

# PHYSICAL CHEMISTRY

FIFTH EDITION

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where  $C$  is an integration constant. Comparison of this equation with equation 4.46 shows that it may be written

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4.49)$$

According to this equation a plot of  $\ln K$  versus  $1/T$  has a slope of  $-\Delta H^\circ/R$  and an intercept at  $1/T = 0$  of  $\Delta S^\circ/R$ . If a straight line is not obtained,  $\Delta H^\circ$  and  $\Delta S^\circ$  depend on the temperature. The value of  $\Delta H^\circ$  at any temperature may be calculated from the slope of the plot at that temperature.

Data are given in Table 4.2 for the equilibrium constants at different temperatures for the reaction  $\text{N}_2(g) + \text{O}_2(g) = 2\text{NO}(g)$ .

**Table 4.2** Equilibrium Constants for the Reaction  $\text{N}_2(g) + \text{O}_2(g) = 2\text{NO}(g)$

$T/\text{K}$	1900	2000	2100	2200	2300	2400	2500	2600
$K_p/10^{-4}$	2.31	4.08	6.86	11.0	16.9	25.1	36.0	50.3

In Fig. 4.3 the values of  $\ln K_p$  are plotted against  $1/T$ , and it is evident that a straight line is produced. The standard enthalpy change for the reaction  $\Delta H^\circ$  in the range 1900–2600 K can be calculated from the slope of the line as follows.

$$\begin{aligned} \Delta H^\circ &= -\text{slope} \times R = -(-2.19 \times 10^4 \text{ K})(1.987 \text{ cal K}^{-1} \text{ mol}^{-1}) \\ &= 43,500 \text{ cal mol}^{-1} \end{aligned}$$

The intercept of Fig. 4.3 at  $1/T = 0$  can be calculated from the experimental value of  $K_p$  at some temperature and the slope. The intercept may be used to calculate the standard entropy change  $\Delta S^\circ$  according to equation 4.49.

$$\frac{\Delta S^\circ}{R} = 12.36$$

$$\Delta S^\circ = (12.36)(1.987 \text{ cal K}^{-1} \text{ mol}^{-1}) = 24.5 \text{ cal K}^{-1} \text{ mol}^{-1}$$

If  $\Delta H^\circ$  is independent of temperature, the integral of equation 4.47 from  $T_1$  to  $T_2$  yields

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ(T_2 - T_1)}{RT_1 T_2} \quad (4.50)$$

**Example 4.8** Calculate the enthalpy change for the reaction  $\text{N}_2(g) + \text{O}_2(g) = 2\text{NO}(g)$  from the equilibrium constants given in Table 4.2 for 2000 K and 2500 K.

$$\ln \frac{K_{2500\text{K}}}{K_{2000\text{K}}} = \ln \frac{3.60 \times 10^{-3}}{4.08 \times 10^{-4}} = \frac{\Delta H^\circ(2500 \text{ K} - 2000 \text{ K})}{(1.987 \text{ cal K}^{-1} \text{ mol}^{-1})(2500 \text{ K})(2000 \text{ K})}$$

and

$$\Delta H^\circ = 43,300 \text{ cal mol}^{-1}$$

According to Le Châtelier's principle, when an equilibrium system is perturbed, the equilibrium will always be displaced in such a way as to oppose the applied change. When the temperature of an equilibrium system is raised, this change cannot be prevented by the system, but what happens is that the equilibrium shifts