Equilibrium between immiscible liquids

Distribution Law:

States that **a solute distributes itself between immiscible solvents such that a constant temperature and pressure the ratio of its concentrations in the two solvents is constant at a given temperature**

That is,

If C is the solute, and A and B are the immiscible solvents, them

$$\frac{[C]in\ A}{[C]in\ B} = constant\ or\ partition\ coefficient$$

Limitations

- Solute should be in the same molecular state in both solvents
- Temperature should be constant
- None of the solvent should be saturated / solutions should be dilute.

Definition

Partition Coefficient or distribution constant is ratio of the concentration of the solute in immiscible solvents at equilibrium.

Experiment to determine partition coefficient

- By finding the ration of concentrations of a solute in one solvent over the concentration a solute in another immiscible solvent at equilibrium.
- The concentration of a solute in a solvent may be obtained by titration or other reliable method.

Application of distribution laws

1. Extraction of organic compound

Example 1

A solution of 6g of a substance X in 50cm^3 of aqueous is in equilibrium at room temperature with an ethereal solution of X containing 108g of x in 100cm^3.

Calculate the mass of x that could be extracted by shaking 100cm^3 of an aqueous solution containing 10g of X with:

(i) 100cm^3 of ether

(ii) $50cm^3$ of ether twice at room temperature.

Solution

First determine the partition constant Kd

Kd = $\frac{concentration\ of\ x\ in\ ether}{concentration\ of\ x\ in\ water}$

Concentration = $\frac{mass}{volume}$

⇨ Kd = $\frac{\frac{108}{100}}{\frac{6}{50}}$ = 9

(i) Let the mass of X extracted be K g

Mass of X left in aqueous solution = (10 –K) g

Kd = 9 = $\frac{\frac{K}{100}}{\frac{(10-K)}{100}}$; thus mass of X , K extracted = 9g

(ii) Let the mas of X extracted by the first 50 cm^3 portion of ether be q g

Mass of x left in aqueous layer = (10 – q) g

Kd = 9 = $\frac{\frac{q}{50}}{\frac{(10-q)}{100}}$; q = 8.2 g

Mass of X left in water = 1 – 8.2 = 1.8g

Let the mass of X extracted by the second 50cm3 portion be p g

Mas of x left in water = (1.8 – p) g

Kd = 9 = $\frac{\frac{p}{50}}{\frac{(1.8-p)}{100}}$; p = 1.5 g

Total mass of X extracted by $50cm^3$ of ether twice = q + p = 8.2 + 1.5 = 9.7g

2. Study of complexes

- The moles of a ligand that forms a complex with a metal ion = to the total moles of ligand in aqueous solution – moles of ligand that did not form a complex
- The mole of a ligand that did not a complex can be found partition coefficient, Kd
- The moles of ligand that form a complex per mole of a metal cation is obtained by division of the moles that formed a complex by the moles of metal ions

Example 2

Excess ammonia was shaken with equal volume of trichloromethane

And a 0.05M aqueous solution of copper (II) ions to form a complex $(Cu(NH_3)_n]^{2+}$. At equilibrium, the concnentrations of ammonia in the trichloromethane and in the aqueous layer were $0.021moll^{-1}$ and $0.725moll^{-1}$ respectively.

(the partition coefficient, KD, of ammonia between water and trichloromethane is 25)

Calculate:

(i) The concentration of free ammonia in aqueous layer

(ii) The concentration of ammonia that formed the complex with copper ions

(iii) The values of n in the complex

(i) From Kd = $\frac{[free\ ammonina]in\ water}{[ammonia]in\ chloroform}$

25 = $\frac{[free\ ammonina]in\ water}{0.021}$

Free ammonia in water = 25 x 0.021 =0.525

(ii) Ammonia that formed a complex with copper ion = total ammonia in water – free ammonia

= 0.725 – 0..525

= 0. 2moles

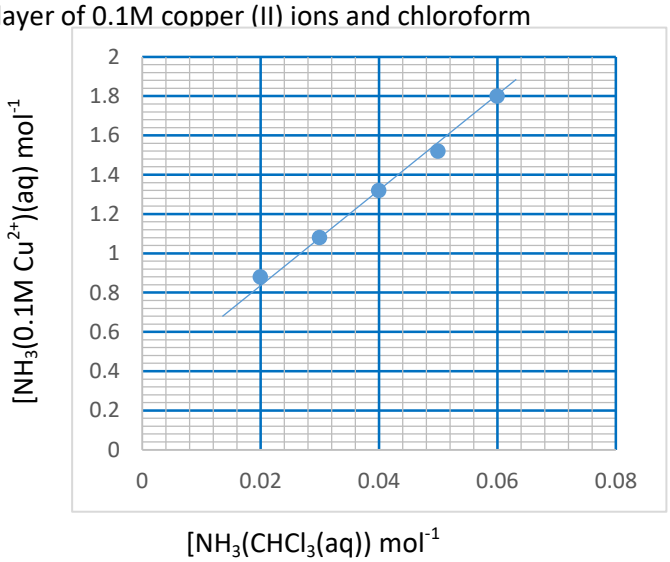
(iii) n = $\frac{moles\ of\ ammonia\ that\ formed\ a\ complex\ with\ copper\ ions}{moles\ of\ copper\ ions}$

= $\frac{0.2}{0.05}$ = 4

3. **Chromatography**.

Exercise

<table>
<tr><td>1.</td><td>(a)</td><td>(i)</td><td>Define the term " partition coefficient" and state conditions under which it is valid</td><td>(3marks)</td></tr>
<tr><td></td><td></td><td>(ii)</td><td>Briefly describe how the partition coefficient for the distribution of iodine between water and trichloromethane can be determined</td><td>(5marks)</td></tr>
<tr><td></td><td>(b)</td><td>(i)</td><td>60cm^3 of an aqueous solution containing 0.3g of compound Y was shaken with 30 cm^3 of ethoxyethane and a mixture allowed to stand. Calculate the mass of Y which was extracted into the ethoxyethane layer. (the partition coefficient of Y between ethoxyethane and water is 4.7</td><td></td></tr>
<tr><td></td><td></td><td>(ii)</td><td>The aqueous solution in (i) was extracted with two successive 15cm^3 of ether. Calculate the mass of Y that was extracted by ether.</td><td>(6marks)</td></tr>
<tr><td></td><td>(c)</td><td></td><td>The table below shows the result of partition of aminoethane between trichloromethane and o.1M copper (II) sulphate solution
<table>
<tr><td>[CH_3NH_2(0.1M$CuSO_4$)]</td><td>0.87</td><td>1.10</td><td>1.33</td><td>1.57</td><td>1.80</td></tr>
<tr><td>[CH_3NH_2($CHCl_3$)]</td><td>0.02</td><td>0.03</td><td>0.04</td><td>0.05</td><td>0.06</td></tr>
</table></td><td></td></tr>
<tr><td></td><td></td><td>(i)</td><td>Plot a graph of [CH_3NH_2(0.1M$CuSO_4$)] against [CH_3NH_2($CHCl_3$)]</td><td></td></tr>
<tr><td></td><td></td><td>(ii)</td><td>Determine the number of moles of aminoethane that formed a complex with copper II ions</td><td></td></tr>
<tr><td></td><td></td><td>(iii)</td><td>Write equation for the reaction between copper II ions and aminoethane.</td><td></td></tr>
<tr><td>2.</td><td></td><td></td><td>100cm^3 of a solution containing 0.171g of ammonia in trichloromethane was shaken with 10cm^3 of water until equilibrium was attained at room temperature. Calculate the number of moles of ammonia in trichloromethane layer. (the partition coefficient of ammonia between water and trichloromethane at room temperature is 27.5)</td><td>(3marks</td></tr>
<tr><td>3.</td><td></td><td></td><td>A copper ore was dissolved in excess concentrated ammonia and the solution made up to 1dm^3. The resultant solution was shaken with 1dm^3 of trichloromethane and left to settle. 50cm^3 of the organic layer needed 25.0cm^3 of 0.05M hydrochloric acid for neutralization. 25cm^3 of the aqueous layer was neutralized by 40cm^3 of 0.5M hydrochloric acid.
Calculate the concentration of copper II ions in molesdm^{-3}. (the distribution coefficient of ammonia between water and trichloromethane is 25.</td><td>6marks)</td></tr>
</table>

4			The graph shows the distribution of ammonia between aqueous layer of 0.1M copper (II) ions and chloroform  	
	(a)	(i)	Determine the distribution coeficient, K_D of ammonia between aqueous copper (II) ions and chloroform.	(3marks)
		(ii)	State what the value you have detrmine indicates about the distribution of ammonia.	(2marks)
	(b)		The graph does not pass through the origin because ammonia with copper (II) ions	
		(i)	Dertermine the number of moles of ammonia that reactionweith one mole copper (II) ions.	(2 ½ marks)
		(ii)	Write equation for the reaction between ammonia and copper II ion	1 ½ marks)
5	(a)		State	
		(i)	The distribution (partition) law	(3 ½ marks)
		(ii)	The condition under which the distributionlaw is valid	(1 ½ marks)
	(b)		$100cm^3$ of an aqueous solution containing 10g of a compound Q was shaken with $100cm^3$ of benzene. Q is more soluble in benzene and the partion coefficient of Q between benzene and water is 12.2 Calculate the mass of Q left in aqueous layer	
	(c)		State one application of partion of solutes	(1mark)
6			$100cm^3$ of an aqueous solution containing 20 g of W was shaken with $50cm^3$ of ether.	
	(a)		Calculate the massof W extracted by ether (the partition coefficient, K_D of W between ether and water is 4)	(2marks)
	(b)		Calcualte the mass of W that would be extracted by shaking the solution twice with $25cm^3$ of ether	(4marks)
7	(a)		State distribution law	(2marks)
	(b)		Describe how the distribution coefficient of butane-1,4-dioic acid (succinic acid) between water and ethoxyethane can be determined.	(5marks)
	(c)		$100cm^3$ of a solution contains 30g of substance Z. calculate the mass of Z that can be extracted by shaking the solution with:	

		(i)	100cm^3 of ethoxyethane	(03marks)
		(ii)	Two 50cm^3 portion of ethoxyethane (the distribution coefficient of Z between ethoxyethane and water is 5)	(05marks)
	(d)		Briefly describe how the distribution law can be used to determine the formula of the complex formed between copper (II) ion ammonia	(05mark)

Suggested answer

1 (a)(i) **Partition Coefficient or distribution constant** is ratio of the concentration of the solute in immiscible solvents at equilibrium.

(ii) – Equal volumes of iodine solution and trichloromethane are mixed and left to stand in order to establish an equilibrium

- The layers are separated by a separating funnel and the concentration of iodine in each layer is determined by titration with standard sodium thiosulphate solution using starch indicator

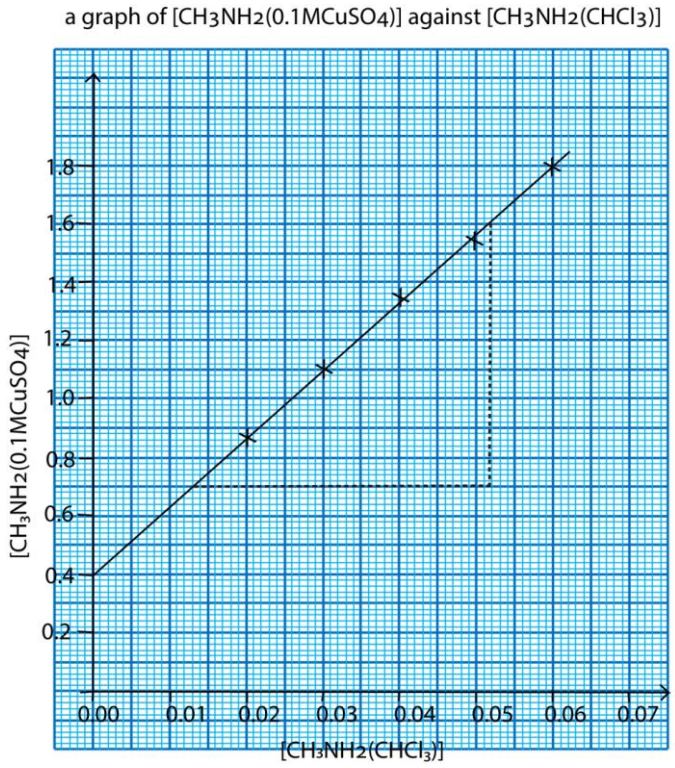
  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

- Partition coefficient Kd = $\frac{[NH_3]\ in\ water}{[NH_3]\ in\ trichloromethane}$

(b) (i) 0.21g

(ii)0.23g

(c)(i)



(ii) Moles of methylamine that formed a complex with copper ion = intercept = 0.4

Moles of methylamine that formed a complex per mole of copper ion = $\frac{0.4}{0.1}$ = 4

(iii) $Cu^{2+}(aq) + 4CH_3NH_2\ (aq) \rightarrow [Cu(CH_3NH_2)_4]^{2+}(aq)$

2. 0.0027 moles

3. Moles of ammonia in 1000cm3 of organic layer

50 cm^3 of organic layer contains the same number of moles of ammonia = moles HCl

$$= \frac{25\ x\ 0.05}{1000}$$

1000cm^3 of organic layer contain = $\frac{25\ x\ 0.05}{1000}\ x\ \frac{1000}{50}$ 0.025moles

Moles of ammonia in 1000cm^3 of water

25 cm^3 of organic layer contains the same number of moles of ammonia = moles HCl

$$= \frac{40\ x\ 0.5}{1000}$$

1000cm^3 of organic layer contain = $\frac{40\ x\ 0.5}{1000}\ x\ \frac{1000}{25}$ 0.8moles

Moles of non complexed ammonia = Kd x moles of ammonia

= 25 x 0.025

= 0.625 moles

Moles of ammonia that formed a complex with copper ions = 0.8 – 0.625

= 0.175 moles

Moles of $Cu^{2+}(aq)$ = $\frac{0.175}{4}$ = 0.044$moldm^3$.

4. (a) (i) kd = slope = 25
   (ii) ammonia is 25 times soluble in water than in trichloromethane
   (b) (i) 4 [intercept/mole of copper ions]

   (ii) $Cu^{2+}(aq) + 4NH_3\ (aq) \rightarrow [Cu(NH_3)_4]^{2+}(aq)$

5. 0.74 g
6. (a) (i) 13.3g
   (ii) 15g
7. (c)(i) 25g
   (ii) 27.5g