

# Some Observations Concerning the van't Hoff Equation

From a survey of several textbooks of introductory physical chemistry (1-6) which are, taken together, in very wide use at the present time, the impression is obtained that the integrated form of the van't Hoff equation

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + C \quad (1)$$

where  $K_a$  is the thermodynamic equilibrium constant in terms of activities,  $\Delta H^\circ$  is the standard enthalpy change for the reaction,  $R$  is the gas constant,  $T$  is the absolute temperature, and  $C$  is a constant of integration, is usually obtained by an unnecessarily complicated procedure. First, the Gibbs-Helmholtz equation is derived, making use of, among other things, the Maxwell equations, and then the relationship

$$\Delta G^\circ = -RT \ln K_a \quad (2)$$

where  $\Delta G^\circ$  is the standard Gibbs free energy change, is used to obtain the differential form of eqn. (1), i.e.,

$$(d \ln K_a / dT) = \Delta H^\circ / RT^2 \quad (3)$$

An integration on the assumption that  $\Delta H^\circ$  is independent of the temperature then yields eqn. (1). (The derivative in eqn. (3) sometimes appears as a partial derivative with the pressure constant, but since, by virtue of their definitions, neither  $K_a$  nor  $\Delta H^\circ$  can depend at all on the pressure of the system of interest, this partial derivative must be equal to the total derivative.) Not only is this procedure unnecessarily complicated, it gives no physical significance to the constant of integration. (It is not very illuminating to say that  $C$  is the value that  $\ln K_a$  would have at infinite temperature if  $\Delta H^\circ$  were independent of  $T$  over its entire range.)

It is difficult to understand why a much more simple procedure has been avoided so consistently. If one makes use of the relationship

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

which is valid for any isothermal change, and equates the right-hand members of eqns. (2) and (4) the result

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (5)$$

is obtained immediately. Not only is this procedure more simple, the result is more general. Equation (5) gives the correct physical interpretation of the "constant"  $C$  and has the additional advantage of being valid whether  $\Delta H^\circ$  and  $\Delta S^\circ$  are constant or not. It would not be correct to challenge the above derivation with the statement: "Equation (4) applies only to isothermal processes while eqn. (5) is supposed to apply at different temperatures." Equation (4) is valid at any temperature. All that is required is that the "reactants" and "products" be at the same temperature—which is the

only situation in which  $K_a$  has meaning. It is interesting to note that at least one textbook of chemistry for freshmen (7) gives the above derivation and several textbooks give, in another connection, the relationship

$$K = \exp(-\Delta H^\circ / RT) \exp(\Delta S^\circ / R)$$

without pointing out the equivalence of this to the van't Hoff equation.

If  $\Delta C_p^\circ$ , the heat capacity of all products in their standard states minus the heat capacity of all reactants in their standard states, is zero for a given range of  $T$  then  $\Delta H^\circ$  and  $\Delta S^\circ$  will be independent of  $T$  over this range and eqn. (5) indicates that a plot of  $\ln K_a$  versus  $1/T$  should be a straight line from whose slope  $\Delta H^\circ$  may be evaluated in the usual way. Using eqn. (5) instead of eqn. (1) makes it clear that the intersection of this line with the  $\ln K_a$  axis (at  $1/T = 0$ ) may be multiplied by  $R$  to get  $\Delta S^\circ$ . Even if  $\Delta C_p^\circ$  is not zero but is some function of  $T$ , so that the plot of  $\ln K_a$  versus  $1/T$  is not a straight line, the value of  $\Delta H^\circ$  for a particular temperature may still be obtained from the slope of the line tangent to the curve at the corresponding value of  $1/T$ , and the intersection of this tangent line with the  $\ln K_a$  axis will give  $\Delta S^\circ / R$  for this temperature. This would not be true if  $\Delta H^\circ$  and  $\Delta S^\circ$  were completely independent functions of the temperature, but in fact they are related since

$$\frac{d\Delta H^\circ}{dT} = \Delta C_p^\circ \quad (6)$$

and

$$\frac{d\Delta S^\circ}{dT} = \frac{\Delta C_p^\circ}{T}$$

Here, again, since the enthalpy and entropy changes refer to standard states, the derivatives are total and do not have to be restricted to constant pressure. Setting  $1/T = x$  and differentiating eqn. (5) with respect to  $x$ , noting that  $dT/dx = -1/x^2 = -T^2$ , yields

$$(d \ln K_a / dx) = -\Delta H^\circ / R - (1/RT)(d\Delta H^\circ / dT)(-T^2) + (1/R)(d\Delta S^\circ / dT)(-T^2) \quad (7)$$

Substitution of eqn. (6) into eqn. (7) yields

$$(d \ln K_a / dx) = -\Delta H^\circ / R \quad (8)$$

so it is seen that the slope of the tangent line bears the same relation to  $\Delta H^\circ$  as did the slope of the linear function in the case of  $\Delta C_p^\circ = 0$ . Furthermore, since the equation of the line which is tangent to the curve at the point  $x'$  is  $y = (-\Delta H^\circ(T')/R)x + I$ , where  $\Delta H^\circ(T')$  is the value of  $\Delta H^\circ$  at the temperature  $T' = 1/x'$ , and  $I$  is the intersection of this line with the  $\ln K_a$  axis, and must also satisfy the conditions  $y = \ln K_a(T')$  when  $x = x'$ , it can be seen that  $I = \Delta S^\circ(T')/R$ .

Although no assumptions of ideality are made in the foregoing discussion, it must be remembered when applying the above relationships to the analysis of experimental results that the value of "equilibrium constants" obtained in many experiments are in terms of pressures or concentrations rather than activities and thus may differ appreciably from  $K_a$ . Use of such values in the above equations may, of course, yield only rough values for  $\Delta H^\circ$  and  $\Delta S^\circ$ .

Of course, none of these observations is really new. The point of interest is that the very simple derivation given above has been almost generally ignored by textbooks and thus, presumably, by most instructors, in favor of a somewhat more complicated and less general procedure. When a derivation may be simplified without loss of rigor or generality might it not be to the advantage of the student that this be done?

#### Literature Cited

- (1) BARROW, G. M., "Physical Chemistry" (2nd ed.), McGraw Hill Book Co., New York, 1966, pp. 230-2.
- (2) CASTELLAN, G. W., "Physical Chemistry," Addison-Wesley Publishing Co., Reading, Mass., 1964, pp. 215-17.
- (3) DANIELS, F., AND ALBERTY, R. A., "Physical Chemistry" (3rd ed.), John Wiley & Sons, Inc., New York, 1966, pp. 207-8.
- (4) EGGERS, D. F., JR., GREGORY, N. W., HALSEY, G. D., JR., AND RABINOVITCH, B. S., "Physical Chemistry," John Wiley & Sons, Inc., New York, 1964, pp. 312-15.
- (5) MARON, S. H., AND PRUTTON, C. F., "Principles of Physical Chemistry," (4th ed.), The Macmillan Co., New York, 1965, pp. 248-51.
- (6) MOORE, W. J., "Physical Chemistry" (3rd ed.), Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, pp. 180-1.
- (7) MAHAN, B. H., "College Chemistry," Addison-Wesley Publishing Co., Reading, Mass., 1966, pp. 307-9.

