , and ξ . Equation 5.1 becomes

$$dF = - (S + a_{p\xi}) dT + (V - a_{T\xi}) dp - a_{pT} d\xi \quad (5.4)$$

During the reaction the variables p , T , and ξ are functions of time only:

$$\left. \begin{aligned} p &= p(t) \\ T &= T(t) \\ \xi &= \xi(t) \end{aligned} \right\} \quad (5.5)$$

Eliminating t we may write:

$$\left. \begin{aligned} p &= p(\xi) \\ T &= T(\xi) \end{aligned} \right\} \quad (5.6)$$

from which the derivatives $\frac{dp}{d\xi}$ and $\frac{dT}{d\xi}$ can be calculated. Equation 5.3 may be written:

$$\frac{dQ'}{d\xi} = a_{p\xi} \cdot \frac{dT}{d\xi} + a_{T\xi} \cdot \frac{dp}{d\xi} + a_{pT} \quad (5.7)$$

and 5.4:

$$\frac{dF}{d\xi} = -(S + a_{p\xi}) \frac{dT}{d\xi} + (V - a_{T\xi}) \frac{dp}{d\xi} - a_{pT} \quad (5.8)$$

For the particular case of a reaction taking place at constant p and T , equations 5.7 and 5.8 become, respectively,

$$\left(\frac{dQ'}{d\xi} \right)_{pT} = a_{pT} \quad (5.9)$$

and

$$\left(\frac{dF}{d\xi} \right)_{pT} = -a_{pT} \quad (5.16)$$

We shall now introduce a fundamental hypothesis entirely in agreement with the accepted methods of thermodynamics which indeed implicitly apply it. This hypothesis was first clearly stated by De Donder (1): $\frac{dQ'}{d\xi}$ is always equal to a_{pT} whatever the manner in which p and T depend on ξ may be, i.e., whatever the relations 5.6 may be. In other words we must have:

$$\frac{dQ'}{d\xi} = a_{p\xi} \frac{dT}{d\xi} + a_{T\xi} \frac{dp}{d\xi} + a_{pT} \equiv a_{pT} \quad (5.11)$$

for all values of $\frac{dT}{d\xi}$ and $\frac{dp}{d\xi}$. Hence the necessary conditions

$$a_{p\xi} = a_{T\xi} = 0 \quad (5.12)$$

The formulas 5.7 and 5.8 become

$$\frac{dQ'}{d\xi} = a_{pT} \quad (5.13)$$

$$dF = -SdT + Vdp - a_{pT}d\xi \quad (5.14)$$

In particular:

$$\left(\frac{\partial F}{\partial \xi}\right)_{pT} = -a_{pT} \quad (5.15)$$

Let us show that equation 5.13 is independent of the choice of variables. If, for instance, we take V, T, ξ instead of p, T, ξ , equation 5.11 becomes

$$\begin{aligned} \frac{dQ'}{d\xi} = & \left[a_{p\xi} + a_{T\xi} \cdot \left(\frac{\partial p}{\partial T}\right)_{V\xi} \right] \frac{dT}{d\xi} \\ & + a_{T\xi} \cdot \left(\frac{\partial p}{\partial V}\right)_{T\xi} \cdot \frac{dV}{d\xi} + a_{pT} + a_{T\xi} \cdot \left(\frac{\partial p}{\partial \xi}\right)_{VT} \end{aligned} \quad (5.16)$$

which, according to equation 5.12, reduces to equation 5.13 whatever $\frac{dT}{d\xi}$ and $\frac{dV}{d\xi}$ may be. We could have started our reasoning with the other thermodynamic functions and we would have found that

$$\frac{dQ'}{d\xi} = a_{SV} = a_{Sp} = a_{VT} = a_{pT} = \mathcal{A} \quad (5.17)$$

The quantity \mathcal{A} is independent of the type of transformation undergone by the system, i.e., it does not depend on the particular way in which the variables S, V, T , or p depend on ξ . It is a function of the state of the system like U, H, A , or F . This function \mathcal{A} was called by De Donder the *affinity* of the system.

Corollary: In the case of transformations such that ξ is constant, i.e., transformations in which the masses of all the constituents in all the phases stay constant (purely physical transformations), we have, according to equation 5.17,

$$dQ' = \mathcal{A}d\xi = 0 \quad (5.18)$$

Hence these transformations are reversible.

From equations 2.10, 2.14, 2.15, 2.16, and 5.17 we deduce the important relations

$$\left(\frac{\partial U}{\partial \xi}\right)_{SV} = \left(\frac{\partial H}{\partial \xi}\right)_{Sp} = \left(\frac{\partial A}{\partial \xi}\right)_{VT} = \left(\frac{\partial F}{\partial \xi}\right)_{pT} = -\mathcal{A} \quad (5.19)$$

We also have

$$\left(\frac{\partial U}{\partial S}\right)_{V\xi} = T \quad (5.20.1) \quad \left(\frac{\partial U}{\partial V}\right)_{S\xi} = -p \quad (5.20.2)$$

$$\left(\frac{\partial H}{\partial S}\right)_{p\xi} = T \quad (5.20.3) \quad \left(\frac{\partial H}{\partial p}\right)_{S\xi} = V \quad (5.20.4)$$

$$\left(\frac{\partial A}{\partial T}\right)_{V\xi} = -S \quad (5.20.5) \quad \left(\frac{\partial A}{\partial V}\right)_{T\xi} = -p \quad (5.20.6)$$

$$\left(\frac{\partial F}{\partial T}\right)_{p\xi} = -S \quad (5.20.7) \quad \left(\frac{\partial F}{\partial p}\right)_{T\xi} = V \quad (5.20.8)$$

and

$$dU = TdS - pdV - \mathcal{A}d\xi \quad (5.21)$$

$$dH = TdS + Vdp - \mathcal{A}d\xi \quad (5.22)$$

$$dA = -SdT - pdV - \mathcal{A}d\xi \quad (5.23)$$

$$dF = -SdT + Vdp - \mathcal{A}d\xi \quad (5.24)$$

It is important to point out that this quantity \mathcal{A} has all the properties usually associated in a qualitative manner with the name "affinity." Since dQ' is always positive and at least equal to zero we have

$$dQ' = \mathcal{A}d\xi \geq 0 \quad (5.25)$$

1. When \mathcal{A} is positive, $d\xi$ is also positive and the process represented by the general reaction 4.8 actually takes place from left to right.

2. When \mathcal{A} is negative, $d\xi$ is also negative and the process represented by equation 4.8 takes place from right to left. The reaction from left to right is impossible.

3. If \mathcal{A} is equal to zero, $d\xi$ may be positive or negative or equal to zero. The system is indifferent with respect to the reaction 4.8.

When ξ stays constant we have, of course,

$$\mathcal{A}d\xi = 0 \quad (5.26)$$

and \mathcal{A} may be different from or equal to zero. When \mathcal{A} is equal to zero and ξ is constant the system is said to be in a state of *true equilibrium*. When \mathcal{A} is different from zero and ξ is constant the system is said to be in a state of *false equilibrium*. The notion of false equilibrium was first introduced by Duhem (2).

VI. RELATION BETWEEN THE AFFINITY AND THE CHEMICAL POTENTIALS

The usual form of the formulas 2.10, 2.14, 2.15, and 2.16 is that due to Gibbs:

$$dU = TdS - pdV + \sum_{\gamma} \sum_{\alpha} \mu_{\gamma\alpha} dn_{\gamma\alpha} \quad (6.1)$$

$$dH = TdS + Vdp + \sum_{\gamma} \sum_{\alpha} \mu_{\gamma\alpha} dn_{\gamma\alpha} \quad (6.2)$$

$$dA = -SdT - pdV + \sum_{\gamma} \sum_{\alpha} \mu_{\gamma\alpha} dn_{\gamma\alpha} \quad (6.3)$$

$$dF = -SdT + Vdp + \sum_{\gamma} \sum_{\alpha} \mu_{\gamma\alpha} dn_{\gamma\alpha} \quad (6.4)$$

in which $\mu_{\gamma\alpha}$ is the chemical potential of the constituent γ in the phase α . These relations are usually meant to apply to reversible changes, i.e., changes such that $dQ' = 0$. Comparing, for instance, equation 6.4 with equation 5.24, and making use of equation 5.18 we obtain the general condition for equilibrium:

$$dQ' = \mathcal{A}d\xi = - \sum_{\gamma} \sum_{\alpha} \mu_{\gamma\alpha} dn_{\gamma\alpha} = 0 \quad (6.5)$$

We obviously have

$$\mu_{\gamma 1} = \mu_{\gamma 2} = \dots = \mu_{\gamma \phi} \quad (6.6)$$

Equation 6.5 becomes then:

$$\mathcal{A}d\xi = - \sum_{\gamma} \mu_{\gamma} \sum_{\alpha} dn_{\gamma\alpha} = 0 \quad (6.7)$$

but, according to equation 4.15,

$$\sum_{\alpha} dn_{\gamma\alpha} = \nu_{\gamma} \cdot d\xi \quad (6.8)$$

Hence the condition of equilibrium:

$$\mathcal{A} = - \sum_{\gamma} \nu_{\gamma} \mu_{\gamma} = 0 \quad (6.9)$$

The various formulas of the previous sections apply to irreversible changes. We thus have in general:

$$\mathcal{A}d\xi = - \sum_{\gamma} \sum_{\alpha} \mu_{\gamma\alpha} dn_{\gamma\alpha} \quad (6.10)$$

The fact that \mathcal{A} and the $\mu_{\gamma\alpha}$'s are here assumed to be defined for states of non-equilibrium should cause no surprise, since such quantities as ΔF , ΔH , ΔS , etc., of current thermodynamics are measured or calculated for irreversible changes. Indeed the method of deducing ΔF from electromotive

force measurements implies the existence of definite chemical potentials for states of non-equilibrium.

For the particular case where there is only one $dn_{\gamma a}$ for each reactant, i.e., when the variation of the total number of moles of the component γ takes place in only one of the phases, formula 6.10 could be written:

$$\mathcal{A} = - \sum_{\gamma} \mu_{\gamma(a)} \cdot \frac{dn_{\gamma(a)}}{d\xi} = - \sum_{\gamma} \mu_{\gamma(a)} \cdot \nu_{\gamma} \quad (6.11)$$

In the case of systems consisting of only one phase, we always have:

$$\mathcal{A} = - \sum_{\gamma} \mu_{\gamma} \nu_{\gamma} \quad (6.12)$$

When several independent reactions take place simultaneously formula 6.10 becomes:

$$\sum_{\rho} \mathcal{A}_{\rho} d\xi_{\rho} = - \sum_{\gamma} \sum_{a} \mu_{\gamma a} dn_{\gamma a} \quad (6.13)$$

VII. COMPARISON WITH CURRENT CHEMICAL THERMODYNAMICS

In this section we shall review some of the fundamental relations of thermodynamics as commonly used and show how they are modified in the present theory. ΔF at constant temperature and pressure becomes

$$\Delta F \rightarrow \left(\frac{\partial F}{\partial \xi} \right)_{pT} = - \mathcal{A} \quad (7.1)$$

ΔH is usually the ΔH that satisfies the relation:

$$\Delta F = \Delta H - T \Delta S \quad (7.2)$$

valid for processes taking place at constant temperature. It should be written:

$$\left(\frac{\partial F}{\partial \xi} \right)_{pT} = \left(\frac{\partial H}{\partial \xi} \right)_{pT} - T \left(\frac{\partial S}{\partial \xi} \right)_{pT} \quad (7.3)$$

$\left(\frac{\partial H}{\partial \xi} \right)_{pT}$ is the heat of reaction at constant temperature and pressure. We shall represent it by $-z_{pT}$. According to formulas 7.1 and 7.3 we have:

$$\mathcal{A} = z_{pT} + T \left(\frac{\partial S}{\partial \xi} \right)_{pT} \quad (7.4)$$

which is one of the exact forms of Berthelot's principle: the affinity is in general different from the heat of reaction but the difference decreases with temperature and vanishes at the absolute zero.

Kirchhoff's formula

$$\left(\frac{\partial \Delta H}{\partial T} \right)_p = \Delta C_p \quad (7.5)$$

in which ΔC_p is the sum of the heat capacities of the products less the corresponding sum for the reagents, assumes the elegant and accurate form:

$$\left(\frac{\partial z_{pT}}{\partial T}\right)_{p\xi} = - \sum_{\gamma} \nu_{\gamma} C_{p\gamma} \quad (7.6)$$

in which $C_{p\gamma}$ is the partial molar heat capacity of the constituent γ at constant p .

The Gibbs-Helmholtz formula

$$\Delta F - T\left(\frac{\partial \Delta F}{\partial T}\right)_p = \Delta H \quad (7.7)$$

becomes

$$F - T\left(\frac{\partial F}{\partial T}\right)_{p\xi} = H \quad (7.8)$$

or also

$$\left(\frac{\partial\left(\frac{F}{T}\right)}{\partial T}\right)_{p\xi} = - \frac{H}{T^2} \quad (7.9)$$

Formula 7.7 may also be written

$$\left(\frac{\partial F}{\partial \xi}\right)_{pT} - T\left(\frac{\partial^2 F}{\partial T \partial \xi}\right)_p = - z_{pT} \quad (7.10)$$

which, according to formula 7.1, is equivalent to

$$z_{pT} + T^2 \left[\frac{\partial}{\partial T} \left(\frac{A}{T} \right) \right]_{p\xi} = 0 \quad (7.11)$$

a formula which De Donder called Kelvin's formula. This list of formulas could be considerably extended. We shall limit ourselves to the foregoing examples, reserving for other communications the theory of the shifts of equilibrium and of the perturbations of chemical systems, a field in which this method is particularly powerful and yields results of great compactness and elegance. The method has been used in connection with several other fundamental problems for which formal solutions will be found in De Donder's monographs.

SUMMARY

The fundamental laws and formulas of chemical thermodynamics are given an exact and general form, thanks to the systematic use of a new variable called the degree of advancement of the reaction. A function of

the state of the system called the affinity is introduced, and its properties are studied according to De Donder's method.

Current chemical thermodynamics is critically reviewed from this point of view.

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