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The Meaning of Δ

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ABSTRACT: It is suggested that the Δ terms for state variables in thermodynamics be arranged in a hierarchical order, because it simplifies terminology and resolves a discrepancy in the use of Δ between chemistry and other disciplines. A term higher in the hierarchy can be used for any lower term but with loss of some information. An example, commonly said to be a mistake, is the use of $\Delta\mu$ or $\Delta_r\mu$ in place of the derivative $\partial G/\partial\xi$.

KEYWORDS: *Upper Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Thermodynamics, Nomenclature/Units/Symbols*

Usage of the Δ symbol and related subjects such as units, the extent of reaction variable ξ, and the derivative $(\partial G/\partial\xi)_{T,p}$ have been extensively discussed in this journal ever since Bent[1] famously described the use of Δ in place of $\partial/\partial\xi$ as "a weed in the field of thermodynamics". Bent says that "the problem of *per*", as in miles *per* hour, Joules *per* mole, even transcends thermodynamics. He says

> *It divides society, intellectually, into two cultures: mathematicians, scientists, and engineers whose work per permeates and those for whom per in any form is perplexing.... [In] themochemistry [sic], phase equilibria, chemical equilibria, and electrochemistry ... most of the Δ's should be uprooted and replaced with the operator ... ∂/∂ξ.*

Several authors (Craig,[2] Spencer,[3] Macdonald[4]) have suggested alternative units and symbols to avoid this supposed incorrect usage of Δ. Related to this there are many discussions of how to use the extent of reaction variable ξ, and the meaning of $(\partial G/\partial\xi)_{T,p}$.

The IUPAC (Cohen et al.,[5] p 60) seems to agree with Bent. It says that "Δ denotes a change in an extensive quantity for a process" (having, e.g., units of J or kJ), but they go on to say that adding a subscript (subscript r) "denotes a change in the property" (having, e.g., units of kJ mol^{-1}). Bent did not offer an alternative symbol for a difference in intensive units but would certainly not agree to the use of any kind of delta, even a subscripted one. Engineers would find these distinctions strange. Chemists are free to define symbols as they wish, but there is some disadvantage in having a common mathematical symbol used differently than in other subjects. Bent[1] says, "Nowhere else does 'Δ' stand for 'per.'" This is true but too restrictive. A more general statement is that nowhere else in science are units of *any* kind associated with the notation Δ (or a subscripted version such as Δ_r). The delta symbol refers to any finite difference; it cares nothing about units. It could be a difference of 10 kg in the weight of a bag of potatoes after more are added, a difference of 10 mph as a car accelerates from 40 to 50 mph, a difference of 10 m^3/min in the discharge of a turbine, a difference of 10 cm^3 of beer in a bottle after some is poured. Some are *per* terms, some are not, it makes no difference to the use of Δ. In other words, it seems that nonchemists would make no distinction between kJ and kJ mol^{-1} or cm^3 and cm^3 mol^{-1} in the use of Δ.

THE HIERARCHY OF DELTAS

A logical relationship between the deltas of state variables in thermodynamics is suggested in Figure 1, using enthalpy as an example. The most general term for a change is simply ΔH. In a hierarchical scheme this would refer to any change in enthalpy, whatever the units involved. A special case is the ΔH between the products and reactants of a chemical reaction called $\Delta_r H$, so this represents a subset of the more general term ΔH. A special kind of chemical reaction involves only pure compounds or solutes in ideal states whose thermodynamic parameters can be found in standard reference tables, and so a subset of all $\Delta_r H$ values can be called $\Delta_r H^\circ$, to indicate that all products and reactants are in their standard states. A special case of $\Delta_r H^\circ$ is the reaction in which a compound is formed from its elements, all in their standard states, called $\Delta_f H^\circ$.

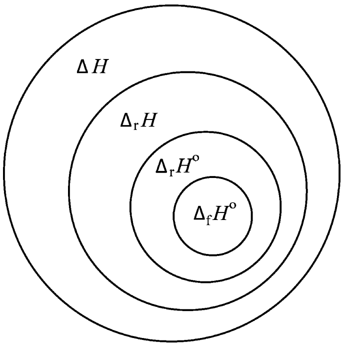

Figure 1. Hierarchy of the deltas of state variables, using enthalpy as an example.

All these terms may have units of kJ or kJ mol^{-1}, depending on what process is referred to. ΔH with no qualifying subscripts or superscripts will often refer to an entire system changing from one equilibrium state to another and, hence, will have extensive (e.g., J or kJ) units, but this need not be a rule, it is just normal practice. In Figure 1 it includes all the other varieties, so it could be used to refer collectively to them, or, if it should happen to be used in place of any of the other more

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explicit terms, it would be less informative but not illegal. An example of this involving $\Delta\mu$ is discussed later. All the other terms having the symbol Δ_r refer to chemical reactions. Commonly data from standard reference sources for individual species are simply added algebraically to give the difference term for the generalized reaction and will have intensive or molar units, but in specific cases where the masses of some or all of the reacting species are required the units will be extensive.

THE MEANING OF $(\partial G/\partial \xi)_{T,P}$

A more important question is the usage and meaning of $(\partial G/\partial\xi)_{T,p}$. To discuss this we take an example from McQuarrie and Simon[6] (p 1058). They consider the reaction

$$N_2O_4(g) = 2NO_2(g) \tag{1}$$

where $\Delta_f G°_{N_2O_4} = 97.787$ kJ mol^{-1} and $\Delta_f G°_{NO_2} = 51.258$ kJ mol^{-1}. This example is also discussed by Raff.[7] Briefly, after defining the mole fractions

$$x_{N_2O_4} = \frac{1-\xi}{1+\xi} \quad \text{and} \quad x_{NO_2} = \frac{2\xi}{1+\xi} \tag{2}$$

the Gibbs energy of the system as a function of ξ at 1 bar and 298.15 K is shown to be (McQuarrie and Simon's[6] eq 26.22).

$$G = (1-\xi)(97.987 \text{ kJ mol}^{-1}) + 2\xi(51.258 \text{ kJ mol}^{-1}) + (1-\xi)RT\ln\frac{(1-\xi)}{(1+\xi)} + 2\xi RT\ln\frac{2\xi}{(1+\xi)} \tag{3}$$

G on the left side is actually $(G - G°_{N_2O_4} - 2G°_{NO_2})$, but McQuarrie and Simon define the two standard state terms to be zero. In any case being constants they drop out on differentiation. The slope of the tangent to the curve is

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,p} = 2\mu_{NO_2} - \mu_{N_2O_4} \tag{4}$$

which equals 9.592 kJ mol^{-1} at $\xi = 0.8$ mol.

The right side of eq 4 is clearly a difference in μ terms. According to the hierarchy of delta terms in Figure 1, referring to this difference as a finite difference with the symbol $\Delta_r\mu$ or even $\Delta\mu$ is not wrong or even misleading, it just conveys less information than does the derivative.

Bent,[1] Craig[2] and others say that the units involved are actually only a symptom of the real problem, which is that all "per" terms (such as a difference in chemical potentials in this case) are rates of change and, therefore, are *not finite differences*. For example Craig[2] (p 668) says that an expression such as eq 4 is a *measure of a process* in which the reaction advances to only an *incremental* extent, so no perceptible change takes place in any state variables. Alternatively, one can imagine a very large system (Cohen and Whitmer[8] suggest "a dirigible full of an isomer mixture, for example") for which a finite change in the chemical potentials does not alter any other state variables. This point of view conflates the properties of real systems with the mathematical formalism of thermodynamics. The curve in Figure 2 represents a continuous differentiable function (eq 3) representing an idealized reaction, not a real one. At each point on the curve the derivative is a fixed and known quantity, and therefore the difference in chemical potentials also has a fixed value. Gibbs[9] (p 39) and many others have pointed out that only equilibrium states can be plotted on diagrams such as Figure 2, which is another way to say the same thing. The real irreversible process for this reaction cannot be plotted on a diagram. There is no need to suggest a different symbol for $\Delta\mu$ as do Craig,[2] Spencer,[3] and MacDonald.[4] Anderson[10] has discussed this in more detail.

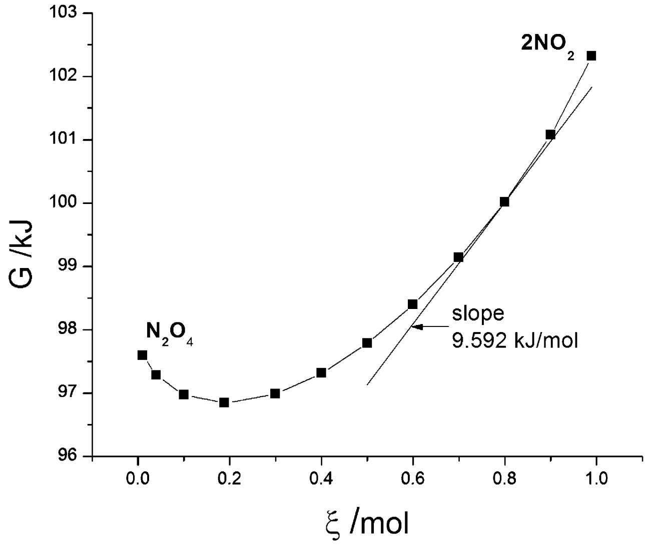

Figure 2. Gibbs energy in kJ of the system N_2O_4−NO_2 as a function of extent of reaction ξ mol. The tangent $(\partial G/\partial\xi)_{T,p}$ having a slope of 9.592 kJ mol^{-1} is shown at $\xi = 0.8$ mol.

G vs ξ is plotted in Figure 2 and $(\partial G/\partial\xi)_{T,p}$ in Figure 3. An example of a tangent obeying eq 4 is shown in Figure 2. The minimum, where stable equilibrium is established, occurs at $\xi = 0.1892$ mol.

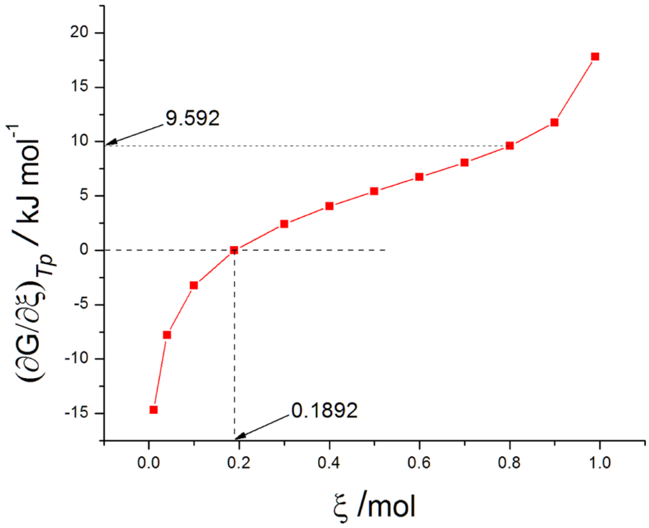

Figure 3. Derivative $(\partial G/\partial\xi)_{T,p}$ of the curve in Figure 2 as a function of ξ.

The value of $\xi = 0.1892$ mol (eq 4 and Figure 3) can be used to calculate the equilibrium mole fractions of the two species in this reaction using eqs 2. The fact that we can calculate equilibrium compositions in real systems is of course one of the most useful functions of thermodynamics. Equations 2 can also be used to calculate the equilibrium constant, as shown by McQuarrie and Simon. Equation 3 and Figure 2 constitute a nice demonstration of a system achieving a minimum in Gibbs energy, but they are idealized and have no connection with how the real reaction actually proceeds, which is the subject of reaction kinetics and reaction mechanisms.

Finally, returning to the subject of the notation used for extensive vs intensive variables, an important fact about the derivative $(\partial G/\partial \xi)_{T,p}$ is that G represents the Gibbs energy of the *system*, not the reaction. The reaction, eq 1, reaches equilibrium, but it is the *system*, with all its phases and components, which achieves a minimum Gibbs energy. This implies that all possible reactions and phase changes, not just the one being considered, also reach equilibrium. The chemical potential is another example of the importance of distinguishing between the system G and individual species G_m. So in emphasizing the difference between a change involving a total system and a change in a specific reaction Bent[1] was emphasizing an important point. But the difference is not and should not be signaled by the delta symbol, it is signaled by a difference in the symbol used for the thermodynamic variable itself, i.e., H and H_m, V and V_m, etc. This difference is more important than the mere adding of a subscript would suggest.

■ CONCLUSIONS

The suggested hierarchy of delta terms in thermodynamics simplifies discussions as to their proper use and resolves a discrepancy in the use of Δ between chemistry and other disciplines. Alternative symbols suggested by Craig[2] and others become unnecessary.

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Notes

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