

ON THE EXACT SIGNIFICANCE OF THE THERMODYNAMIC QUANTITIES ΔF AND ΔF^0

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It has been customary in recent years to consider the absolute value of ΔF as a measure of the affinity of chemical reactions (3, 4). This ΔF is the finite difference between the free energy in the final state and that in the initial state, these states being separated by one occurrence of the reaction, as written in ordinary chemistry, at constant pressure and temperature. A close theoretical examination of the properties of ΔF and of the various methods used in its determination reveals certain difficulties as to its significance. In particular, what is the exact physical meaning of the so-called standard free energy change ΔF^0 defined by the relation

$$\Delta F^0 = - RT \ln K \quad (1)$$

in which K is the equilibrium constant expressed in terms of mole fractions? The closely related ΔF_1^0 defined by

$$\Delta F_1^0 = - RT \ln K_p \quad (2)$$

in which K_p is the equilibrium constant expressed in terms of partial pressures (in the case of gas reactions) also requires investigation.

Putting aside any discussion of previous writings on the subject, we shall give the exact and general definitions of these two quantities by means of a straightforward thermodynamic reasoning. Let us first indicate the notations and recall certain thermodynamic formulas. We shall present the reasoning in terms of a general chemical reaction

$$0 = \sum_{\gamma''} \nu_{\gamma''} M_{\gamma''} + \sum_{\gamma'} \nu_{\gamma'} M_{\gamma'} \quad (3)$$

The $M_{\gamma''}$'s are the chemical symbols of the components which are usually written on the left-hand side of the chemical reaction. Their coefficients $\nu_{\gamma''}$ are hence negative. The $M_{\gamma'}$'s are the chemical symbols of the components on the right-hand side. Their coefficients $\nu_{\gamma'}$ are positive. The

number of moles of the component γ will be represented by n_γ . The mole fraction of the component γ will be represented by N_γ , with

$$N_\gamma = \frac{n_\gamma}{\sum_\gamma n_\gamma} = \frac{n_\gamma}{n} \quad (4)$$

The chemical potential or partial molar free energy will be called μ_γ . We have (1, 2)

$$\mu_\gamma = \mu_\gamma^0(p, T) + RT \ln N_\gamma f_\gamma \quad (5)$$

μ_γ^0 is a function of pressure and temperature alone and is characteristic of the chemical species γ . f_γ is the activity coefficient. The equilibrium constant $K(p, T)$ is defined by

$$\ln K(p, T) = -\frac{1}{RT} \sum_\gamma \nu_\gamma \mu_\gamma^0(p, T) \quad (6)$$

The degree of advancement of the reaction will be called ξ (1). It is defined by the differential relations

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_\gamma}{\nu_\gamma} = \dots = d\xi \quad (7)$$

Calling n_γ^0 the number of moles of component γ at time zero, we have

$$n_\gamma = n_\gamma^0 + \nu_\gamma \xi \quad (8)$$

The free energy at any time t is given by

$$F = \sum_\gamma n_\gamma \mu_\gamma \quad (9)$$

or, according to equation 5,

$$F = \sum_\gamma n_\gamma \mu_\gamma^0 + RT \sum_\gamma n_\gamma \ln N_\gamma f_\gamma \quad (10)$$

In the initial state the free energy is given by equation 10 and ξ is assumed to be zero. At the time t the reaction 1 has occurred once and ξ is equal to 1. Temperature and pressure are kept constant and F becomes, according to equations 10, 8, and 4,

$$F + \Delta F = \sum_\gamma (n_\gamma + \nu_\gamma) \mu_\gamma^0 + RT \sum_\gamma (n_\gamma + \nu_\gamma) \ln \frac{n_\gamma + \nu_\gamma}{n + \nu} f_\gamma \quad (11)$$

in which

$$\nu = \sum_\gamma \nu_\gamma \quad (12)$$

and the f'_γ 's are the activity coefficients corresponding to the new composition of the system. From equations 11 and 10 we deduce

$$\Delta F = \sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^0 + RT \sum_{\gamma} \left[(n_{\gamma} + \nu_{\gamma}) \ln \frac{n_{\gamma} + \nu_{\gamma}}{n + \nu} f'_{\gamma} - n_{\gamma} \ln \frac{n_{\gamma}}{n} f_{\gamma} \right] \quad (13)$$

or also, according to equation 6,

$$\Delta F = -RT \ln K + RT \ln \prod_{\gamma} \left(\frac{n_{\gamma} + \nu_{\gamma}}{n + \nu} f'_{\gamma} \right)^{n_{\gamma} + \nu_{\gamma}} \cdot \left(\frac{n}{n_{\gamma} f_{\gamma}} \right)^{n_{\gamma}} \quad (14)$$

ΔF is thus obviously a function, not only of the mole fractions n_{γ}/n , but also of the n_{γ} 's themselves and hence of the size of the system. Let us examine the behavior of ΔF when, the initial mole fractions being kept constant, the various n_{γ} 's tend towards infinity. Formula 14 can be written

$$\Delta F = -RT \ln K + RT \ln \prod_{\gamma} \frac{\left(1 + \frac{\nu_{\gamma}}{n_{\gamma}} \right)^{n_{\gamma} + \nu_{\gamma}}}{\left(1 + \frac{\nu}{n} \right)^{n_{\gamma} + \nu_{\gamma}}} \cdot \left(\frac{n_{\gamma}}{n} \right)^{\nu_{\gamma}} \cdot \frac{f'_{\gamma}{}^{n_{\gamma} + \nu_{\gamma}}}{f_{\gamma}{}^{n_{\gamma}}} \quad (15)$$

or also

$$\Delta F = -RT \ln K + RT \ln \left\{ \frac{\prod_{\gamma} \left(1 + \frac{1}{\frac{n_{\gamma}}{\nu_{\gamma}}} \right)^{n_{\gamma}}}{\left(1 + \frac{1}{\frac{n}{\nu}} \right)^n} \cdot \prod_{\gamma} \left(\frac{n_{\gamma} + \nu_{\gamma}}{n + \nu} \right)^{\nu_{\gamma}} \cdot \frac{f'_{\gamma}{}^{n_{\gamma} + \nu_{\gamma}}}{f_{\gamma}{}^{n_{\gamma}}} \right\} \quad (16)$$

When the various n_{γ}/ν_{γ} 's tend towards infinity we have

$$\lim \left(1 + \frac{1}{\frac{n_{\gamma}}{\nu_{\gamma}}} \right)^{n_{\gamma}} = e^{\nu_{\gamma}} \quad (17.1)$$

$$\lim \left(1 + \frac{1}{\frac{n}{\nu}} \right)^n = e^{\nu} \quad (17.2)$$

$$\lim \frac{n_{\gamma} + \nu_{\gamma}}{n + \nu} = \lim \frac{n_{\gamma}}{n} = N_{\gamma} \quad (17.3)$$

and, since initial and final composition become now identical,

$$\lim f'_{\gamma} = f_{\gamma} \quad (17.4)$$

From formula 16 we then deduce

$$\lim (\Delta F)_{\text{all } n_{\gamma} \rightarrow \infty} = -RT \ln K + RT \ln \prod_{\gamma} (N_{\gamma} f_{\gamma})^{\nu_{\gamma}} \quad (18)$$

Formula 18 gives the free energy change involved in one occurrence of the reaction in an infinitely large system whose composition is defined by the N_γ 's. We thus see that the standard free energy change

$$\Delta F^0 = -RT \ln K \quad (19)$$

is a particular case of formula 18 corresponding to a composition such that

$$\prod_{\gamma} (N_{\gamma} f_{\gamma})^{\nu_{\gamma}} = 1 \quad (20.1)$$

or

$$\prod_{\gamma'} (N_{\gamma'} f_{\gamma'})^{\nu_{\gamma'}} = \prod_{\gamma''} (N_{\gamma''} f_{\gamma''})^{|\nu_{\gamma''}|} \quad (20.2)$$

This condition expresses that the product of the activities of the various components on the right-hand side of the reaction, taken with their respective exponents $\nu_{\gamma'}$, is equal to the corresponding product for the components on the left-hand side. The particular composition for which this condition is satisfied depends on the type of reaction (coefficients ν_{γ}) and on the relations between the various activity coefficients and composition. It would thus have to be determined for each individual case. Formula 20.1 is of course satisfied when all the activities are equal to unity, but such a state is often physically impossible, as can easily be realized by considering the particular case of ideal or nearly ideal systems. One could make all the activities equal to unity by separating the components in such a way that each one forms an independent phase, but the reaction is then often fictitious, although the ΔF could still be calculated (see below). The main result of this discussion is that ΔF , in order to have the exact meaning implied by its mathematical symbol, must refer to an infinitely large system.

It can easily be verified that ΔF , as given by formula 18, is simply, in absolute value, the *affinity* in De Donder's sense (1). The affinity being

$$\mathcal{A} = - \left(\frac{\partial F}{\partial \xi} \right)_{pT} \quad (21)$$

we deduce from formulas 10 and 7 and from the well-known Gibbs-Duhem formula that

$$- \mathcal{A} = -RT \ln K + RT \ln \prod_{\gamma} (N_{\gamma} f_{\gamma})^{\nu_{\gamma}} \quad (22)$$

\mathcal{A} is an intensive property and does not depend on the size of the system. ΔF is thus actually an affinity (in absolute value) and should be written $\left(\frac{\partial F}{\partial \xi} \right)_{pT}$ or $-\mathcal{A}$.

In the case of gas reactions the rather unfortunate custom of using the equilibrium constant K_p is prevalent. Between K and K_p the following relation holds

$$K_p = Kp^\nu \quad (23)$$

with

$$K_p = \prod_{\gamma} (p_{\gamma} f'_{\gamma})^{\nu_{\gamma}} \quad (24)$$

p_{γ} is the partial pressure of component γ , p the total pressure.

We have, in the case of gases

$$p_{\gamma} = N_{\gamma} p \quad (25)$$

From formulas 18 and 23 we easily deduce, for an infinitely large system,

$$\Delta F = -RT \ln K_p + RT \ln p^{\nu} \prod_{\gamma} (N_{\gamma} f_{\gamma})^{\nu_{\gamma}} \quad (26)$$

The standard free energy change

$$\Delta F_1^0 = -RT \ln K_p \quad (27)$$

thus corresponds to a state such that

$$p^{\nu} \prod_{\gamma} (N_{\gamma} f_{\gamma})^{\nu_{\gamma}} = 1 \quad (28)$$

If $\nu = 0$, this condition becomes equivalent to 20.2. If ν is different from 0, formula 28 is satisfied when we have separately

$$p = 1 \quad (29.1)$$

and

$$\prod_{\gamma'} (N_{\gamma'} f_{\gamma'})^{\nu_{\gamma'}} = \prod_{\gamma''} (N_{\gamma''} f_{\gamma''})^{\nu_{\gamma''}} \quad (29.2)$$

or also when all the $p_{\gamma} f_{\gamma}$ defined by formula 25 are equal to unity. Here again ΔF refers to an infinitely large system. One can only dispense with this restriction as to the size of the system by writing $\left(\frac{\partial F}{\partial \xi}\right)_{pT}$ instead of ΔF . Another way of explaining this point is the following: By increasing the size of the system we may have a gradual transition of the type

$$\left(\frac{\partial F}{\partial \xi}\right)_{pT} \longrightarrow \left(\frac{\Delta F}{\Delta \xi}\right)_{pT} \quad (30)$$

meaning that $\left(\frac{\Delta F}{\Delta \xi}\right)_{pT}$ becomes a better approximation for $\left(\frac{\partial F}{\partial \xi}\right)_{pT}$ as the system becomes larger. $\Delta \xi$ can only be considered as infinitesimally small

if the size of the system, i.e., the various n_γ 's, and hence F , are infinitely large. If we now make $\Delta\xi = 1$, formula 30 becomes

$$\left(\frac{\partial F}{\partial \xi}\right)_{pT} = \lim (\Delta F)_{\text{all } n_\gamma \rightarrow \infty} \quad (31)$$

It is obvious that most thermodynamic reasoning and calculations involving these quantities will be made more exact and more straightforward by using $\left(\frac{\partial F}{\partial \xi}\right)_{pT}$ instead of ΔF .

Analogous conclusions could be obtained concerning other familiar thermodynamic quantities such as ΔU , ΔH , ΔC_p , etc. For instance, $\left(\frac{\partial H}{\partial \xi}\right)_{pT}$ is equal to the instantaneous heat of reaction at constant pressure and temperature, while ΔH refers to an infinitely large system or, as is often the case in practice, it is the average heat of reaction between two states of a finite system separated by a $\Delta\xi$ equal to 1.

In practice one frequently calculates the free energy change corresponding to one occurrence of the reaction when each reactant is considered as forming an independent phase. The reaction is then often a fictitious one, but the ΔF can be calculated in a direct manner. Let us note that the building up of galvanic cells is a partial realization of this separation into independent phases. If component γ forms a phase by itself, its partial molar free energy is given by

$$\mu_\gamma = \mu_\gamma^0(p, T) \quad (32)$$

obtained by replacing both N_γ and f_γ by unity in formula 5. Let us consider $|\nu_{\gamma''}|$ moles of each component γ'' appearing in the reaction 1, each group of $|\nu_{\gamma''}|$ moles forming a separate phase. The free energy in the initial state is then

$$F_i = - \sum_{\gamma''} \nu_{\gamma''} \mu_{\gamma''}^0(p, T) \quad (33)$$

The reaction is assumed to go to completion and the final state is chosen such that there are $\nu_{\gamma'}$ moles of each component γ' in as many separate phases as there are components of this type. The free energy in the final state is then

$$F_f = \sum_{\gamma'} \nu_{\gamma'} \mu_{\gamma'}^0(p, T) \quad (34)$$

and ΔF is given by

$$\Delta F = F_f - F_i = \sum_{\gamma'} \nu_{\gamma'} \mu_{\gamma'}^0 + \sum_{\gamma''} \nu_{\gamma''} \mu_{\gamma''}^0 = \sum_{\gamma} \nu_{\gamma} \mu_{\gamma}^0 \quad (35)$$

which, according to formula 6, can also be written

$$\Delta F = - RT \ln K \quad (36)$$

We thus see that this ΔF is identical with the standard ΔF^0 studied above, for which a new interpretation is now provided.

If ΔF^0 is determined by means of the relation

$$\Delta F^0 = \Delta H^0 - T\Delta S^0 \quad (37)$$

both ΔH^0 and ΔS^0 should refer to this system of separated phases. The classical method for the calculation of ΔS^0 from the heat capacity data of the pure compounds is in agreement with this requirement. ΔH^0 is usually obtained from a combination of combustion and other thermochemical data and is only an approximation (although often a very good one) to the true ΔH^0 , since the resulting compounds (carbon dioxide and water, for instance) are mixed instead of being in separate phases. The true ΔH^0 and ΔS^0 must be such that

$$\Delta F^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K \quad (38)$$

The latter interpretation of ΔF^0 actually considers this quantity as a particular case of the ΔF given by formula 13, while in the first interpretation it is a particular case of the ΔF given by formula 18. Only in this latter case is ΔF^0 a particular value of a true function of the state of the system.

As we have shown, this function is the affinity $-\left(\frac{\partial F}{\partial \xi}\right)_{pT}$.

SUMMARY

1. The quantity ΔF is calculated by means of the fundamental thermodynamic formula $F = \sum n_\gamma \mu_\gamma$.

2. It is shown to be a function of the state of the system (pressure, temperature, and mole fractions) only if the system is infinitely large.

3. The standard $\Delta F^0 = -RT \ln K$ is discussed and its exact definition given.

4. A comparison between ΔF and the partial derivative $\left(\frac{\partial F}{\partial \xi}\right)_{pT}$ (ξ is the degree of advancement of the reaction) is presented.

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