

ONCE MORE ON ΔG OF CHEMICAL REACTION

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In a chemical thermodynamics course many students have difficulty understanding the following equation

$$\Delta G^{\circ} = - RT \ln K_p \quad (1)$$

Even gifted students find it difficult to understand the delta function and the dimensions of K_p .

The ambiguity of the delta symbol in chemical thermodynamics is the major contributing factor to this lack of understanding. The IUPAC Commission on Physicochemical Symbols in their so-called **green book (1)** wrote to this end (the IUPAC commission used the symbol H, we have substituted G for H): **Although symbols such as $\Delta_r G$ should denote the integral Gibbs energy of reaction**

$$\Delta_r G = G(\xi_2) - G(\xi_1) \quad (2)$$

in practice this symbol is usually used to denote the change divided by the amount transferred, i.e. the change per extent of reaction, defined by the equation

$$\Delta_r G = \sum_i \nu_i \mu_i = (\partial G / \partial \xi)_{T,p} \quad (3)$$

The quantity $(\partial G / \partial \xi)$ will be referred to as the partial change in the Gibbs energy.

Over the last twenty years much attention has been paid in this journal to eq 1 **(2 - 13)**. Authors seeking to

differentiate the meaning of ΔG in eq 3 from that in eq 2 have proposed the following notations: $\Delta\tilde{G}^\circ$ (4), $\Delta_{P,T}G$ (9), $\Delta\bar{G}^\circ$ (10), ΔG° (13), and the special name **the chemists' delta** (10).

The ambiguity in the delta symbol in equations 2 and 3 arose early on in the history of chemical thermodynamics, where two approaches to ΔG developed within eight years of each other, by Gibbs (1876) (14) and by Van't Hoff (1884) (15).

Gibbs' approach to chemical equilibrium, which has now become the standard in the teaching of chemical thermodynamics, uses the algebraic sum of chemical potentials, $\sum_i \nu_i \mu_i$ (the partial change in the Gibbs energy, eq 3) and does not need eq 2 at all. The historic problem with Gibbs is that he never derived anything like equation 1.

It was Van't Hoff who first wrote an equation close to eq 1. With little modification his equation can be presented as follows¹

$$W = RT \ln K_c \quad (4)$$

W here is the maximum work and is a finite difference of some function of state (say ΔG at constant temperature and pressure) and brings forth the interpretation of the delta symbol in eq 1 with the meaning of eq 2 (integral change of the Gibbs energy).

In the discussion on the problem with the chemist's delta and in the comparison between the Gibbs and Van't Hoff approaches we will follow the notation of the IUPAC Commission (1) employing a variety of subscripts and superscripts. We will start with the notation for changes: ΔZ , ΔZ_m , and $\Delta_r Z_m$ of any extensive property Z (entropy, energy, enthalpy, volume and so on) in a closed system with a single chemical reaction taking

place. Afterwards, employing this notation, we will suggest several interpretations based on both Gibbs' and Van't Hoff's approach for the quantity $\Delta_r Z_m$ and try to show why the symbol Δ may make sense here. Later on, from the criteria of chemical equilibrium we'll obtain the quantity $\Delta_r Z_m^{\circ}$ and, in turn, examine its interpretation. We will finish with a standard equilibrium constant K° and the relation between it and K_p (K_c).

The System Under Study

Let us consider a closed system containing N substances (initial numbers of moles are $n_{o,i}$) in which only one chemical reaction

$$\sum_i \nu_i B_i = 0 \quad (5)$$

can take place. Such a condition can be expressed as

$$\text{rank}(A) = N - 1$$

where A is the formula matrix **(16)**. In this simple case the change in the number of moles of each substance can be described by introducing a chemical variable ξ^2 defined by the equation

$$n_i = n_{o,i} + \xi \nu_i \quad (6)$$

or

$$dn_i = \nu_i d\xi \quad (7)$$

For any inert substances in the system (**e.g.** solvent) that do not take part in the reaction their stoichiometric numbers in eqs 5 to 8 are assumed to be equal zero.

Integral Change of An Extensive Property ΔZ

The simplest and most natural definition of a delta is the integral change of an extensive property

$$\Delta Z = Z_2 - Z_1 \quad (8)$$

where Z_2 and Z_1 are related to two states of the system with different values of ξ (see also eq 2). It is this term that is included in eq 4 and such equations as

$$\Delta U = Q_V$$

$$\Delta H = Q_P$$

$$-(\Delta F)_{V,T} = W_{\max}$$

$$-(\Delta G)_{P,T} = W_{\max}$$

Worth noting is that the value of ΔZ in eq 8 depends not only on the chemical variable, but also on external variables (**e.g.** p , T constant or V , T constant).

ΔZ as defined above is clearly an extensive property. Usually it is easier to deal with an intensive property, and as such, we can consider the mole change of ΔZ while the chemical variable is changed by one mole, $\Delta\xi = 1$. In other words, the ratio

$$\Delta Z_m = \Delta Z / \Delta\xi \quad (9)$$

but it is still the integral change of Z .

Van't Hoff in his works had used only these integral changes. The main problem with his method was that the ratio $\Delta Z / \Delta\xi$ depended on the value of $\Delta\xi$. This means that in the general case ΔZ_m is not defined properly. To cope with it, Van't Hoff had introduced the special huge box (Van't Hoff's box) within which a chemical reaction was taking place (see more below).

Partial Change in An Extensive Property $\Delta_r Z_m$

In the Gibbs' approach a differential of Z (infinitesimally small change) is used

$$dZ = (\partial Z/\partial T)_{p,n_i} dT + (\partial Z/\partial p)_{T,n_i} dp + \sum_i (\partial Z/\partial n_i)_{T,p,n_j} dn_i$$

The derivative at dn_i is known as the partial molar quantity

$$(\partial Z/\partial n_i)_{T,p,n_j} = Z'_i$$

where it is assumed that $j \neq i$.

In the case of a closed system with only one reaction taking place, changes in amounts of each of the substances depend on the chemical variable only and dZ can be rewritten, according to eqs 6 and 7, as follows

$$dZ = (\partial Z/\partial T)_{p,n_i} dT + (\partial Z/\partial p)_{T,n_i} dp + (\sum_i \nu_i Z'_i) d\xi \quad (10)$$

Thus, we have

$$\sum_i \nu_i Z'_i = (\partial Z/\partial \xi)_{T,p} \quad (11)$$

This quantity plays a very important role in chemical equilibria and may be named **a partial change of an extensive property in the chemical reaction**. That is all that is needed in the Gibbs' approach.

According to IUPAC recommendations **(1)**, it is denoted as

$$\Delta_r Z_m \equiv \sum_i \nu_i Z'_i \quad (12)$$

Note that the word **change** is usually dropped and this gives rise to such terms as the entropy of a chemical reaction $\Delta_r S_m$, the enthalpy of a chemical reaction $\Delta_r H_m$ and so on.

If there were no definition such as eq 12, there would be no need for our paper since the ambiguity in delta occurs here. The same delta used for integral changes has also been applied

to partial changes.

Let us now discuss whether the delta in eq 12 is the ordinary one. We start by comparing integral ΔZ_m and partial $\Delta_r Z_m$ in Van't Hoff's approach and continue with the possible interpretation of $\Delta_r Z_m$ in Gibbs' approach. After which we will present two examples.

Interpretation of $\Delta_r Z_m$ in Van't Hoff's Approach

First, let us consider the connection between ΔZ_m and $\Delta_r Z_m$ in the most important case when temperature and pressure of the system are kept constant in transition from the state 1 to 2. By integrating eq 10 we have

$$(\Delta Z_m)_{p,T} = (\int \Delta_r Z_m d\xi) / \Delta\xi$$

Were $\Delta_r Z_m$ not dependent on the value of the chemical variable, the change of the extensive property of the whole system $(\Delta Z_m)_{p,T}$ and the partial change of the extensive property $\Delta_r Z_m$ would be numerically equal each other

$$(\Delta Z_m)_{p,T} = \Delta_r Z_m \quad (13)$$

Equation 13 holds for all chemical reactions where Van't Hoff's box is employed - with the system containing a large number of moles of each substance, reagents and products ($n_{oi} \rightarrow \infty$). Here the change of the chemical variable by a finite value ($\Delta\xi = 1$ for example) brings an infinitesimally small change to the mole fractions (**i.e.** to composition) and leaves the partial molar quantities unchanged.

Equation 13 yields the simplest interpretation of $\Delta_r Z_m$. It shows that $\sum_i \nu_i Z'_i$ is numerically equal to the change of the extensive property of the whole system corresponding to the

change of the chemical variable on one mole at constant temperature and pressure. Thus, such interpretation shows the connection of $\Delta_r G_m$ with eq (2) and may present some explanation why the symbol delta was applied instead of the algebraic sum $\sum_i \nu_i$.

Nonetheless, it should be stressed that there is a great difference between the delta in the sense of eq 2 and 8 (per mole of change in the chemical variable, eq 9) and Δ_r^3 . Generally speaking, equation 13 applies to the case of Van't Hoff's box at constant temperature and pressure only. At the same time, $\Delta_r Z_m$ is the derivative $(\partial Z/\partial \xi)_{p,T}$ (eqs 10 to 12), and it does not correspond to any process at all, but to some state of the system under study at a given value of the chemical variable.

Such a difference gives a different meaning to the subscripts p and T in eqs 11 and 13. In eq 13 they are external variables that are kept constant in the chemical reaction. In eq 11 they are just a remainder that Z is a function of p and T while the derivative is taken. Equation 10 to 12 apply at any given set of external variables (p and T, V and T, U and V and so on).

To make this point clearer let us take the case of constant volume and temperature. To compute $(\Delta Z_m)_{V,T}$ we have to deal with the derivative $(\partial Z/\partial \xi)_{V,T}$. Analogously to eq 11 one can obtain

$$(\partial Z/\partial \xi)_{V,T} = \sum_i \nu_i (\partial Z/\partial n_i)_{V,T,n_j}$$

While considering the compound function $Z\{V(p,T;n_i), T;n_i\}$ it is possible to derive the relationship of $(\partial Z/\partial n_i)_{V,T,n_j}$ with the

correspondent partial molar quantity

$$(\partial Z / \partial n_i)_{V, T, n_j} = Z'_i - (\partial Z / \partial V)_{T, n_i} V'_i$$

From here we have

$$(\partial Z / \partial \xi)_{V, T} = \Delta_r Z_m - (\partial Z / \partial V)_{T, n_i} \Delta_r V_m$$

and

$$(\Delta Z_m)_{V, T} = \left\{ \int_{\xi=0}^{\xi} [\Delta_r Z_m - (\partial Z / \partial V)_{T, n_i} \Delta_r V_m] d\xi \right\} / \Delta \xi$$

Since there are only intensive properties under the integral one should expect, using the same arguments as above, that in the case of Van't Hoff's box the following equation will hold

$$(\Delta Z_m)_{V, T} = \Delta_r Z_m - (\partial Z / \partial V)_{T, n_i} \Delta_r V_m \quad (14)$$

Here a major difference with eq 13 occurs. The maximum work at V with T held constant is the integral change of Helmholtz energy, but $(\Delta A_m)_{V, T}$ is no longer equal to $\sum_i \nu_i A'_i$. Rather, according to eq 14 we obtain

$$(\Delta F_m)_{V, T} = \sum_i \nu_i \mu_i = \Delta_r G_m \quad (15)$$

since

$$\mu_i = A'_i - pV'_i$$

Interpretation of $\Delta_r Z_m$ in Gibbs' Approach

Another interpretation of delta in $\Delta_r Z_m$ is possible within the Gibbs' approach that arises from eq 12 (see also eq 3). In a chemical reaction the stoichiometric numbers associated with reagents are negative while those associated with products are positive. This allows us to write

$$\sum_i \nu_i Z'_i = \sum_{\nu_p > 0} \nu_p Z'_p - \sum_{\nu_r < 0} |\nu_r| Z'_r \quad (16)$$

Thus, it is possible to say that Δ_r is the difference between two states: the sum of the properties of the products minus the

sum of the properties of the reagents. This also allows us to employ the delta symbol as defined in eq 1 (and eq 12) but with a completely different meaning than as in eq 13.

However, there is a problem. The quantity $\sum_i \nu_i Z'_i$ corresponds to some state of a system at the given value of the chemical variable and at the same time it is presented (eq 16) as the difference between two different states of another systems (products and reagents), i.e. it corresponds to some state and some process at the same time.

When $\sum_i \nu_i Z'_i$ is taken as a process (eq 16), reagents and products are assumed to be under the same conditions. This would tempt us to subscript $\Delta_r Z_m$ to emphasize this: for example $(\Delta_r Z_m)_{p,T}$ or $(\Delta_r Z_m)_{V,T}$. Nonetheless, in this particular case this is nonsensical since we are talking about the state of the chemical system under study where all of the state functions are constant: $p, V, T, U, S, \text{ etc.}$ Thus, eq 16 is merely an interpretation of the basic equations 11 and 12.

Example 1. Heterogeneous Reaction Among Pure Substances

In this case each substance exists as a separate phase. The simplest case is the phase transition of an one-component system. We will consider a system comprising CaCO_3 , CaO and CO_2 . Here the overall extensive property is the sum of properties of each phase that, combined with definition of molar quantity ($Z_m = Z/n$), yields the following

$$Z = n_1 Z_{m1} + n_2 Z_{m2} + n_3 Z_{m3}$$

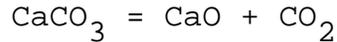
The molar quantity depends only on temperature and pressure and does not depend on amount of substance. Hence

$$(\partial Z / \partial n_i)_{T,p,n_j} = Z_{m,i}$$

For any state of the system in the example the following holds

$$(\partial Z / \partial \xi)_{T,p} = Z_m(\text{CO}_2) + Z_m(\text{CaO}) - Z_m(\text{CaCO}_3) = \Delta_r Z_m$$

while the chemical reaction is chosen as



Thus (employing the Gibbs energy), the rate of change of the Gibbs energy of the system is equal to the change of the Gibbs energy of the process when one mole of CaO and one mole CO₂ are produced from one mole of CaCO₃ at a given temperature and pressure.

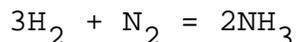
It is worth noting that in this case eq 13 will hold not only for Van't Hoff's box, but for a system of any dimension because molar quantities of separate phases do not depend on the value of the chemical variable at constant temperature and pressure.

Example 2. Homogeneous Reaction Among Ideal Gases

One of the properties of an ideal gas mixture is that the partial molar quantity of each gas depends only on its partial pressure and does not depend on the total pressure or the partial pressures of the other gases. This means that the molar quantity of a pure gas taken at the partial pressure of the gas in the gas mixture is equal to the partial molar quantity of the gas in the mixture

$$(\partial Z / \partial n_i)_{T,p,n_j} = Z_{im}(T, p_i)$$

We will now consider the synthesis of ammonia



Assuming the behavior of all gases to be ideal, one can obtain

$$(\partial Z/\partial \xi)_{T,P} = 2Z_m(\text{NH}_3, P_{\text{NH}_3}) + Z_m(\text{N}_2, P_{\text{N}_2}) - 3Z_m(\text{H}_2, P_{\text{H}_2}) = \Delta_r Z_m$$

Here (again employing the Gibbs energy), the rate of change in the Gibbs energy of the system is equal to the change of the Gibbs energy in the reaction when two moles of ammonia are produced from three moles of hydrogen and one mole of nitrogen: reactants and products being kept in separate boxes at pressures equal to the partial pressures in the system under study.

Equation 13 states that $\Delta_r G_m$ is equal to change of the Gibbs energy of an appropriate Van't Hoff's box while the chemical variable ξ is changed by one mole. This example differs from example 1 as follows. In the synthesis of ammonia eq 13 applies only for Van't Hoff's box. Changing the chemical variable produces changes in the partial pressures of the gases, thus, changing $\Delta_r G_m$ in the small system.

* * *

In the discussion above of delta in eq 12, we have tried to show how this symbol is used. We have also tried to show the possible misconceptions in the interpretation of $\Delta_r G_m$ in light of eq 12. We come to the conclusion that it would be better if eq 12 was not employed. However, since this equation enjoys such wide use, we have no choice but to use it.

Criteria of Equilibria and $\Delta_r Z_m^{\circ}$

Only one value of the chemical variable corresponds to the equilibrium state of the system while other values are associated with non-equilibrium states. The minimum of a

potential function, for example

$$\begin{array}{ll} p, T = \text{const} & \min_{\xi} (G) \\ V, T = \text{const} & \min_{\xi} (A) \end{array}$$

locates the equilibrium state for a given set of external conditions. While the minimum of the function is determined, the bounds of ξ should be kept in mind

$$-\min_{\nu_p > 0} (n_{o,p}/\nu_p) \leq \xi \leq \min_{\nu_r < 0} (n_{o,r}/|\nu_r|) \quad (17)$$

This equation comes from the condition where the amounts of substances have a non-negative value (see eq 6).

Generally speaking, the criteria for equilibrium should be written as follows

$$\begin{aligned} dG_{p,T} &= (\sum_i \nu_i \mu_i) d\xi \geq 0 \\ dA_{V,T} &= (\sum_i \nu_i \mu_i) d\xi \geq 0 \end{aligned}$$

The inequality sign \geq there signifies that at equilibrium (the minimum of the potential function) any allowable change of the chemical variable must not lower the potential function. To this end, the criteria of equilibrium differ from the criteria of spontaneity $dG_{p,T} \leq 0$ and $dA_{V,T} \leq 0$.

If $\sum_i \nu_i \mu_i$ could reach zero inside the allowable area (eq 17) for ξ , the minimum of the potential function (the equilibrium state) would be the steady state point, $dG = 0$, where $d\xi \neq 0$.

However, the situation when $\sum_i \nu_i \mu_i$ is not equal to zero within the allowable area is also quite possible. The simplest example is the system with calcium carbonate (see Example 1 above). $\sum_i \nu_i \mu_i$ in this example at a given temperature and pressure is constant, and in the common case, is not equal to

zero. Here we need inequality sign as written above to apply the criteria of equilibrium. In this case the minimum of the potential function corresponds to the absence of one of the substances when ξ reaches the margin of the allowable area (there are only two substances left at equilibrium in the example with calcium carbonate).

If the latter case is excluded from consideration and only systems where $\sum_i \nu_i \mu_i$ is able to reach zero are considered, the criteria of equilibrium will be

$$\sum_i \nu_i \mu_i \equiv \Delta_r G_m = 0$$

Writing the chemical potential as a function of a partial pressure (a fugacity, an activity) yields

$$\mu_i = \mu_i^\circ + RT \ln (p_i/p^\circ) \quad (18)$$

$$\mu_i = \mu_i^\circ + RT \ln (f_i/p^\circ) \quad (19)$$

$$\mu_i = \mu_i^\circ + RT \ln \mathbf{a}_i \quad (20)$$

Thus,

$$\Delta_r G_m^\circ = \sum_i \nu_i \mu_i^\circ = - RT \ln K^\circ$$

In the common case standard states of substances are described not only by the Gibbs energy, but also by other extensive properties and by the term $\Delta_r Z_m^\circ$.

Interpretation of $\Delta_r Z_m^\circ$

As a first approximation the meaning of $\Delta_r Z_m^\circ$ should not differ from that of $\Delta_r Z_m$. Unfortunately, this is not the case. $\Delta_r Z_m^\circ$ is obtained by introducing the standard state as the reference point for the chemical potential. However, the standard state and $\Delta_r Z_m^\circ$ do not properly apply to our system.

We will now consider the Gibbs energy $\sum_i \nu_i \mu_i^\circ$ ($\Delta_r G_m^\circ$). The

algebraic sum $\sum_i \nu_i \mu_i^\circ$ is obtained where eq 18 to 20 are employed to determine the standard state for each individual substance. However, for the sake of convenience, the standard states may be chosen independently for each substance. For example, in eq 20, the standard state of the solvent may be different from that of a salt in the solution.

Thus, $\Delta_r G_m^\circ$ does not refer straightforwardly to any real or hypothetical system with all the substances inside. On the other hand $\Delta_r G_m$ refers to a real chemical system.

This difference between $\Delta_r G_m^\circ$ and $\Delta_r G_m$ yields eq 16 as the definition for $\sum_i \nu_i \mu_i^\circ$

$$\sum_i \nu_i G_m^\circ = \sum_{\nu_p > 0} \nu_p G_m^\circ - \sum_{\nu_r < 0} |\nu_r| G_m^\circ$$

where reagents and products are in their standard states, with all substances in the separate boxes. We remind the reader that the opposite is true for $\Delta_r G_m$ - eqs 10 to 12 are the definition while eq 16 is the interpretation.

Interpretation of $\sum_i \nu_i \mu_i^\circ$ as the rate of change in the Gibbs energy (eq 11) or where Van't Hoff's box is used (eq 13) demands a special system where all the substances (products and reagents) are in their standard states. In the common case, many restrictions must apply (hypothetical states, one-way membranes and so on).

If we limit ourselves to a mixture of ideal gases (see Example 2 above), a system applying eqs 11 to 13 to interpret $\sum_i \nu_i \mu_i^\circ$ can be easily constructed. In this gas mixture each gas possesses the partial pressure equal to the pressure of the gas in its standard state. Thus, we can apply such concepts as Gibbs G° and Helmholtz A° energies to the "standard" system.

Note that the total pressure of such a system is not equal to the standard pressure but to the sum of the standard pressures of all of the gases. Using the Van't Hoff box one can arrive at the following (see eqs 13 and 15)

$$(\Delta G_m^\circ)_{p,T} = (\Delta A_m^\circ)_{V,T} = \Delta_r G_m^\circ \quad (21)$$

This equation yields a connection between the Gibbs' and Van't Hoff's approaches (see eqs 1 to 4).

K_p and K_c

Finally, we consider the problem in the dimensions of the equilibrium constant and the choice of the standard state. Dimensional analysis of eq 1 shows that the equilibrium constant is a dimensionless quantity and that its numerical value depends on the choice of the standard state (see eqs 18 to 20). As a result, to underscore this, the IUPAC commission (1) introduced the new notation K° and a new term **the standard equilibrium constant**.

The equilibrium constants K_p and K_c , which enjoy widespread use in chemistry, are dimensional. This is confirmed by IUPAC recommendations. Thus, a relationship between K° and K_p (K_c) must exist.

If the standard state is assumed to be an ideal gas at some pressure (p°) one can see from eqs 18 and 21 that

$$(\Delta G_m^\circ)_{p,T} = (\Delta A_m^\circ)_{V,T} = \Delta_r G_m^\circ = -RT \ln \{K_p/p^\circ(\Delta_r \nu)\}$$

On the other hand, if the standard state is assumed to be an ideal gas at some concentration (the symbol $^\ominus$ will denote this), the equation

$$\mu_i = \mu_i^\ominus + RT \ln (c_i/c^\ominus)$$

yields

$$(\Delta G_m^\ominus)_{p,T} = (\Delta A_m^\ominus)_{V,T} = \Delta_r G_m^\ominus = - RT \ln \{K_c / c^{\ominus(\Delta_r \nu)}\}$$

Acknowledgment

In some textbooks the equation

$$\Delta A^\ominus = - RT \ln K_c$$

may be encountered. T.M. Roshchina and her students tried to deduce this equation from eq 1 in the case of ideal gases. They came to the conclusion that if $\Delta_r A_m^\ominus$ is used in place of ΔA^\ominus this equation will not be true. She brought our attention to this matter. We thank her and our other colleagues for their helpful discussions.

We are indebted to Sherman Henzel for his help with editing the manuscript.

Acknowledgement is made to the International Science Foundation for the short term research grant in 1993.

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FOOTNOTES

¹ originally as $\ln K = - E/(2T)$. We will write also another familiar equation, one written by Van't Hoff,

$$(d \ln K)/dT = q/(2T^2)$$

and let you guess what the constant two means there.

² In our paper we prefer to use the term **the chemical variable** instead of the more usual one **the degree of advancement of the chemical reaction**. First, it is shorter, and second, the latter tempts us to think of ξ as a dimensionless value.

³ we suggest naming Δ_r as the operator of the chemical reaction