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The Thermodynamics of Chemical Reactions at High Pressures

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Synopsis. A "thermodynamic" derivation by Jee of a simple proportionality between the effects of pressure on the enthalpy change ΔH and the entropy change ΔS for a chemical reaction in solution, is shown to be erroneous.

In a recent paper,[1)] J.-G. Jee has presented a derivation "from the basic thermodynamic equation(s)," of a simple proportional relationship between the influence of pressure on the molar change of enthalpy ΔH for a chemical reaction and its corresponding influence on the molar change of entropy ΔS.

Jee[1)] began by applying one of the Maxwell relations to derive the formula

$$(\partial H/\partial p)_T = (T - 1/\alpha)(\partial S/\partial p)_T, \tag{1}$$

where p denotes the pressure and T the absolute temperature. This is a standard thermodynamic relation [it is given, for example, by combining Guggenheim's[2)] formulae (1.47.4) and (1.48.4)], linking the pressure derivatives of the total enthalpy H and the total entropy S of a closed homogeneous phase in the absence of a chemical reaction: α denotes the coefficient of thermal expansion of the phase,

$$\alpha = (\partial V/\partial T)_p/V, \tag{2}$$

where V is the total volume of the phase.

Jee[1)] then assumed that a relation similar to Eq. 1 applies to a chemical equilibrium, with H and S being replaced by ΔH and ΔS, denoting changes of enthalpy and entropy accompanying the reaction. On that basis, and assuming α to be independent of p, he integrated Eq. 1 to obtain his relation (Eq. 12):

$$\Delta H^{\mathrm{p}} - \Delta H^{\circ} = (T - 1/\alpha)(\Delta S^{\mathrm{p}} - \Delta S^{\circ}), \tag{3}$$

where the superscripts $^{\mathrm{p}}$ and $^{\circ}$ indicate values at a high pressure and at atmospheric pressure, respectively. He took that formula to mean that there is a "theoretical" linear relationship between $\Delta H^{\mathrm{p}} - \Delta H^{\circ}$ and $\Delta S^{\mathrm{p}} - \Delta S^{\circ}$.

If Jee's relation were correct, it might be useful. However, it is not correct.

In dealing with a chemically reacting system we need to consider, not the total quantities H, S, and V for the mixture, but the behavior of the corresponding *partial molar* quantities for the reacting species and for the products. If, for a particular species J, we write these as H_{J}, S_{J}, and V_{J}, then a relation analogous to Eq. 1 holds between the partial molar functions of J in the form

$$(\partial H_{\mathrm{J}}/\partial p)_T = (T - 1/\alpha_{\mathrm{J}})(\partial S_{\mathrm{J}}/\partial p)_T, \tag{4}$$

where α_{J} is defined[3)] as

$$\alpha_{\mathrm{J}} = (\partial V_{\mathrm{J}}/\partial T)_p/V_{\mathrm{J}}. \tag{5}$$

Taking the simple case of a chemical reaction equilibrium,

$$\mathrm{A} \rightleftarrows \mathrm{B}, \tag{6}$$

between two species A and B in a homogeneous mixture, we have

$$\Delta H = H_{\mathrm{B}} - H_{\mathrm{A}} \tag{7}$$

and

$$\Delta S = S_{\mathrm{B}} - S_{\mathrm{A}}, \tag{8}$$

where ΔH is the difference between the partial molar enthalpy (or standard partial molar enthalpy) of the product and that of the initial species; ΔS is the corresponding difference of entropy.

Combining Eqs. 4, 7, and 8, we obtain

$$(\partial \Delta H/\partial p)_T = (T - 1/\alpha_{\mathrm{B}})(\partial \Delta S/\partial p)_T + (1/\alpha_{\mathrm{A}} - 1/\alpha_{\mathrm{B}})(\partial S_{\mathrm{A}}/\partial p)_T, \tag{9}$$

and if we make an additional (usually unjustified) assumption that α_{A} and α_{B} are independent of p, we can integrate Eq. 9 to obtain

$$\Delta H^{\mathrm{p}} - \Delta H^{\circ} = (T - 1/\alpha_{\mathrm{B}})(\Delta S^{\mathrm{p}} - \Delta S^{\circ}) + (1/\alpha_{\mathrm{A}} - 1/\alpha_{\mathrm{B}})(S_{\mathrm{A}}^{\mathrm{p}} - S_{\mathrm{A}}^{\circ}). \tag{10}$$

More complex relations apply if more than two species take part in the reaction.

Unlike the supposed relation (Eq. 3), the correct formula (Eq. 10) does *not* represent a simple proportionality between $\Delta H^{\mathrm{p}} - \Delta H^{\circ}$ and $\Delta S^{\mathrm{p}} - \Delta S^{\circ}$. It would do so only if additional conditions were met—namely, either (a) that $\alpha_{\mathrm{B}} = \alpha_{\mathrm{A}}$, which is improbable (particularly so for ionic reactions), or (b) that S_{A} and S_{B} have the same functional dependence upon p. These are both *extra*-thermodynamic conditions, and the second resembles El'yanov's[5)] assumption of a "linear free energy relation" for the effects of pressure on equilibrium constants, which enabled him to derive an expression similar to Eq. 3

Criticisms analogous to the above apply also to Jee's[1)] supposed enthalpy/volume and entropy/volume relations.

Finally, when we come to examine Jee's[1)] experimental evidence for linear correlations between ΔH and ΔS, we encounter a difficulty, because it is impossible to reconcile the values of ΔH, ΔS, and ΔV that he has listed in his Table 2 and plotted in Fig. 1, with the experimental values of the equilibrium constants K that he has reported in Table 1. For instance, his listed values of ΔV have both the wrong sign and the wrong magnitude [his formula (Eq. 9) for ΔV is, in any case, incorrect[6)] when applied to values of K having volume concentration units ($\mathrm{dm^3\,mol^{-1}}$)]. Also, the equilibrium constants yield values of ΔH and ΔS that show large and random scatter, with no indication whatever of the smooth trends suggested in Jee's Table 2.

Admittedly, they give good linear plots of ΔH versus ΔS, with slopes near the experimental temperature, ca. 300 K; but that is precisely the behavior that would arise from random errors in the experimental temperature dependences of the K.

References

1) J.-G. Jee, *Bull. Chem. Soc. Jpn.*, **60**, 4483 (1987).

2) E. A. Guggenheim, "Thermodynamics," North Holland, Amsterdam (1967), p. 39.

3) The derivative α_J, defined in this way, should not be confused with the 'partial molar expansivity' of J, which is conventionally defined[4] as $(\partial V_J/\partial T)_p$.

4) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold, New York (1963), p. 370.

5) B. S. El'yanov, *Aust. J. Chem.*, **28**, 933 (1975); B. S. El'yanov and E. M. Vasylvitskaya, *Rev. Phys. Chem. Jpn.*, **50**, 169 (1980).

6) S. D. Hamann and W. J. le Noble, *J. Chem. Educ.*, **61**, 658 (1984).