

CHAPTER 10

Practice Exercises

10.1 Since water is saturated with both oxygen and nitrogen, water contains $0.00134 \times 32 = 4.3 \times 10^{-2}$ g L⁻¹.

10.3 $K_{sp} = (2.15 \times 10^{-3})[2 \times (2.15 \times 10^{-3})]^2 = 3.98 \times 10^{-8}$

10.5 $x = 4.2 \times 10^{-16}$ M = molar concentration of AgI in a 0.20 M NaI solution.

In pure water:

$$K_{sp} = 8.3 \times 10^{-17} = [\text{Ag}^+][\text{I}^-] = (x)(x)$$

$x = 9.1 \times 10^{-9}$ M = molar concentration of AgI in pure water (much more soluble).
on.

10.7 $Q_{sp} = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (5.0 \times 10^{-4})(1.0 \times 10^{-3}) = 5.0 \times 10^{-7}$

Since $Q_{sp} < K_{sp}$ (6.3×10^{-7}), a precipitate of PbSO₄ is not expected.

10.9 $n_{\text{CH}_3\text{OH}} = 0.250 \text{ mol kg}^{-1} \times 2.000 \text{ kg} = 0.500 \text{ mol}$

$$m = nM = 0.500 \text{ mol} \times 32.042 \text{ g mol}^{-1} = 16.0 \text{ g}$$

10.11 $p_{\text{solvent}} = X_{\text{solvent}} \times p^{\circ}_{\text{solvent}} = 0.859 \times 1.38 \times 10^3 \text{ Pa} = 1.19 \times 10^3 \text{ Pa}$

10.13 $T_b = (100.00 + 0.16) ^\circ\text{C} = 100.16 ^\circ\text{C}$

10.15 $\Pi = (0.0115 \times 10^3 \text{ mol m}^{-3})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(310 \text{ K}) = 2.96 \times 10^4 \text{ Pa}$

10.17 If the solute is 100 % dissociated, 1 mole of solute gives 2 moles of ions, therefore:

$$\Delta T = K_f b = (1.86 \text{ K mol}^{-1} \text{ kg})(2 \times 0.237 \text{ mol kg}^{-1}) = 0.882 \text{ K} = 0.882 ^\circ\text{C} \text{ and the freezing point is } (0.000 - 0.882)^\circ\text{C} = -0.882 ^\circ\text{C}.$$

If the solute is 0 % dissociated:

$$\Delta T = K_f b = (1.86 \text{ K mol}^{-1} \text{ kg})(0.237 \text{ mol kg}^{-1}) = 0.441 \text{ K} = 0.441 ^\circ\text{C} \text{ and the freezing point is } (0.000 - 0.441)^\circ\text{C} = -0.441 ^\circ\text{C}.$$

Review Questions

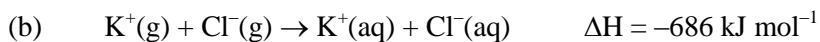
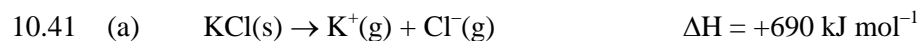
- 10.1 (a) solution: a homogeneous mixture of two or more substances
(b) solvent: the liquid in which the solute is dissolved
(c) solute: the dissolved substance in a solution
(d) solubility: the maximum amount of a solute that dissolves completely in a given amount of solvent at a specified temperature
(e) saturated solution: a solution in which no more solute can be dissolved
(f) dissolution: the process of dissolving a solute in a solvent.

- 10.3 Firstly, the tendency towards maximum entropy drives the solution process and secondly, the new forces of attraction between solute and solvent molecules drive the overall process. Thus, the relative degree of solute–solute, solvent–solvent and solute–solvent interactions determines if a solute is soluble in a solvent.
- 10.5 ‘Immiscible’ means that petrol and water exist as two separate phases, regardless of the mole ratio of the mixture. Water molecules are tightly linked to one another by hydrogen bonding. In petrol however, which is a nonpolar organic liquid, there are only weak attractive dispersion forces and so petrol as a solute in water offers no energetic advantage in attraction to individual water molecules and the solvent is therefore not disrupted to allow the solute to dissolve.
- 10.7 Ethanol molecules are more nonpolar (less polar) than those of water.
- 10.9 As Al^{3+} has a larger positive charge, it has the larger hydration enthalpy.
- 10.11 The disruption of ethanol and the disruption of hexane cost more energy than is gained on formation of the solution. This is because the two liquids are not alike. Ethanol is a polar substance which exhibits hydrogen bonding, whereas hexane is a nonpolar liquid having only dispersion forces.
- 10.13 We can estimate from the graph in figure 10.15 that the solubility of NH_4NO_3 in 100 g of H_2O is 500 g at 70°C and 150 g at 10°C . The mass of solid that crystallises is the difference between these two solubilities, namely $500 - 150 = 350$ g.
- 10.15 Oxygen solubility increases as temperature decreases. The larger fish therefore needs more oxygen and is found in the colder regions of lake bottoms.
- 10.17 The atmospheric pressure on a mountain is less than the atmospheric pressure at sea level. From Henry's law, as the partial pressure of oxygen decreases, the concentration of oxygen also decreases. Therefore, there is less oxygen to sustain life in mountain streams.
- 10.19 K_{sp} refers only to the equilibrium concentrations of ions in a saturated solution of a salt, whereas Q_{sp} refers to the concentrations of ions at any condition.
- 10.21 The common ion effect is the lowering of the solubility of a sparingly soluble ionic salt on addition of a common ion to a saturated solution of the salt. Addition of a common ion to a saturated solution instantaneously increases Q_{sp} and the equilibrium therefore shifts to the left to decrease Q_{sp} . This results in the precipitation of the sparingly soluble salt. In the case of AgCl , the balanced chemical equation for the dissolution reaction is:

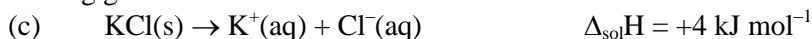
$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \text{ for which } K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}.$$
Addition of NaCl to a saturated solution containing Ag^+ and Cl^- result in the precipitation of AgCl(s) . The common ion in this case is Cl^- .
- 10.23 K_{sp} values assume 100% dissociation of the ions. However, in solution, the component ions are often not fully separated since ion pairs are often formed.
- 10.25 The molarity will be greater than 1.0. Since the density of the solution is greater than 1, the mass of the solution in kilograms will be greater than its volume in litres.

- 10.27 There are fewer molecules of solvent at the surface of a solution containing a non-volatile solute than there are in the pure solvent. Consequently, the vapour pressure is reduced relative to that of the pure solvent.
- 10.29 A positive deviation from Raoult's law indicates that the vapour pressure of the 'real' solution is greater than that of the corresponding 'ideal' solution. Such positive deviations result from the formation of mixtures whereby the intermolecular forces of attraction in the mixture are less than those in the pure components.
- 10.31 (a) When a solute is dissolved in a solvent, the vapour pressure of the resulting solution is lower than that of the pure solvent. Boiling point is defined as the temperature at which the vapour pressure of the solution is equal to atmospheric pressure. Since the vapour pressure of a solution is less than that of the solvent, a solution has a higher boiling point than that of the solvent.
- (b) A solution has a lower freezing point than that of the pure solvent so a non-volatile solute dissolved in water has a lower freezing point than that of pure water.
- 10.33 An osmotic membrane allows only solvent to pass, whereas a dialysing membrane allows solvated ions of minimum size to pass as well as solvent molecules. A dialysing membrane prevents the passage of large solute particles, such as colloid particles.
- 10.35 The side of the membrane less concentrated in solute is more concentrated in solvent. The solvent passes through the membrane from the side more concentrated in solvent (less concentrated in solute) to the side less concentrated in solvent (more concentrated in solute) in order to equalise the concentration of solvent on both sides of the membrane.
- 10.37 If a cell is placed in a solution, the concentration of salts in the solution affects those in the cell. If the solution is hypertonic, the concentration of salts in solution is higher than the concentration of salts in the cell. If the solution is hypotonic, then the concentration of salts in solution is lower than the concentration of salts in the cell.
- 10.39 The van't Hoff factor is the ratio of the value of a colligative property as measured to that expected in the complete absence of solute dissociation. A van't Hoff factor of one applies for all non-dissociating molecular solutes. A van't Hoff factor greater than one indicates a dissociation of the solute (if it is only slightly greater than one, it means that the dissociation is not extensive). A van't Hoff factor less than one indicates association of the solute. A van't Hoff factor of 0.5 indicates the formation of dimers.

Review Problems



Adding gives:



10.43 lattice enthalpy + hydration enthalpy = enthalpy of solution

Therefore:

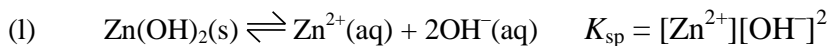
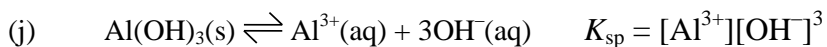
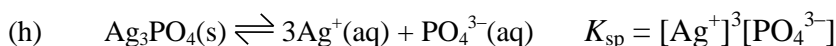
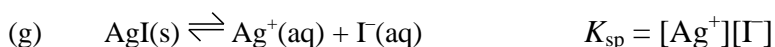
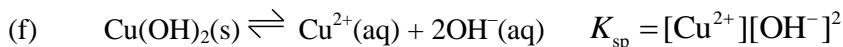
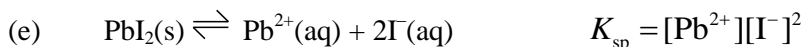
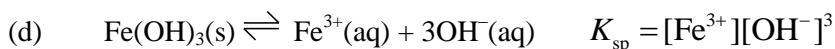
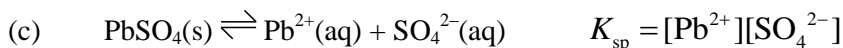
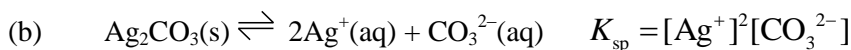
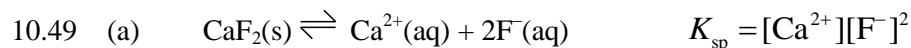
$$(+630 \text{ kJ mol}^{-1}) + \text{hydration enthalpy} = +14 \text{ kJ mol}^{-1}$$

$$\text{So hydration enthalpy} = -616 \text{ kJ mol}^{-1}$$

10.45 $c_2 = \frac{(1.5 \times 10^5 \text{ Pa})(0.025 \text{ g L}^{-1})}{1.0 \times 10^5 \text{ Pa}} = 0.038 \text{ g L}^{-1}$

10.47 Henry's law states that the solubility of a gas in a liquid is proportional to the gas pressure above the liquid. Since the pressure doubles, the solubility must also double:

$$\text{Therefore, solubility} = 2 \times (0.010 \text{ g L}^{-1}) = 0.020 \text{ g L}^{-1}.$$



10.51 $K_{\text{sp}} = [\text{Ag}^+][\text{CH}_3\text{COO}^-] = (4.79 \times 10^{-2} \text{ M})^2 = 2.29 \times 10^{-3}$

10.53 $K_{\text{sp}} = [\text{Ca}^{2+}][\text{CrO}_4^{2-}] = (0.0267)^2 = 7.13 \times 10^{-4}$

10.55 $K_{\text{sp}} = (4.2 \times 10^{-8})^3(2.8 \times 10^{-8})^2 = 5.8 \times 10^{-38}$

10.57 LiF has a greater molar solubility than BaF₂

10.59 $K_{\text{sp}} = 27(1.8 \times 10^{-5})^4 = 2.8 \times 10^{-18}$

- 10.61 (a) $x = 4.4 \times 10^{-4} \text{ M}$ = molar solubility of CuCl in pure water
(b) $x = 9.5 \times 10^{-6} \text{ M}$ = molar solubility of CuCl in 0.0200 M HCl
(c) $x = 9.5 \times 10^{-7} \text{ M}$ = molar solubility of CuCl in 0.200 M HCl
(d) $x = 6.3 \times 10^{-7} \text{ M}$ = molar solubility of CuCl in 0.150 M CaCl₂

- 10.63 (a) The molar solubility is $3.0 \times 10^{-11} \text{ M}$
(b) $x = 1.2 \times 10^{-6} \text{ M}$ = molar solubility of AuCl₃ in 0.010 M Au(NO₃)₃.

10.65 $x = 1.6 \times 10^{-3} \text{ M}$ = molar solubility of CaSO₄ in 0.015 M CaCl₂ solution

10.67 $K_{\text{sp}} = [\text{Fe}^{2+}][\text{OH}^-]^2 = 7.9 \times 10^{-16}$

For 0.250 L of solution, the number of moles of Fe(OH)₂ that dissolve is $n = cV = 2.0 \times 10^{-12} \text{ mol L}^{-1} \times 0.250 \text{ L} = 5.0 \times 10^{-13} \text{ mol}$. In terms of mass, $m = nM = 5.0 \times 10^{-13} \text{ mol} \times 89.866 \text{ g mol}^{-1} = 4.5 \times 10^{-11} \text{ g}$. This is negligible, and so all of the Fe²⁺ in solution is precipitated as Fe(OH)₂.

- 10.69 (a) $x = 0.013 \text{ M}$ = molar solubility of Ca(OH)₂ in 0.10 M CaCl₂
(b) $x = 0.0065 \text{ M}$ = molar solubility of Ca(OH)₂ in 0.10 M NaOH

10.71 Since $Q_{\text{sp}} > K_{\text{sp}}$, a precipitate forms.

10.73 Since $Q_{\text{sp}} < K_{\text{sp}}$, no precipitate forms.

- 10.75 (a) $[\text{SO}_4^{2-}] = 1.6 \times 10^{-4}$, CaSO₄ starts to precipitate
(b) Since $[\text{Sr}^{2+}] = 4.9 \times 10^{-4} \text{ M}$, the percentage of Sr²⁺ precipitated is:

$$\frac{0.15 - 4.9 \times 10^{-4}}{0.15} \times 100\% = 99.7\%$$

10.77 $b = \frac{\text{amount of solute}}{\text{mass of solvent}} = \frac{0.143 \text{ mol}}{0.991 \text{ kg}} = 0.144 \text{ mol kg}^{-1}$

10.79 $b = \frac{\text{amount of solute}}{\text{mass of solvent}} = \frac{0.250 \text{ mol}}{0.0135 \text{ kg}} = 18.5 \text{ mol kg}^{-1}$

10.81 $p_{\text{solution}} = X_{\text{solvent}} \times p_{\text{solvent}}^{\circ} = 0.959 \times (3.13 \times 10^3 \text{ Pa}) = 3.00 \times 10^3 \text{ Pa}$

10.83 $p_{\text{total}} = p_{\text{C}_5\text{H}_{12}} + p_{\text{C}_7\text{H}_{16}} = 3.21 \times 10^4 \text{ Pa} + 1.99 \times 10^3 \text{ Pa} = 3.41 \times 10^4 \text{ Pa}$

$$10.85 \quad (a) \quad X_{\text{CHCl}_3} = \frac{p_{\text{CHCl}_3}}{p_{\text{CHCl}_3}^0} = \frac{6.72 \times 10^4 \text{ Pa}}{6.92 \times 10^4 \text{ Pa}} = 0.971$$

$$\text{As } X_{\text{CHCl}_3} + X_{\text{solute}} = 1, \text{ therefore } X_{\text{solute}} = 1 - X_{\text{CHCl}_3} = 1 - 0.971 = 0.029$$

$$(b) \quad X_{\text{CHCl}_3} = \frac{n_{\text{CHCl}_3}}{n_{\text{CHCl}_3} + n_{\text{solute}}} = \frac{1.00}{1.00 + n_{\text{solute}}} = 0.971$$

$$1.00 + n_{\text{solute}} = \frac{1.00}{0.971} = 1.03$$

$$n_{\text{solute}} = 1.03 - 1.00 = 0.03 \text{ mol}$$

$$(c) \quad M_{\text{solute}} = \frac{m}{n} = \frac{8.3 \text{ g}}{0.030 \text{ mol}} = 2.8 \times 10^2 \text{ g mol}^{-1}$$

$$10.87 \quad \Delta T_b = K_b b = (0.51 \text{ K mol}^{-1} \text{ kg})(2.00 \text{ mol kg}^{-1}) = 1.0 \text{ K} = 1.0 \text{ }^\circ\text{C}$$

$$T_b = 100.0 + 1.0 = 101 \text{ }^\circ\text{C}$$

$$\Delta T_m = K_f b = (1.86 \text{ K mol}^{-1} \text{ kg})(2.00 \text{ mol kg}^{-1}) = 3.72 \text{ K} = 3.72 \text{ }^\circ\text{C}$$

$$T_f = 0.00 - 3.72 = -3.72 \text{ }^\circ\text{C}$$

10.89 In 100 g of water:

$$n_{\text{sucrose}} = 1.61 \text{ mol kg}^{-1} \times 0.100 \text{ kg} = 0.161 \text{ mol}$$

$$m_{\text{sucrose}} = nM = 0.161 \text{ mol} \times 342.296 \text{ g mol}^{-1} = 55.1 \text{ g}$$

10.91 In 200.0 g of benzene:

$$n_{\text{solute}} = 0.394 \text{ mol kg}^{-1} \times 0.200 \text{ kg} = 0.0788 \text{ mol}$$

$$M_{\text{solute}} = \frac{m}{n} = \frac{12.00 \text{ g}}{0.0788 \text{ mol}} = 152 \text{ g mol}^{-1}$$

10.93 In 500 g of benzene:

$$n_{\text{solute}} = 0.0606 \text{ mol kg}^{-1} \times 0.500 \text{ kg} = 0.0303 \text{ mol}$$

$$M_{\text{solute}} = \frac{m}{n} = \frac{3.84 \text{ g}}{0.0303 \text{ mol}} = 127 \text{ g mol}^{-1}$$

The empirical formula has $M = [(4 \times 12.01) + (2 \times 1.008) + 14.01] \text{ g mol}^{-1} = 64.066 \text{ g mol}^{-1}$.
Therefore the molecular formula is $2 \times \text{empirical formula} = \text{C}_8\text{H}_4\text{N}_2$.

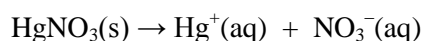
$$10.95 \quad n_{\text{solute}} = \frac{(2.76 \text{ Pa})(1.00 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 1.1 \times 10^{-6} \text{ mol}$$

$$M_{\text{solute}} = \frac{m}{n} = \frac{2.0 \text{ g}}{1.1 \times 10^{-6} \text{ mol}} = 1.8 \times 10^6 \text{ g mol}^{-1}$$

10.97 The vapour pressure is: $p_{\text{solution}} = X_{\text{solvent}} \times p^{\circ}_{\text{solvent}} = 0.942 \times (2.30 \times 10^3 \text{ Pa}) = 2.17 \times 10^3 \text{ Pa}$.

10.99 Adding these gives $\Pi = 2.87 \times 10^6 \text{ Pa}$. Thus, a pressure greater than $2.87 \times 10^6 \text{ Pa}$ is needed to desalinate seawater by reverse osmosis.

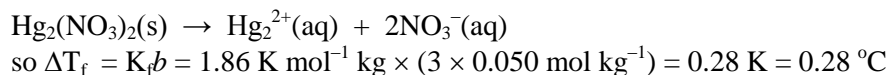
10.101 Mercury(I) nitrate, HgNO_3 , dissociates to give two moles of ions in solution according to the equation:



$$\text{so } \Delta T_f = K_f b = 1.86 \text{ K mol}^{-1} \text{ kg} \times (2 \times 0.10 \text{ mol kg}^{-1}) = 0.37 \text{ K} = 0.37 ^\circ\text{C}$$

$$\text{Freezing point} = (0.00 - 0.37)^\circ\text{C} = -0.37 ^\circ\text{C}$$

However, the observed freezing point depression is less than this so the formula is $\text{Hg}_2(\text{NO}_3)_2$ and the mercury ion is dimeric and divalent (Hg_2^{2+}). The concentration of the solution is $0.050 \text{ mol kg}^{-1}$ and $\text{Hg}_2(\text{NO}_3)_2$ gives 3 moles of ions on dissociation, according to the equation:



The freezing point is therefore $(0.00 - 0.28)^\circ\text{C} = -0.28 ^\circ\text{C}$.

$$10.103 \quad \% \text{ ionisation} = \frac{\text{amount ionised}}{\text{amount available}} = \frac{0.015}{0.125} \times 100\% = 12\%$$

10.105 If fully dissociated, K_2SO_4 has a van't Hoff factor of 3

$$10.107 \quad \Pi = cRT = (223 \text{ mol m}^{-3})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(283 \text{ K}) = 5.25 \times 10^5 \text{ Pa}$$

Additional Exercises

10.109 A simple molecular model of gas solubility predicts that the solvent expands to allow the gas to enter which is an endothermic process. Gas molecules occupy the spaces and intermolecular attractions between the gas and the solvent hold the gas in the solution and this is an exothermic process. Since helium is a small, nonpolar atom, the interaction between helium and blood is not sufficient to overcome the energy required to expand the solvent. As a result, helium is not soluble in blood.

10.111

$$X_{\text{CCl}_4} = \frac{n_{\text{CCl}_4}}{n_{\text{CCl}_4} + n_{\text{unknown}}}, \text{ so:}$$

$$n_{\text{unknown}} = n_{\text{CCl}_4} \left(\frac{1}{X_{\text{CCl}_4}} - 1 \right)$$

$$n_{\text{CCl}_4} = \left(\frac{400 \text{ g}}{153.81 \text{ g mol}^{-1}} \right) = 2.60 \text{ mol}$$

$$n_{\text{unknown}} = (2.60 \text{ mol}) \left(\frac{1}{0.895} - 1 \right) = 0.305 \text{ mol}$$

$$\text{molar mass} = \frac{43.3 \text{ g}}{0.305 \text{ mol}} = 142 \text{ g mol}^{-1}$$

10.113 $[\text{Fe}^{2+}] = 0.100 - x = 0.001 \text{ M}$ and $[\text{Mn}^{2+}] = 0.0995 \text{ M}$

10.115 concentration of Ca^{2+} is 0.072 ppm

10.117 (a) The liquid level height difference is proportional to the osmotic pressure. Therefore Π is calculated by converting the height difference to the height of a mercury column in mm, which is equal to the pressure in torr (1 mm Hg =

1 torr):

$$h_{\text{Hg}} = h_{\text{solution}} \times (\rho_{\text{solution}}/\rho_{\text{Hg}}) = (12.6 \text{ mm}) \times (1.00 \text{ g mL}^{-1}/13.6 \text{ g mL}^{-1})$$

$$= 0.926 \text{ mm Hg}$$

Since atmospheric pressure = 760 mm Hg = $1.013 \times 10^5 \text{ Pa}$ this is converted to Pa:

$$\Pi(\text{Pa}) = \frac{0.926 \text{ mm Hg}}{760 \text{ mm Hg}} \times 1.013 \times 10^5 \text{ Pa} = 1.23 \times 10^2 \text{ Pa}.$$

(b) $\Pi = cRT$

$$c = \Pi/RT = \frac{1.23 \times 10^2 \text{ Pa}}{(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K})} = 4.96 \times 10^{-2} \text{ mol m}^{-3}$$

$$= 4.96 \times 10^{-5} \text{ M}.$$

(c) Since this is a dilute solution and the solute does not dissociate, the molarity and molality are equivalent so:

$$\Delta T_f = K_f b = (1.86 \text{ K mol}^{-1} \text{ kg})(4.98 \times 10^{-5} \text{ mol kg}^{-1})$$

$$= 9.26 \times 10^{-5} \text{ K} = 9.26 \times 10^{-5} \text{ }^\circ\text{C}$$

Therefore the freezing point is $-9.26 \times 10^{-5} \text{ }^\circ\text{C}$

(d) The magnitude of the temperature change is too small to measure.

- 10.119 (a) Consider 100.0000 mol of solution and so there is 0.9159 mol KNO_3 and $(100.0000 - 0.9159) = 99.0841$ mol of water.

$$m_{\text{H}_2\text{O}} = nM = 99.0841 \text{ mol} \times 18.016 \text{ g mol}^{-1} = 1785 \text{ g} = 1.785 \text{ kg}.$$

$$\text{Therefore the molality is } b = \frac{0.9159 \text{ mol}}{1.785 \text{ kg}} = 0.5131 \text{ mol kg}^{-1}.$$

$$(b) \quad \%(w/w) \text{ KNO}_3 = \frac{\text{mass KNO}_3}{(\text{mass KNO}_3 + \text{mass H}_2\text{O})} \times 100\%$$

$$m_{\text{KNO}_3} = nM = 0.9159 \text{ mol} \times 101.11 \text{ g mol}^{-1} = 92.6 \text{ g}$$

$$\%(w/w) \text{ KNO}_3 = \frac{92.6 \text{ g KNO}_3}{(92.6 \text{ g} + 1785 \text{ g})} \times 100\% = 4.93\%$$

- (c) The total mass of the solution is $(1785 \text{ g} + 92.6 \text{ g}) = 1878 \text{ g}$. The density of the solution = 1.0489 g mL^{-1} . Therefore $V = \frac{m}{\rho} = \frac{1878 \text{ g}}{1.0489 \text{ g mL}^{-1}} = 1790 \text{ mL}$.

In 1790 mL there is 0.9159 mol KNO_3 . Therefore:

$$c = \frac{n}{V} = \frac{0.9159 \text{ mol}}{1.790 \text{ L}} = 0.5117 \text{ M}$$

Practice Questions

- 11.3
- conjugate pair
- $$\text{PO}_4^{3-}(\text{aq}) + \text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{HPO}_4^{2-}(\text{aq}) + \text{CH}_3\text{COO}^{-}(\text{aq})$$
- base acid acid base
- conjugate pair

The solution is acidic, since the pH is less than 7.0.

11.9 $[\text{H}_3\text{O}^+] = 10^{-5.5} = 3.2 \times 10^{-6} \text{ M}$

- 11.11 The stronger acid has the lower pK_a , therefore HX is the stronger acid. The K_a values are:
 For HX: $K_a = 10^{-pK_a} = 10^{-3.16} = 6.9 \times 10^{-4}$
 For HY: $K_a = 10^{-pK_a} = 10^{-4.14} = 7.2 \times 10^{-5}$
- 11.13 $x = 8.4 \times 10^{-4} \text{ M} = [\text{H}_3\text{O}^+]$
 $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(8.4 \times 10^{-4}) = 3.08$
- 11.15 $x = 4.4 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$
 $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(4.4 \times 10^{-6}) = 5.36$
- 11.17 $x = 1.2 \times 10^{-6} \text{ M} = [\text{OH}^-]$
 $\text{pOH} = -\log[\text{OH}^-] = -\log(1.2 \times 10^{-6}) = 5.93$
 $\text{pH} = 14.00 - \text{pOH} = 8.07.$
- 11.19 Since $K_b(\text{CN}^-)$ is larger than $K_a(\text{NH}_4^+)$, the NH_4CN solution is basic.
- 11.21 (a) HBr is the stronger acid since binary acid strength increases across a period.
 (b) H_2Te is the stronger acid since binary acid strength increases down a group.
 (c) CH_3SH since acid strength increases down a group.
- 11.23 In all cases, the acid with the greater number of O atoms is the stronger.
 (a) HIO_4
 (b) H_2TeO_4
 (c) H_3AsO_4
- 11.25 Use the Henderson–Hasselbalch equation:

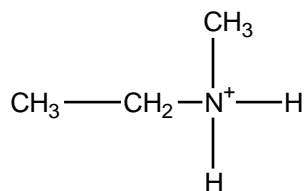
$$\text{pH} = pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$= 9.26 + \log \frac{0.08}{0.15} = 8.99$$
- 11.27 pH change is $(9.17 - 9.08) = 0.09$ pH units
- 11.29 H_2O , NH_3 and PH_3 all have at least one lone pair on the central atom and are therefore Lewis bases. ‘Hardness’ increases across a period and decreases down a group so the order of increasing hardness is $\text{PH}_3 < \text{NH}_3 < \text{H}_2\text{O}$.

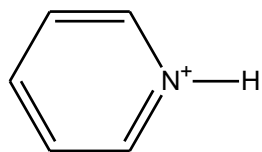
Review Questions

- 11.1 A Brønsted–Lowry acid is a proton donor and a Brønsted–Lowry base is a proton acceptor.
- 11.3 H_2SO_4 is not the conjugate acid of SO_4^{2-} because H_2SO_4 has two more hydrogen ions than SO_4^{2-} .

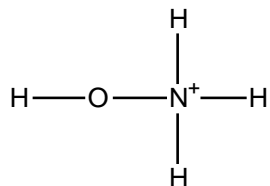
11.5 (a)



(b)

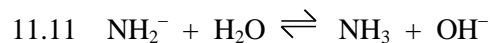


(c)

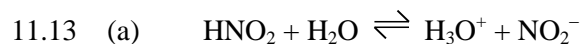


11.7 In pure water, the concentration of H_3O^+ and OH^- are equal and their product is K_w . As $K_w = 1.0 \times 10^{-14}$ at 25°C , the maximum possible concentration of H_3O^+ at this temperature is 1.0×10^{-7} (the square root of K_w).

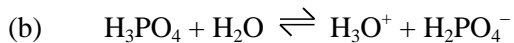
11.9 A strong acid is one that reacts completely with water to give quantitative formation of H_3O^+ .



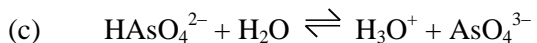
As NH_2^- is such a strong base, this reaction proceeds to completion. The NH_2^- ion accepts a proton from water and gives quantitative formation of NH_3 . As NH_3 is a very weak acid, the reverse reaction does not occur.



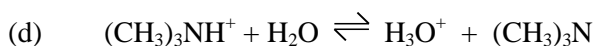
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]}$$



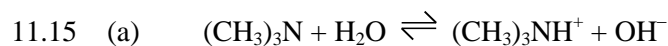
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$



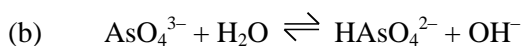
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{AsO}_4^{3-}]}{[\text{HAsO}_4^{2-}]}$$



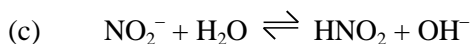
$$K_a = \frac{[\text{H}_3\text{O}^+][(\text{CH}_3)_3\text{N}]}{[(\text{CH}_3)_3\text{NH}^+]}$$



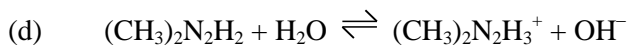
$$K_b = \frac{[(\text{CH}_3)_3\text{NH}^+][\text{OH}^-]}{[(\text{CH}_3)_3\text{N}]}$$



$$K_b = \frac{[\text{HAsO}_4^{2-}][\text{OH}^-]}{[\text{AsO}_4^{3-}]}$$



$$K_b = \frac{[\text{HNO}_2][\text{OH}^-]}{[\text{NO}_2^-]}$$



$$K_b = \frac{[(\text{CH}_3)_2\text{N}_2\text{H}_3^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{N}_2\text{H}_2]}$$

11.17 The sodium salt of acetylsalicylic acid contains the conjugate base of this acid, the acetylsalicylate ion. Being the conjugate base of a weak acid, this ion has appreciable basic properties and a solution of the sodium salt is therefore basic.

11.19 Since ammonium ion is the conjugate acid of a weak base (NH_3), it is appreciably acidic. The anion in the fertiliser, NO_3^- , is the conjugate base of a strong acid and is therefore, neutral. Consequently, adding ammonium nitrate lowers the pH of soil.

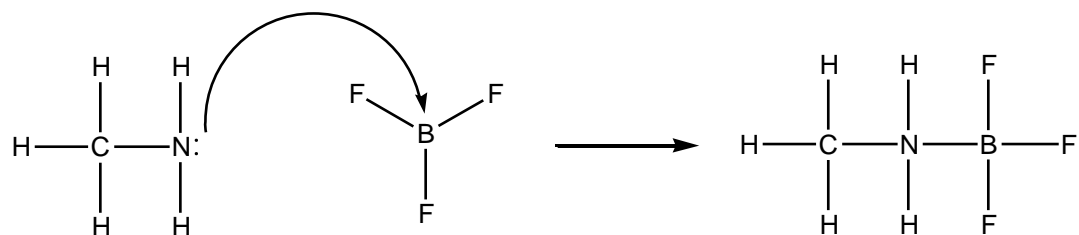
11.21 If $[\text{HA}]_{\text{initial}} \geq 400 \times K_a$, the initial concentration of the acid is equal to the equilibrium concentration. The same criterion applies to bases.

11.23 Acid strength increases across a period and down a group.

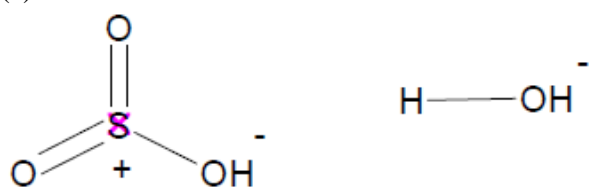
11.25 In nitric acid, there are more oxygen atoms bound to the nitrogen atom than in nitrous acid. As the number of oxygen atoms increases, the 'pull' on the electrons in the OH bond increases, withdrawing electrons away from the hydrogen atom and increasing the polarity of the O—H bond which makes it easier to lose a proton.

- 11.27 NO_2^- is a stronger base than SO_3^{2-} because its conjugate acid, HNO_2 , is a weaker acid than the conjugate acid of SO_3^{2-} , HSO_3^- . HSO_3^- is a stronger acid than HNO_2 since it contains a greater number of lone oxygen atoms.
- 11.29 The equilibrium lies to the left, in the direction which favours formation of the weaker acid and base; so the strongest base reacts with the strongest acid.
- 11.31 This equilibrium lies almost completely to the left, since HNO_3 is a strong acid and NO_3^- is a weak base.
- 11.33 In water, formic acid and acetic acid have slightly different dissociation constants. Hence, it is possible to differentiate their acid strengths. In liquid NH_3 however, formic acid and acetic acid are fully dissociated and appear to be the same strength because NH_3 is a much stronger base than H_2O and can more readily accept a proton.
- 11.35 Buffer 1 is made with an excess of NH_3 and is therefore, better able to resist changes in pH on addition of acid, as this reacts with the NH_3 in the buffer. Buffer 2 is made with an excess of NH_4^+ and is therefore, better able to resist changes in pH on addition of base. Consequently, buffer 1 maintains a steady pH on addition of a strong acid.
- 11.37 At the equivalence point, the titrated hydrazine solution is acidic and is a solution of hydrazinium chloride. The hydrazinium ion, being the conjugate acid of a weak base, has appreciable acidic properties.
- 11.39 An acid-base indicator is a weak acid that changes colour when it converts from its acidic form to its basic form. Because indicators are weak acids, they react with the titrant and consequently, small amounts of indicator are used so the results are not affected excessively by interaction of the titrant with the indicator.
- 11.41 Potassium hydroxide is a strong base and hydrobromic acid is a strong acid. Consequently, the pH at the equivalence point is 7. Any indicator that changes colour around pH 7 is appropriate. Phenolphthalein is also a good indicator since the pH changes rapidly near the equivalence point in titrations of a strong acid with a strong base. Only a small volume of added acid, frequently less than one drop, causes a large change in pH. In addition, since the colour change for phenolphthalein is from colourless to pink, it is easily observed.
- 11.43 A Lewis acid is an electron pair acceptor. A Lewis base is an electron pair donor.

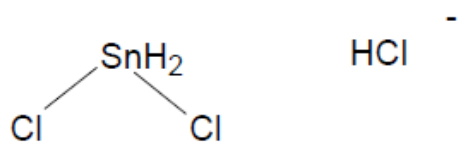
11.45



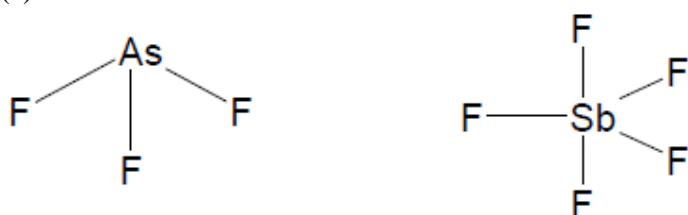
11.47 (a)



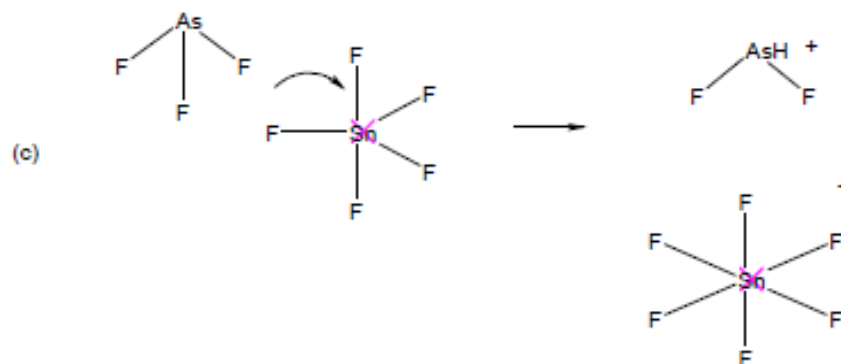
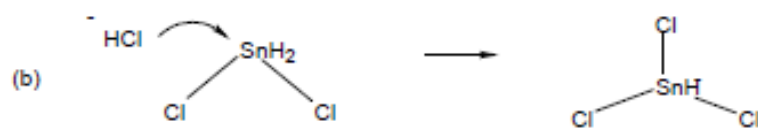
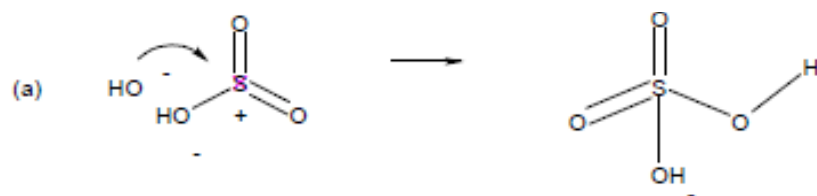
(b)



(c)

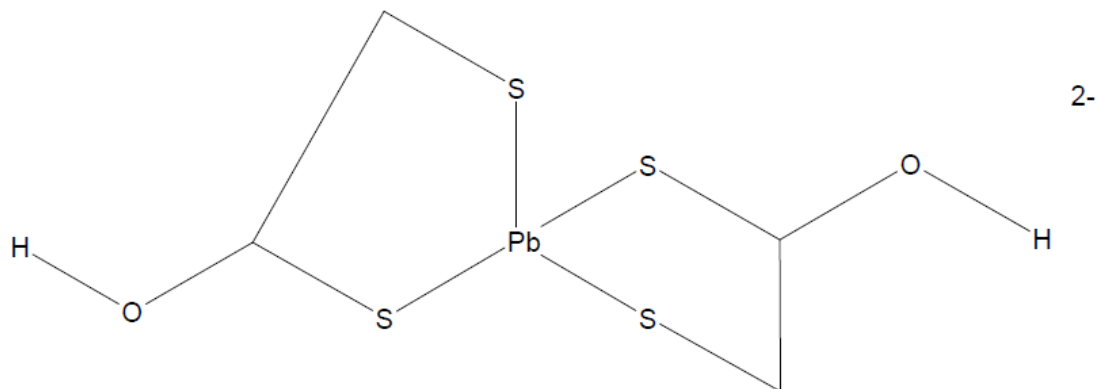


11.49



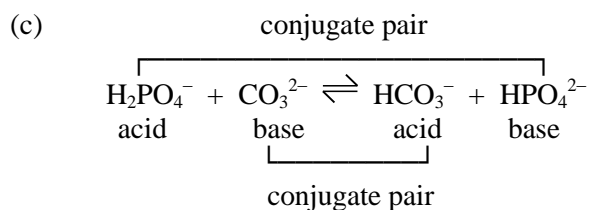
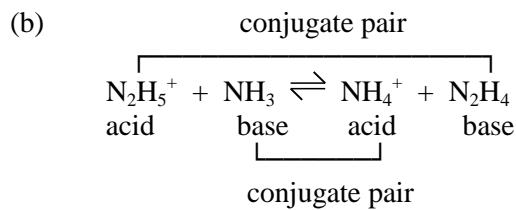
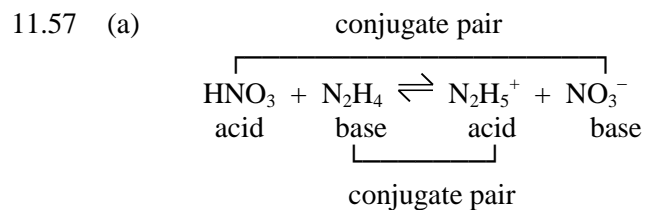
- 11.51 (a) $\text{NH}_3 < \text{NCl}_3 < \text{NF}_3$ (NF_3 is hardest)
 (b) $\text{ClO}_2^- < \text{ClO}_3^- < \text{ClO}_4^-$ (ClO_4^- is hardest)
 (c) $\text{Pb}^{2+} < \text{Pb}^{4+} < \text{Zn}^{2+}$ (Zn^{2+} is hardest)
 (d) $\text{SbCl}_3 < \text{PCl}_3, \text{PF}_3$ (PF_3 is hardest)

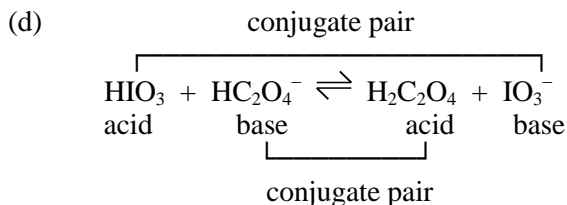
11.53



Review Problems

- 11.55 (a) HF
 (b) N_2H_5^+
 (c) $\text{C}_5\text{H}_5\text{NH}^+$
 (d) HO_2^-
 (e) H_2CrO_4





11.59 At 25 °C, $K_w = 1.0 \times 10^{-14} = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$

(a) $[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (0.0024) = 4.2 \times 10^{-12} \text{ M}$

(b) $[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (1.4 \times 10^{-5}) = 7.1 \times 10^{-10} \text{ M}$

(c) $[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (5.6 \times 10^{-9}) = 1.8 \times 10^{-6} \text{ M}$

(d) $[\text{H}_3\text{O}^+] = (1.0 \times 10^{-14}) / (4.2 \times 10^{-13}) = 2.4 \times 10^{-2} \text{ M}$

11.61 $\text{pH} = -\log[\text{H}_3\text{O}^+]$

$[\text{H}_3\text{O}^+] = 4.2 \times 10^{-12} \text{ M}$ $\text{pH} = 11.38$

$[\text{H}_3\text{O}^+] = 7.1 \times 10^{-10} \text{ M}$ $\text{pH} = 9.15$

$[\text{H}_3\text{O}^+] = 1.8 \times 10^{-6} \text{ M}$ $\text{pH} = 5.74$

$[\text{H}_3\text{O}^+] = 2.4 \times 10^{-2} \text{ M}$ $\text{pH} = 1.62$

11.63 (a) $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-8.26} = 5.5 \times 10^{-9} \text{ M}$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 8.26 = 5.74$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.74} = 1.8 \times 10^{-6} \text{ M}$

(b) $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-10.25} = 5.6 \times 10^{-11} \text{ M}$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 10.25 = 3.75$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-3.75} = 1.8 \times 10^{-4} \text{ M}$

(c) $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-4.65} = 2.2 \times 10^{-5} \text{ M}$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 4.65 = 9.35$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-9.35} = 4.5 \times 10^{-10} \text{ M}$

(d) $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-6.18} = 6.6 \times 10^{-7} \text{ M}$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 6.18 = 7.82$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-7.82} = 1.5 \times 10^{-8} \text{ M}$

(e) $[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-9.70} = 2.0 \times 10^{-10} \text{ M}$
 $\text{pH} = 14.00 - \text{pOH} = 14.00 - 9.70 = 4.30$
 $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.30} = 5.0 \times 10^{-5} \text{ M}$

11.65 $n_{\text{NaOH}} = \frac{m}{M} = \frac{6.0 \text{ g}}{39.998 \text{ g mol}^{-1}} = 1.5 \times 10^{-1} \text{ mol}$

$$c = \frac{n}{V} = \frac{1.5 \times 10^{-1} \text{ mol}}{1 \text{ L}} = 1.5 \times 10^{-1} \text{ M}$$

As NaOH is a strong base, it dissociates completely. Thus $[\text{OH}^-] = 1.5 \times 10^{-1} \text{ M}$.

$$\text{pOH} = -\log[\text{OH}^-] = -\log(0.15) = 0.82$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 0.82 = 13.18$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-13.18} = 6.6 \times 10^{-14} \text{ M}$$

$$11.67 \quad V = \frac{n}{c} = \frac{1.69 \times 10^{-3} \text{ mol}}{0.100 \text{ mol L}^{-1}} = 1.69 \times 10^{-2} \text{ L} = 16.9 \text{ mL}$$

$$11.69 \quad \text{At } 25^\circ\text{C}, K_a \times K_b = 1.0 \times 10^{-14}$$

$$K_a = K_w / K_b = 1.0 \times 10^{-14} / 1.0 \times 10^{-10} = 1.0 \times 10^{-4}$$

$$11.71 \quad K_a \times K_b = 1.0 \times 10^{-14}$$

$$K_a = K_w / K_b = 1.0 \times 10^{-14} \div 4.4 \times 10^{-4} = 2.3 \times 10^{-11}$$

$$11.73 \quad (\text{a}) \quad \text{The conjugate base is } \text{IO}_3^-$$

$$\text{p}K_b = 14.00 - \text{p}K_a = 14.00 - 0.23 = 13.77$$

$$K_b = 10^{-\text{p}K_b} = 10^{-13.77} = 1.7 \times 10^{-14}$$

(b) IO_3^- is a weaker base than acetate anion, because its K_b is smaller than that of acetate anion. Conversely, HIO_3 is a stronger acid than CH_3COOH , so its conjugate base is weaker than that of CH_3COOH .

$$11.75 \quad K_a = \frac{(0.038)(0.038)}{0.06} = 2 \times 10^{-2}$$

$$\text{p}K_a = -\log(K_a) = -\log(2 \times 10^{-2}) = 1.7$$

$$11.77 \quad K_b = \frac{(1.3 \times 10^{-4})(1.3 \times 10^{-4})}{0.15} = 1.1 \times 10^{-7}$$

$$\text{p}K_b = -\log(K_b) = -\log(1.1 \times 10^{-7}) = 6.96$$

$$11.79 \quad K_a = \frac{[\text{x}][\text{x}]}{0.15} = 1.8 \times 10^{-5} \quad \text{x} = 1.6 \times 10^{-3} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 2.78$$

$$11.81 \quad \text{pH} = 14.00 - \text{pOH} = 14.00 - 3.74 = 10.26$$

$$11.83 \quad \text{Initial concentration of } \text{NH}_3 \text{ is } 0.15 \text{ M. } 500 \text{ mL} = 0.5 \text{ L of solution, therefore } n_{\text{NH}_3} = cV = 0.15 \text{ mol L}^{-1} \times 0.5 \text{ L} = 0.075 \text{ mol.}$$

$$11.85 \quad K_b = \frac{(\text{x})(\text{x})}{0.40 - \text{x}} = 1.4 \times 10^{-11}$$

Since $(0.40 - x) \approx 0.40$:

$$x = 2.4 \times 10^{-6} \text{ M} = [\text{OH}^-] = [\text{HNO}_2]$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log(2.4 \times 10^{-6}) = 5.63$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.63 = 8.37$$

$$11.87 \quad K_a = \frac{(x)(x)}{0.10} = 5.9 \times 10^{-9} \quad x = 2.4 \times 10^{-5} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 4.62$$

$$11.89 \quad K_a \times K_b = K_w, K_b = K_w / K_a = 1.0 \times 10^{-14} / 1.8 \times 10^{-8} = 5.6 \times 10^{-7}$$

11.91

$$K_b = \frac{(x)(x)}{0.67} = 3.3 \times 10^{-7} \quad x = 4.7 \times 10^{-4} = [\text{OH}^-]$$

$$\text{pOH} = 3.33$$

$$\text{pH} = 10.67$$

$$11.93 \quad \text{pH} = -\log(4.6 \times 10^{-3}) = 2.34$$

$$11.95 \quad \text{pH} = -\log(1.4 \times 10^{-3}) = 2.85$$

11.97 (a) HBr: Br larger than Cl therefore HBr bond is longer and weaker.

(b) HF: more electronegative F polarises and weakens the HF bond.

(c) HBr: Br larger than S therefore HBr bond is longer and weaker.

11.99 (a) HClO_2 , because it has more lone oxygen atoms.

(b) H_2SeO_4 , because it has more lone oxygen atoms.

11.101 (a) HClO_3 , because Cl is more electronegative,

(b) HClO_3 , because it has more lone oxygen atoms and Cl is more electronegative than I.

(c) HBrO_4 , because it has more lone oxygen atoms.

11.103 The equilibrium reaction is: $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$

Using the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$= 9.26 + \log \frac{0.25}{0.45} = 9.00$$

$$11.105 \quad \Delta[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COOH}]_{\text{final}} - [\text{CH}_3\text{COOH}]_{\text{initial}} = 0.080 \text{ M} - 0.15 \text{ M} = -0.07 \text{ M}$$

$$\Delta[\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COO}^-]_{\text{final}} - [\text{CH}_3\text{COO}^-]_{\text{initial}} = 0.21 \text{ M} - 0.25 \text{ M} = -0.04 \text{ M}$$

$$11.107 \quad m = Mn = 82.0 \text{ g mol}^{-1} \times 0.27 \text{ mol} = 22 \text{ g NaOOCCH}_3$$

$$11.109 \quad m = Mn = 53.492 \text{ g mol}^{-1} \times 1.8 \times 10^{-2} \text{ mol} = 0.96 \text{ g NH}_4\text{Cl}$$

11.111 Initial pH

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{n_{A^-}}{n_{HA}} \\ &= 4.74 + \log \frac{0.110}{0.100} = 4.78 \end{aligned}$$

Final pH

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{n_{A^-}}{n_{HA}} \\ &= 4.74 + \log \frac{0.108}{0.103} = 4.76 \end{aligned}$$

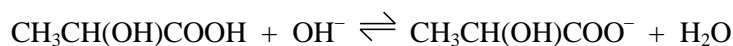
If the same volume of HCl was added to 125 mL of pure water, remembering that HCl dissociates completely:

$$c = \frac{n}{V} = \frac{0.00250 \text{ mol}}{0.150 \text{ L}} = 0.0167 \text{ mol L}^{-1} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log(0.0167) = 1.78$$

Hence, the pH change is $(7.00 - 1.78) = 5.22$ pH units which shows how a buffer solution maintains a constant pH.

11.113 Lactic acid, $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$, is a monoprotic acid which reacts with NaOH in a 1:1 mole ratio according to the equation:



$$n_{\text{NaOH}} = cV = 0.155 \text{ mol L}^{-1} \times (17.25 \times 10^{-3} \text{ L}) = 2.67 \times 10^{-3} \text{ mol}$$

From the reaction stoichiometry, this must also be the number of moles of lactic acid present.

11.115 The % NaCl by mass in the original mixture is:

$$(\text{mass NaCl}/\text{total mass}) \times 100 = (0.72 \text{ g} / 1.243 \text{ g}) \times 100 = 58 \% \text{ NaCl.}$$

$$11.117 \quad \text{pH} = 14.00 - \text{pOH} = 14.00 - 5.77 = 8.23$$

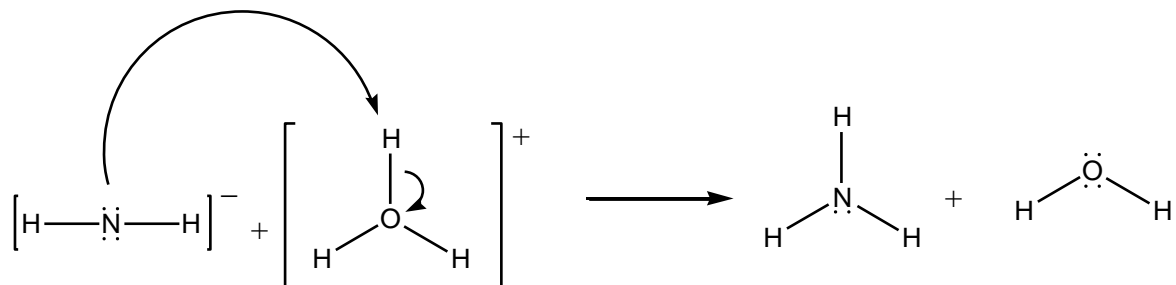
$$11.119 \quad \text{pH} = 12.85$$

$$11.121 \text{ (a)} \quad \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (1.342 \times 10^{-3}) = 2.87.$$

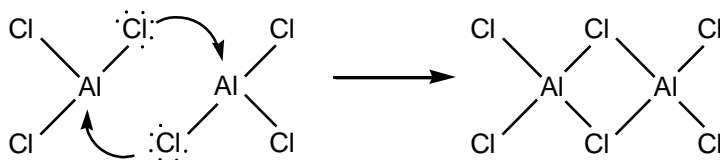
$$\text{(b)} \quad \text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]} = 4.74 + \log \frac{2.857 \times 10^{-2}}{4.286 \times 10^{-2}} = 4.56$$

- (c) $\log \frac{[A^-]}{[HA]} = 0$ and $\text{pH} = \text{p}K_a = 4.74$
 (d) $\text{pH} = 14.00 - \text{pOH} = 14.00 - 5.28 = 8.72$

11.123 NH_2^- is the Lewis base and H_3O^+ is the Lewis acid.



11.125 Each Al atom acts as a Lewis acid, accepting an electron pair from Cl.



- 11.127 (a) Lewis acid is AlCl_3 : Lewis base is Cl^-
 (b) Lewis acid is Zn^{2+} : Lewis base is CN^-
 (c) Lewis acid is I_2 : Lewis base is I^-
 (d) Lewis acid is CO_2 : Lewis base is O^{2-}

11.129 The order of increasing polarisability is : $\text{V}^{3+} < \text{Fe}^{3+} < \text{Fe}^{2+} < \text{Pb}^{2+}$.
 Polarisability increases as ionic size increases.

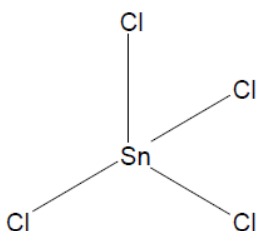
11.131 The order of increasing softness is :

- (a) $\text{BF}_3 < \text{BCl}_3 < \text{AlCl}_3$
 (b) $\text{Al}^{3+} < \text{Tl}^{3+} < \text{Tl}^+$
 (c) $\text{AlCl}_3 < \text{AlBr}_3 < \text{AlI}_3$

Softness increases down groups.

11.133 Both SO_2 and SO_3 have a lone pair of electrons on S but SO_3 is less polarisable than SO_2 because this lone pair is closer to S in SO_3 than in SO_2 , due to the greater electronegativity effect of 3 oxygens compared to 2 oxygens.

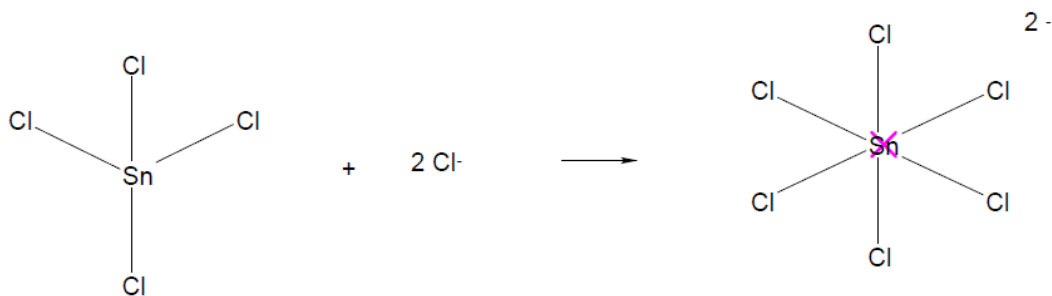
11.135



There are no lone pairs on Sn so

SnCl_4 has a regular tetrahedral structure.

However, the Sn octet can be expanded such that SnCl_4 can function as a Lewis acid by accepting 2 Cl^- to form $[\text{SnCl}_6]^{2-}$



Additional Exercises

11.137 Conjugate acid: $(\text{CH}_3)_2\text{NH}_2^+$ and conjugate base: $(\text{CH}_3)_2\text{N}^-$

11.139 $\text{pH} = -\log(5.1 \times 10^{-5}) = 4.29$

11.141 $\text{pH} = \text{pK}_a + \log \frac{n_{\text{A}^-}}{n_{\text{HA}}} = 9.26 + \log \frac{0.100}{0.0500} = 9.56$

11.143 Since the ammonium ion is the salt of the weak base NH_3 , it is acidic. The cyanide ion is the salt of the weak acid, HCN , so it is basic. In order to determine if the solution is acidic or basic, the relative strengths of these two components need to be determined:

$$K_a(\text{NH}_4^+) = K_w / K_b(\text{NH}_3) = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$$

$$K_b(\text{CN}^-) = K_w / K_a(\text{HCN}) = 1.0 \times 10^{-14} / 6.2 \times 10^{-9} = 1.6 \times 10^{-5}$$

Since $K_b(\text{CN}^-)$ is larger than $K_a(\text{NH}_4^+)$, CN^- acts as a base to a larger extent than NH_4^+ acts as an acid. Therefore the NH_4CN solution is basic.

- 11.145 This is an example of a titration of a strong acid with a strong base. Prior to reaching the equivalence point, there is an excess of acid present. The number of moles of acid present is determined by subtracting the number of moles of base added from the amount of acid initially present. The new concentration of acid is determined taking the volume change into account to calculate the pH. After the equivalence point, there is an excess of base. The excess is determined by subtracting the initial number of moles of acid present from the number of moles of base added. The resulting concentration of base is determined to calculate the pH.

The number of moles of H_3O^+ initially present are:

$$n_{\text{H}_3\text{O}^+} = cV = 0.1000 \text{ mol L}^{-1} \times (25.00 \times 10^{-3} \text{ L}) = 2.500 \times 10^{-3} \text{ mol}$$

- (a) Initially, there is only 0.1000 M HCl present: $[\text{H}_3\text{O}^+] = 0.1000 \text{ M}$,
 $\text{pH} = -\log[\text{H}_3\text{O}^+] = 1.00$.
- (b) After 10.00 mL of added base, the solution volume is 35.00 mL
 $n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (10.00 \times 10^{-3} \text{ L}) = 1.000 \times 10^{-3} \text{ mol}$
 $n_{\text{H}_3\text{O}^+} = 2.5000 \times 10^{-3} \text{ mol} - 1.000 \times 10^{-3} \text{ mol} = 1.500 \times 10^{-3} \text{ mol}$

$$[\text{H}_3\text{O}^+] = \frac{1.500 \times 10^{-3} \text{ mol}}{35.00 \times 10^{-3} \text{ L}} = 4.286 \times 10^{-2} \text{ M}$$

 $\text{pH} = -\log[\text{H}_3\text{O}^+] = 1.37$
- (c) After 24.90 mL of added base, the solution volume is 49.90 mL
 $n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (24.90 \times 10^{-3} \text{ L}) = 2.490 \times 10^{-3} \text{ mol}$
 $n_{\text{H}_3\text{O}^+} = 2.5000 \times 10^{-3} \text{ mol} - 2.490 \times 10^{-3} \text{ mol} = 1.000 \times 10^{-5} \text{ mol}$

$$[\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-5} \text{ mol}}{49.90 \times 10^{-3} \text{ L}} = 2.004 \times 10^{-4} \text{ M}$$

 $\text{pH} = -\log[\text{H}_3\text{O}^+] = 3.70$
- (d) After 24.99 mL of added base, the solution volume is 49.99 mL
 $n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (24.90 \times 10^{-3} \text{ L}) = 2.490 \times 10^{-3} \text{ mol}$
 $n_{\text{H}_3\text{O}^+} = 2.5000 \times 10^{-3} \text{ mol} - 2.499 \times 10^{-3} \text{ mol} = 1.000 \times 10^{-6} \text{ mol}$

$$[\text{H}_3\text{O}^+] = \frac{1.00 \times 10^{-6} \text{ mol}}{49.99 \times 10^{-3} \text{ L}} = 2.000 \times 10^{-5} \text{ M}$$

 $\text{pH} = -\log[\text{H}_3\text{O}^+] = 4.70$
- (e) After 25.00 mL of added base, the solution volume is 50.00 mL

The solution now contains equal numbers of moles of acid and base, so it is neutral.
 $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.00 \times 10^{-7} \text{ M}$

$$\text{pH} = -\log(1.00 \times 10^{-7}) = 7.00$$

- (f) After 25.01 mL of added base, the solution volume is 50.01 mL

From here on, the solutions contain excess base and the any excess over 2.500×10^{-3} mol, the amount of base required to reach the equivalence point, is the total hydroxide ion concentration in the solution.

$$n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (25.01 \times 10^{-3} \text{ L}) = 2.501 \times 10^{-3} \text{ mol}$$

$$n_{\text{OH}^- \text{ excess}} = 2.501 \times 10^{-3} \text{ mol} - 2.500 \times 10^{-3} \text{ mol} = 1.000 \times 10^{-6} \text{ mol}$$

$$[\text{OH}^-] = \frac{n}{V} = \frac{1.000 \times 10^{-6} \text{ mol}}{50.01 \times 10^{-3} \text{ L}} = 2.000 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 4.70$$

$$\text{pH} = 14.00 - \text{pOH} = 9.30$$

- (g) After 25.10 mL of added base, the solution volume is 50.10 mL

$$n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (25.10 \times 10^{-3} \text{ L}) = 2.510 \times 10^{-3} \text{ mol}$$

$$n_{\text{OH}^- \text{ excess}} = 2.510 \times 10^{-3} \text{ mol} - 2.500 \times 10^{-3} \text{ mol} = 1.000 \times 10^{-5} \text{ mol}$$

$$[\text{OH}^-] = \frac{n}{V} = \frac{1.000 \times 10^{-5} \text{ mol}}{50.10 \times 10^{-3} \text{ L}} = 1.996 \times 10^{-4} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 3.70$$

$$\text{pH} = 14.00 - \text{pOH} = 10.30$$

- (h) After 26.00 mL of added base, the solution volume is 51.00 mL

$$n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (26.00 \times 10^{-3} \text{ L}) = 2.600 \times 10^{-3} \text{ mol}$$

$$n_{\text{OH}^- \text{ excess}} = 2.600 \times 10^{-3} \text{ mol} - 2.500 \times 10^{-3} \text{ mol} = 1.000 \times 10^{-4} \text{ mol}$$

$$[\text{OH}^-] = \frac{n}{V} = \frac{1.000 \times 10^{-4} \text{ mol}}{51.00 \times 10^{-3} \text{ L}} = 1.961 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 2.71$$

$$\text{pH} = 14.00 - \text{pOH} = 11.29$$

- (i) After 50.00 mL of added base, the solution volume is 75.00 mL

$$n_{\text{OH}^- \text{ added}} = cV = 0.1000 \text{ mol L}^{-1} \times (50.00 \times 10^{-3} \text{ L}) = 5.000 \times 10^{-3} \text{ mol}$$

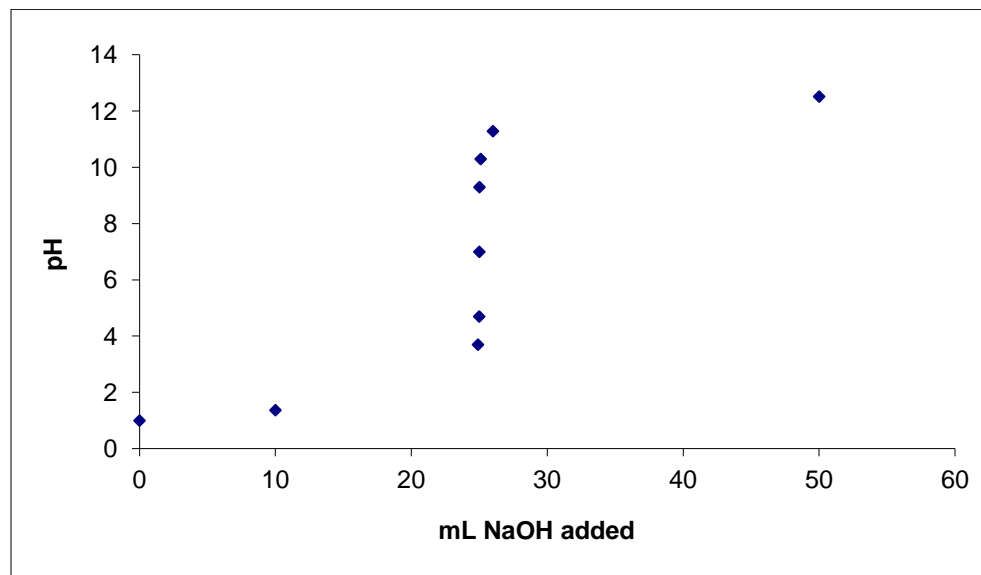
$$n_{\text{OH}^- \text{ excess}} = 5.000 \times 10^{-3} \text{ mol} - 2.500 \times 10^{-3} \text{ mol} = 2.500 \times 10^{-3} \text{ mol}$$

$$[\text{OH}^-] = \frac{n}{V} = \frac{2.500 \times 10^{-3} \text{ mol}}{75.00 \times 10^{-3} \text{ L}} = 3.333 \times 10^{-2} \text{ M}$$

$$\text{pOH} = -\log[\text{OH}^-] = 1.48$$

$$\text{pH} = 14.00 - \text{pOH} = 12.52$$

The titration graph is on the next page:



- 11.147 (a) $\text{AlCl}_3 + \text{LiCH}_3 \rightarrow \text{Li}^+ [\text{AlCH}_3\text{Cl}_3]^-$
 (b) $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$
 (c) $\text{SbF}_5 + \text{LiF} \rightarrow \text{Li}^+ [\text{SbF}_6]^-$
 (d) $\text{SF}_4 + \text{AsCl}_5 \rightarrow \text{AsCl}_3 + \text{SF}_4\text{Cl}_2$