Chemistry (A-level)

Equilibria (Chapter 7)

- Water is able to act as acid (proton-donor, H^+) or base (proton-acceptor), where in equilibrium:

H+ donated

$$H_2O(l) + H_2O(l) \rightleftharpoons \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{OH^-(aq)}$$

  - Where simplifying gives:

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

  - The equilibrium expression given by:

$$K_c = \frac{[H^+(aq)]\,[OH^-(aq)]}{[H_2O(l)]}$$

  - Due to the low extend of ionisation, the concentrations of the ions are negligible, hence we regard the concentration of water as constant, thus:

$$K_w = [H^+]\,[OH^-]$$

  - K_w is the **ionic product of water**; value at 298 K: 1.00×10^{-14} $mol^2\ dm^{-6}$; is defined as the equilibrium constant for the ionisation of water
  - Hydrogen ion concentration of pure water can then be found; for each molecule of water that ionises, one H^+ ion and one OH^- ion are produced:

$$[H^+] = [OH^-]$$

  - Rewriting the equilibrium expression:

$$K_w = [H^+]^2$$

  - Rearranging:

$$[H^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}\ mol\ dm^{-3}$$

- **pH** is defined as the negative logarithm to the base 10 of the hydrogen ion concentration, written as:

$$pH = -\log_{10}[H^+]$$

Calculate the pH of a solution whose H^+ ion concentration is $5.32 \times 10^{-4}\ mol\ dm^{-3}$.

$pH = -\log_{10}[H^+]$

$= -\log_{10}(5.32 \times 10^{-4})$

$= 3.27$

Calculate the hydrogen ion concentration of a solution whose pH is 10.5.

$pH = -\log_{10}[H^+]$

$[H^+] = 10^{-pH}$

$= 10^{-10.5}$

$= 3.16 \times 10^{-11}\ mol\ dm^{-3}$

- Monobasic acids contain only one replaceable hydrogen atom per molecule
- Strong monobasic acids, e.g. HCl, completely ionises in solution
  - The concentration of hydrogen ions in solution is approximately the same as the concentration of the acid (assumption that the concentration of H^+ ions arising from the ionisation of water molecules is negligible compared with those arising from the acid)
- Calculating the H^+ of a solution of strong base (ionises completely in solution) given by:

$$K_w = [H^+][OH^-] \qquad [H^+] = \frac{K_w}{[OH^-]}$$

  - Hence pH can be obtained:

Calculate the pH of a solution of sodium hydroxide of concentration 0.0500 mol dm^{-3}.

$K_w = 1.00 \times 10^{-14}$ mol^2 dm^{-6} (at 298 K).

Step 1 Write the expression relating $[H^+]$ to K_w and $[OH^-]$

$$[H^+] = \frac{K_w}{[OH^-]}$$

Step 2 Substitute the values into the expression to calculate $[H^+]$.

$$[H^+] = \frac{1.00 \times 10^{-14}}{0.0500} = 2.00 \times 10^{-13} \text{ mol dm}^{-3}$$

Step 3 Calculate the pH.

$$\begin{aligned} pH &= -\log_{10}[H^+] \\ &= -\log_{10}(2.00 \times 10^{-13}) \\ &= 12.7 \end{aligned}$$

- **Acid dissociation constant, K_a**: the equilibrium constant for a weak acid, given by:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

  - The value of K_a indicates the extend of dissociation of the acid:
    - High value (e.g. 40 mol dm^{-3}), equilibrium lies to the right, acid almost completely ionised
    - Low value (e.g. 1.0×10^{-4} mol dm^{-3}), equilibrium lies to the left, acid only slightly ionised and exist mainly as HA molecules
- **pK_a**: the values of K_a expressed as a logarithm to base 10, given by:

$$pK_a = -\log_{10}K_a$$

  - To compare the strengths of low K_a acids
- Calculating K_a and pH for a weak acid:
  - Given the general equation:

$$HA(aq) \rightleftharpoons H^+ + A^-$$

  - Hence:

$$[H^+] = [A^-]$$

  - Rewriting the equilibrium expression:

$$K_a = \frac{[H^+]^2}{[HA]}$$

- Assumptions:
  - Ignore the concentration of hydrogen ions produced by the ionisation of the water molecules in the solution, as the ionic product of water (1.00×10^{-14} $mol^2\ dm^{-6}$) is negligible compared with the values for most weak acids
  - Assume that the ionisation of the weak acid is negligible, hence the concentration of undissociated HA molecules present is approximately the same as that of the original acid.

Calculate the pH of $0.100\ mol\ dm^{-3}$ ethanoic acid, CH_3COOH.

($K_a = 1.74 \times 10^{-5}\ mol\ dm^{-3}$)

Step 1 Write the equilibrium expression for the reaction.

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

$$K_a = \frac{[H^+]^2}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+]^2}{[CH_3COOH]}$$

Step 2 Enter the values into the expression.

$$1.74 \times 10^{-5} = \frac{[H^+]^2}{(0.100)}$$

Step 3 Rearrange the equation.

$$[H^+]^2 = 1.74 \times 10^{-5} \times 0.100 = 1.74 \times 10^{-6}$$

Step 4 Take the square root.

$$[H^+] = \sqrt{1.74 \times 10^{-6}} = 1.32 \times 10^{-3}\ mol\ dm^{-3}$$

Step 5 Calculate pH.

$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(1.32 \times 10^{-3})$$
$$= 2.88 \text{ (to 3 significant figures)}$$

Calculate the value of K_a for methanoic acid. A solution of $0.010\ mol\ dm^{-3}$ methanoic acid, HCOOH, has a pH of 2.90.

Step 1 Convert pH to $[H^+]$.

$$[H^+] = 10^{-2.90}$$
$$= 1.26 \times 10^{-3}\ mol\ dm^{-3}$$

Step 2 Write the equilibrium expression.

$$K_a = \frac{[H^+]^2}{[HA]} \quad \text{or} \quad K_a = \frac{[H^+]^2}{[HCOOH]}$$

Step 3 Enter the values into the expression and calculate the answer.

$$K_a = \frac{(1.26 \times 10^{-3})^2}{(0.010)}$$
$$= 1.59 \times 10^{-4}\ mol\ dm^{-3}$$

- An **acid-base indicator** is a dye or mixture of dyes that changes colour over a specific pH range; many indicators can be considered as weak acids in which the acid (HIn) and conjugate base (In^-) have different colours:

$$HIn \rightleftharpoons H^+ + In^-$$

HIn: un-ionised indicator colour A; In^-: conjugate base colour B

  - Adding an acid to this indicator solution shifts the position of equilibrium to the left
  - Adding an alkali shifts the position of equilibrium to the right
  - The colour of the indicator during a titration depends on the concentration of H^+ ions present.

Name of dye	Colour at lower pH	pH range	End-point	Colour at higher pH
methyl violet	yellow	0.0–1.6	0.8	blue
methyl yellow	red	2.9–4.0	3.5	yellow
methyl orange	red	3.2–4.4	3.7	yellow
bromophenol blue	yellow	2.8–4.6	4.0	blue
bromocresol green	yellow	3.8–5.4	4.7	blue
methyl red	red	4.2–6.3	5.1	yellow
bromothymol blue	yellow	6.0–7.6	7.0	blue
phenolphthalein	colourless	8.2–10.0	9.3	pink/violet
alizarin yellow	yellow	10.1–13.0	12.5	orange/red

Table 21.3 Some of the chemical indicators used to monitor pH, with their pH ranges of use and pH of end-point.

- Titration of strong acids with strong bases (e.g. 0.100 mol dm^{-3} NaOH titrated with 0.100 mol dm^{-3} HCl in the presence of bromothymol blue indicator):

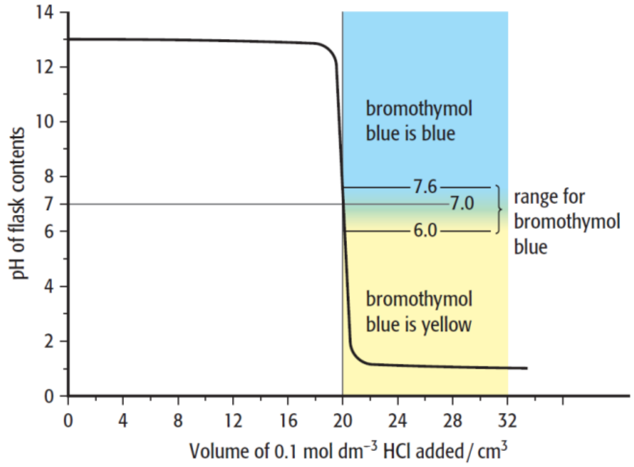

Figure 21.7 A strong acid–strong base titration with bromothymol blue as indicator.

  - ➢ A sharp fall between pH 10.5 and pH 3.5; in this region tiny additions of H^+ ions result in a rapid change in pH
  - ➢ A midpoint of steep at pH 7, corresponds to the end-point of the titration
  - ➢ Bromothymol blue indicator changed from blue to yellow over the range 7.6 to 6.0 where the slope is steepest
  - ➢ Due to the sharp change in pH, other indicators can be used which change within this region (e.g. phenolphthalein – pH range 8.2 to 10.0):

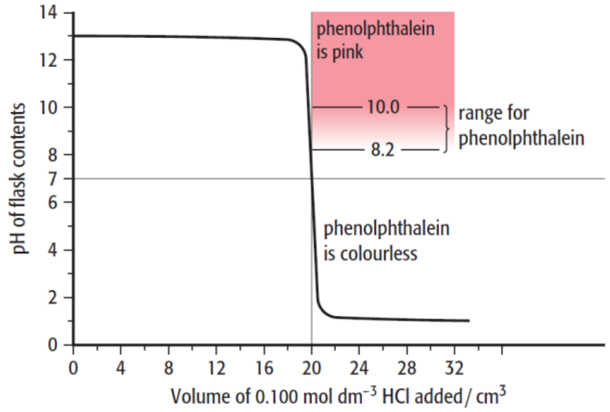

Figure 21.8 A strong acid–strong base titration with phenolphthalein as indicator.

- Titration of strong acids with weak bases (e.g. 0.100 mol dm^{-3} aqueous ammonia titrated with 0.100 mol dm^{-3} nitric acid):

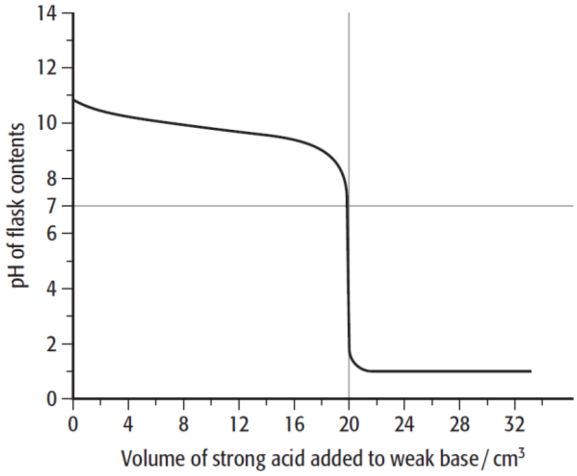

Figure 21.9 A typical strong acid–weak base titration.

- A sharp fall between pH 7.5 and pH 3.5
- Midpoint of the steep slope at about pH 5
- Indicators chosen should be within the sharp fall

- Titration of weak acids with strong bases (e.g. 0.100 mol dm^{-3} aqueous NaOH titrated with 0.100 mol dm^{-3} benzoic acid):

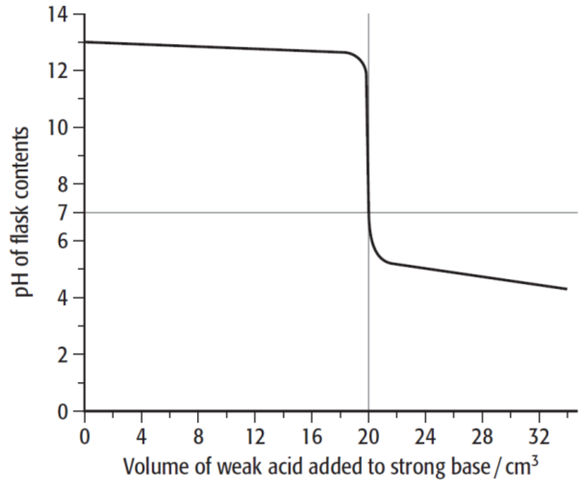

Figure 21.10 A typical weak acid–strong base titration.

- A sharp fall between pH 11 and pH 7.5
- Midpoint of steep slope at about pH 9

- Titration of weak acids with weak bases (e.g. 0.100 mol dm^{-3} aqueous ammonia titrated with 0.100 mol dm^{-3} aqueous benzoic acid):

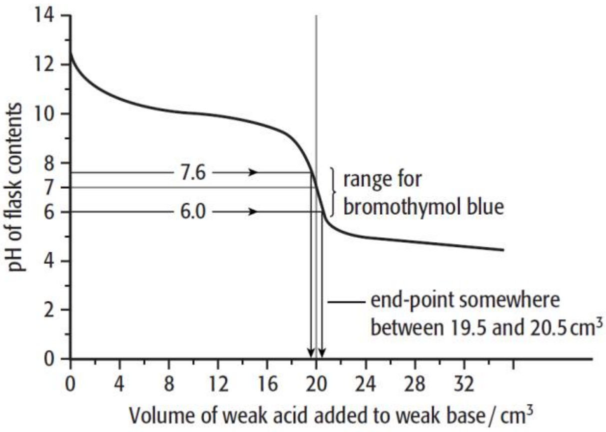

Figure 21.11 A typical weak acid–weak base titration.

- No sharp fall
- No acid-base indicator is suitable to determine the end-point of the reaction

- A **buffer solution** is a solution which the pH does not change significantly when small amounts of acids or alkalis are added
  - A mixture of a weak acid and one of its salts (e.g. aqueous mixture of ethanoic acid and sodium ethanoate, buffers between pH values of 4 and 7):

$$\underset{\text{ethanoic acid}}{CH_3COOH(aq)} \rightleftharpoons H^+(aq) + \underset{\text{ethanoate ion}}{CH_3COO^-(aq)}$$

  - To increase the concentration of ethanoate ion, the sodium ethanoate is used:

$$\underset{\text{sodium ethanoate}}{CH_3COONa(s)} + aq \longrightarrow Na^+(aq) + \underset{\text{ethanoate ion}}{CH_3COO^-(aq)}$$

- Hence the buffer solution contains high concentrations of both CH_3COOH and CH_3COO^-:

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

relatively high concentration of ethanoic acid — relatively high concentration of ethanoate ions

- Addition of H^+ ions shift the equilibrium position to the left, as more H^+ ions combine with CH_3COO^-; the large reserve supply of CH_3COO^- and CH_3COOH ensure that concentration does not change significantly; hence the pH does not change significantly
- Addition of OH^- ions combine with H^+ ions to form water; reducing the H^+ concentration; equilibrium position shifts to the right; CH_3COOH molecules ionise to form more H^+ and CH_3COO^- until the equilibrium is re-established; $^-$; the large reserve supply of CH_3COO^- and CH_3COOH ensure that concentration does not change significantly; hence the pH does not change significantly
- Another example would be aqueous ammonia and ammonium chloride:

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

and

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

- Calculate the pH of a buffer solution:

Calculate the pH of a buffer solution containing $0.600\ mol\ dm^{-3}$ propanoic acid and $0.800\ mol\ dm^{-3}$ sodium propanoate.
(K_a propanoic acid $= 1.35 \times 10^{-5}\ mol\ dm^{-3}$)

Step 1 Write the equilibrium expression.

$$K_a = \frac{[H^+][C_2H_5COO^-]}{[C_2H_5COOH]}$$

Step 2 Rearrange the equilibrium expression to make $[H^+]$ the subject.

$$[H^+] = \frac{K_a \times [C_2H_5COOH]}{[C_2H_5COO^-]}$$

Note that in this expression, the ratio determining $[H^+]$, and hence pH, is the ratio of the concentration of the acid to the salt (conjugate base).

Step 3 Substitute the data given.

$$[H^+] = 1.35 \times 10^{-5} \times \frac{(0.600)}{0.800}$$
$$= 1.01 \times 10^{-5}\ mol\ dm^{-3}$$

Step 4 Calculate the pH.

$$pH = -\log_{10}[H^+]$$
$$= -\log_{10}(1.01 \times 10^{-5})$$
$$= -(-4.99)$$
$$= 4.99$$

$$[H^+] = K_a \times \frac{[acid]}{[salt]}$$

or

$$pH = pK_a + \log_{10}\left(\frac{[salt]}{[acid]}\right)$$

- In humans, the pH of blood is kept between 7.35 and 7.45 by several buffers, such as hydrogencarbonate ions (HCO_3^-); due to aerobic respiration, CO_2 is produced which combines with water, producing hydrogen ions:

$$CO_2(aq) + H_2O(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

hydrogencarbonate ion

- If H^+ ion increases, equilibrium position shifts to the left, which reduces the concentration of the H^+ ions in the blood and keeps the pH constant

- If H^+ ion decreases, equilibrium position shifts to the right, increasing the concentration of H^+ and keeps a constant pH

- **Solubility product**, K_{sp}, is the product of the concentrations of each ion in a saturated solution of a sparingly soluble salt at 298 K, raised to the power of their relative concentrations
  - E.g. Fe_2S_3 the equilibrium expression given by:

$$K_{sp} = [Fe^{3+}(aq)]^2[S^{2-}(aq)]^3$$

  - Solubility product only applies to ionic compounds which are slightly soluble
  - Units:

$$\begin{aligned} K_{sp} &= [Mg^{2+}(aq)] \times [OH^-(aq)]^2 \\ &= mol\,dm^{-3} \times (mol\,dm^{-3})^2 \\ &= mol^3\,dm^{-9} \end{aligned}$$

Calculating solubility product from solubility.

A saturated solution of magnesium fluoride, MgF_2, has a solubility of 1.22×10^{-3} mol dm^{-3}. Calculate the solubility product of magnesium fluoride.

Step 1 Write down the equilibrium equation.

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

Step 2 Calculate the concentration of each ion in solution.

When 1.22×10^{-3} mol dissolves to form 1 dm^3 of solution the concentration of each ion is:

$[Mg^{2+}] = 1.22 \times 10^{-3}$ mol dm^{-3}

$[F^-] = 2 \times 1.22 \times 10^{-3}$ mol dm^{-3} $= 2.44 \times 10^{-3}$ mol dm^{-3}

(The concentration of F^- is $2 \times 1.22 \times 10^{-3}$ mol dm^{-3} because each formula unit contains $2 \times F^-$ ions.)

Step 3 Write down the equilibrium expression.

$K_{sp} = [Mg^{2+}][F^-]^2$

Step 4 Substitute the values.

$K_{sp} = (1.22 \times 10^{-3}) \times (2.44 \times 10^{-3})^2$
$= 7.26 \times 10^{-9}$

Step 5 Add the correct units.

$(mol\,dm^{-3}) \times (mol\,dm^{-3})^2 = mol^3\,dm^{-9}$

Answer $= 7.26 \times 10^{-9}$ mol^3 dm^{-9}

Calculating solubility from solubility product

Calculate the solubility of copper(II) sulfide in mol dm^{-3}.

(K_{sp} for CuS $= 6.3 \times 10^{-36}$ mol^2 dm^{-6})

Step 1 Write down the equilibrium equation.

$CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq)$

Step 2 Write the equilibrium expression in terms of one ion only.

From the equilibrium equation $[Cu^{2+}] = [S^{2-}]$

So $K_{sp} = [Cu^{2+}][S^{2-}]$ becomes $K_{sp} = [Cu^{2+}]^2$

Step 3 Substitute the value of K_{sp}.

$(6.3 \times 10^{-36}) = [Cu^{2+}]^2$

Step 4 Calculate the concentration.

In this case we take the square root of K_{sp}.

$[Cu^{2+}] = \sqrt{K_{sp}}$

$[Cu^{2+}] = \sqrt{6.3 \times 10^{-36}} = 2.5 \times 10^{-18}$ mol dm^{-3}

- The **common ion effect** is the reduction in the solubility of a dissolved salt achieved by adding a solution of a compound salt which has an ion in common with the dissolved salt, often results to ppt
  - $Q > K_{sp}$: no ppt & $Q > K_{sp}$: ppt & $Q = K_{sp}$: saturated

- E.g.AgCl(aq):

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

- The addition of the common ion, Cl^-, causes the increase in concentration of $[Cl^-]$; hence $[Ag^+]$ $[Cl^-]$ is greater than the K_{sp}, silver chloride ppt will form

For example, the solubility of barium sulfate, $BaSO_4$, in water is 1.0×10^{-5} mol dm^{-3} and the solubility of barium sulfate in 0.100 mol dm^{-3} sulfuric acid, H_2SO_4, is only 1.0×10^{-9} mol dm^{-3}.

We can explain the lower solubility in sulfuric acid by referring to the solubility product of barium sulfate:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = 1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

If we ignore the very small amount of $SO_4^{2-}(aq)$ from the barium sulfate then $[SO_4^{2-}]$ is 0.1 mol dm^{-3} (from the sulfuric acid). This gives:

$$1.0 \times 10^{-10} = [Ba^{2+}] \times [0.1]$$

$$[Ba^{2+}] = 1.0 \times 10^{-9} \text{ mol dm}^{-3}$$

- **Partition coefficient**, K_{pc}, is the equilibrium constant which relates the concentration of a solute partitioned between two immiscible solvents at a particular temperature

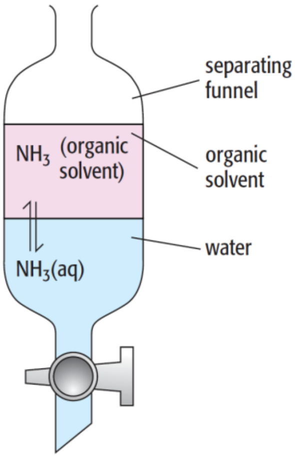

Figure 21.16 Ammonia (the solute) dissolves in both solvents, water and the organic solvent. A state of dynamic equilibrium is established.

$$NH_3(aq) \rightleftharpoons NH_3(\text{organic solvent})$$

The partition coefficient of a solute X between two solvents A and B is described by the equilibrium expression:

$$K_{pc} = \frac{[X(\text{solvent A})]}{[X(\text{solvent B})]}$$

- Worked example:

100 cm^3 of a 0.100 mol dm^{-3} solution of ammonia in water at 20 °C was shaken with 50 cm^3 of an organic solvent and left in a separating funnel for equilibrium to be established.

A 20.0 cm^3 portion of the aqueous layer was run off and titrated against 0.200 mol dm^{-3} dilute hydrochloric acid. The end-point was found to be 9.40 cm^3 of acid.

What is the partition coefficient of ammonia between these two solvents at 20 °C?

The alkaline ammonia solution is neutralised by dilute hydrochloric acid:

$$NH_3(aq) + HCl(aq) \longrightarrow NH_4Cl(aq)$$

1 mole of ammonia reacts with 1 mole of the acid.

In the titration we used:

$$\frac{9.40}{1000} \times 0.200 \text{ moles of HCl}$$

$= 1.88 \times 10^{-3}$ moles

This reacts with ammonia in the ratio 1 : 1 so there must be 1.88×10^{-3} moles of NH_3 in the 20.0 cm^3 portion titrated.

Therefore in the 100 cm^3 aqueous layer there are

$$1.88 \times 10^{-3} \times \frac{100}{20.0} \text{ mol}$$

$= 9.40 \times 10^{-3}$ mol

The number of moles of ammonia in the organic layer must be equal to the initial number of moles of ammonia minus the amount left in the aqueous layer at equilibrium

initial number of moles of ammonia

$$= 0.100 \times \frac{100}{1000}$$

$= 0.0100$ mol

final number of moles of ammonia in organic layer

$= 0.0100 - 9.40 \times 10^{-3}$ mol

$= 6.00 \times 10^{-4}$ mol

Now we need to change the numbers of moles of ammonia in each layer into concentrations (i.e. the number of moles in 1000 cm^3 or 1 dm^3) to substitute into the equilibrium expression for the partition coefficient, K_{pc}.

The concentration of ammonia in 100 cm^3 of the aqueous layer

$$= 9.40 \times 10^{-3} \times \frac{1000}{100}$$

$= 0.094$ mol dm^{-3}

The concentration of ammonia in 50 cm^3 of the organic solvent

$$= 6.00 \times 10^{-4} \times \frac{1000}{50}$$

$= 0.012$ mol dm^{-3}

The expression for the partition coefficient, K_{pc} is:

$$K_{pc} = \frac{[NH_3(\text{organic solvent})]}{[NH_3(aq)]} = \frac{0.012}{0.094}$$

$= 0.128$ (no units)

This value is less than 1, which shows us that ammonia is more soluble in water than in the organic solvent.

In general for a solute X partitioned between two solvents A and B, the equilibrium expression is given by

$$K_{pc} = \frac{[X(\text{solvent A})]}{[X(\text{solvent B})]}$$