CORRECT CALCULATION OF ΔH^0, ΔC_p^0, AND ΔV^0 FROM TEMPERATURE AND PRESSURE DEPENDENCES OF EQUILIBRIUM CONSTANTS: THE IMPORTANCE OF THERMAL EXPANSION AND COMPRESSIBILITY OF THE SOLVENT

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ABSTRACT

Activities of solutes and compositions of solutions may be expressed correctly in terms of molarity (c), molality (m) or mole fraction (x), leading to corresponding equilibrium constants K_c, K_m, or K_x. Equations for differences between ΔG_c^0, ΔG_m^0, and ΔG_x^0 values are derived. Common errors in calculations involving ($\mathrm{d}\ln K_c/\mathrm{d}T$) and ($\mathrm{d}\ln K_c/\mathrm{d}P$) are identified and remedies for these errors are presented.

INTRODUCTION

It is common and useful to calculate enthalpies, entropies, and heat capacities from equilibrium constants at different temperatures. Similarly, it is possible to obtain changes in volume and compressibilities from equilibrium constants at different pressures. Unfortunately, these calculations are often carried out incorrectly. It is the purpose of this paper to identify these errors and to show how to eliminate or correct them.

THERMODYNAMIC CALCULATIONS

We begin by considering a reaction that we represent by

$$y\ \mathrm{Y} = z\ \mathrm{Z} \ \text{(all in solvent A)} \tag{1}$$

The thermodynamic equilibrium constant for this reaction is

$$K = [\mathrm{Z}]^z/[\mathrm{Y}]^y \tag{2}$$

in which brackets indicate appropriate activities of the solute species Y and Z. Activities of solutes are related to compositions of solutions and to chosen standard states as described in various textbooks [1—3]. Most investigations of interest here are based on activities defined so that activity coefficients approach unity at infinite dilution. Compositions of solutions are generally expressed in terms of molarity (c), molality (m), or mole fraction

(x), and thence equilibrium constants as in eqn. (2) can be represented by K_c, K_m, or K_x. Each of these equilibrium constants can be thermodynamically sound and each can offer advantages in terms of convenience of evaluation from experimental results or suitability for theoretical interpretation in relation to some particular model. We do not imply here or later that one kind of K is in any way inferior to other kinds. But we do point out that K_c, K_m, and K_x are not generally numerically equal; these different K values lead to different standard free energies (ΔG_c^0, ΔG_m^0, and ΔG_x^0) calculated from $\Delta G^0 = -RT\ln K$. Further, we especially emphasize that some calculations with K_c values are frequently done incorrectly. The principal focus of this paper is on these incorrect calculations with K_c values at different temperatures or pressures.

Equilibrium constants for reaction (1) are related to each other as in

$$K_x = K_m(s)^{y-z} = K_c(s\rho)^{y-z} \tag{3}$$

in which s represents the number of moles of solvent A per kilogram of solvent and ρ is the density of solvent A. Differences between standard free energy changes associated with the various equilibrium constants are given by the following

$$\Delta G_c^0 - \Delta G_m^0 = (y-z)RT\ln(\rho) \tag{4}$$

$$\Delta G_m^0 - \Delta G_x^0 = (y-z)RT\ln(s) \tag{5}$$

$$\Delta G_c^0 - \Delta G_x^0 = (y-z)RT\ln(s\rho) \tag{6}$$

Application of $d\Delta G^0/dT = -\Delta S^0$ to eqns. (4)—(6) leads to equations for the differences between ΔS_c^0, ΔS_m^0, and ΔS_x^0. Because ΔG^0 and ΔS^0 values for a given reaction depend partly on human choices of standard states and composition scales, it is necessary to be careful about interpreting these values.

It is common to obtain the standard enthalpy of reaction by application of the van't Hoff equation

$$\Delta H^0 = RT^2(d\ln K/dT) = -T^2[d(\Delta G^0/T)dT] \tag{7}$$

The corresponding change in heat capacity can be obtained from

$$\Delta C_p^0 = d\Delta H^0/dT = R[2T(d\ln K/dT) + T^2(d^2\ln K/dT^2)] \tag{8}$$

Because s in eqns. (3) and (5) is independent of temperature, we obtain exactly the same (correct) ΔH^0 from application of eqn. (7) to either K_m or K_x values. This ΔH^0 value is the same as can be obtained (in principle, at least) from calorimetric measurements. It follows that ΔC_p^0 values may be obtained correctly by way of eqn. (8) applied to either K_x or K_m values.

Because ρ in eqns. (3), (4) and (6) depends on temperature, application of eqn. (7) to K_c values leads to a different ΔH^0 value than is obtained by way of K_x or K_m values. This "ΔH_c^0" value obtained by direct application of eqn. (7) to K_c values is incorrect. Formal proof that this "ΔH_c^0" value is not the correct "standard state-infinite dilution" ΔH^0 follows from Wall's treatment of the temperature dependence of activities [3]. Because it is incorrect to apply eqn. (7) directly to K_c values, it is also incorrect to apply eqn. (8) directly to K_c values.

It is possible to obtain ΔH^0 and ΔC_p^0 values correctly from K_c values at different temperatures as follows. One way is to use the solvent density at each temperature in eqn. (3) to convert K_c values to corresponding K_m values, or to use both s and ρ values in eqn. (3) to convert K_c values to K_x values, and then apply eqns. (7) and (8). Another way is based on the substitution of $K_c(\rho)^{y-z}$ for K_m or $K_c(s\rho)^{y-z}$ for K_x in eqn. (7) to obtain

$$\Delta H^0 = RT^2(\mathrm{d}\ln K_c/\mathrm{d}T) + (y-z)RT^2(\mathrm{d}\ln\rho/\mathrm{d}T) \qquad (9)$$

Equation (9) can also be expressed in terms of the coefficient of thermal expansion of the solvent, $\alpha = V^{-1}(\mathrm{d}V/\mathrm{d}T)$

$$\Delta H^0 = RT^2(\mathrm{d}\ln K_c/\mathrm{d}T) - (y-z)RT^2\alpha \qquad (10)$$

Equation (10) was derived long ago by Guggenheim [4].

For water as solvent at 298 K, the "correction term" on the far right of eqns. (9) and (10) is calculated from densities or the coefficient of thermal expansion [5] to be $(y-z)188$ J mole^{-1}. Most organic solvents have considerably larger coefficients of thermal expansion than has water, leading to correspondingly larger "correction terms". The "correction term" in eqns. (9) and (10) becomes larger at higher temperatures.

Further differentiation of eqn. (10) leads to

$$\Delta C_p^0 = R[2T(\mathrm{d}\ln K_c/\mathrm{d}T) + T^2(\mathrm{d}^2\ln K_c/\mathrm{d}T^2)] - \\ (y-z)R[2T\alpha + T^2(\mathrm{d}\alpha/\mathrm{d}T)] \qquad (11)$$

For water at 298 K the "correction term" here amounts to $(y-z)$ 8.6 J K^{-1} mole^{-1}.

A treatment analogous to eqns. (9) and (10) is sometimes needed in connection with "distribution constants" and calculated enthalpies of transfer. Consider the equilibrium distribution of Y between two solvents represented by

$$Y \text{ (in A)} = Y \text{ (in B)} \qquad (12)$$

and the corresponding equilibrium constant

$$K = [Y]_B/[Y]_A \qquad (13)$$

Again, eqn. (7) is directly applicable to K_x and K_m values, while direct application to K_c values is incorrect. Instead, the correct equation is

$$\Delta H^0 = RT^2(\mathrm{d}\ln K_c/\mathrm{d}T) + RT^2(\alpha_B - \alpha_A) \qquad (14)$$

in which α_A and α_B are the coefficients of thermal expansion of solvents A and B. For water and an organic solvent at 298 K the "correction term" on the far right of eqn. (14) is usually greater than 0.5 kJ mole^{-1}.

Equilibrium constants at different pressures lead to the standard state change in volume by way of

$$\Delta V^0 = -RT(\mathrm{d}\ln K/\mathrm{d}P) \qquad (15)$$

This equation is directly applicable to K_m and K_x values, but it is not correct to apply eqn. (15) to K_c values. Instead, K_c values should be used in

$$\Delta V^0 = -RT(\mathrm{d}\ln K_c/\mathrm{d}P) - (y-z)RT\kappa \qquad (16)$$

in which $\kappa = -V^{-1}(dV/dP)$, the compressibility coefficient of the solvent. This equation has been derived previously by Guggenheim [4] and by Hamann [6]. For water at 298 K the "correction term" on the far right of eqn. (16) amounts to $(y - z)$ 1.1 cm^3 mole^{-1}.

SUMMARY

Equations (7), (8) and (15) are directly applicable only to equilibrium constants expressed in terms of activities that are themselves defined in terms of temperature and pressure independent measures of composition, such as K_x or K_m, but not K_c. Correct calculations with K_c values must include coefficients of thermal expansion and compressibility. Equations presented here illustrate the importance of clearly specifying standard states and composition scales.

As Guggenheim [4] has previously pointed out, the principles and equations presented here also apply to $(dlnk/dT)$ and $(dlnk/dP)$ calculations with rate constants.

ACKNOWLEDGEMENTS

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