Further Exercises

Chapter 4

W1. Write the expressions for the thermodynamic equilibrium constant K for the following reactions.

$$3\ O_{2\ (g)} \rightleftharpoons 2\ O_{3\ (g)}$$

$$H_2(g) + Br_2(g) \rightleftharpoons 2\ HBr(g)$$

$$3\ Zn_{(s)} + 2\ Fe^{3+}_{(aq)} \rightleftharpoons 2\ Fe_{(s)} + 3\ Zn^{2+}_{(aq)}$$

$$NOBr_{(g)} \rightleftharpoons NO_{(g)} + \tfrac{1}{2}\ Br_{2(g)}$$

W2. Use the enthalpy and entropy data in Appendix 1 to calculate the standard Gibbs energy change and the equilibrium constant at 298 K for the reaction:

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)}$$

W3. 0.1 mol of carbon disulfide and 0.5 mol of chlorine reacted at constant temperature.

$$CS_2\ (g) + 3\ Cl_2\ (g) \rightleftharpoons S_2Cl_2\ (g) + CCl_4\ (g)$$

At equilibrium, 0.03 mol of tetrachloromethane were formed. How much of each of the other components were present at equilibrium?

W4. Calculate the value of $\Delta_r G°$ required for a complete (>99.99%) reaction at 1000 K.

W5. An equimolar mixture of carbon monoxide and hydrogen is allowed to come to equilibrium over a catalyst which promotes their conversion to methanol, $CH_3OH_{(g)}$. Use values of standard Gibbs energies (Appendix 1) to calculate the value of K for this reaction. At an equilibrium pressure p, the fraction of CO converted to methanol is x. Formulate an expression for K as a function of p and x. Show that, for very low conversions, the conversion is proportional to the square of the pressure.

W6. Nitric oxide, NO, and carbon monoxide, CO. are air pollutants emitted by car engines. One potential reaction to remove them is

$$2NO_{(g)} + 2\ CO_{(g)} \rightarrow N_{2(g)} + CO_{2(g)}$$

From the data in Appendix 1, estimate the equilibrium constant for the reaction at 298 K. In a series of measurements, the pressures of each component in the air were $p(N_2)$= 0.78 bar, $p(CO_2) = 4 \times 10^{-4}$ bar $p(NO) = 5 \times 10^{-7}$ bar and $p(CO) = 5 \times 10^{-5}$ bar. In what direction would the reaction proceed under these conditions? Suggest why this may not be a practical method of removing NO from car emissions.

W7. At 2500 K and 1 bar pressure, carbon dioxide is 15% dissociated into CO and oxygen. Calculate the equilibrium constant in terms of partial pressures and the standard Gibbs energy change at this temperature for the dissociation. What would be the effect of changing the pressure?

W8. For the $N_2O_4 \rightleftharpoons 2NO_2$ reaction (Section 4.4), express the equation for K in terms of the degree of dissociation, α, and the total pressure, and so prove that α decreases with increasing total pressure.

W9. For the a general reaction $\alpha A + \beta B \rightleftharpoons \gamma C + \delta D$ derive the relationship between the Gibbs energy change of the reaction and the reaction quotient. Use the relationship to show that $\Delta_r G^{\ominus} = - RT \ln K$.

W10. For the reaction $N_2O_{4(g)} \rightleftharpoons NO_{2(g)}$, if the degree of dissociation is α at a total pressure of p_{total}, show that the equilibrium constant K is given by

$$K = \frac{4\alpha^2}{1-\alpha^2} \times p_{total}$$