15

Chemical equilibrium

Answers to worked examples

WE 15.1 Writing expressions for thermodynamic equilibrium constants (on p. 700 in *Chemistry*^{3})

Write expressions for the thermodynamic equilibrium constants for the following reactions.

(a) $4\ NH_3\ (g) + 5\ O_2\ (g) \rightleftharpoons 4\ NO\ (g) + 6\ H_2O\ (l)$

(b) $Ca(OH)_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2\ OH^-\ (aq)$

(c) $Ni(CO)_4\ (g) \rightleftharpoons Ni\ (s) + 4\ CO\ (g)$

Strategy

Use Equation 15.1 to derive the form of the equilibrium constant in terms of the activities of each of the components. Substitute an appropriate expression for the activity of each component, paying attention to whether the components is present as a solid, liquid or gas, or whether it is in solution.

Solution

The equilibrium constant may be expressed in terms of activities in the form of Equation 15.1

$$K = \frac{\prod\left[a(\text{products})_{\text{eqm}}\right]^{\nu_\text{P}}}{\prod\left[a(\text{reactants})_{\text{eqm}}\right]^{\nu_\text{R}}}$$

where ν_P and ν_R are the stoichiometric coefficients of the reactants and products respectively. The activity of a component J that exists as a pure solid, liquid or gas in its standard state is, from Section 15.1,

$$a_J = 1$$

For mixtures, the activity of a component of a gas is, from Section 15.1

$$a_J = p_J/p^{\ominus}$$

where p_J is the partial pressure of J, whilst for dilute solutions, from Section 15.1,

$$a_J = [J]/c^{\ominus}$$

The inclusion of the terms in the standard pressure

$$p^{\ominus} = 1\ \text{bar} = 10^5\,\text{Pa}$$

and standard concentration

$$c^{\ominus} = 1\ \text{mol dm}^{-3}$$

ensure that the activities are dimensionless.

(a) For the reaction,

$$4\,NH_3\,(g) + 5\,O_2\,(g) \rightleftharpoons 4\,NO\,(g) + 6\,H_2O\,(l)$$

then, substituting the stoichiometric coefficients, and noting that the ammonia, NH_3, oxygen, O_2 and nitric oxide, NO are present as a gaseous mixture, with the water, H_2O, as a pure liquid,

$$\begin{aligned} K &= \frac{(a_{NO})^{\nu_{NO}}\left(a_{H_2O}\right)^{\nu_{H_2O}}}{\left(a_{NH_3}\right)^{\nu_{NH_3}}\left(a_{O_2}\right)^{\nu_{O_2}}} \\ &= \frac{(p_{NO}/p^{\ominus})^4(1)^6}{\left(p_{NH_3}/p^{\ominus}\right)^4\left(p_{O_2}/p^{\ominus}\right)^5} \\ &= \frac{(p_{NO}/1\ \text{bar})^4}{\left(p_{NH_3}/1\ \text{bar}\right)^4\left(p_{O_2}/1\ \text{bar}\right)^5} \end{aligned}$$

where the eqm subscript has been dropped from each term for clarity.

(b) For the reaction

$$Ca(OH)_2\,(s) \rightleftharpoons Ca^{2+}\,(aq) + 2\,OH^-\,(aq)$$

then because the reactant is a pure solid and the two products are present in dilute solution,

$$K = \frac{(a_{\mathrm{Ca^{2+}}})^{\nu_{\mathrm{Ca^{2+}}}}(a_{\mathrm{OH^-}})^{\nu_{\mathrm{OH^-}}}}{(a_{\mathrm{Ca(OH)_2}})^{\nu_{\mathrm{Ca(OH)_2}}}}$$

$$= \frac{([\mathrm{Ca^{2+}}]/c^{\ominus})([\mathrm{OH^-}]/c^{\ominus})^2}{1}$$

$$= ([\mathrm{Ca^{2+}}]/1\ \mathrm{mol\ dm^{-3}})([\mathrm{OH^-}]/1\ \mathrm{mol\ dm^{-3}})^2$$

(c) For the reaction

$$\mathrm{Ni(CO)_4\ (g) \rightleftharpoons Ni\ (s) + 4\ CO\ (g)}$$

then

$$K = \frac{(a_{\mathrm{Ni}})^{\nu_{\mathrm{Ni}}}(a_{\mathrm{CO}})^{\nu_{\mathrm{CO}}}}{(a_{\mathrm{Ni(CO)_4}})^{\nu_{\mathrm{Ni(CO)_4}}}}$$

$$= \frac{(1)(p_{\mathrm{CO}}/p^{\ominus})^4}{(p_{\mathrm{Ni(CO)_4}}/p^{\ominus})}$$

$$= \frac{(p_{\mathrm{CO}}/1\ \mathrm{bar})^4}{(p_{\mathrm{Ni(CO)_4}}/1\ \mathrm{bar})}$$

where, once again, the quantities refer to the values are equilibrium.

WE 15.2 Calculating the thermodynamic equilibrium constant, *K* (on p. 700 in *Chemistry*[3])

At 298 K, the thermodynamic equilibrium constant, *K*, for the reaction

$$\mathrm{N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)}$$

is 0.150. An equilibrium mixture contains a partial pressure of 0.05 bar of NO_2 (g). Calculate the equilibrium partial pressure of N_2O_4 (g).

<u>Strategy</u>

Use Equation 15.1, and the definition of activity for the components of a gaseous mixture in Section 15.1, to write an expression for the equilibrium constant in terms of the partial pressures. Solve the equation for the only unknown, the equilibrium partial pressure of N_2O_4 (g)

Solution

Using Equation 15.1 gives

$$K = \frac{(a_{NO_2})^{\nu_{NO_2}}}{(a_{N_2O_4})^{\nu_{N_2O_4}}}$$

which, because the activity of a component of a gaseous mixture is

$$a_J = p_J/p^{\ominus}$$

may be expressed as

$$K = \frac{(p_{NO_2}/p^{\ominus})^2}{p_{N_2O_4}/p^{\ominus}} = \frac{p_{NO_2}{}^2}{p_{N_2O_4}}/p^{\ominus}$$

so that, rearranging

$$p_{N_2O_4} = p_{NO_2}{}^2/\times p^{\ominus}/K = (0.05\ \text{bar})^2/(1\ \text{bar})/0.150 = 0.0167\ \text{bar}$$

WE 15.3 Using the reaction quotient, *Q* (on p. 704 in *Chemistry*[3])

What will happen in the above reaction if the starting pressures of H_2 (g), I_2 (g) and HI (g) are 0.2 bar, 0.5 bar and 1.4 bar, respectively?

Strategy

Use the expression derived for the reaction quotient for the reaction and substitute the new values. Compare the resulting value for the reaction quotient with that for the equilibrium constant.

Solution

Substituting directly gives

$$Q = \frac{(p_{HI}/p^{\ominus})^2}{(p_{H_2}/p^{\ominus})(p_{I_2}/p^{\ominus})} = \frac{p_{HI}^2}{p_{H_2}p_{I_2}} = \frac{(1.4\ \text{bar})^2}{0.2\ \text{bar} \times 0.5\ \text{bar}} = 19.6$$

Thus, because the equilibrium constant K = 46 at this temperature

$$Q < K$$

so that the forward reaction will proceed spontaneously to create more HI until equilibrium is established.

WE 15.4 Using $\Delta_r G^\circ_{298}$ to calculate a value for *K* (on p. 707 in *Chemistry*³)

The thermodynamic equilibrium constant, *K*, is 15.51 at 100°C for the following reaction: N_2O_4 (g) ⇌ 2 NO_2 (g). Calculate the standard Gibbs energy change for the reaction.

Strategy

Use Equation 15.4, substituting the values for the equilibrium constant and the temperature. Remember to express the temperature in units of kelvin.

Solution

Using Equation 15.4, and noting that the temperature

$$T/\mathrm{K} = \theta/{}^\circ\mathrm{C} + 273.15 = 273.15 + 100 = 373$$

then

$$\begin{aligned}\Delta_r G^\circ &= -RT \ln K \\ &= -8.314\ \mathrm{J\ K^{-1} mol^{-1}} \times 373\ \mathrm{K} \times \ln 15.51 \\ &= -8500\ \mathrm{J\ mol^{-1}} = -8.50\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Note that because the equilibrium constant, $K > 1$, the standard Gibbs energy change is negative, implying that the reactants will react spontaneously at this temperature.

WE 15.5 $\Delta_r G^\circ$ for a reaction that goes to completion at 750 K (on p. 709 in *Chemistry*³)

What is the Gibbs energy change for a reaction R ⇌ P that comes to equilibrium with equal concentrations of product and reactant at 473 K. Comment on the answer.

Strategy

Use Equation 15.1 to write an expression for the equilibrium constant of the reaction. Express the activities of the reactants and products in terms of concentration and substitute.

Solution

For the reaction

$$\mathrm{R} \rightleftharpoons \mathrm{P}$$

then the equilibrium constant has the form

$$K = \frac{(a_\mathrm{P})_\mathrm{eqm}}{(a_\mathrm{R})_\mathrm{eqm}}$$

which, because the activity of a component J in a dilute solution is, from the discussion in Section 15.1,

$$a_\mathrm{J} = [\mathrm{J}]/c^{\ominus}$$

becomes

$$K = \frac{[\mathrm{P}]/c^{\ominus}}{[\mathrm{R}]/c^{\ominus}}$$

If the concentrations of the products and reactants are equal then so are the activities,

$[\mathrm{P}]_\mathrm{eqm} = [\mathrm{R}]_\mathrm{eqm}$ so $(a_\mathrm{P})_\mathrm{eqm} = (a_\mathrm{R})_\mathrm{eqm}$

so that all terms cancel and

$$K = \frac{\left(a_{(\mathrm{P})}\right)_\mathrm{eqm}}{\left(a_{(\mathrm{R})}\right)_\mathrm{eqm}} = 1$$

Then using equilibrium

$$\begin{aligned}\Delta_\mathrm{r}G^{\ominus} &= -RT\ln K \\ &= -(8.314\ \mathrm{J\ K^{-1}mol^{-1}}) \times (473\ \mathrm{K}) \times (\ln 1) \\ &= 0\end{aligned}$$

For a reaction with equal concentrations of product and reactant, $K = 1$, and so $\Delta_\mathrm{r}G^{\ominus}$ is zero at *any* temperature.

WE 15.6 Calculating the partial pressure of a product at equilibrium (on p. 710 in *Chemistry*^{3})

The thermodynamic equilibrium constant, K, is 15.5 at 100°C for the reaction

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

In an equilibrium mixture at 100°C, the partial pressure of N_2O_4 (g) is 0.14 bar. What is the partial pressure of NO_2 (g) at equilibrium?

Strategy

Use Equation 15.1 to derive an expression for the equilibrium constant for the reaction in terms of the activities, and therefore the partial pressures, of the components. Rearrange the expression and substitute the values for the equilibrium constant and partial pressure of N_2O_4 (g) to determine the unknown pressure of NO_2 (g).

Solution

Using Equation 15.1 gives

$$K = \frac{(a_{NO_2})^{\nu_{NO_2}}}{(a_{N_2O_4})^{\nu_{N_2O_4}}}$$

which, because the activity of a component of a gaseous mixture is, from Section 15.1

$$a_J = p_J/p^{\ominus}$$

may be expressed as

$$K = \frac{(p_{NO_2}/p^{\ominus})^2}{p_{N_2O_4}/p^{\ominus}} = \frac{{p_{NO_2}}^2}{p_{N_2O_4}}/p^{\ominus}$$

so that, rearranging, the partial pressure of NO_2 is

$$p_{NO_2} = (K \times p_{N_2O_4}/p^{\ominus})^{1/2} = \{15.5 \times (0.14\ \text{bar}) \times (1\ \text{bar})\}^{1/2} = 1.5\ \text{bar}$$

WE 15.7 Calculating equilibrium yields from starting quantities (on p. 712 in *Chemistry*^{3})

The thermodynamic equilibrium constant, K, is 15.5 at 100°C for the reaction

$$N_2O_4\,(g) \rightleftharpoons 2\,NO_2\,(g)$$

1 mol of N_2O_4 (g) is introduced into a sealed container at 100 °C. The final pressure in the container is 1.5 bar when the system comes to equilibrium. Find the composition of the mixture at equilibrium.

Strategy

Use the stoichiometry of the reaction to derive expressions for the mole fraction, and hence partial pressure, of each component in terms of the initial amount of N_2O_4 and the proportion that has reacted. Use these expressions for the partial pressures to produce an expression that relates the equilibrium constant to the proportion of N_2O_4 that has reacted. Rearrange and solve the resulting quadratic equation to determine the proportion of N_2O_4 that has reacted.

Solution

If 1 mol of N_2O_4 is present initially, and a fraction α reacts, then the amount of N_2O_4 present at equilibrium is

$$n_{\mathrm{N_2O_4}} = (1-\alpha)\ \mathrm{mol}$$

Because for every molecule of N_2O_4 that reacts, two molecules of NO_2 are formed, the amount of NO_2 present at equilibrium is

$$n_{\mathrm{NO_2}} = 2\alpha\ \mathrm{mol}$$

The total amount is

$$n_{\mathrm{total}} = n_{\mathrm{N_2O_4}} + n_{\mathrm{NO_2}} = (1-\alpha)\mathrm{mol} + 2\alpha\ \mathrm{mol} = (1+\alpha)\mathrm{mol}$$

The partial pressures of the two components depend upon the mole fractions and are therefore

$$p_{\mathrm{N_2O_4}} = x_{\mathrm{N_2O_4}}p = \frac{n_{\mathrm{N_2O_4}}}{n_{\mathrm{total}}} \times p = \frac{(1-\alpha)\mathrm{mol}}{(1+\alpha)\mathrm{mol}} \times p = \frac{(1-\alpha)}{(1+\alpha)}p$$

and

$$p_{\mathrm{NO_2}} = x_{\mathrm{NO_2}}p = \frac{n_{\mathrm{NO_2}}}{n_{\mathrm{total}}} \times p = \frac{2\alpha\ \mathrm{mol}}{(1+\alpha)\mathrm{mol}} \times p = \frac{2\alpha}{(1+\alpha)}p$$

The equilibrium constant is, from Worked Example 15.6,

$$K = \frac{(p_{NO_2}/p^{\ominus})^2}{p_{N_2O_4}/p^{\ominus}} = \frac{p_{NO_2}{}^2}{p_{N_2O_4}}/p^{\ominus}$$

and substituting gives

$$K = \frac{[2\alpha p/(1+\ \alpha)]^2}{[(1-\alpha)p/(1+\alpha)]}/p^{\ominus} = \frac{4\alpha^2}{(1-\alpha)(1+\alpha)}p/p^{\ominus} = \frac{4\alpha^2}{1-\alpha^2}\ p/p^{\ominus}$$

Multiplying out this expression gives

$$K(1-\alpha^2) = 4\alpha^2 p/p^{\ominus}$$

Entering the values,

$$15.5(1-\alpha^2) = 4\alpha^2 \times 1.5\ \text{bar}/1\ \text{bar}$$

Multiplying and cancelling terms,

$15.5 – 15.5\ \alpha^2 = 4\ \alpha^2 \times 1.5$

$15.5 – 15.5\ \alpha^2 = 6\ \alpha^2$

$15.5 = 21.5\ \alpha^2$

$\alpha^2 = 15.5\ /\ 21.5 = 0.72$

Hence $\alpha = (0.72)^{½} = 0.85$

Thus, at equilibrium the amount of N_2O_4 present is

$$n_{N_2O_4} = (1-\alpha)\text{mol} = (1-0.85)\text{mol} = 0.15\ \text{mol}$$

and the amount of NO_2 is

$$n_{NO_2} = 2\alpha\ \text{mol} = 2 \times 0.85\ \text{mol} = 1.70\ \text{mol}$$

WE 15.8 Effect of pressure on an equilibrium (on p. 715 in *Chemistry*³)

Without using Le Chatelier's principle, predict the effect of changing the pressure in a vessel containing the following equilibrium reaction at constant temperature:

$$C\ (s) + CO_2\ (g) \rightleftharpoons 2\ CO\ (g)$$

Strategy

Use Equation 15.1 to derive an expression for the equilibrium constant for the reaction. Use the expressions for the activity of a pure solid, or a component in a gaseous mixture to show how the equilibrium constant varies with partial pressure and hence mole fraction.

Solution

The equilibrium constant for the reaction is

$$K = \frac{(a_{\mathrm{CO}})^2}{a_{\mathrm{C}} \times a_{\mathrm{CO_2}}}$$

where, because in general, the activity of a solid in its standard state is, from Section 15.1,

$$a_{\mathrm{J}} = 1$$

and the activity of a gaseous component is

$$a_{\mathrm{J}} = p_{\mathrm{J}}/p^{\ominus} = x_{\mathrm{J}}p/1\ \mathrm{bar}$$

then

$$K = \frac{(x_{\mathrm{CO}}p/1\ \mathrm{bar})^2}{1 \times (x_{\mathrm{CO_2}}p/1\ \mathrm{bar})} = \frac{x_{\mathrm{CO}}^2}{x_{\mathrm{CO_2}}} \times p/1\ \mathrm{bar}$$

The value of the equilibrium constant does not change with pressure. Thus, if the pressure increases, to keep K constant, x_{CO}^2 must reduce and $x_{\mathrm{CO_2}}$ must go up to compensate. An increase in pressure therefore leads to a reduction in the amount of CO so the position of the equilibrium moves towards the reactants. Conversely, if the pressure decreases, the proportion of CO must increase, meaning that the position of equilibrium moves towards the products.

This is consistent with Le Chatelier's principle; increasing the pressure will drive the reaction towards the side containing the lower amount of gas.

WE 15.9 Temperature dependence of *K* (on p. 717 in *Chemistry*[3])

The equilibrium constant for a reaction was measured and found to fit the straight-line relationship: $\ln K = 7.55 - 4844 / T$. Calculate: (a) $\Delta_r H^\ominus$ and $\Delta_r S^\ominus$; (b) $\Delta_r G^\ominus$ for the reaction at 500 K.

Strategy

Compare the experimentally derived expression with the van't Hoff equation, Equation 15.10, and identify the various terms. Hence determine the standard enthalpy and entropy of reaction and use the definition of Gibbs energy, Equation 14.16 to calculate the standard Gibbs energy.

Solution

The van't Hoff equation, Equation 15.10, has the form

$$\ln K = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$$

which if rewritten as

$$\ln K = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R} \times 1/T$$

is of the form

$$\ln K = c + m/T$$

where m is the gradient and c the intercept of a graph of ln K against temperature. Note that the gradient of the graph must have the same units as temperature, i.e. kelvin, in order that all terms are dimensionless. Thus, by inspection,

$$-\frac{\Delta_r H^\ominus}{R} = m = -4844\ \mathrm{K}$$

so that

$$\Delta_r H^\ominus = 4844 \times R = (4844\ \mathrm{K}) \times (8.314\ \mathrm{J\ K^{-1} mol^{-1}})$$
$$= +40300\ \mathrm{J\ mol^{-1}} = +40.3\ \mathrm{kJ\ mol^{-1}}$$

and

$$\frac{\Delta_r S^\ominus}{R} = c = 7.55$$

so that

$$\Delta_r S^\ominus = 7.55 \times R = 7.55 \times (8.314\ \mathrm{J\ K^{-1} mol^{-1}}) = +62.8\ \mathrm{J\ K^{-1} mol^{-1}}$$

Combining these two results gives

$$\begin{aligned}\Delta_r G^{\ominus} &= \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} \\ &= (+40.3 \times 10^3\ \mathrm{J\ mol^{-1}}) - \{(500\ \mathrm{K})500\ \mathrm{K} \times (62.8\ \mathrm{J\ K^{-1} mol^{-1}})\} \\ &= +8900\ \mathrm{J\ mol^{-1}} = +8.90\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Note that it is good practice to state explicitly the sign of thermodynamic changes, even though mathematically it is not strictly necessary always to include the + sign before a positive quantity.

Answers to boxes

Box 15.1 Solubility equilibria (on p. 701 in *Chemistry*^{3})

(a) Write expressions for the solubility products for MgF_2, Ag_2CO_3, $Al(OH)_3$ and Bi_2S_3 in terms of activities.

Strategy

Write a chemical equation for the dissolution process and use Equation 15.1 to write the equilibrium constant in terms of the activities of the solid and dissolved species using the expressions given in Section 15.1. Remember that the activity of a pure solid is 1, so that the terms for the activities of the solid species will disappear.

Solution

For dissolution of MgF_2,

$$MgF_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2\,F^-(aq)$$

and so

$$K = (a_{Mg^{2+}})_{eqm}(a_{F^-})^2_{eqm}/(a_{MgF_2})_{eqm} = (a_{Mg^{2+}})_{eqm}(a_{F^-})^2_{eqm}$$

Similarly, for Ag_2CO_3,

$$Ag_2CO_3\,(s) \rightleftharpoons 2\,Ag^+\,(aq) + CO_3^{2-}(aq)$$

and so

$$K = (a_{Ag^+})^2_{eqm}(a_{CO_3^{2-}})_{eqm}/(a_{Ag_2CO_3})_{eqm} = (a_{Ag^+})^2_{eqm}(a_{CO_3^{2-}})_{eqm}$$

and for $Al(OH)_3$

$$Al(OH)_3\,(s) \rightleftharpoons Al^{3+}\,(aq) + 3\,OH^-(aq)$$

and so

$$K = (a_{Al^{3+}})_{eqm}(a_{OH^-})^3_{eqm}/(a_{Al(OH)_3})_{eqm} = (a_{Al^{3+}})_{eqm}(a_{OH^-})^3_{eqm}$$

and for Bi_2S_3

$$Bi_2S_3\,(s) \rightleftharpoons 2\,Bi^{3+}\,(aq) + 3\,S^{2-}(aq)$$

and so

$$K = (a_{Bi^{3+}})^2_{eqm}(a_{S^{2-}})^3_{eqm}/\left(a_{Bi_2S_3}\right)_{eqm} = (a_{Bi^{3+}})^2_{eqm}(a_{S^{2-}})^3_{eqm}$$

(b) Write the solubility products for MgF_2, Ag_2CO_3, $Al(OH)_3$ and Bi_2S_3 in terms of their molar solubilities, *s*.

Strategy

Replace the activities of the ions in the answers to part (a) by their concentrations. Express the concentrations in terms of the molar solubility, remembering to pay attention to the stoichiometry of the salt.

Solution

For MgF_2, because for every 1 mol of MgF_2 that dissolves, 1 mol of Mg^{2+} (aq) and 2 mol of F^- (aq) are formed, then

$$a_{Mg^{2+}} = [Mg^{2+}]/c^{\circ} = s/\text{mol dm}^{-3}$$

and

$$a_{F^-} = [F^-] = 2s/c^{\circ} = 2s\ /\ \text{mol dm}^{-3}$$

where *s* is the molar solubility, which is the amount of salt that is dissolved in 1 dm^3 of solution. Thus,

$$K = \left(a_{Mg^{2+}}\right)_{eqm}(a_{F^-})^2_{eqm} = [Mg^{2+}][F^-]^2/c^{\circ 3}$$
$$= s \times (2s)^2/(\text{mol dm}^{-3})^3 = 4s^3\ /\ (\text{mol dm}^{-3})^3$$

In the same way, for Ag_2CO_3,

$$K = \left(a_{Ag^+}\right)^2_{eqm}\left(a_{CO_3^{2-}}\right)_{eqm} = [Ag^+]^2[CO_3^{2-}]/c^{\circ 3}$$
$$= (2s)^2 \times s/(\text{mol dm}^{-3})^3 = 4s^3\ /\ (\text{mol dm}^{-3})^3$$

for $Al(OH)_3$,

$$K = (a_{Al^{3+}})_{eqm}(a_{OH^-})^3_{eqm} = [Al^{3+}][OH^-]^3/c^{\circ 4}$$
$$= s \times (3s)^3/(\text{mol dm}^{-3})^4 = 27\,s^4/(\text{mol dm}^{-3})^4$$

and Bi_2S_3

$$K = (a_{Bi^{3+}})^2_{eqm}(a_{S^{2-}})^3_{eqm} = [Bi^{2+}]^2[S^{2-}]^3/c^{\ominus 5}$$
$$= (2s)^2 \times (3s)^3/(\text{mol dm}^{-3})^5 = 108\, s^5/(\text{mol dm}^{-3})^5$$

(c) K for MgF_2 is 6.4×10^{-9} and K for $Al(OH)_3$ is 1.0×10^{-33}. Calculate the molar solubility of each compound in water.

Strategy

Use the expressions derived in part(b), for the solubility product in terms of the molar solubility. Rearrange the equations and solve for the molar solubility.

Solution

For MgF_2, if

$$K = 4s^3 \,/\, (\text{mol dm}^{-3})^3 = 6.4 \times 10^{-9}$$

then

$$s = (6.4 \times 10^{-9}\, (\text{mol dm}^{-3})^3/4)^{1/3} = 1.2 \times 10^{-3}\ \text{mol dm}^{-3}$$

and for $Al(OH)_3$:

$$K = 27\, s^4/(\text{mol dm}^{-3})^4 = 1.0 \times 10^{-33}$$

then

$$s = (1.0 \times 10^{-33}\, (\text{mol dm}^{-3})^4/27)^{1/4} = 2.5 \times 10^{-9}\ \text{mol dm}^{-3}$$

(d) Calculate the molar solubility of (i) MgF_2 in 0.1 mol dm^{-3} sodium fluoride solution; (ii) $Al(OH)_3$ in 0.02 mol dm^{-3} sodium hydroxide solution.

Strategy

Replace the activities of the ions in the answers to part (a) by their concentrations. Express the concentrations of the remaining ions in terms of the molar solubility, paying attention to the stoichiometry of the salt.

Solution

(i) In 0.1 mol dm^{-3} sodium fluoride solution, NaF (aq),

$$[F^-] = 0.1\ \text{mol dm}^{-3}$$

Magnesium fluoride is a sparingly soluble salt, so will add very little to the concentration of F^- ions present in solution above that from the sodium fluoride. The Mg^{2+} ions come only from dissolution of the magnesium fluoride, so that

$$[\mathrm{Mg}^{2+}] = s$$

and therefore

$$\begin{aligned} K &= [\mathrm{Mg}^{2+}][\mathrm{F}^-]^2/c^{\ominus 3} \\ &= s \times (0.1\ \mathrm{mol\ dm^{-3}})^2/(1\ \mathrm{mol\ dm^{-3}})^3 \\ &= 0.01\ s\ /\ \mathrm{mol\ dm^{-3}} \end{aligned}$$

Rearranging,

$$s = (K/0.01)\ \mathrm{mol\ dm^{-3}} = (6.4 \times 10^{-9}\ /\ 0.01)\ \mathrm{mol\ dm^{-3}} = 6.4 \times 10^{-7} \mathrm{mol\ dm^{-3}}$$

(ii) In 0.02 mol dm^{-3} NaOH (aq),

$$[\mathrm{OH}^-] = \ 0.02\ \mathrm{mol\ dm^{-3}}$$

because the dominant source of OH^- ions in solution comes from the sodium hydroxide, whilst

$$[\mathrm{Al}^{3+}] = s$$

and so

$$\begin{aligned} K = [\mathrm{Al}^{3+}][\mathrm{OH}^-]^3/c^{\ominus 4} &= s \times (0.02\ \mathrm{mol\ dm}\ \ ^3)^3/(\mathrm{mol\ dm^{-3}})^4 \\ &= 8 \times 10^{-6}\ s\ /\mathrm{mol\ dm^{-3}} \end{aligned}$$

and therefore

$$\begin{aligned} s &= (K/0.02)\ \mathrm{mol\ dm^{-3}} = \{(1.0 \times 10^{-33})\ /(\ 8 \times 10^{-6})\ \}\ \mathrm{mol\ dm^{-3}} \\ &= 1.3 \times 10^{-28} \mathrm{mol\ dm^{-3}} \end{aligned}$$

In both cases, the presence of the common ion already in solution reduces the solubility of the sparingly soluble salt.

Box 15.2 Equilibrium in fizzy water (on p. 704 in *Chemistry*^{3})

(a) A bottle of fizzy water is opened at room temperature and the water is poured into a glass. The glass is then left to stand for several hours. What happens to (i) K, (ii) Q, over this period of time?

Strategy

Consider Equation 15.5 and the factors that affect the value of the equilibrium constant to decide how the value of K and Q might change. Use Le Chatelier's principle to determine how the point of equilibrium changes as the system adjusts to the new conditions once the bottle is opened.

Solution

(i) The equilibrium constant, K, depends only upon the change in the standard Gibbs energy and temperature. The value of K is thus a constant at a fixed temperature and so does not change with time.

(ii) The fizzy water is initially at equilibrium and will remain after the bottle has been opened so that

$$Q = K$$

The pressure, however, will be lower after the bottle is opened, so that even though the value of K, and hence Q, will not change, the point of equilibrium will be different. At the lower pressure, more carbon dioxide comes out of solution, because, according to Le Chatelier's principle, the system will respond to minimize the effect of the change.

(b) What will be the solubility of CO_2 in mol dm^{-3} at 293 K (20°C) if the gas is injected into pure water at 2 bar pressure?

Strategy

Write an expression for the equilibrium constant in terms of the pressure of carbon dioxide gas and concentration of carbon dioxide in solution. Substitute the value for the equilibrium constant given in Box 15.2, along with the pressure, and solve for the concentration of carbon dioxide in solution.

Solution

The equilibrium may be written as

$$CO_2\,(aq) \rightleftharpoons CO_2\,(g)$$

so that the equilibrium constant is

$$K = \frac{\left(a_{CO_2(g)}\right)_{eqm}}{\left(a_{CO_2(aq)}\right)_{eqm}} = \frac{\left(p_{CO_2(g)}\right)_{eqm}/p^{\ominus}}{[CO_2(aq)]_{eqm}/c^{\ominus}}$$

where the activity of the carbon dioxide in solution may be expressed as a concentration because the solution is dilute. The concentration of carbon dioxide in solution is the molar solubility,

$$[CO_2(aq)] = s$$

so that

$$K = \frac{\left(p_{CO_2(g)}\right)_{eqm}/1\ \text{bar}}{s/1\ \text{mol dm}^{-3}} = 28$$

where the value of the equilibrium constant is given in Box 15.2 and is correct for a temperature of 20°C. Rearranging,

$$\begin{aligned} s &= \frac{p_{CO_2(g)}{}_{eqm}}{28} \times (c^{\ominus}/p^{\ominus}) \\ &= \frac{2\ \text{bar}}{28} \times \{(1\ \text{mol dm}^{-3})/(1\ \text{bar})\} \\ &= 0.071\ \text{mol dm}^{-3} \end{aligned}$$

Doubling the pressure therefore results in a doubling of the molar solubility of carbon dioxide.

Box 15.4 Contrails from jet aircraft (on p. 708 in *Chemistry*³)

The Leeds group obtained values of $\Delta_r H^{\ominus}_{298} = -113.3$ kJ mol^{-1} and $\Delta_r S^{\ominus}_{298} = -142$ J K^{-1} mol^{-1} for the forward reaction in reaction 1.

(a) Write an expression for the equilibrium constant, K, in reaction 1.

Strategy

Use Equation 15.1 to express the equilibrium constant in terms of the partial pressures of the components.

Solution

Using Equation 15.1, and remembering that the activity of a gas may be expressed as the ratio of the partial pressure to the standard pressure,

$$K = \frac{(a_{\mathrm{HOSO_2(g)}})_{\mathrm{eqm}}}{(a_{\mathrm{SO_2(g)}})_{\mathrm{eqm}}(a_{\mathrm{OH(g)}})_{\mathrm{eqm}}}$$

$$= \frac{(p_{\mathrm{HOSO_2(g)}})_{\mathrm{eqm}}/p^{\circ}}{(p_{\mathrm{SO_2(g)}})_{\mathrm{eqm}}(p_{\mathrm{OH(g)}})_{\mathrm{eqm}}/p^{\circ 2}}$$

$$= \frac{(p_{\mathrm{HOSO_2(g)}})_{\mathrm{eqm}}}{(p_{\mathrm{SO_2(g)}})_{\mathrm{eqm}}(p_{\mathrm{OH(g)}})_{\mathrm{eqm}}/1\ \mathrm{bar}}$$

(b) Calculate $\Delta_r G^{\circ}$ and the equilibrium constant K at 298 K.

Strategy

Use Equation 14.16, which shows how the change in Gibbs energy depends upon the change in enthalpy and entropy for a given temperature. Calculate the equilibrium constant from the change in Gibbs energy using Equation 15.4.

Solution

Substituting directly into Equation 14.16

$$\begin{aligned}\Delta_r G^{\circ}_{298} &= \Delta_r H^{\circ}_{298} - T\Delta_r S^{\circ}_{298} \\ &= (-113.3 \times 10^3\ \mathrm{J\ mol^{-1}}) - \{(298\ \mathrm{K}) \times (-142\ \mathrm{J\ K^{-1} mol^{-1}})\} \\ &= -71.0 \times 10^3\ \mathrm{J\ mol^{-1}} = -71.0\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Using Equation 15.4, if

$$\Delta_r G^{\circ} = -RT \ln K$$

then

$$\ln K = -\Delta_r G^{\circ}/RT$$

and so

$$\begin{aligned}K &= \mathrm{e}^{-\Delta_r G^{\circ}/RT} \\ &= \mathrm{e}^{-(-71.0\times 10^3\ \mathrm{J\ mol^{-1}})/\{8.314\ \mathrm{J\ K^{-1} mol^{-1}} \times (298\ \mathrm{K})\}} \\ &= 2.8 \times 10^{12}\end{aligned}$$

(c) Assuming $\Delta_r S^{\circ}$ and $\Delta_r H^{\circ}$ are independent of temperature, calculate K at 500 K and 1100 K.

Strategy

Repeat the calculations of $\Delta_r G^{\ominus}$ and K for the different temperatures.

Solution

At 500 K:

$$\begin{aligned}\Delta_r G^{\ominus}_{500} &= \Delta_r H^{\ominus}_{500} - T\Delta_r S^{\ominus}_{500}\\ &= (-113.3 \times 10^3\ \mathrm{J\ mol^{-1}}) - \{500\ \mathrm{K} \times (-142\ \mathrm{J\ K^{-1} mol^{-1}})\}\\ &= -42.3 \times 10^3\ \mathrm{J\ mol^{-1}} = -42.3\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

and so

$$\begin{aligned}K &= \mathrm{e}^{-\Delta_r G^{\ominus}/RT}\\ &= \mathrm{e}^{-(-42.3\times 10^3\ \mathrm{J\ mol^{-1}})/\{8.314\ \mathrm{J\ K^{-1} mol^{-1}} \times (500\ \mathrm{K})\}}\\ &= 2.6 \times 10^4\end{aligned}$$

At 1100 K:

$$\begin{aligned}\Delta_r G^{\ominus}_{1100} &= \Delta_r H^{\ominus}_{1100} - T\Delta_r S^{\ominus}_{1100}\\ &= (-113.3 \times 10^3\ \mathrm{J\ mol^{-1}}) - \{1100\ \mathrm{K} \times (-142\ \mathrm{J\ K^{-1} mol^{-1}})\}\\ &= +42.9 \times 10^3\ \mathrm{J\ mol^{-1}} = +42.9\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

and so

$$\begin{aligned}K &= \mathrm{e}^{-\Delta_r G^{\ominus}/RT}\\ &= \mathrm{e}^{-(-42.9\times 10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1} mol^{-1}}) \times (1100\ \mathrm{K})\}}\\ &= 9.2 \times 10^{-3}\end{aligned}$$

(d) Suggest what effect the temperature of the exhaust gases has on the ratio of SO_2 to SO_3 + H_2SO_4 in the jet exhaust.

Strategy

Apply Le Chatelier's principle to determine the effect of changing the temperature on the position of the equilibrium for reaction 1.

Solution

For Reaction1, the standard reaction enthalpy change is negative and so the reaction is exothermic. According to Le Chatelier's principle, the position of equilibrium will change in such as way as to minimize the effect of any change in conditions. Thus, is the temperature increases, the position of equilibrium in reaction 1 will lies further to the left in favour of SO_2 and OH· radicals. This means that at the higher temperatures there will be less tendency to form SO_3 and H_2SO_4.

Box 15.5 Chalk, lime and mineral water – an example of heterogeneous equilibrium (on p. 713 in *Chemistry*^{3})

(a) Write an expression for the equilibrium constant, K, for the decomposition of $CaCO_3$ (s).

<u>Strategy</u>

Use Equation 15.1 to write an expression for the equilibrium constant in terms of the activities of the components. Susbtitute expressions for the activities of the various solid and gas-phase components.

<u>Solution</u>

From Equation 15.1

$$K = \frac{\left(a_{\mathrm{CO_2(g)}}\right)_{\mathrm{eqm}}\left(a_{\mathrm{CaO(s)}}\right)_{\mathrm{eqm}}}{\left(a_{\mathrm{CaCO_3(s)}}\right)_{\mathrm{eqm}}}$$

The calcium carbonate and calcium oxide are present as solids in their standard state, so that

$$a_{\mathrm{CaO(s)}} = a_{\mathrm{CaCO_{3(s)}}} = 1$$

whilst the carbon dioxide is present as gas so that the activity may be expressed in terms of the partial pressure and therefore the mole fraction of carbon dioxide

$$a_{\mathrm{CO_2(g)}} = p_{\mathrm{CO_2(g)}}/p^{\ominus} = x_{\mathrm{CO_2(g)}} \times p/p^{\ominus}$$

and therefore, substituting,

$$K = p_{\mathrm{CO_2(g)}}/p^{\ominus}$$

(b) Suppose you roast some $CaCO_3$ (s) in a closed oven. You then add some more $CaCO_3$ (s) (without changing the temperature). What happens to the pressure of CO_2 (g)?

Strategy

Consider how the equilibrium constant, and hence the partial pressure of carbon dioxide, depends upon the amount of calcium carbonate present.

Solution

The partial pressure of carbon dioxide depends upon the equilibrium constant as

$$p_{CO_2(g)} = K \times p^{\ominus}$$

and thus does not depend upon the amount of either the calcium carbonate or calcium oxide present. The pressure of carbon dioxide is thus unaffected by the addition of more calcium carbonate.

(c) In contrast, you heat some $CaCO_3$ (s) in an open crucible. What happens?

Strategy

Consider how the use of an open crucible affects the possibility of achieving equilibrium.

Solution

In an open system, some CO_2 will escape and its pressure will fall below the equilibrium value. More $CaCO_3$ (s) will react to replace it. This will continue until all the $CaCO_3$ (s) has reacted to form CaO (s).

(d) Calculate $\Delta_r G^{\ominus}$ and K for the decomposition of $CaCO_3$ (s) at 298 K and estimate their values at 1273 K. Comment on the results of your calculations.

Strategy

Use Equation 14.16 and the values for the standard enthalpy and entropy of reaction, $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ to find the change in the Gibbs energy of reaction $\Delta_r G^{\ominus}$. Then use Equation 15.4 to find K.

Solution

At 298 K, substituting directly into Equation 14.16

$$\begin{aligned}\Delta_r G^{\ominus}_{298} &= \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298}\\ &= (+178.3 \times 10^3 \text{ J mol}^{-1}) - \{298 \text{ K} \times (+160.6 \text{ J K}^{-1}\text{mol}^{-1})\}\\ &= +130.4 \times 10^3 \text{ J mol}^{-1} = +130.4 \text{ kJ mol}^{-1}\end{aligned}$$

Using Equation 15.4, if

$$\Delta_r G^\ominus = -RT \ln K$$

then

$$\ln K = -\Delta_r G^\ominus / RT$$

and so

$$\begin{aligned} K &= e^{-\Delta_r G^\ominus / RT} \\ &= e^{-(130.4\times10^3\ \mathrm{J\ mol^{-1}})/\{8.314\ \mathrm{J\ K^{-1} mol^{-1}}\times(298\ \mathrm{K})\}} \\ &= 1.39 \times 10^{-23} \end{aligned}$$

Assuming that the enthalpy and entropy of reaction do not vary significantly with temperature, then at 1273 K:

$$\begin{aligned} \Delta_r G^\ominus_{1273} &= \Delta_r H^\ominus_{1273} - T\Delta_r S^\ominus_{1273} \\ &= (+178.3 \times 10^3\ \mathrm{J\ mol^{-1}}) - \{1273\ \mathrm{K} \times (+160.6\ \mathrm{J\ K^{-1} mol^{-1}})\} \\ &= -26.1 \times 10^3\ \mathrm{J\ mol^{-1}} = -26.1\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

and so

$$\begin{aligned} K &= e^{-\Delta_r G^\ominus / RT} \\ &= e^{-(-26.1\times10^3\ \mathrm{J\ mol^{-1}})/\{8.314\ \mathrm{J\ K^{-1} mol^{-1}}\times(1273\ \mathrm{K})\}} \\ &= 11.8 \end{aligned}$$

As expected, at 298 K, the standard Gibbs energy of reaction is positive and so the reaction is not spontaneous. The equilibrium constant $K < 1$ and so little CO_2 is formed. At 1273 K, however, the standard Gibbs energy of reaction is negative and the reaction is spontaneous. The equilibrium therefore lies in favour of the products.

(e) Estimate the temperature at which the decomposition of $CaCO_3$ (s) just becomes spontaneous at 1 bar.

Strategy

Use the conditions for a reaction to be spontaneous to decide the value of the Gibbs energy of reaction at which the formation of products is favoured. Rearrange Equation 14.16 and substitute the known values for the standard enthalpy and entropy of reaction to determine the temperature at which the condition is met.

Solution

We know from Section 14.6 that a reaction becomes spontaneous when $\Delta_r G^\ominus < 0$. Thus, using Equation 14.16,

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = 0$$

so that

$$T = \frac{\Delta_r H^\ominus}{\Delta_r S^\ominus} = \frac{+178.3 \times 10^3 \text{ J mol}^{-1}}{+160.6 \text{ J K}^{-1}\text{mol}^{-1}} = 1110 \text{ K}$$

(f) What is the equilibrium partial pressure of CO_2 at 1273 K?

Strategy

Use the expression derived in part (a), together with the value determined in part (d).

Solution

If

$$p_{CO_2(g)} = K \times p^\ominus$$

and

$$K = 11.8$$

then

$$p_{CO_2(g)} = 11.8 \times 1 \text{ bar} = 11.8 \text{ bar}$$

Box 15.6 A case study in reaction thermodynamics—the Haber process (on p. 720 in *Chemistry*^{3})

(a) Use data from Appendix 7 (p.1350) on enthalpy change of formation and heat capacity to calculate $\Delta_r H^\ominus$ for the synthesis of ammonia at: (i) 298 K; (ii) 773 K; (iii) 1000 K.

Strategy

Use the data in the appendix and Equation 13.6 to calculate the enthalpy of reaction at 298 K, $\Delta_r H^\ominus_{298}$, for the Haber process from the difference between the enthalpies of formation of the products and the reactants. Using Equation 13.11, apply the same approach to calculate the change in the standard heat capacities of the products and reactants, $\Delta C^{\ominus}_{p,298}$ at the same temperature. Combine the two results using the Kirchoff equation, Equation 13.10, to determine the enthalpy change on formation at 773 and 1000 K.

Solution

(i) The Haber process is the reaction of hydrogen, H_2, and nitrogen, N_2 to form ammonia, NH_3.

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3(g)$$

Appendix 7 gives the enthalpy of formation of ammonia, NH_3, as $\Delta_f H^{\ominus}_{298}(NH_3\,(g)) = -46.1$ kJ mol^{-1}. The enthalpies of formation of hydrogen and nitrogen are both zero, $\Delta_f H^{\ominus}_{298}(H_2\,(g)) = \Delta_f H^{\ominus}_{298}(N_2\,(g)) = 0$ because H_2 (g) and N_2 (g) are defined as the standard states for hydrogen and nitrogen. Then, using Equation 13.6 to find $\Delta_r H^{\ominus}$ at 298 K,

$$\Delta_r H^{\ominus}_{298} = \sum_i \nu_i \Delta_f H^{\ominus}_{298}(\text{products}) - \nu_i \Delta_f H^{\ominus}_{298}(\text{reactants})$$

$$= \overbrace{\{2 \times \Delta_f H^{\ominus}_{298}(\mathrm{NH_3(g)})\}}^{\text{products}} - \overbrace{\{\underbrace{\Delta_f H^{\ominus}_{298}(\mathrm{N_2(g)})}_{0} + (3 \times \underbrace{\Delta_f H^{\ominus}_{298}(\mathrm{H_2(g)})}_{0})\}}^{\text{reactants}}$$

$$= 2 \times (-46.1\ \mathrm{kJ\ mol^{-1}}) = -92.2\ \mathrm{kJ\ mol^{-1}} = -92.2 \times 10^3\ \mathrm{J\ mol^{-1}}$$

(ii) and (iii) In order to apply the Kirchoff equation, Equation 13.10, it is necessary to calculate the change in the heat capacity upon reaction. Using Equation 13.11, and assuming that the heat capacities themselves remain constant with temperature,

$$\Delta_r C^{\ominus}_p = \sum_i \nu_i C^{\ominus}_p(\text{products}) - \nu_i C^{\ominus}_p(\text{reactants})$$

$$= \overbrace{\{2 \times C^{\ominus}_p(\mathrm{NH_3(g)})\}}^{\text{products}} - \overbrace{\{C^{\ominus}_p(\mathrm{N_2(g)}) + \left(3 \times C^{\ominus}_p(\mathrm{H_2(g)})\right)\}}^{\text{reactants}}$$

$$= \{2 \times (35.1\ \mathrm{J\ K^{-1} mol^{-1}})\} - [(29.1\ \mathrm{J\ K^{-1} mol^{-1}}) + \{3 \times (28.8\ \mathrm{J\ K^{-1} mol^{-1}})\}]$$

$$= -45.3\ \mathrm{J\ K^{-1} mol^{-1}}$$

Then, applying Kirchhoff's law, Equation 13.10,

$$\Delta_r H^{\ominus}_{T_2} = \Delta_r H^{\ominus}_{T_2} + \Delta C^{\ominus}_p (T_2 - T_1)$$

to find $\Delta_r H^\circ$ at 773 K

$$\Delta_r H^\circ_{773} = \Delta_r H^\circ_{298} + \Delta C_p^\circ (773\text{ K} - 298\text{ K})$$
$$= (-92.2 \times 10^3 \text{ J mol}^{-1}) + \{-45.3 \text{ J K}^{-1}\text{mol}^{-1} \times (475\text{ K})\}$$
$$= -113.7 \times 10^3 \text{ J mol}^{-1} = -113.7 \text{ kJ mol}^{-1}$$

and 1000 K

$$\Delta_r H^\circ_{1000} = \Delta_r H^\circ_{298} + \Delta C_p^\circ (1000\text{ K} - 298\text{ K})$$
$$= (-92.2 \times 10^3 \text{ J mol}^{-1}) + \{-45.3 \text{ J K}^{-1}\text{mol}^{-1} \times (702\text{ K})\}$$
$$= -124.0 \times 10^3 \text{ J mol}^{-1} = -124.0 \text{ kJ mol}^{-1}$$

(b) Calculate the standard Gibbs energy change of the reaction at: (i) 298 K; (ii) 773 K; (iii) 1000 K.

Strategy

Calculate the standard entropy change for the reaction at 298 K using by substituting the data in the Appendix for the standard entropies of the products and reactants into Equation 14.12. Then apply Equation 14.7 to determine the entropy change at the other temperatures. Finally, use Equation 14.16 and the values for the standard enthalpy and entropy changes to determine the change in the standard Gibbs energy of reaction.

Solution

From Appendix 7, the standard entropies at 298 K are $S^\circ_{298}(NH_3(g)) = 192.45 \text{ J K}^{-1}\text{mol}^{-1}$, $S^\circ_{298}(N_2(g)) = 191.6 \text{ J K}^{-1}\text{mol}^{-1}$, and $S^\circ_{298}(H_2(g)) = 130.7 \text{ J K}^{-1}\text{mol}^{-1}$. Thus, using Equation 14.12,

$$\Delta_r S^\circ_{298} = \sum_i \nu_i S^\circ_{298}(\text{products}) - \nu_i S^\circ_{298}(\text{reactants})$$
$$= \overbrace{\left(2 \times S^\circ_{298}(NH_3(g))\right)}^{\text{products}} - \overbrace{\left\{S^\circ_{298}(N_2(g)) + \left(3 \times S^\circ_{298}(H_2(g))\right)\right\}}^{\text{reactants}}$$
$$= \{2 \times (192.45 \text{ J K}^{-1}\text{mol}^{-1})\}$$
$$- [(191.6 \text{ J K}^{-1}\text{mol}^{-1}) + \{3 \times (130.7 \text{ J K}^{-1}\text{mol}^{-1})\}]$$
$$= -198.8 \text{ J K}^{-1}\text{mol}^{-1}$$

Then, using Equation 15.7

$$\Delta_r S^{\ominus}_{T_2} = \Delta_r S^{\ominus}_{T_1} + \Delta C_p \ln(T_2/T_1)$$

to determine the entropy change at 773 K

$$\begin{aligned}\Delta_r S^{\ominus}_{773} &= \Delta_r S^{\ominus}_{298} + \Delta C_p \ln(773\ \text{K}/298\ \text{K}) \\ &= (-198.8\ \text{J K}^{-1}\text{mol}^{-1}) + \{(-45.3\ \text{J K}^{-1}\text{mol}^{-1}) \times \ln(773\ \text{K}/298\ \text{K})\} \\ &= -242.0\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

and 1000 K

$$\begin{aligned}\Delta_r S^{\ominus}_{1000} &= \Delta_r S^{\ominus}_{298} + \Delta C_p \ln(1000\ \text{K}/298\ \text{K}) \\ &= (-198.8\ \text{J K}^{-1}\text{mol}^{-1}) + \{(-45.3\ \text{J K}^{-1}\text{mol}^{-1}) \times \ln(1000\ \text{K}/298\ \text{K})\} \\ &= -253.6\ \text{J K}^{-1}\text{mol}^{-1}\end{aligned}$$

Then, using Equation 14.16

$$\Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$$

to calculate $\Delta_r G^{\ominus}$ at 298 K,

$$\begin{aligned}\Delta_r G^{\ominus}_{298} &= \Delta_r H^{\ominus}_{298} - T\Delta_r S^{\ominus}_{298} \\ &= (-92.2 \times 10^3\ \text{J mol}^{-1}) - \{(298\ \text{K}) \times (-198.8\ \text{J K}^{-1}\text{mol}^{-1})\} \\ &= -33.0 \times 10^3\ \text{J mol}^{-1} = -33.0\ \text{kJ mol}^{-1}\end{aligned}$$

at 773 K

$$\begin{aligned}\Delta_r G^{\ominus}_{773} &= \Delta_r H^{\ominus}_{773} - T\Delta_r S^{\ominus}_{773} \\ &= (-113.7 \times 10^3\ \text{J mol}^{-1}) - \{(773\ \text{K}) \times (-242.0\ \text{J K}^{-1}\text{mol}^{-1})\} \\ &= +73.4 \times 10^3\ \text{J mol}^{-1} = +73.4\ \text{kJ mol}^{-1}\end{aligned}$$

and 1000 K

$$\begin{aligned}\Delta_r G^{\ominus}_{1000} &= \Delta_r H^{\ominus}_{1000} - T\Delta_r S^{\ominus}_{1000} \\ &= (-124.0 \times 10^3\ \text{J mol}^{-1}) - \{(1000\ \text{K}) \times (-253.6\ \text{J K}^{-1}\text{mol}^{-1})\} \\ &= +129.6 \times 10^3\ \text{J mol}^{-1} = +129.6\ \text{kJ mol}^{-1}\end{aligned}$$

(c) Comment on the significance of the results from (b).

Strategy

Consider how the magnitude and sign of the Gibbs energy of reaction changes as the temperature increases.

Solution

The Gibbs energy of reaction increases with temperature. At 298 K, the Gibbs energy is negative, meaning that the reaction is spontaneous in the direction shown. However, as the temperature increases, the Gibbs energy becomes positive, so that at 773 and 1000 K, the reaction is not spontaneous. At these temperatures, the equilibrium will lie in favour of the reactants.

(d) Write the expression for the equilibrium constant and use it, together with the van't Hoff equation (Equation 15.10, p.714), to explain the effect on the yield of ammonia of: (i) increasing the pressure; (ii) increasing temperature; (iii) adding hydrogen gas to the reaction mixture; (iv) changing the amount of catalyst in the reaction chamber.

Strategy

Use Equation 15.1 to write the equilibrium constant in terms of activities. Express the activities of the various components as functions of the mole fractions and the total pressure.

Solution

Using Equation 15.1,

$$K = \frac{\left(a_{\mathrm{NH_3(g)}}\right)_{\mathrm{eqm}}^2}{\left(a_{\mathrm{N_2(g)}}\right)_{\mathrm{eqm}}\left(a_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}}^3}$$

and because for a gas, the activity is related to the partial pressure, which in turn depends upon the mole fraction

$$a_{\mathrm{J}} = p_{\mathrm{J}}/p^{\ominus} = x_{\mathrm{J}}p/p^{\ominus}$$

then

$$K = \frac{\left(p_{\mathrm{NH_3(g)}}\right)_{\mathrm{eqm}}^2}{\left(p_{\mathrm{N_2(g)}}\right)_{\mathrm{eqm}}\left(p_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}}^3} \times p^{\ominus 2} = \frac{\left(x_{\mathrm{NH_3(g)}}\right)_{\mathrm{eqm}}^2}{\left(x_{\mathrm{N_2(g)}}\right)_{\mathrm{eqm}}\left(x_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}}^3} \times (1\ \mathrm{bar}/p)^2$$

(i) The equilibrium constant does not vary with pressure. Thus, if the total pressure, p, increases, the magnitude of the first term must also increase in order that the value of the equilibrium constant does not change. The position of equilibrium moves towards the products, as predicted by Le Chatelier's principle. Thus, the mole fraction of ammonia, $x_{\mathrm{NH_3(g)}}$, will increase and the mole fraction of nitrogen and hydrogen, $x_{N_2(g)}$ and $x_{H_2(g)}$, will decrease if the total pressure increases.

(ii) According to the van't Hoff equation, Equation 15.11,

$$\ln K = \text{constant} - \frac{\Delta_r H^{\ominus}}{R} \times \left(\frac{1}{T}\right)$$

The effect of varying the temperature therefore depends upon the sign of the standard enthalpy of reaction. The reaction is exothermic at 298, 773 and 1000 K, so that

$$\Delta_r H^{\ominus} < 0$$

Thus, according to Table 15.2, increasing the temperature will cause the value of the equilibrium constant to decrease. If the pressure remains constant, the equilibrium will move in favour of reactants, meaning that less ammonia is produced.

(iii) Using the expression derived in part (i) for the equilibrium constant in terms of the mole fraction of the various components, if the amount, and hence proportion of hydrogen increases, then the mole fraction of ammonia must also increase. Once again, this observation is consistent with Le Chatelier's principle, because the system responds to reduce the amount of hydrogen by converting it into ammonia.

(iv) Addition of a catalyst affects the kinetics and not the thermodynamics of a reaction. The catalyst does not, therefore, influence the position of equilibrium and so will not affect the yield of ammonia. However, the maximum yield may be established more quickly.

(e) Calculate and comment on the equilibrium constant for the reaction at: (i) 298 K; (ii) 773 K; (iii) 1000 K.

Strategy

Use the values for the standard Gibbs energy of reaction and Equation 15.5.

Solution

Using Equation 15.5 and substituting directly,

$$K_{298} = e^{-\Delta_r G^{\ominus}/RT} = e^{-(-33.0\times10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1} mol^{-1}})\times(298\ \mathrm{K})\}} = 6.1\times10^5$$

$$K_{773} = e^{-\Delta_r G^\ominus/RT} = e^{-(+73.4\times10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(773\ \mathrm{K})\}} = 1.1\times10^{-5}$$

$$K_{1000} = e^{-\Delta_r G^\ominus/RT} = e^{-(+129.6\times10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(1000\ \mathrm{K})\}} = 1.7\times10^{-7}$$

(f) A reaction mixture at 298 K has the following partial pressures: 1 bar N_2, 3 bar H_2, and 0.5 bar NH_3. In which direction will the reaction move towards equilibrium?

Strategy

Write an expression for the reaction quotient in terms of the partial pressures of the components. Substitute the values for the partial pressures into the expression and compare the value with that for the equilibrium constant at this temperature.

Solution

The reaction quotient is, by comparison with the expression for the equilibrium constant derived in part (d),

$$Q_{298} = \frac{\left(p_{\mathrm{NH_3(g)}}\right)^2}{\left(p_{\mathrm{N_2(g)}}\right)\ \left(p_{\mathrm{H_2(g)}}\right)^3} \times p^{\ominus 2}$$

$$= \frac{(0.5\ \mathrm{bar})^2}{(1\ \mathrm{bar})\times(3\ \mathrm{bar})^3} \times (1\ \mathrm{bar})^2 = 9.3\times10^{-3}$$

Thus, $Q_{298} < K_{298}$, and the forward reaction will occur until the reaction reaches equilibrium.

Answers to end of chapter questions

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

(a) $4\ NH_3\ (g) + 7\ O_2\ (g) \rightleftharpoons 4\ NO_2\ (g) + 6\ H_2O\ (l)$

(b) $HCN\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CN^-\ (aq)$

(c) $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

(d) $3\ O_2\ (g) \rightleftharpoons 2\ O_3\ (g)$

(e) $2\ H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$

(f) $3\ Zn\ (s) + 2\ Fe^{3+}\ (aq) \rightleftharpoons 2\ Fe\ (s) + 3\ Zn^{2+}\ (aq)$

Strategy

Use Equation 15.1 to express the equilibrium constant in terms of the activities of the components, paying particular attention to the stoichiometry of the reaction. Substitute the appropriate expressions from Section 15.1 for the activities of the components, according to whether they are in their standard state,

$$a_\mathrm{J} = 1$$

or are present as gaseous

$$a_\mathrm{J} = p_\mathrm{J}/p^\ominus = a_\mathrm{J} = x_\mathrm{J}p/p^\ominus$$

or dilute mixtures

$$a_\mathrm{J} = [\mathrm{J}]/c^\ominus$$

Solution

(a) The water is present in its standard state, so that

$$a_{\mathrm{H_2O}} = 1$$

whilst the other components are present as a mixture of gases, so that

$$a_{\mathrm{NO_2}} = p_{\mathrm{NO_2}}/p^\ominus$$

and so on, so that

$$K = \frac{(a_{H_2O})^6_{eqm}(a_{NO_2})^4_{eqm}}{(a_{NH_3})^6_{eqm}(a_{O_2})^7_{eqm}}$$

$$= \frac{(p_{NO_2}/p^{\ominus})^4_{eqm}}{(p_{NH_3}/p^{\ominus})^6_{eqm}(p_{O_2}/p^{\ominus})^7_{eqm}}$$

$$= \frac{(p_{NO_2}/1\ \text{bar})^4_{eqm}}{(p_{NH_3}/1\ \text{bar})^6_{eqm}(p_{O_2}/1\ \text{bar})^7_{eqm}}$$

(b) Assuming that the solution is dilute, so that the water may be assumed to be almost pure,

$$a_{H_2O} = 1$$

and, because the other components are present in solution

$$a_{H_3O^+(aq)} = [H_3O^+(aq)]/c^{\ominus}]$$

so that

$$K = \frac{(a_{H_3O^+(aq)})_{eqm}(a_{CN^-(aq)})_{eqm}}{(a_{HCN(aq)})_{eqm}(a_{H_2O(l)})_{eqm}}$$

$$= \frac{[H_3O^+\ (aq)]_{eqm}/\ c^{\ominus} \times [CN^-(aq)]_{eqm}/c^{\ominus}}{[HCN\ (aq)]_{eqm}/\ c^{\ominus}}$$

$$= \frac{[H_3O^+\ (aq)]_{eqm}[CN^-(aq)]_{eqm}}{[HCN\ (aq)]_{eqm}\ \times 1\ \ \text{mol dm}^{-3}}$$

(c) All components are presents as gases, for which

$$a_{PCl_3} = p_{PCl_3}/p^{\ominus} = x_{PCl_3}p/p^{\ominus}$$

and so on, so that

$$K = \frac{(a_{PCl_3})_{eqm}(a_{Cl_2})_{eqm}}{(a_{PCl_5})_{eqm}}$$

$$= \frac{(p_{PCl_3}/p^{\ominus})_{eqm}(p_{Cl_2}/p^{\ominus})_{eqm}}{(p_{PCl_5}/p^{\ominus})_{eqm}}$$

$$= \frac{(p_{PCl_3}/1\ \text{bar})_{eqm}(p_{Cl_2}/1\ \text{bar})_{eqm}}{(p_{PCl_5}/1\ \text{bar})_{eqm}}$$

(d) Using the same method,

$$K = \frac{(a_{O_3})^2_{eqm}}{(a_{O_2})^3_{eqm}} = \frac{(p_{O_3}/p^{\ominus})^2_{eqm}}{(p_{O_2}/p^{\ominus})^3_{eqm}} = \frac{(p_{O_3}/1\ \text{bar})^2_{eqm}}{(p_{O_2}/1\ \text{bar})^3_{eqm}}$$

(e) Water molecules do not dissociate readily, so that we may assume that the water is present in its standard state, so that

$$a_{H_2O} = 1$$

with the ions present as if in dilute solution, so that

$$a_{H_3O^+(aq)} = [H_3O^+(aq)]/c^{\ominus}]$$

and so on. Thus,

$$K = \frac{(a_{H_3O^+(aq)})_{eqm}(a_{OH^-(aq)})_{eqm}}{(a_{H_2O(l)})_{eqm}}$$

$$= \frac{[H_3O^+\ (aq)]_{eqm}/\ 1\ \ \text{mol dm}^{-3} \times [OH^-(aq)]_{eqm}/1\ \ \text{mol dm}^{-3}}{1}$$

$$= [H_3O^+\ (aq)]_{eqm}[OH^-(aq)]_{eqm}$$

(f) The solids are in their standard states, so that

$$(a_{Fe(s)})_{eqm} = (a_{Zn(s)})_{eqm} = 1$$

with the ions in dilute solution so that

$$a_{Fe^{3+}\ (aq)} = [Fe^{3+}(aq)]/1\ \ \text{mol dm}^{-3}]$$

and therefore

$$K = \frac{(a_{Fe(s)})^2_{eqm}(a_{Zn^{2+}(aq)})^3_{eqm}}{(a_{Fe^{3+}(aq)})^2_{eqm}(a_{Zn(s)})^3_{eqm}} = \frac{([Zn^{2+}(aq)]/1\ \ \text{mol dm}^{-3})^3_{eqm}}{([Fe^{3+}(aq)]/1\ \ \text{mol dm}^{-3})^2_{eqm}}$$

2. The solubility of silver chloride in water at 25 °C is 1.27×10^{-5} mol dm^{-3}. Calculate

(a) the solubility product of AgCl

(b) the solubility of AgCl in 0.01 mol dm^{-3} aqueous sodium chloride solution.

(Section 15.1)

Strategy

Follow the method used in Box 15.1. Write an expression for the solubility product of silver chloride in terms of concentration and hence solubility. Having calculated the solubility product, use the expression to determine the solubility of silver chloride in the presence of a known concentration of chloride ions.

Solution

(a) The solubility product of silver chloride may expressed in terms of activities as

$$K = a_{Ag^+} a_{Cl^-}$$

Silver chloride is a sparingly soluble salt, so we may assume that the concentration of the resulting solution is sufficiently low that we may approximate activities by concentrations

$$K = \left([Ag^+]_{eqm}/c^{\ominus}\right)\left([Cl^-]_{eqm}/c^{\ominus}\right) = [Ag^+]_{eqm}[Cl^-]_{eqm}/(1\ \text{mol dm}^{-3})^2$$

The concentrations of the two ions are equal, and represent the solubility, *s*, of the salt

$$[Ag^+]_{eqm} = [Cl^-]_{eqm} = s$$

so that

$$K = (s/c^{\ominus})^2$$

Hence,

$$K = \{(1.27 \times 10^{-5}\ \text{mol dm}^{-3})/(1\ \text{mol dm}^{-3})\}^2 = 1.61 \times 10^{-10}$$

(b) In the presence of a solution of sodium chloride, the concentration of Cl^- ions depends upon the contribution from both salts

$$[\mathrm{Cl^-}]_{\mathrm{eqm}} = \{s + (0.01\ \mathrm{mol\ dm^{-3}})\}$$

Thus

$$K = [\mathrm{Ag^+}]_{\mathrm{eqm}}[\mathrm{Cl^-}]_{\mathrm{eqm}}/c^{\ominus 2} = s \times \{s + (0.01\ \mathrm{mol\ dm^{-3}})\}/c^{\ominus 2}$$

We could solve this equation exactly for the solubility s. However, because AgCl is a sparingly soluble salt, we may assume that $s \ll (0.01\ \mathrm{mol\ dm^{-3}})$ and so

$$\{s + (0.01\ \mathrm{mol\ dm^{-3}})\} \approx (0.01\ \mathrm{mol\ dm^{-3}})$$

This approximation allows us to solve for the solubility much more easily,

$$s = Kc^{\ominus 2}/(0.01\ \mathrm{mol\ dm^{-3}}) = (1.61 \times 10^{-10}/0.01)\ \mathrm{mol\ dm^{-3}}$$
$$= 1.61 \times 10^{-8} \mathrm{mol\ dm^{-3}}$$

Thus, as expected, the AgCl is less soluble in a solution of sodium chloride than in pure water.

3. The equilibrium constants for two gas phase reactions at 1000 °C are shown.

$$CO_2(g) \rightleftharpoons CO(g) + \tfrac{1}{2}\ O_2\ (g) \qquad K_1 = 9.1 \times 10^{-12}$$

$$H_2O(g) \rightleftharpoons H_2(g) + \tfrac{1}{2}\ O_2\ (g) \qquad K_2 = 7.1 \times 10^{-12}$$

Use these data to find the equilibrium constant at the same temperature for the reaction:

$$CO_2\ (g) + H_2\ (g) \rightleftharpoons CO(g) + H_2O(g)$$

(Section 15.1)

Strategy

Apply Equation 15.4 to calculate the standard reaction Gibbs energy for the two reactions. Then calculate the standard reaction Gibbs energy of the required reaction as the difference between the values for the two individual reactions. Finally, use Equation 15.5 to calculate the corresponding equilibrium constant.

Solution

Applying Equation 15.4, the standard reaction Gibbs energy for the two reactions are

$$\Delta_r G^\circ(1) = -RT\ln K_1 = -(8.314\ \mathrm{J\ K^{-1}mol^{-1}}) \times (1273\ \mathrm{K}) \times \ln(9.1\times10^{-12})$$
$$= +269\times10^3\ \mathrm{J\ mol^{-1}}$$
$$\Delta_r G^\circ(2) = -RT\ln K_2 = -(8.314\ \mathrm{J\ K^{-1}mol^{-1}}) \times (1273\ \mathrm{K}) \times \ln(7.1\times10^{-12})$$
$$= +272\times10^3\ \mathrm{J\ mol^{-1}}$$

The reaction

$$CO_2\,(g) + H_2\,(g) \rightleftharpoons CO(g) + H_2O(g)$$

may be expressed as the difference between the two reactions given, so that

$$\Delta_r G^\circ(3) = \Delta_r G^\circ(1) - \Delta_r G^\circ(2)$$
$$= (+269\times10^3\ \mathrm{J\ mol^{-1}}) - (+272\times10^3\ \mathrm{J\ mol^{-1}}) = -2.6\times10^3\ \mathrm{J\ mol^{-1}}$$

The corresponding equilibrium constant is therefore, from Equation 15.5,

$$K_3 = \frac{K_1}{K_2} = \mathrm{e}^{-\Delta_r G^\circ(3)/RT} = \mathrm{e}^{-\{(-2.6\times10^3\ \mathrm{J\ mol^{-1}})/(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(1273\ \mathrm{K})\}} = 1.28$$

Note that although it is often convenient to break down calculations into steps, rounding errors can sometimes be avoided by combining the various equations and performing one single calculation. Thus, we could have obtained the same result by writing

$$K_3 = \mathrm{e}^{-\frac{\Delta_r G^\circ(3)}{RT}} = \mathrm{e}^{-\frac{\{\Delta_r G^\circ(1) - \Delta_r G^\circ(2)\}}{RT}} = \mathrm{e}^{-\frac{\Delta_r G^\circ(1)}{RT}}/\mathrm{e}^{-\frac{\Delta_r G^\circ(2)}{RT}}$$
$$= K_1/K_2 = 9.1\times10^{-12}/7.1\times10^{-12} = 1.28$$

4. The equilibrium constant for the following reaction is $K = 1.5 \times 10^4$.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

In a reaction vessel, the partial pressures of the reaction mixture are: $COCl_2$ 0.050 bar, CO 0.0010 bar, and Cl_2 0.0001 bar.

(a) Calculate the value for the reaction quotient, Q, for this mixture.

(b) What will happen to the composition of the reaction mixture as it moves to equilibrium? (Section 15.2)

Strategy

Write the reaction quotient in terms of the partial pressures of the products and reactants. Compare the calculated value for the reaction quotient under these conditions with the equilibrium constant and decide whether the composition moves towards products or reactants as it approaches equilibrium.

Solution

(a) We may write the reaction quotient as

$$Q = \frac{a_{\mathrm{COCl_2(g)}}}{a_{\mathrm{CO(g)}}a_{\mathrm{Cl_2(g)}}} = \frac{p_{\mathrm{COCl_2(g)}}/p^{\ominus}}{(p_{\mathrm{CO(g)}}/p^{\ominus})(p_{\mathrm{Cl_2(g)}}/p^{\ominus})} = \frac{p_{\mathrm{COCl_2(g)}}p^{\ominus}}{p_{\mathrm{CO(g)}}p_{\mathrm{Cl_2(g)}}}$$

$$= \frac{(0.050\ \mathrm{bar}) \times (1\ \mathrm{bar})}{(0.0010\ \mathrm{bar}) \times (0.0001\ \mathrm{bar})} = 5 \times 10^{5}$$

(b) The reaction quotient under these conditions is larger than the equilibrium constant. Thus, as the reaction approaches equilibrium, the partial pressure of the $COCl_2$ product will decrease and the partial pressure of CO and Cl_2 reactants will increase. The value of the reaction quotient will therefore decrease and converge towards that of the equilibrium constant.

5. An important reaction in the formation of smog is:

$$O_3(g) + NO(g) \rightleftharpoons O_2(g) + NO_2(g)$$

Under certain conditions, the equilibrium constant for this reaction is $K = 6.0 \times 10^{34}$. If the partial pressures of each gas in the air over your home town were 1.0×10^{-6} bar O_3, 1.0×10^{-5} bar NO, 2.5×10^{-4} bar NO_2, and 8.2×10^{-3} bar O_2, what could you say about the course of the reaction as it moves to equilibrium? (Section 15.2)

Strategy

Write the reaction quotient in terms of the partial pressures of the products and reactants. Compare the calculated value with that given for the equilibrium constant.

Solution

We may write the reaction quotient as

$$Q = \frac{a_{\mathrm{O_2(g)}}a_{\mathrm{NO_2(g)}}}{a_{\mathrm{O_3(g)}}a_{\mathrm{NO(g)}}} = \frac{(p_{\mathrm{O_2(g)}}/p^{\ominus})(p_{\mathrm{NO_2(g)}}/p^{\ominus})}{(p_{\mathrm{O_3(g)}}/p^{\ominus})(p_{\mathrm{NO(g)}}/p^{\ominus})} = \frac{p_{\mathrm{O_2(g)}}p_{\mathrm{NO_2(g)}}}{p_{\mathrm{O_3(g)}}p_{\mathrm{NO(g)}}}$$

$$= \frac{(2.5 \times 10^{-4}\ \text{bar}) \times (8.2 \times 10^{-3}\ \text{bar})}{(1.0 \times 10^{-6}\ \text{bar}) \times (1.0 \times 10^{-5}\ \text{bar})} = 2.1 \times 10^{5}$$

Thus, under these conditions, the value of the reaction quotient is much less than that of the equilibrium constant. Thus, as equilibrium is approached, the partial pressures of the products must increase and those of the reactants decrease.

6. Calculate the equilibrium constant, *K*, at 298 K for the reaction

$$H_2O\ (l) \rightleftharpoons H_2\ (g) + ½\ O_2\ (g)$$

The standard Gibbs energy change of formation of H_2O (l) at 298 K is –237.1 kJ mol^{-1}.

Strategy

Use Equation 15.5 and substitute the value for the standard Gibbs energy change of formation of H_2O (l).

Solution

As written, the reaction is the reverse of that for the formation of H_2O (l) from its elements in their standard states

$$H_2\ (g) + ½\ O_2\ (g) \rightleftharpoons H_2O\ (l)$$

so that

$$\Delta_r G^{\circ}_{298} = -\Delta_f G^{\circ}_{298} = +237.1\ \text{kJ mol}^{-1} = +237.1 \times 10^{3}\ \text{J mol}^{-1}$$

Thus

$$K_{298} = e^{-\Delta_r G^{\circ}_{298}/RT} = e^{-(+237.1\times10^{3}\ \text{J mol}^{-1})/\{(8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})\}}$$
$$= 2.75 \times 10^{-42}$$

7. Use the data below to calculate the standard Gibbs energy change and the equilibrium constant, *K*, at 298 K for the reaction

$$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$$

	$\Delta_f H^{\circ}_{298}$ / kJ mol^{-1}	S°_{298} / J K^{-1} mol^{-1}
CO (g)	–110.5	197.7

H_2O (g)	–241.8	188.8
CO_2 (g)	–393.5	213.7
H_2 (g)	0	130.7

Strategy

Use Equations 13.6 and 14.11 to determine the standard enthalpy and entropy change for the reaction. Substitute the values into Equation 15.16 to find the corresponding change in Gibbs energy and then Equation 15.7 to determine the equilibrium constant.

Solution

Using Equation 13.6 to calculate $\Delta_r H^{\ominus}_{298}$

$$\Delta_r H^{\ominus}_{298} = \sum_i \nu_i \Delta_f H^{\ominus}_{298}(\text{products}) - \nu_i \Delta_f H^{\ominus}_{298}(\text{reactants})$$

$$= \overbrace{\left(\Delta_f H^{\ominus}_{298}(CO_2(g)) + \Delta_f H^{\ominus}_{298}(H_2(g))\right)}^{\text{products}} - \overbrace{\left(\Delta_f H^{\ominus}_{298}(CO(g)) + \Delta_f H^{\ominus}_{298}(H_2O(g))\right)}^{\text{reactants}}$$

$$= \{(-393.5\ \text{kJ mol}^{-1}) + (0\ \text{kJ mol}^{-1})\} - \{(-110.5\ \text{kJ mol}^{-1}) + (-241.8\ \text{kJ mol}^{-1})\}$$

$$= -41.2\ \text{kJ mol}^{-1} = -41.2 \times 10^3\ \text{J mol}^{-1}$$

and Equation 14.11 to determine $\Delta_r S^{\ominus}_{298}$

$$\Delta_r S^{\ominus}_{298} = \sum_i \nu_i S^{\ominus}_{298}(\text{products}) - \nu_i S^{\ominus}_{298}(\text{reactants})$$

$$= \overbrace{\left(S^{\ominus}_{298}(CO_2(g)) + S^{\ominus}_{298}(H_2(g))\right)}^{\text{products}} - \overbrace{\left(S^{\ominus}_{298}(CO(g)) + S^{\ominus}_{298}(H_2O(g))\right)}^{\text{reactants}}$$

$$= \{(213.7\ \text{J K}^{-1}\text{mol}^{-1}) + (130.7\ \text{J K}^{-1}\text{mol}^{-1})\} - \{(197.7\ \text{J K}^{-1}\text{mol}^{-1}) + (188.8\ \text{J K}^{-1}\text{mol}^{-1})\}$$

$$= -42.1\ \text{J K}^{-1}\text{mol}^{-1}$$

then

$$\begin{aligned}\Delta_r G^{\circ}_{298} &= \Delta_r H^{\circ}_{298} - T\Delta_r S^{\circ}_{298}\\ &= (-41.2 \times 10^3\ \mathrm{J\ mol^{-1}}) - \{(298\ \mathrm{K}) \times (-42.1\ \mathrm{J\ K^{-1}\ mol^{-1}})\}\\ &= -28700\ \mathrm{J\ mol^{-1}} = -28.7\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

from Equation 14.16. Then, using Equation 15.5,

$$\begin{aligned}K_{298} &= \mathrm{e}^{-\Delta_r G^{\circ}_{298}/RT} = \mathrm{e}^{-(-28.7\times10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1} mol^{-1}})\times(298\ \mathrm{K})\}}\\ &= 1.07 \times 10^5\end{aligned}$$

8. A vessel initially contains graphite and partial pressures of O_2 (g) and CO_2 (g) of 0.02 bar, and 0.001 bar respectively, at 298 K. The reaction that occurs is

$$\mathrm{C\ (s) + O_2\ (g) \rightleftharpoons CO_2\ (g)}$$

In what direction will the reaction proceed? (The standard Gibbs energy change of formation of CO_2 (g) is –394.4 kJ mol^{-1} at 298 K.)

Strategy

Calculate the reaction quotient using Equation 15.2, and the equilibrium constant using Equation 15.7. Compare the two values and use the arguments explained in Section 15.2 to predict the direction in which the reaction will proceed.

Solution

The reaction quotient is, from Equation 15.2

$$Q = \frac{(a_{\mathrm{CO_2(g)}})}{(a_{\mathrm{O_2(g)}})\ (a_{\mathrm{C(s)}})} = \frac{(p_{\mathrm{CO_2(g)}})\ /p^{\circ}}{(p_{\mathrm{O_2(g)}})\ /p^{\circ}} = \frac{(p_{\mathrm{CO_2(g)}})/1\ \mathrm{bar}}{(p_{\mathrm{O_2(g)}})/1\ \mathrm{bar}}$$

$$= \frac{0.001\ \mathrm{bar}}{0.02\ \mathrm{bar}} = 0.05$$

From Section 15.1,

$$a_{\mathrm{C(s,graphite)}} = 1$$

since graphite is defined as the standard state of solid carbon. The activities of the gases are, from Section 15.1,

$$a_{\mathrm{CO_2(g)}} = p_{\mathrm{CO_2(g)}}/p^{\circ}$$

The reaction corresponds to the formation of carbon dioxide from its elements in their standard states, so that

$$\Delta_r G^{\ominus}_{298} = \Delta_f G^{\ominus}_{298} = -394.4 \text{ kJ mol}^{-1} = -394.4 \times 10^3 \text{J mol}^{-1}$$

and using Equation 15.5

$$K = e^{-\Delta_r G^{\ominus}_{298}/RT}$$
$$= e^{-(-394.4\times10^3 \text{ J mol}^{-1})/\{(8.314 \text{ J K}^{-1}\text{mol}^{-1})\times(298 \text{ K})\}}$$
$$= 1.35 \times 10^{69}$$

Thus,

$$Q \ll K$$

and, from the arguments in Section 15.2, the reaction will proceed in the forward direction.

9. 2.0 mol of carbon disulfide and 4.0 mol of chlorine react at constant temperature according to this equation:

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

At equilibrium, 0.30 mol of tetrachloromethane are formed. How much of each of the other components is present in this equilibrium mixture?

Strategy

Use the principle of mass balance to write expressions for the amount of each component, both initially and at equilibrium. Substitute the known values and rearrange to find the amounts of the unknown components.

Solution

Initially, the amount of carbon disulfide and chlorine are

$$\left(n_{CS_2}\right)_0 = 2.0 \text{ mol}$$

and

$$\left(n_{Cl_2}\right)_0 = 4.0 \text{ mol}$$

If the amount of tetrachloromethane present at equilibrium is

$$\left(n_{\mathrm{CCl_4}}\right)_{\mathrm{eqm}} = 0.30\ \mathrm{mol}$$

then this implies that 0.03 mol of carbon disulfide and 0.03 mol of chlorine have reacted, so that

$$\left(n_{\mathrm{CS_2}}\right)_{\mathrm{eqm}} = \left(n_{\mathrm{CS_2}}\right)_0 - \left(n_{\mathrm{CCl_4}}\right)_{\mathrm{eqm}} = 2.0\ \mathrm{mol} - 0.30\ \mathrm{mol} = 1.7\ \mathrm{mol}$$

The stoichiometry of the reaction is such that three molecules of chlorine react for every molecule of crabon disulfide produced, so that

$$\left(n_{\mathrm{Cl_2}}\right)_{\mathrm{eqm}} = \left(n_{\mathrm{Cl_2}}\right)_0 - 3\times\left(n_{\mathrm{CCl_4}}\right)_{\mathrm{eqm}} = 4.0\ \mathrm{mol} - 3\times 0.30\ \mathrm{mol} = 3.1\ \mathrm{mol}$$

The amount of S_2Cl_2 will be the same as the amount of chlorine produced, so that

$$\left(n_{\mathrm{S_2Cl_2}}\right)_{\mathrm{eqm}} = \left(n_{\mathrm{Cl_2}}\right)_{\mathrm{eqm}} = 0.30\ \mathrm{mol}$$

10. Nitrosyl chloride (NOCl) decomposes to nitric oxide and chlorine when heated

$$2\ \mathrm{NOCl\ (g)} \rightleftharpoons 2\ \mathrm{NO\ (g)} + \mathrm{Cl_2\ (g)}$$

In a mixture of all three gases at 600 K, the partial pressure of NOCl is 0.88 bar, that of NO is 0.06 bar, and the partial pressure of chlorine is 0.03 bar. At 600 K, the equilibrium constant, *K,* is 0.060.

(a) What is the value of the reaction quotient for this mixture? Is the mixture at equilibrium?

(b) In which direction will the system move to reach equilibrium?

(c) What would happen if an additional amount of NOCl (g) was injected into the reaction?

Strategy

(a) Write an expression for the reaction quotient using Equation 15.2 and substitute the appropriate forms of the activities of the various components from Section 15.1. (b) Compare the calculated value for the reaction quotient with the quoted value for the equilibrium constant. (c) Consider the effect on the value of the reaction quotient relative to that of the equilibrium constant, of increasing the amount of NOCl (g).

Solution

(a) According to Equation 15.2,

$$Q = \frac{\left(a_{\mathrm{NO\,(g)}}\right)^2 \left(a_{\mathrm{Cl_2\,(g)}}\right)}{\left(a_{\mathrm{NOCl\,(g)}}\right)^2}$$

where, because the components are present as gases, we may replace the activities, using the relations given in Section 15.1, by expressions involving partial pressures

$$\begin{aligned} Q &= \frac{\left(p_{\mathrm{NO\,(g)}}/p^{\ominus}\right)^2 \left(p_{\mathrm{Cl_2\,(g)}}/p^{\ominus}\right)}{\left(p_{\mathrm{NOCl\,(g)}}/p^{\ominus}\right)^2} \\ &= \frac{\left(p_{\mathrm{NO\,(g)}}\right)^2 \left(p_{\mathrm{Cl_2\,(g)}}\right)}{\left(p_{\mathrm{NOCl\,(g)}}\right)^2 \times p^{\ominus}} \\ &= \frac{(0.06\ \mathrm{bar})^2 \times 0.03\ \mathrm{bar}}{(0.88\ \mathrm{bar})^2 \times 1\ \mathrm{bar}} \\ &= 1.4 \times 10^{-4} \end{aligned}$$

(b) Thus, because $K = 0.060$, $Q < K$. The arguments presented in Section 15.2 therefore predict that the reaction will proceed in the forward direction.

(c) The value of the equilibrium constant will not change as long as the temperature remains constant. Thus, if the amount of NOCl were to be increased, some would react in order to form more NO and Cl_2 so that the equilibrium was re-established. This is consistent with Le Chatelier's principle; the system responds to minimise the effect of the addition of the NOCl by moving the position of the equilibrium towards the products.

11. The following reaction is exothermic

$$\mathrm{Ti\ (s) + 2\ Cl_2\ (g) \rightleftharpoons TiCl_4\ (g)}$$

How could the yield of $TiCl_4$ be increased?

Strategy

Write an equation for the equilibrium constant using Equation 15.1 and the expressions for the activities in Section 15.1. Use Le Chatelier's principle to consider how the system would respond to an imposed change in temperature and pressure.

Solution

The equilibrium constant for the reaction may be written as

$$K = \frac{\left(a_{\mathrm{TiCl_4\,(g)}}\right)_{\mathrm{eqm}}}{\left(a_{\mathrm{Ti\,(s)}}\right)_{\mathrm{eqm}}\left(a_{\mathrm{Cl_2\,(g)}}\right)_{\mathrm{eqm}}^2} = \frac{\left(p_{\mathrm{TiCl_4\,(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}}{1 \times \left(p_{\mathrm{Cl_2\,(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}^2} = \frac{\left(p_{\mathrm{TiCl_4\,(g)}}\right)_{\mathrm{eqm}} p^{\ominus}}{\left(p_{\mathrm{Cl_2\,(g)}}\right)_{\mathrm{eqm}}^2}$$

Rearranging therefore gives

$$\left(p_{\mathrm{TiCl_4\,(g)}}\right)_{\mathrm{eqm}} = K \times \left(p_{\mathrm{Cl_2\,(g)}}\right)_{\mathrm{eqm}}^2 / 1\ \mathrm{bar}$$

The amount of $TiCl_4$ may therefore be increased either by increasing the value of the equilibrium constant, or by changing the pressure.

The reaction is exothermic. Thus, if the temperature is reduced, the point of equilibrium will move further in favour of products, so that the effect of the change is, effectively, minimised. We may prove this using the van't Hoff equation, Equation 15.10, which has the form

$$\ln K = \frac{\Delta_r S^{\ominus}}{R} - \frac{\Delta_r H^{\ominus}}{RT}$$

and shows that if

$$\Delta_r H^{\ominus} < 0$$

which is true for an exothermic reaction such as this, then the value of the equilibrium constant will increase if the temperature is reduced.

We may rewrite the expression for the partial pressure of $TiCl_4$ in terms of the mole fraction of chlorine as

$$\left(p_{\mathrm{TiCl_4\,(g)}}\right)_{\mathrm{eqm}} = K\left(x_{\mathrm{Cl_2\,(g)}}\right)_{\mathrm{eqm}}^2 p/p^{\ominus}$$

Increasing the pressure, either by increasing the amount of chlorine or by introducing an inert buffer gas will therefore increase the amount of $TiCl_4$ at equilibrium.

12. The following gas phase reaction is exothermic

$$CO\ (g) + \tfrac{1}{2}\ O_2\ (g) \rightleftharpoons CO_2\ (g)$$

What will be the effect of (a) increasing the pressure, (b) increasing the temperature, and (c) adding a catalyst on (i) the equilibrium constant, K and, (ii) the yield of CO_2?

Strategy

Apply Le Chatelier's Principle to each situation.

Solution

(a) Changing the pressure has no effect on the value of the equilibrium constant. According to Le Chatelier's principle, because the amount of gas is reduced by the reaction, increasing the pressure will favour the formation of products, increasing the amount of CO_2 at equilibrium.

(b) The reaction is exothermic, so that increasing the temperature will, according to the van't Hoff equation, Equation 15.10, reduce the value of the equilibrium constant. If the value of the equilibrium constant falls as a result of the increase in temperature, the amount of CO_2 present at equilibrium must be reduced.

(c) Adding a catalyst has no effect on the equilibrium constant or the amounts of each component at equilibrium. Equilibrium is, however, established more quickly.

13. For the gas phase reaction

$$COCl_2\ (g) \rightleftharpoons CO\ (g) + Cl_2\ (g)$$

at 100°C and 2 bar pressure, the fraction, α, of phosgene ($COCl_2$) that reacts is 6.3×10^{-5}. Calculate the equilibrium constant, K, for the reaction.

Strategy

Write an expression for the equilibrium constant in terms of the mole fractions of the components and the total pressure, using Equation 15.1 and the definition of activity given in Section 15.1. Express the mole fractions of the components in terms of the fraction α of phosgene that has reacted.

Solution

The equilibrium constant has, according to Equation 15.1, the general form

$$K = \frac{\left(a_{\mathrm{CO\,(g)}}\right)_{\mathrm{eqm}}\left(a_{\mathrm{Cl_2\,(g)}}\right)_{\mathrm{eqm}}}{\left(a_{\mathrm{COCl_2\,(g)}}\right)_{\mathrm{eqm}}}$$

which because the activities of gaseous components may expressed, according to Section 15.1, in terms of their partial pressure and hence mole fraction, may be written

$$K = \frac{\left(p_{\mathrm{CO\,(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}\left(p_{\mathrm{Cl_2\,(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}}{\left(p_{\mathrm{COCl_2\,(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}}$$

$$= \frac{\left(x_{\mathrm{CO\,(g)}}p/p^{\ominus}\right)_{\mathrm{eqm}}\left(x_{\mathrm{Cl_2\,(g)}}p/p^{\ominus}\right)_{\mathrm{eqm}}}{\left(x_{\mathrm{COCl_2\,(g)}}p/p^{\ominus}\right)_{\mathrm{eqm}}} \times (p/p^{\ominus})$$

$$= \frac{\left(x_{\mathrm{CO\,(g)}}\right)_{\mathrm{eqm}}\left(x_{\mathrm{Cl_2\,(g)}}\right)_{\mathrm{eqm}}}{\left(x_{\mathrm{COCl_2\,(g)}}\right)_{\mathrm{eqm}}} \times p/1\ \mathrm{bar}$$

The mole fraction of a component is the ratio of the amount of that component to the total of all components

$$x_{\mathrm{J}} = n_J/n$$

so that

$$x_{\mathrm{CO(g)}} = n_{\mathrm{CO(g)}}/\left(n_{\mathrm{CO(g)}} + n_{\mathrm{Cl_2(g)}} + n_{\mathrm{COCl_2(g)}}\right)$$

and so on. If the amount of phosgene present initially is $\left(n_{\mathrm{COCl_2(g)}}\right)_0$ then the amounts present at equilibrium are

$$\left(n_{\mathrm{COCl_2(g)}}\right)_{\mathrm{eqm}} = (1-\alpha)\left(n_{\mathrm{COCl_2(g)}}\right)_0$$

$$\left(n_{\mathrm{CO(g)}}\right)_{\mathrm{eqm}} = \alpha\left(n_{\mathrm{COCl_2(g)}}\right)_0$$

$$\left(n_{\mathrm{Cl_2(g)}}\right)_{\mathrm{eqm}} = \alpha\left(n_{\mathrm{COCl_2(g)}}\right)_0$$

so that at equilibrium

$$\begin{aligned} n_{\text{total}} &= \left(n_{\text{CO(g)}} + n_{\text{Cl}_2\text{(g)}} + n_{\text{COCl}_2\text{(g)}}\right) \\ &= \alpha\left(n_{\text{COCl}_2\text{(g)}}\right)_0 + \alpha\left(n_{\text{COCl}_2\text{(g)}}\right)_0 + (1-\alpha)\left(n_{\text{COCl}_2\text{(g)}}\right)_0 \\ &= (1+\alpha)\left(n_{\text{COCl}_2\text{(g)}}\right)_0 \end{aligned}$$

and hence

$$\begin{aligned} \left(x_{\text{COCl}_2\text{(g)}}\right)_{\text{eqm}} &= \left(n_{\text{COCl}_2\text{(g)}}/n_{\text{total}}\right)_{\text{eqm}} \\ &= (1-\alpha)\left(n_{\text{COCl}_2\text{(g)}}\right)_0/(1+\alpha)\left(n_{\text{COCl}_2\text{(g)}}\right)_0 \\ &= (1-\alpha)/(1+\alpha) \end{aligned}$$

and

$$\begin{aligned} \left(x_{\text{CO(g)}}\right)_{\text{eqm}} &= \left(n_{\text{CO(g)}}/n_{\text{total}}\right)_{\text{eqm}} \\ &= \alpha\left(n_{\text{COCl}_2\text{(g)}}\right)_0/(1+\alpha)\left(n_{\text{COCl}_2\text{(g)}}\right)_0 \\ &= \alpha/(1+\alpha) \end{aligned}$$

$$\begin{aligned} \left(x_{\text{Cl}_2\text{(g)}}\right)_{\text{eqm}} &= \left(n_{\text{Cl}_2\text{(g)}}/n_{\text{total}}\right)_{\text{eqm}} \\ &= \alpha\left(n_{\text{COCl}_2\text{(g)}}\right)_0/(1+\alpha)\left(n_{\text{COCl}_2\text{(g)}}\right)_0 \\ &= \alpha/(1+\alpha) \end{aligned}$$

The mole fractions of the components are thus independent of the initial amount of phosgene. Substituting into the expression for the equilibrium constant,

$$\begin{aligned} K &= \frac{\left(x_{\text{CO (g)}}\right)_{\text{eqm}}\left(x_{\text{Cl}_2\text{ (g)}}\right)_{\text{eqm}}}{\left(x_{\text{COCl}_2\text{ (g)}}\right)_{\text{eqm}}} \times \frac{p}{p^{\ominus}} \\ &= \frac{\alpha/(1+\alpha) \times \alpha/(1+\alpha)}{(1-\alpha)/(1+\alpha)} \times \frac{p}{p^{\ominus}} \\ &= \frac{\alpha^2}{(1-\alpha)(1+\alpha)} \times \frac{p}{p^{\ominus}} \\ &= \frac{\alpha^2}{1-\alpha^2} \times \frac{p}{p^{\ominus}} \end{aligned}$$

Substituting the values given $\alpha = 6.3 \times 10^{-5}$ and $p = 2$ bar

gives

$$K = \frac{(6.3 \times 10^{-5})^2}{1 - (6.3 \times 10^{-5})^2} \times \frac{2\ \text{bar}}{1\ \text{bar}} = 7.9 \times 10^{-9}$$

14. Bromine and chlorine react to produce bromine monochloride according to the equation

$$Br_2\ (g) + Cl_2\ (g) \rightleftharpoons 2\ BrCl\ (g)$$

0.2 mol of bromine gas and 0.2 mol of chlorine gas are introduced into a sealed flask with a volume of 5.0 dm^3. Under the conditions of the experiment, $K = 36.0$. How much BrCl will be present at equilibrium?

Strategy

Write an expression for the equilibrium constant in terms of activities using Equation 15.1. Substitute expressions for the activities of the various components given in Section 15.1 to obtain an equation for the equilibrium constant in terms of the partial pressures. By considering the stoichiometry of the reaction, determine the partial pressures of each component at equilibrium. Substitute and rearrange to find the partial pressure and hence amount of BrCl present at equilibrium.

Solution

Using Equation 15.1,

$$K = \frac{\left(a_{\text{BrCl (g)}}\right)^2_{\text{eqm}}}{\left(a_{\text{Cl}_2\text{ (g)}}\right)_{\text{eqm}}\left(a_{\text{Br}_2\text{ (g)}}\right)_{\text{eqm}}}$$

The activities of a component in a gas-phase mixture is, from Section 15.1,

$$a_{\text{J(g)}} = p_{\text{J(g)}}/p^{\ominus} = x_{\text{J(g)}}p/p^{\ominus}$$

so that

$$K = \frac{\left(p_{\text{BrCl (g)}}/p^{\ominus}\right)^2_{\text{eqm}}}{\left(p_{\text{Cl}_2\text{ (g)}}/p^{\ominus}\right)_{\text{eqm}}\left(p_{\text{Br}_2\text{ (g)}}/p^{\ominus}\right)_{\text{eqm}}} = \frac{\left(x_{\text{BrCl (g)}}\right)^2_{\text{eqm}}}{\left(x_{\text{Cl}_2\text{ (g)}}\right)_{\text{eqm}}\left(x_{\text{Br}_2\text{ (g)}}\right)_{\text{eqm}}}$$

where the terms in the total pressure, p, and standard pressure $p^{\ominus}$, cancel. The mole fractions are given by Equation 8.9,

$$x_J = n_J/n_{total}$$

where the total amount is given by

$$n_{total} = n_{Br_2} + n_{Cl_2} + n_{BrCl}$$

The total amount of substance does not change, so that

$$(n_{total})_{eqm} = (n_{total})_0 = (n_{Br_2})_0 + (n_{Cl_2})_0 = 0.2 \text{ mol} + 0.2 \text{ mol} = 0.4 \text{ mol}$$

At equilibrium, if we assume that a fraction α of Br_2 reacts, then

$$(n_{Br_2})_{eqm} = (1-\alpha)(n_{Br_2})_0 = 0.2(1-\alpha) \text{ mol}$$

$$(n_{Cl_2})_{eqm} = (1-\alpha)(n_{Cl_2})_0 = 0.2(1-\alpha) \text{ mol}$$

$$(n_{BrCl})_{eqm} = 2\alpha(n_{Br_2})_0 = 2 \times 0.2\alpha \text{ mol} = 0.4\alpha \text{ mol}$$

because for every molecule of Br_2 that reacts, two molecules of BrCl are produced. Hence

$$(x_{Br_2})_{eqm} = (n_{Br_2}/n_{total})_{eqm} = 0.2(1-\alpha) \text{ mol}/0.4 \text{ mol} = 0.5(1-\alpha)$$

$$(x_{Cl_2})_{eqm} = (n_{Cl_2}/n_{total})_{eqm} = 0.2(1-\alpha) \text{ mol}/0.4 \text{ mol} = 0.5(1-\alpha)$$

$$(x_{BrCl})_{eqm} = (n_{BrCl}/n_{total})_{eqm} = 0.4\alpha \text{ mol}/0.4 \text{ mol} = \alpha$$

Thus, substituting,

$$K = \frac{(x_{BrCl\,(g)})^2_{eqm}}{(x_{Cl_2\,(g)})_{eqm}(x_{Br_2\,(g)})_{eqm}} = \frac{\alpha^2}{0.5(1-\alpha) \times 0.5(1-\alpha)} = \frac{4\alpha^2}{(1-\alpha)^2} = 36$$

Rearranging gives

$$36(1-\alpha)^2 = 4\alpha^2$$

Taking the square root of each side

$$6(1-\alpha) = \pm 2\alpha$$

so that either

$$6 - 6\alpha = +2\alpha$$

so that

$$\alpha = 6/8 = 0.75$$

or

$$6 - 6\alpha = -2\alpha$$

so that

$$\alpha = 6/4 = 1.5$$

We may ignore the second value because we know that since α is the fraction of Br_2 that has reacted, its value must be less than 1.

Thus,

$$(n_{\mathrm{BrCl}})_{\mathrm{eqm}} = 2\alpha\left(n_{\mathrm{Br_2}}\right)_0 = 2 \times 0.75 \times (0.2\ \mathrm{mol}) = 0.3\ \mathrm{mol}$$

15. When ammonia is dissolved in water, the following equilibrium is established

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

Calculate the hydroxide ion concentration in the solution formed when 0.10 mol of ammonia are dissolved in sufficient water to make 500 cm^3 of solution. (At the temperature of the reaction, $K = 1.8 \times 10^{-5}$).

Strategy

Write the equilibrium constant in terms of the concentrations of the various components using Equation 15.1 and the expressions given in Section 15.1. Use the stoichiometry of the reaction to express the concentrations of all species in terms of the concentration of hydroxide ions and the initial concentration of ammonia. Rearrange this expression and solve for the unknown concentration of hydroxide ions.

Solution

From Equation 15.1, and because the activities of ions in dilute solution may be expressed using the expressions in Section 15.1 as

$$a_{\mathrm{J(aq)}} = [\mathrm{J}]/c^{\ominus}$$

and the activity of a pure solid or liquid component in its standard state is

$$a_{\mathrm{J}} = 1$$

Therefore

$$K = \frac{[NH_4^+(aq)]_{eqm}[OH^-(aq)]_{eqm}/1 \text{ mol dm}^{-3}}{[NH_3(aq)]_{eqm}}$$

From the stoichiometry of the reaction

$$[NH_4^+(aq)]_{eqm} = [OH^-(aq)]_{eqm}$$

and

$$[NH_3(aq)]_{eqm} = [NH_3(aq)]_0 - [OH^-(aq)]_{eqm}$$

then

$$K = \frac{[OH^-(aq)]_{eqm}^2/1 \text{ mol dm}^{-3}}{[NH_3(aq)]_0 - [OH^-(aq)]_{eqm}} = 1.8 \times 10^{-5}$$

The initial solution is made up by dissolving 0.10 mol of NH_3 in 500 cm^3 = 0.5 dm^3 of solution so the initial concentration is

$$[NH_3(aq)]_0 = n_0/V = (0.10 \text{ mol})/(0.5 \text{ dm}^3) = 0.2 \text{ mol dm}^{-3}$$

so that

$$K = \frac{[OH^-(aq)]_{eqm}^2}{(0.2 \text{ mol dm}^{-3}) - [OH^-(aq)]_{eqm}} = 1.8 \times 10^{-5} \times 1 \text{ mol dm}^{-3}$$

This expression is a quadratic equation in $[OH^-(aq)]_{eqm}$, of the form

$$a[OH^-(aq)]_{eqm}^2 + b[OH^-(aq)]_{eqm} + c = 0$$

but a good approximation of the solution can be obtained by assuming that the concentration of OH^- ions is very low, so that

$$0.2 \text{ mol dm}^{-3} \gg [OH^-(aq)]_{eqm}$$

and therefore

$$0.2 \text{ mol dm}^{-3} - [OH^-(aq)]_{eqm} \approx 0.2 \text{ mol dm}^{-3}$$

so that

$$K = \frac{[OH^-(aq)]_{eqm}^2}{0.2 \text{ mol dm}^{-3}} = 1.8 \times 10^{-5} \times 1 \text{ mol dm}^{-3}$$

and so

$$[\mathrm{OH^-(aq)}]^2_{\mathrm{eqm}} = (1.8 \times 10^{-5}) \times 1\ \mathrm{mol\ dm^{-3}} \times (0.2\ \mathrm{mol\ dm^{-3}})$$
$$= 0.36 \times 10^{-5}\ \mathrm{mol^2\ dm^{-6}}$$

Hence,

$$[\mathrm{OH^-(aq)}]_{\mathrm{eqm}} = 1.9 \times 10^{-3}\ \mathrm{mol\ dm^{-3}}$$

16. The standard Gibbs energy change for the gas phase isomerization of *cis*-2-pentene to *trans*-2-pentene is –3.67 kJ mol^{-1}. (Section 15.4)

(a) Calculate the equilibrium constant for the reaction.

(b) What are the equilibrium mole fractions of the *cis* and *trans* isomers at 298 K?

Strategy

Use Equation 15.5 to calculate the equilibrium constant from the standard Gibbs energy change. Write an expression for the equilibrium constant in terms of the partial pressures and hence the mole fractions of the two isomers.

Solution

(a) From Equation 15.5,

$$K = \mathrm{e}^{-\Delta_\mathrm{r}G/RT} = \mathrm{e}^{-(-3.67\times10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(298\ \mathrm{K})\}} = 4.40$$

(b) We may write the equilibrium constant for the isomerization reaction as

$$K = \frac{p_{\mathrm{trans}}/p^{\ominus}}{p_{\mathrm{cis}}/p^{\ominus}} = \frac{p_{\mathrm{trans}}}{p_{\mathrm{cis}}}$$

But, the partial pressure is related to the mole fraction through Equation 8.10

$$p_\mathrm{J} = x_\mathrm{J} p_{\mathrm{total}}$$

so that

$$K = \frac{x_{\mathrm{trans}} p_{\mathrm{total}}}{x_{\mathrm{cis}} p_{\mathrm{total}}} = \frac{x_{\mathrm{trans}}}{x_{\mathrm{cis}}} = \frac{x_{\mathrm{trans}}}{1 - x_{\mathrm{trans}}}$$

Substituting the value for the equilibrium constant and rearranging,

$$4.40(1 - x_{\text{trans}}) = x_{\text{trans}}$$
$$5.40x_{\text{trans}} = 4.40$$
$$x_{\text{trans}} = 0.815$$

and

$$x_{\text{C}} = 1 - 0.815 = 0.185$$

17. What is the standard enthalpy change for a reaction in which the equilibrium constant doubles when the temperature increases from 298 K to 308 K?

Strategy

Apply the van't Hoff equation, Equation 15.10.

Solution

We may use the van't Hoff equation, Equation 15.10, to write expressions for the equilibrium constant at the two temperatures

$$\ln K_{298} = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (298\ \text{K})}$$

and

$$\ln K_{308} = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (308\ \text{K})}$$

Subtracting the two equations from each other allows the standard reaction entropy to be eliminated

$$\begin{aligned}\ln K_{308} - \ln K_{298} &= \left\{\frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (308\ \text{K})}\right\} - \left\{\frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (298\ \text{K})}\right\}\\ &= -\frac{\Delta_r H^\ominus}{R \times (308\ \text{K})} + \frac{\Delta_r H^\ominus}{R \times (298\ \text{K})}\\ &= -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{308\ \text{K}} - \frac{1}{298\ \text{K}}\right)\\ &= -\frac{\Delta_r H^\ominus}{8.314\ \text{J K}^{-1}\text{mol}^{-1}} \times (-1.90 \times 10^{-4}\ \text{K}^{-1})\\ &= 1.31 \times 10^{-5} (\text{J mol}^{-1})^{-1} \times \Delta_r H^\ominus\end{aligned}$$

But,

$$\ln K_{308} - \ln K_{298} = \ln(K_{308}/K_{298}) = \ln 2$$

so that

$$\ln 2 = 1.31 \times 10^{-5} (\text{J mol}^{-1})^{-1} \times \Delta_r H^{\ominus}$$

then

$$\Delta_r H^{\ominus} = \{\ln 2 / (1.31 \times 10^{-5})\} \text{J mol}^{-1} = +52.9 \times 10^3 \text{ J mol}^{-1} = +52.9 \text{ kJ mol}^{-1}$$

18. CO_2 decomposes into CO and O_2 over a platinum catalyst

$$2\,CO_2\,(g) \rightleftharpoons 2\,CO\,(g) + O_2\,(g)$$

At 1 bar pressure, the fraction, α, of CO_2 that reacted was 0.014 at 1395 K, 0.025 at 1443 K and 0.047 at 1498 K.

(a) Calculate the equilibrium constant at 1443 K.

(b) Calculate $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ for the reaction.

Strategy

Use Equations 15.1 and 14.19 to write expressions for the equilibrium constant in terms of the fraction of CO that reacted. Substitute the values of α to calculate the values of the equilibrium constants at the three temperatures. Follow the method described in W.E. 15.9 and plot a graph of ln K against 1 / T and determine $\Delta_r H^{\ominus}$ and $\Delta_r S^{\ominus}$ from the gradient and intercept.

Solution

(a) The equilibrium constant has the form

$$K = \frac{\left(a_{CO(g)}\right)^2_{eqm}\left(a_{O_2(g)}\right)_{eqm}}{\left(a_{CO_2(g)}\right)^2_{eqm}}$$

$$= \frac{\left(p_{CO(g)}/p^{\ominus}\right)^2_{eqm}\left(p_{O_2(g)}/p^{\ominus}\right)_{eqm}}{\left(p_{CO_2(g)}/p^{\ominus}\right)^2_{eqm}}$$

$$= \frac{\left(x_{CO(g)}\right)^2_{eqm}\left(x_{O_2(g)}\right)_{eqm}}{\left(x_{CO_2(g)}\right)^2_{eqm}} \times (p/p^{\ominus})$$

The mole fractions of the components are, according to Equation 8.9,

$$x_{CO(g)} = n_{CO(g)}/n_{total} = n_{CO(g)}/\left(n_{CO(g)} + n_{CO_2(g)} + n_{O_2(g)}\right)$$

and so on. But if α is the fraction of CO_2 that has reacted, then

$$\left(n_{CO_2(g)}\right)_{eqm} = (1-\alpha)\left(n_{CO_2(g)}\right)_0$$
$$\left(n_{CO(g)}\right)_{eqm} = \alpha\left(n_{CO_2(g)}\right)_0$$
$$\left(n_{O_2(g)}\right)_{eqm} = ½\alpha\left(n_{CO_2(g)}\right)_0$$

so that

$$n_{total} = (1-\alpha)\left(n_{CO_2(g)}\right)_0 + \alpha\left(n_{CO_2(g)}\right)_0 + ½\alpha\left(n_{CO_2(g)}\right)_0 = (1+½\alpha)\left(n_{CO_2(g)}\right)_0$$

and therefore

$$\left(x_{CO_2(g)}\right)_{eqm} = (1-\alpha)\left(n_{CO_2(g)}\right)_0/(1+½\alpha)\left(n_{CO_2(g)}\right)_0 = (1-\alpha)/(1+½\alpha)$$
$$\left(x_{CO(g)}\right)_{eqm} = \alpha\left(n_{CO_2(g)}\right)_0/(1+½\alpha)\left(n_{CO_2(g)}\right)_0 = \alpha/(1+½\alpha)$$
$$\left(x_{O_2(g)}\right)_{eqm} = ½\alpha\left(n_{CO_2(g)}\right)_0/(1+½\alpha)\left(n_{CO_2(g)}\right)_0 = ½\alpha/(1+½\alpha)$$

so that

$$K = \frac{\alpha^2 \times ½\alpha}{(1-\alpha)^2(1+½\alpha)} \times (p/p^{\ominus})$$

Thus if, at 1443 K and p = 1 bar, α = 0.025, then

$$K_{1443} = \frac{½ \times 0.025^3}{0.975^2 \times 1.0125} = 8.12 \times 10^{-6}$$

and in the same way

$$K_{1395} = 1.40 \times 10^{-6}$$

and

$$K_{1498} = 5.85 \times 10^{-5}$$

(b) The van’t Hoff equation, Equation 15.10

$$\ln K = \frac{\Delta_r S^{\ominus}}{R} - \frac{\Delta_r H^{\ominus}}{RT}$$

which if rewritten as

$$\ln K = \frac{\Delta_r S^{\ominus}}{R} - \frac{\Delta_r H^{\ominus}}{R} \times 1/T$$

has the form of a straight-line graph

$$\ln K = c + m/T$$

Thus a graph of ln K against 1 / T has a gradient of $-\Delta_r H^{\ominus}/R$ and intercept of $+\Delta_r S^{\ominus}$. Plotting the data results in a graph with a gradient of

$$m = -\frac{\Delta_r H^{\ominus}}{R} = -75.4 \times 10^3\,\text{K}$$

so that

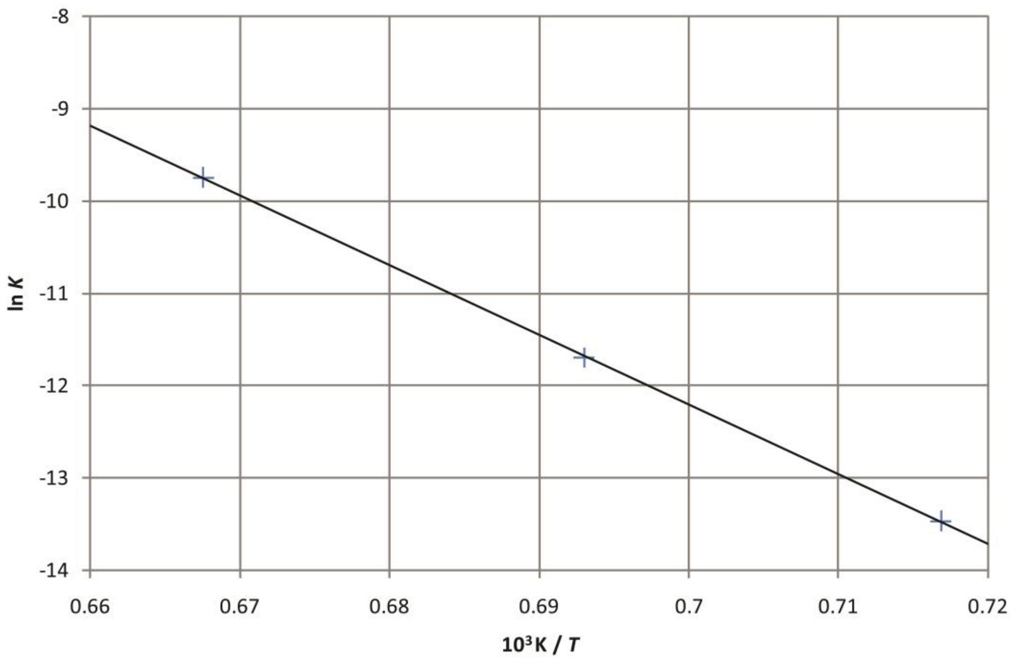
$$\Delta_r H^{\ominus} = -(-75.4 \times 10^3\,\text{K}) \times (8.314\,\text{J K}^{-1}\text{mol}^{-1})$$
$$= +626 \times 10^3\,\text{J mol}^{-1} = +626\,\text{kJ mol}^{-1}$$

and an intercept of

$$c = \frac{\Delta_r S^{\ominus}}{R} = +40.6$$

so that

$$\Delta_r S^{\ominus} = +40.6 \times (8.314\,\text{J K}^{-1}\text{mol}^{-1}) = +338\,\text{J K}^{-1}\text{mol}^{-1}$$



19. For a general reaction

$$\alpha\text{A} + \beta\text{B} \rightleftharpoons \gamma\text{C} + \delta\text{D}$$

Derive the relationship between the Gibbs energy change of the reaction and the reaction quotient. Use the relationship to show that $\Delta_r G^\ominus = -RT \ln K$.

Strategy

Start from the general definition of the Gibbs energy of the components and write an expression for the change in Gibbs energy on reaction.

Solution

In general, the Gibbs energy of a component J is

$$G_\mathrm{J} = G_\mathrm{J}^\ominus + RT \ln (a_\mathrm{J})$$

We may rewrite this as

$$G_\mathrm{J}^\ominus = G_\mathrm{J} - RT \ln (a_\mathrm{J})$$

The standard Gibbs energy change of reaction is

$$\Delta_\mathrm{r} G^\ominus = \sum_i \nu_i G^\ominus (\text{products}) - \nu_i G^\ominus (\text{reactants})$$

which for the reaction given becomes

$$\begin{aligned}\Delta_\mathrm{r} G^\ominus &= \gamma G_\mathrm{C}^\ominus + \delta G_\mathrm{D}^\ominus - \alpha G_\mathrm{A}^\ominus - \beta G_\mathrm{B}^\ominus \\ &= \gamma (G_\mathrm{C} - RT \ln a_\mathrm{C}) + \delta (G_\mathrm{D} - RT \ln a_\mathrm{D}) \\ &\qquad - \alpha (G_\mathrm{A} - RT \ln a_\mathrm{C}) - \beta (G_\mathrm{B} - RT \ln a_\mathrm{C}) \\ &= (\gamma G_\mathrm{C} + \delta G_\mathrm{D} - \alpha G_\mathrm{A} - \beta G_\mathrm{B}) - RT(\gamma \ln a_\mathrm{C} + \delta \ln a_\mathrm{D} - \alpha \ln a_\mathrm{A} - \beta \ln b_\mathrm{B}) \\ &= \Delta_\mathrm{r} G - RT \ln \frac{a_\mathrm{C}^\gamma a_\mathrm{D}^\delta}{a_\mathrm{A}^\alpha a_\mathrm{B}^\beta} \\ &= \Delta_\mathrm{r} G - RT \ln Q\end{aligned}$$

because

$$\Delta_\mathrm{r} G = (\gamma G_\mathrm{C} + \delta G_\mathrm{D} - \alpha G_\mathrm{A} - \beta G_\mathrm{B})$$

and according to the rules for manipulation of logarithms that are described in Section MT3 of the Maths Toolkit,

$$x \ln y = \ln x^y$$

When the reaction reaches equilibrium, $\Delta_\mathrm{r} G = 0$ and $Q = K$, so that

$$\Delta_\mathrm{r} G^\ominus = \Delta_\mathrm{r} G - RT \ln Q$$

$$= 0 - RT \ln K$$
$$= -RT \ln K$$

20. Silver carbonate decomposes on heating. Calculate the equilibrium constant at 383 K for the reaction. Would it be appropriate to dry a sample of silver carbonate in an oven at 383 K?

	Ag_2CO_3 (s)	Ag_2O (s)	CO_2 (g)
$\Delta_f H^{\ominus}_{298}$ / kJ mol^{-1}	–501.4	–31.1	–393.5
$S^{\ominus}_{298}$ / J K^{-1} mol^{-1}	167.3	121.3	213.7
C_p / J K^{-1} mol^{-1}	109.6	65.9	37.1

Strategy

Write a balanced chemical equation for the thermal decomposition of silver carbonate. Calculate the standard reaction enthalpy and entropy change at 298 K and hence, by determining the change in the heat capacity, at 383 K. Use your values to determine the change in the Gibbs energy of reaction and thus the equilibrium constant at 383 K.

Solution

The products of the thermal decomposition of silver carbonate are silver oxide and carbon dioxide.

$$Ag_2CO_3\,(s) \rightleftharpoons Ag_2O\,(s) + CO_2\,(g)$$

Using Equation 13.6,

$$\Delta_r H^{\ominus}_{298} = \sum_i \nu_i \Delta_f H^{\ominus}_{298}(\text{products}) - \nu_i \Delta_f H^{\ominus}_{298}(\text{reactants})$$

$$= \overbrace{\left(\Delta_f H^{\ominus}_{298}(Ag_2O(s)) + \Delta_f H^{\ominus}_{298}(CO_2(g))\right)}^{\text{products}} - \overbrace{\Delta_f H^{\ominus}_{298}(Ag_2CO_3(s))}^{\text{reactant}}$$

$$= \{(-31.1\ \text{kJ mol}^{-1}) + (-393.5\ \text{kJ mol}^{-1})\} - (-501.4\ \text{kJ mol}^{-1})$$

$$= +76.8\ \text{kJ mol}^{-1} = +76.8 \times 10^3\,\text{J mol}^{-1}$$

and Equation 14.11 to determine $\Delta_r S^{\circ}_{298}$

$$\Delta_r S^{\circ}_{298} = \sum_i \nu_i S^{\circ}_{298}(\text{products}) - \nu_i S^{\circ}_{298}(\text{reactants})$$
$$= \{S^{\circ}_{298}(\text{Ag}_2\text{O(s)}) + S^{\circ}_{298}(\text{CO}_2(\text{g}))\} - S^{\circ}_{298}(\text{Ag}_2\text{CO}_3(\text{s}))$$
$$= \{(121.3\ \text{J K}^{-1}\text{mol}^{-1}) + (213.7\ \text{J K}^{-1}\text{mol}^{-1})\} - (167.3\ \text{J K}^{-1}\text{mol}^{-1})$$
$$= +167.7\ \text{J K}^{-1}\text{mol}^{-1}$$

Using Equation 13.11, and assuming that the heat capacities themselves remain constant with temperature,

$$\Delta_r C^{\circ}_p = \sum_i \nu_i C^{\circ}_p(\text{products}) - \nu_i C^{\circ}_p(\text{reactants})$$
$$= C^{\circ}_p(\text{Ag}_2\text{O(s)}) + C^{\circ}_p(\text{CO}_2(\text{g})) - C^{\circ}_p(\text{Ag}_2\text{CO}_3(\text{g}))$$
$$= (65.9\ \text{J K}^{-1}\text{mol}^{-1}) + (37.1\text{J K}^{-1}\text{mol}^{-1}) - (109.6\ \text{J K}^{-1}\text{mol}^{-1})$$
$$= -6.6\ \text{J K}^{-1}\text{mol}^{-1}$$

Then, applying Kirchhoff's law, Equation 13.10,

$$\Delta_r H^{\circ}_{T_2} = \Delta_r H^{\circ}_{T_2} + \Delta C^{\circ}_p(T_2 - T_1)$$

to find $\Delta_r H^{\circ}$ at 383 K

$$\Delta_r H^{\circ}_{383} = \Delta_r H^{\circ}_{298} + \Delta C^{\circ}_p(383\ \text{K} - 298\ \text{K})$$
$$= +76.8 \times 10^3 \text{J mol}^{-1} + \{(-6.6\ \text{J K}^{-1}\text{mol}^{-1}) \times (85\ \text{K})\}$$
$$= +76.2 \times 10^3\ \text{J mol}^{-1} = +76.2\ \text{kJ mol}^{-1}$$

and using Equation 14.12

$$\Delta_r S^{\circ}_{T_2} = \Delta_r S^{\circ}_{T_1} + \Delta C_p \ln(T_2/T_1)$$

to determine the entropy change at 383 K

$$\Delta_r S^{\circ}_{383} = \Delta_r S^{\circ}_{298} + \Delta C_p \ln(383\ \text{K}/298\ \text{K})$$
$$= (+167.7\ \text{J K}^{-1}\text{mol}^{-1}) + \{(-6.6\ \text{J K}^{-1}\text{mol}^{-1}) \times \ln(383/298)\}$$
$$= +166.0\ \text{J K}^{-1}\text{mol}^{-1}$$

so that

$$\Delta_r G^{\circ}_{383} = \Delta_r H^{\circ}_{383} - T\Delta_r S^{\circ}_{383}$$
$$= (+76.2 \times 10^3\ \text{J mol}^{-1}) - \{(383\ \text{K}) \times (166.0\ \text{J K}^{-1}\ \text{mol}^{-1})\}$$

$$= +12.6 \times 10^3\ \mathrm{J\ mol^{-1}} = +12.6\ \mathrm{kJ\ mol^{-1}}$$

from Equation 14.16. Then, using Equation 15.5,

$$K_{383} = \mathrm{e}^{-\Delta_r G^\ominus/RT} = \mathrm{e}^{-(12.6\times10^3\ \mathrm{J\ mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1} mol^{-1}})\times(383\ \mathrm{K})\}} = 0.019$$

The reaction quotient may be written, using Equations 15.2 and 14.19 as

$$Q = \frac{a_{\mathrm{Ag_2O(s)}}a_{\mathrm{CO_2(g)}}}{a_{\mathrm{Ag_2CO_3(s)}}} = p_{\mathrm{CO_2(g)}}/p^\ominus$$

because the activities of the two solids, which are in their standard states are both 1. For the reaction to proceed spontaneously,

$$Q < K$$

so that

$$Q < 0.019$$

meaning that $\quad p_{\mathrm{CO_2(g)}} < 0.019\ \mathrm{bar}$

Thus, if silver carbonate is heated to a temperature of 383 K in an atmosphere with a partial pressure of carbon dioxide of less than 0.019 bar then the silver carbonate will decompose. In air, $p(CO_2)$ is usually around 4×10^{-4} bar (400 ppm) so that some decomposition will occur.

21. For the following esterification reaction

$$C_2H_5OH\ (aq) + CH_3CO_2H\ (aq) \rightleftharpoons CH_3CO_2C_2H_5\ (aq) + H_2O\ (l)$$

The equilibrium constant at 298 K is 3.8. A mixture containing 0.5 mol dm^{-3} each of ethanol and ethanoic acid was reacted in a sealed flask at 298 K. After a certain time, the concentrations of each had changed to 0.39 mol dm^{-3}.

(a) Had the reaction reached equilibrium?

(b) If not, what would the concentration of $CH_3CO_2C_2H_5$ (aq) be at equilibrium?

(c) In practice, the reaction is carried out so as to remove the water as it forms. Explain why this is so.

Strategy

Write an expression for the reaction quotient in terms of the activities and hence the mole fractions of the various components using Equation 15.2 and the relations given in Section 15.1. Compare the value of the reaction quotient with the value of the equilibrium constant to determine whether the mixture had reached equilibrium.

Solution

(a) The reaction quotient is, according to Equation 15.2,

$$Q = \frac{\left(a_{\mathrm{CH_3CO_2C_2H_5(aq)}}\right)\ \left(a_{\mathrm{H_2O(l)}}\right)}{\left(a_{\mathrm{C_2H_5OH(aq)}}\right)\ \left(a_{\mathrm{CH_3CO_2H(aq)}}\right)}$$

The activity of a component in solution is, according to Section 15.1,

$$a_{\mathrm{J}} = [\mathrm{J}]/1\ \mathrm{mol\ dm^{-3}}$$

The relationship is strictly only valid for dilute solutions, which is not necessarily the case for this reaction, but if the assumption is applied in this case

$$Q = \frac{[\mathrm{CH_3CO_2C_2H_5(l)}] \times [\mathrm{H_2O(l)}]}{[\mathrm{C_2H_5OH(l)}] \times [\mathrm{CH_3CO_2H(l)}]}$$

If the concentration of ethanol and ethanoic acid is 0.50 mol dm^{-3} initially, and 0.39 mol dm^{-3} at equilibrium, then

$$\begin{aligned}[\mathrm{CH_3CO_2C_2H_5(l)}] = [\mathrm{H_2O(l)}] &= [\mathrm{C_2H_5OH(l)}]_0 - [\mathrm{C_2H_5OH(l)}] \\ &= 0.50\ \mathrm{mol\ dm^{-3}} - 0.39\ \mathrm{mol\ dm^{-3}} \\ &= 0.11\ \mathrm{mol\ dm^{-3}}\end{aligned}$$

so that

$$Q = \frac{0.11\ \mathrm{mol\ dm^{-3}} \times 0.11\ \mathrm{mol\ dm^{-3}}}{0.39\ \mathrm{mol\ dm^{-3}} \times 0.39\ \mathrm{mol\ dm^{-3}}} = 0.079$$

Since this is less than K the reaction has not reached equilibrium and the forward reaction will proceed.

(b) The equilibrium constant

$$K = 3.8 = \frac{\left([\mathrm{C_2H_5OH(l)}]_0 - [\mathrm{C_2H_5OH(l)}]_{\mathrm{eqm}}\right)^2}{[\mathrm{C_2H_5OH(l)}]_{\mathrm{eqm}}[\mathrm{CH_3CO_2H(l)}]_{\mathrm{eqm}}}$$

$$3.8 = \frac{\left(0.5\ \mathrm{mol\ dm^{-3}} - [\mathrm{C_2H_5OH(l)}]_{\mathrm{eqm}}\right)^2}{[\mathrm{C_2H_5OH(l)}]^2_{\mathrm{eqm}}}$$

Taking the square root of both sides,

$$\sqrt{3.8} = 1.95 = \frac{(0.5 \text{ mol dm}^{-3} - [C_2H_5OH(l)]_{eqm})}{[C_2H_5OH(l)]_{eqm}}$$

$$1.95\ [C_2H_5OH(l)]_{eqm} = (0.5 \text{ mol dm}^{-3} - [C_2H_5OH(l)]_{eqm})$$

$$2.95\ [C_2H_5OH(l)]_{eqm} = 0.5 \text{ mol dm}^{-3}$$

Which leads to $[C_2H_5OH(l)]_{eqm}$ = 0.17 mol dm^{-3}.

Hence, since

$$\begin{aligned}[CH_3CO_2C_2H_5(l)]_{eqm} &= [C_2H_5OH(l)]_0 - [C_2H_5OH(l)]_{eqm} \\ &= (0.50 - 0.17) \text{ mol dm}^{-3} \\ &= 0.33 \text{ mol dm}^{-3}\end{aligned}$$

Thus the concentration of the ester at equilibrium is 0.33 mol dm^{-3}.

(c) Removing the water will reduce the value of Q and so drive the equilibrium towards formation of the ester.

22. The equilibrium constant for the reaction:

$$SO_3\ (g) \rightleftharpoons SO_2\ (g) + \tfrac{1}{2}\ O_2\ (g)$$

has been measured as 0.157 at 900 K and 0.513 at 1000 K. Assuming the values of ΔH and ΔS are constant over this temperature range, calculate the standard enthalpy change and the entropy change for the reaction.

Strategy

Use the van't Hoff equation, Equation 15.10, to write two simultaneous equations. Solve for the unknown enthalpy and entropy of reaction.

Solution

The van't Hoff Equation, Equation 15.10, has the form

$$\ln K = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$$

so that at 900 K,

$$\ln 0.157 = -1.85 = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (900\ \text{K})}$$

and at 1000 K,

$$\ln 0.513 = -0.67 = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (1000\ \text{K})}$$

Subtracting the two equations to eliminate $\Delta_r S^\ominus$

$$-1.85 - (-0.67) = -\frac{\Delta_r H^\ominus}{R \times (900\ \text{K})} - \frac{\Delta_r H^\ominus}{R \times (1000\ \text{K})}$$

$$-1.18 = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{900\ \text{K}} - \frac{1}{1000\ \text{K}}\right)$$

$$\frac{\Delta_r H^\ominus}{R} = +10.62 \times 10^3\,\text{K}$$

$$\Delta_r H^\ominus = (+10.62 \times 10^3\,\text{K}) \times (8.314\ \text{J K}^{-1}\text{mol}^{-1})$$

$$\Delta_r H^\ominus = +88.3\ \text{kJ mol}^{-1}$$

Substituting to find $\Delta_r S^\ominus$

$$\frac{\Delta_r S^\ominus}{R} = \frac{\Delta_r H^\ominus}{R \times 900\ \text{K}} - 1.85 = \frac{+10.62 \times 10^3\,\text{K}}{900\ \text{K}} - 1.85 = +9.95$$

so that

$$\Delta_r S^\ominus = +9.95 \times R = +9.95 \times (8.314\ \text{J K}^{-1}\text{mol}^{-1}) = +82.7\ \text{J K}^{-1}\text{mol}^{-1}$$

23. An equilibrium constant, K, is five times larger when a reaction is performed at 200 K than at 150 K. Assuming the enthalpy change is constant over this temperature range, calculate $\Delta_r H^\ominus$ for the reaction

<u>**Strategy**</u>

Use the van't Hoff equation, Equation 15.10, to write expressions for the equilibrium constant at the two temperatures. Combine the two equations to give an expression for the ratio of the equilibrium constants in terms of the enthalpy change.

Solution

The van't Hoff Equation, Equation 15.10, has the form

$$\ln K = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$$

so that

$$\ln K_{200} = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (200\ \text{K})}$$

and

$$\ln K_{150} = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (150\ \text{K})}$$

Subtracting the equations

$$\ln K_{200} - \ln K_{150} = \left(\frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (200\ \text{K})}\right) - \left(\frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{R \times (150\ \text{K})}\right)$$

$$\ln(K_{200}/K_{150}) = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{200\ \text{K}} - \frac{1}{150\ \text{K}}\right)$$

But

$$K_{200}/K_{150} = 5$$

so that

$$\ln(5) = -\frac{\Delta_r H^\ominus}{R}\left(\frac{1}{200\ \text{K}} - \frac{1}{150\ \text{K}}\right)$$

Rearranging gives

$$\Delta_r H^\ominus = +966\ \text{K} \times R = +966\ \text{K} \times (8.314\ \text{J K}^{-1}\text{mol}^{-1})$$

$$= +8.0 \times 10^3\ \text{J mol}^{-1} = +8.0\ \text{kJ mol}^{-1}$$

24. If the following reaction was at equilibrium in a closed vessel at a controlled temperature, what would be the effect of adding more H_2 to the reaction vessel and permitting the reaction to approach equilibrium again?

$$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$$

Strategy

Write the expression for the equilibrium constant using Equation 15.1 and consider the effect of increasing the hydrogen pressure on the other components, remembering that K remains constant at a fixed temperature.

Solution

The equilibrium constant is given by:

$$K = \frac{(a_{CO_2(g)})_{eqm}(a_{H_2(g)})_{eqm}}{(a_{CO(g)})_{eqm}(a_{H_2O(g)})_{eqm}} = \frac{(p_{CO_2(g)}/1\text{bar})_{eqm}(p_{H_2(g)}/1\text{bar})_{eqm}}{(p_{CO(g)}/1\text{bar})_{eqm}(p_{H_2O(g)}/1\text{bar})_{eqm}}$$

If $p_{H_2(g)}$ increases then, in order to keep K constant, $p_{CO_2(g)}$must reduce while $p_{CO(g)}$ and $p_{H_2O(g)}$increase. i.e. the reverse reaction is promoted.

25. The folding and unfolding of proteins have important biological effects (see Chapter 14, p.653). Studies have been carried out on protein G which shows a reversible transition from a folded to an unfolded form as the temperature is raised.

$$\text{protein G (folded)} \rightleftharpoons \text{protein G (unfolded)}$$

For the unfolding of protein G at the normal cell temperature of 37 °C (310 K), $\Delta H^{\ominus}$ = +210.9 kJ mol^{-1} and $\Delta S^{\ominus}$ = +616.7 J K^{-1} mol^{-1}.

(a) Write an expression for K for this equilibrium.

(b) What is the value of K at the temperature when the protein is half-folded and half-unfolded?

(c) What is the value of $\Delta G^{\ominus}$ at this temperature?

(d) Calculate $\Delta G^{\ominus}$ for the unfolding process at 310 K.

(e) Calculate K at 310 K and comment on the value you obtain.

(f) Calculate a value for K at 69°C (342 K) and comment on the value you obtain.

Strategy

Use Equation 14.16 and 15.4 to determine the Gibbs energy change and equilibrium constant. Assume that the enthalpy and entropy of reaction do not vary significantly with temperature.

Solution

(a) The equilibrium constant for the process is, according to Equation 15.1,

$$K = \frac{\left(a_{\mathrm{G(unfolded)}}\right)_{\mathrm{eqm}}}{\left(a_{\mathrm{G(folded)}}\right)_{\mathrm{eqm}}}$$

Assuming that the proteins are in dilute solution, then we may use the expression in Section 15.1 to replace the activities by the concentrations

$$K = \frac{[\mathrm{G(unfolded)}]_{\mathrm{eqm}}/c^{\ominus}}{[\mathrm{G(folded)}]_{\mathrm{eqm}}/c^{\ominus}} = \frac{[\mathrm{G(unfolded)}]_{\mathrm{eqm}}}{[\mathrm{G(folded)}]_{\mathrm{eqm}}}$$

(b) If the concentrations of the folded and unfolded proteins are equal, then $K = 1$.

(c) Using Equation 15.4,

$$\Delta_r G^{\ominus} = -RT \ln K = -RT \ln 1 = 0$$

(d) Using Equation 14.16,

$$\begin{aligned}\Delta_r G^{\ominus}_{310} &= \Delta_r H^{\ominus}_{310} - T\Delta_r S^{\ominus}_{310} \\ &= (+210.9 \times 10^3 \,\mathrm{J\ mol^{-1}}) - (310\ \mathrm{K}) \times (616.7\ \mathrm{J\ K^{-1} mol^{-1}}) \\ &= +19.7 \times 10^3 \mathrm{J\ K^{-1} mol^{-1}} = +19.7\ \mathrm{kJ\ K^{-1} mol^{-1}}\end{aligned}$$

(e) Rearranging Equation 15.4,

$$\begin{aligned}\ln K_{310} &= -\Delta_r G^{\ominus}_{310}/RT \\ &= -(19.7 \times 10^3\ \mathrm{J\ K^{-1} mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1} mol^{-1}}) \times (310\ \mathrm{K})\} \\ &= -7.65\end{aligned}$$

so that

$$K_{310} = \mathrm{e}^{-7.65} = 4.8 \times 10^{-4}$$

Thus, at this temperature, $K < 1$, implying that the protein G is largely in the folded state at 310 K.

(f) Assuming that the Gibbs energy does not vary significantly with temperature,

$$\begin{aligned}\ln K_{342} &= -\Delta_r G^{\ominus}_{342}/RT \\ &= -(19.7 \times 10^3\ \mathrm{J\ K^{-1} mol^{-1}})/\{(8.314\ \mathrm{J\ K^{-1} mol^{-1}}) \times (342\ \mathrm{K})\} \\ &= -6.93\end{aligned}$$

so that

$$K_{342} = \mathrm{e}^{-6.93} = 9.8 \times 10^{-4}$$

Thus,

$$K_{342} > K_{310}$$

implying that at this higher temperature, the protein has become more unfolded.

26. For the reaction

$$CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$$

	$\Delta_f H^{\ominus}_{298}$ / **kJ mol^{-1}**	$S^{\ominus}_{298}$ / **J K^{-1} mol^{-1}**	C_p / **J K^{-1} mol^{-1}**
CO (g)	–110.5	197.7	29.1
H_2O (g)	–241.8	188.8	33.6
CO_2 (g)	–393.5	213.7	37.1
H_2 (g)	0	130.7	28.8

(a) Use the data to calculate the Gibbs energy change and the equilibrium constant at 798 K.

(b) 1 mol of CO and 1 mol of H_2O (g) are introduced into a container at 798 K and allowed to come to equilibrium at a total pressure of 0.1 bar. Write an expression to relate the equilibrium constant to the number of moles of each component in the equilibrium mixture and calculate the number of moles of H_2 gas present at equilibrium.

$$CO\ (g) + H_2O\ (g) \rightarrow CO_2\ (g) + H_2\ (g)$$

Strategy

(a) Use Equations 13.6 and 14.11 to determine the standard enthalpy and entropy change for the reaction at 298 K. Then calculate the change in the heat capacity and use Equations 13.10 and 14.7 to determine the standard enthalpy and entropy change for the reaction at 798 K. Substitute the values into Equation 14.16 to find the corresponding change in Gibbs energy at the new temperature and then Equation 15.5 to determine the equilibrium constant.

(b) Use Equation 15.1 to write a general expression for the equilibrium constant in terms of the activities of the components. Then use the relations in Section 15.1 to express the activities in terms of the mole fractions of each component. Substitute the known initial amounts of CO and H_2O and hence find the unknown amount of H_2 at equilibrium.

Solution

Using Equation 13.6,

$$\Delta_r H^{\circ}_{298} = \sum_i \nu_i \Delta_f H^{\circ}_{298}(\text{products}) - \nu_i \Delta_f H^{\circ}_{298}(\text{reactants})$$

$$= \overbrace{\left(\Delta_f H^{\circ}_{298}(\mathrm{CO_2(g)}) + \Delta_f H^{\circ}_{298}(\mathrm{H_2(g)})\right)}^{\text{products}}$$

$$- \overbrace{\left(\Delta_f H^{\circ}_{298}(\mathrm{CO(g)}) + \Delta_f H^{\circ}_{298}(\mathrm{H_2O(g)})\right)}^{\text{reactants}}$$

$$= \{(-393.5\ \mathrm{kJ\ mol^{-1}}) + (0\ \mathrm{kJ\ mol^{-1}})\}$$

$$-\{(-110.5\ \mathrm{kJ\ mol^{-1}}) + (-241.8\ \mathrm{kJ\ mol^{-1}})\}$$

$$= -41.2\ \mathrm{kJ\ mol^{-1}} = -41.2 \times 10^3\ \mathrm{J\ mol^{-1}}$$

and Equation 14.11 to determine $\Delta_r S^{\circ}{}_{298}$

$$\Delta_r S^{\circ}_{298} = \sum_i \nu_i S^{\circ}_{298}(\text{products}) - \nu_i S^{\circ}_{298}(\text{reactants})$$

$$= \overbrace{\left(S^{\circ}_{298}(\mathrm{CO_2(g)}) + S^{\circ}_{298}(\mathrm{H_2(g)})\right)}^{\text{products}}$$

$$- \overbrace{\left(S^{\circ}_{298}(\mathrm{CO(g)}) + S^{\circ}_{298}(\mathrm{H_2O(g)})\right)}^{\text{reactants}}$$

$$= \{(213.7\ \mathrm{J\ K^{-1}mol^{-1}}) + (130.7\ \mathrm{J\ K^{-1}mol^{-1}})\}$$

$$-\{(197.7\ \mathrm{J\ K^{-1}mol^{-1}}) + (188.8\ \mathrm{J\ K^{-1}mol^{-1}})\}$$
$$= -42.1\ \mathrm{J\ K^{-1}mol^{-1}}$$

Using Equation 13.11, and assuming that the heat capacities themselves remain constant with temperature,

$$\Delta_r C_p^{\ominus} = \sum_i \nu_i C_p^{\ominus}(\text{products}) - \nu_i C_p^{\ominus}(\text{reactants})$$

$$= \overbrace{\left(C_p^{\ominus}(\mathrm{CO_2(g)}) + C_p^{\ominus}(\mathrm{H_2(g)})\right)}^{\text{products}} - \overbrace{\left(C_p^{\ominus}(\mathrm{CO(g)}) + C_p^{\ominus}(\mathrm{H_2O(g)})\right)}^{\text{reactants}}$$

$$= \{(37.1\ \mathrm{J\ K^{-1}mol^{-1}}) + (28.8\ \mathrm{J\ K^{-1}mol^{-1}})\}$$
$$-\{(29.1\ \mathrm{J\ K^{-1}mol^{-1}}) + (33.6\ \mathrm{J\ K^{-1}mol^{-1}})\}$$
$$= +3.2\ \mathrm{J\ K^{-1}mol^{-1}}$$

Then, applying the Kirchhoff equation, Equation 13.10,

$$\Delta_r H_{T_2}^{\ominus} = \Delta_r H_{T_2}^{\ominus} + \Delta C_p^{\ominus}(T_2 - T_1)$$

to find $\Delta_r H^{\ominus}$ at 798 K

$$\Delta_r H_{798}^{\ominus} = \Delta_r H_{298}^{\ominus} + \Delta C_p^{\ominus}(798\ \mathrm{K} - 298\ \mathrm{K})$$
$$= (-41.2\times 10^3\,\mathrm{J\ mol^{-1}}) + \{(3.2\ \mathrm{J\ K^{-1}mol^{-1}})\times(500\ \mathrm{K})\}$$
$$= -39.6\times 10^3\ \mathrm{J\ mol^{-1}} = -39.6\ \mathrm{kJ\ mol^{-1}}$$

and using Equation 14.7

$$\Delta_r S_{T_2}^{\ominus} = \Delta_r S_{T_1}^{\ominus} + \Delta C_p \ln(T_2/T_1)$$

to determine the entropy change at 798 K

$$\Delta_r S_{798}^{\ominus} = \Delta_r S_{298}^{\ominus} + \Delta C_p \ln(798\ \mathrm{K}/298\ \mathrm{K})$$
$$= (-42.1\ \mathrm{J\ K^{-1}mol^{-1}}) + \{(3.2\ \mathrm{J\ K^{-1}mol^{-1}})\times \ln(798/298)\}$$
$$= -38.9\ \mathrm{J\ K^{-1}mol^{-1}}$$

so that

$$\Delta_r G_{798}^{\ominus} = \Delta_r H_{798}^{\ominus} - T\Delta_r S_{798}^{\ominus}$$
$$= (-39.6\times 10^3\ \mathrm{J\ mol^{-1}}) - \{(798\ \mathrm{K})\times(-38.9\ \mathrm{J\ K^{-1}\ mol^{-1}})\}$$
$$= -8.6\times 10^3\ \mathrm{J\ mol^{-1}} = -8.6\ \mathrm{kJ\ mol^{-1}}$$

from Equation 14.16. Then, using Equation 15.5,

$$K_{798} = \mathrm{e}^{-\Delta_r G^{\ominus}/RT} = \mathrm{e}^{-(-8.6\times10^{3}\,\mathrm{J\,mol^{-1}})/\{(8.314\,\mathrm{J\,K^{-1}mol^{-1}})\times(798\,\mathrm{K})\}} = 3.7$$

(b) The general form of the equilibrium constant in terms of activities

$$K = \frac{\left(a_{\mathrm{CO_2(g)}}\right)_{\mathrm{eqm}}\left(a_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}}}{\left(a_{\mathrm{CO(g)}}\right)_{\mathrm{eqm}}\left(a_{\mathrm{H_2O(g)}}\right)_{\mathrm{eqm}}}$$

may be rewritten in terms of mole fractions because for a gaseous component,

$$a_{\mathrm{J(g)}} = p_{\mathrm{J}}/p^{\ominus} = x_{\mathrm{J}}p/p^{\ominus}$$

so that

$$K = \frac{\left(p_{\mathrm{CO_2(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}\left(p_{\mathrm{H_2(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}}{\left(p_{\mathrm{CO(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}\left(p_{\mathrm{H_2O(g)}}/p^{\ominus}\right)_{\mathrm{eqm}}} = \frac{\left(x_{\mathrm{CO_2(g)}}\right)_{\mathrm{eqm}}\left(x_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}}}{\left(x_{\mathrm{CO(g)}}\right)_{\mathrm{eqm}}\left(x_{\mathrm{H_2O(g)}}\right)_{\mathrm{eqm}}} =$$

There is no term in the total pressure because there is no change in the amount of gas on reaction. The mole fraction of a component is defined by Equation 8.9

$$x_{\mathrm{J}} = n_{\mathrm{J}}/n_{\mathrm{total}}$$

so that

$$K = \frac{\left(n_{\mathrm{CO_2(g)}}\right)_{\mathrm{eqm}}\left(n_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}}}{\left(n_{\mathrm{CO(g)}}\right)_{\mathrm{eqm}}\left(n_{\mathrm{H_2O(g)}}\right)_{\mathrm{eqm}}}$$

where once again, the term in the total amount, n_{total}, cancel.

If the fraction of CO that reacts is defined as α then the amounts of the reactants present at equilibrium are

$$\left(n_{\mathrm{CO(g)}}\right)_{\mathrm{eqm}} = (1-\alpha)\left(n_{\mathrm{CO(g)}}\right)_0$$

$$\left(n_{\mathrm{H_2O(g)}}\right)_{\mathrm{eqm}} = (1-\alpha)\left(n_{\mathrm{H_2O(g)}}\right)_0 = (1-\alpha)\left(n_{\mathrm{CO(g)}}\right)_0$$

if the initial amount of CO and H_2O are the same, and the amounts of the products are

$$\left(n_{\mathrm{CO_2(g)}}\right)_{\mathrm{eqm}} = \alpha\left(n_{\mathrm{CO(g)}}\right)_0$$

$$\left(n_{\mathrm{H_2(g)}}\right)_{\mathrm{eqm}} = \alpha\left(n_{\mathrm{CO(g)}}\right)_0$$

Thus, substituting these expression for the amount of each component into our equation for the equilibrium constant,

$$K = \frac{\alpha \times \alpha}{(1-\alpha)(1-\alpha)} = \frac{\alpha^2}{(1-\alpha)^2}$$

Taking square roots and rearranging

$$\frac{\alpha}{(1-\alpha)} = \pm\sqrt{K}$$

so that

$$\alpha = \pm\sqrt{K} \mp \sqrt{K}\alpha$$
$$\alpha\left(1 \pm \sqrt{K}\right) = \pm\sqrt{K}$$
$$\alpha = \pm\sqrt{K}/(1 \pm \sqrt{K})$$

Thus, at 798 K, because $K = 3.7$,

$$\alpha = \pm\sqrt{3.7}/\left(1 \pm \sqrt{3.7}\right) = 0.66 \ \text{ or } \ 1.9$$

We may ignore the second solution because α is the fraction of CO that has reacted, so must be less than 1. If the initial amount of CO was 1 mol, then at equilibrium, the amount of CO_2 must be

$$\left(n_{CO_2(g)}\right)_{eqm} = \alpha\left(n_{CO(g)}\right)_0 = 0.66 \times 1.0 \text{ mol} = 0.66 \text{ mol}$$

Note that for a reaction such as this, in which the amount of gas does not change as the reactants are converted into products, the position of the equilibrium is independent of the pressure.

27. Calculate the maximum quantity (in mol) of KIO_3 that can be added to 250 cm^3 of a solution containing 1.00×10^{-3} mol dm^{-3} of Cu^{2+} (*aq*) without precipitating $Cu(IO_3)_2$ (*s*). $K_{sp} = 1.4\times10^{-7}$ for $Cu(IO_3)_2$ (s).

Strategy

Write the expression for the solubility product in terms of the concentrations of the various ions involved. The $Cu(IO_3)_2$ will precipitate when its concentration reaches the solubility at that temperature.

Solution

The solubility product of $Cu(IO_3)_2$ is given by

$$K = (a_{Cu^{2+}}) \times (a_{IO_3^-})^2 = 1.4 \times 10^{-7}$$

where a is given by the molar concentration divided by 1 mol dm^{-3}.

$$K = \left(\frac{[Cu^{2+}]}{1\ \text{mol dm}^{-3}}\right) \times \left(\frac{[IO_3^-]}{1\ \text{mol dm}^{-3}}\right) = 1.4 \times 10^{-7}$$

Since $[Cu^{2+}] = 1.00 \times 10^{-3}$ mol dm^{-3}

$$\left(\frac{1 \times 10^{-3}\ \text{mol dm}^{3}}{1\ \text{mol dm}^{3}}\right) \times \left(\frac{[IO_3^-]}{1\ \text{mol dm}^{3}}\right)^2 = 1.4 \times 10^{-7}$$

So, $[IO_3^-] = (1.4 \times 10^{-4})^{½}$ mol dm^{-3} = 0.012 mol dm^{-3}

Since 1 mol of KIO_3 gives 2 mol of IO_3^-, the solubility of KIO_3 is 0.006 mol dm^{-3}

Hence in 250 cm^3, 0.006 / 4 = 0.0015 mol could be added.

28. For the reaction, H_2 (g) + I_2 (s) $\rightleftharpoons$ 2 HI (g), $\Delta_r G^\circ$ = 3.40 kJ mol^{-1} at 298.15 K.

(a) Calculate the equilibrium constant.

(b) Does the reaction favour the products or reactants?

(c) If additional H_2 (g) was added to the equilibrium mixture at the same temperature, predict what would happen to the position of equilibrium.

Strategy

Write the expression for the equilibrium constant in terms of the Gibbs energy change for the reaction, Equation 15.4. The value of *K* shows whether the products or reactants are favoured. The expression for the equilibrium constant in terms of the activities of the components will show the effect of adding or removing a component.

Solution

(a) $K = \exp\left(\frac{-\Delta_r G^\circ}{RT}\right) = \exp\left(\frac{-3.40\times10^3 \text{ J mol}^{-1}}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\times(298.15 \text{ K})}\right) = 0.25$

(b) The equilibrium favours the reactants since $K < 1$. However, not by very much so the equilibrium mixture contains amounts of both products and reactants

(c) $K = \left(\frac{a_{HI}^2}{a_{H_2}\times 1}\right)$

If H_2 was added, since the equilibrium constant does not change at constant temperature, the amount of HI would have to increase so it would promote the forward reaction.

29. Use data in Appendix 7 to answer the following for the reaction.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

(a) Calculate the enthalpy change and the entropy change for the reaction at 25°C. Is the reaction spontaneous at this temperature?

(b) Find the equilibrium constant under these conditions?

Strategy

The enthalpy and entropy changes can be found using Equations 13.6 and 14.11 at 298 K. Substitute the values into Equation 14.16 to find the corresponding change in Gibbs energy, the value of which will indicate whether the reaction is spontaneous. The equilibrium constant can be found using Equation 15.4.

Solution

(a) calculate $\Delta_r H^\ominus_{298}$.

$$\Delta_r H^\circ_{298} = \sum v_i \Delta_f H^\circ_{298}(\text{products}) - \sum v_i \Delta_f H^\circ_{298}(\text{reactants})$$
$$= [2\times(+33.2\,\text{kJmol}^{-1})] - [2\times(+90.3\,\text{kJmol}^{-1})]$$
$$= -114.2\,\text{kJmol}^{-1}$$

calculate $\Delta_r S^\circ_{298}$.

$$\Delta_r S^\circ_{298} = \sum v_i S^\circ_{298}(\text{products}) - \sum v_i S^\circ_{298}(\text{reactants})$$
$$= [2\times 240.1\,\text{JK}^{-1}\text{mol}^{-1}] - [2\times 210.8\,\text{JK}^{-1}\text{mol}^{-1} + 205.1\,\text{JK}^{-1}\text{mol}^{-1}]$$
$$= -146.5\,\text{JK}^{-1}\text{mol}^{-1}$$

calculate $\Delta_r G^\circ_{298}$.

$$\Delta_r G^\circ_{298} = \Delta_r H^\circ_{298} - T\Delta_r H^\circ_{298}$$
$$= -114.2\,\text{kJmol}^{-1} - [298\cancel{\text{K}} \times (-146.5\times10^{-3}\,\text{kJ}\cancel{\text{K}}^{-1}\text{mol}^{-1})]$$
$$= -43.5\,\text{kJmol}^{-1}$$

$\Delta_r G^\circ < 0$ so, the reaction is spontaneous

(b)

$$K = exp\left(\frac{-\Delta_r G^\circ}{RT}\right) = exp\left(\frac{-(-43.5\times10^3\,\text{J mol}^{-1})}{(8.314\,\text{J K}^{-1}\,\text{mol}^{-1})\times(298.15\,\text{K})}\right) = 4.18\times10^7$$

30. A student was investigating the following equilibrium reaction which has an equilibrium constant of 0.220 at 800 °C

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

and did four experiments.

(i) 0.2 g of $CaCO_3$ (s) was heated to 800 °C in a 1.0 dm^3 container

(ii) 2.0 g of $CaCO_3$ (s) was heated to 800 °C in a 1.0 dm^3 container

(iii) 0.2 g of $CaCO_3$ (s) was heated to 800 °C in a 500 cm^3 container

(iv) 2.0 g of $CaCO_3$ (s) was heated to 800 °C in a 500 cm^3 container

The pressure of CO_2(g) measured in each case was (i) 0.18 bar, (ii) 0.22 bar, (iii) 0.22 bar, (iv) 0.22 bar. Explain these observations.

Solution

For this reaction, $K = \dfrac{(a_{CO_2})(a_{CaO})}{(a_{CaCO_3})}$ $K = \dfrac{(p_{CO_2}/\text{bar})\times 1}{1} = (p_{CO_2}/\text{bar})$

Hence, $CaCO_3$ (s) will react to form CO_2 until the pressure reaches 0.22 bar after which the solid and gas will be in equilibrium.

For (i), if all the $CaCO_3$ (s) reacts, it will form 0.2 g / 100 g mol^{-1} = 0.002 mol of CO_2. Using the ideal gas equation,

$$pV = nRT$$
$$p = \frac{nRT}{V} = \frac{0.002\,\text{mol} \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times (800 + 273.15)\,\text{K}}{1\times 10^{-3}\,\text{dm}^{-3}}$$
$$= 1.8\times 10^{4}\,\text{Pa}$$

So all the $CaCO_3$ (s) reacts to give a pressure of 0.18 bar. There is insufficient $CaCO_3$ (s) to produce any further CO_2 gas.

For (ii), (ii) and (iv), sufficient $CaCO_3$ (s) reacts to bring the reaction to equilibrium, hence the pressure is 0.22 bar with some solid remaining in the container.

31. The equilibrium constants for the gas-phase dissociation of molecular iodine,
$I_2\ (g) \rightleftharpoons 2\,I\,(g)$
have been measured at the following temperatures:

$T\,/\,K$	872	973	1073	1173
K	1.8×10^{-4}	1.8×10^{-3}	1.08×10^{-2}	4.8×10^{-2}

(a) Use a graphical method to determine $\Delta_r H^{\circ}$ and $\Delta_r S^{\circ}$ for this reaction.

(b) Determine $\Delta_r G^{\circ}$ at 1000 K.

(c) What would be the effect on the position of equilibrium of increasing the temperature?

Strategy

The equilibrium constant is related to temperature through the van't Hoff equation, Equation 15.10. This shows that a plot of ln K versus reciprocal temperature should give a linear relation, the slope of which gives the enthalpy change. The entropy change can be found from the slope of the graph. The Gibbs energy change can be found from the equilibrium constant using Equation 15.4.

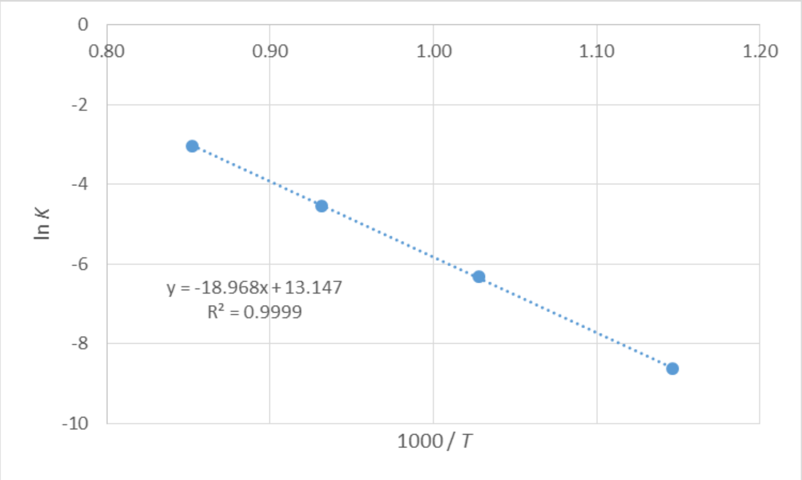
Solution

(a) Using the equation $\ln K = \frac{\Delta_r S^{\circ}}{R} - \frac{\Delta_r H^{\circ}}{RT}$, a graph of ln$K$ against $1/T$ should be linear with a gradient of $-\Delta_r H^{\circ}/R$ and intercept equal to $\Delta_r S^{\circ}/R$.

Calculating the data:

T / K	**1000/T 1/K**	K	**ln K**
872	**1.15**	1.80E-04	**-8.623**
973	**1.03**	1.80E-03	**-6.32**
1073	**0.93**	1.08E-02	**-4.528**
1173	**0.85**	4.80E-02	**-3.037**

Which gives a graph



The equation of the straight line is y = -18968 + 13.147.

Therefore, slope = -18970 K and intercept = + 13.15

$\frac{\Delta_r H^\circ}{R}$ = -(gradient) = -(-18970 K)

$\Delta_r H^\circ$ = (+ 18970 K) × (8.314 J K^{-1} mol^{-1}) = + 157.7 kJ mol^{-1}

$\frac{\Delta_r S^\circ}{R}$ = (intercept) = 13.15

$\Delta_r S^\circ$ = (+13.15) × (8.314 J K^{-1} mol^{-1}) = + 109.3 J K^{-1} mol^{-1}

(ii) $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ so

$\Delta_r G^\circ$ = (+ 157.7 kJ mol^{-1}) – (1000 K) × (+ 109.3 × 10^{-3} kJ K^{-1} mol^{-1})
= + 48.3 kJ mol^{-1}

(iii) Increasing the temperature would (a) increase the entropic contribution which favours dissociation (b) it is an endothermic reaction so Le Chatelier's principle predicts that the forward reaction will increase.