# Unit 13

(1) **2000 A/L**

c) $A$ and $B$ are two fully miscible volatile liquids. On mixing A and B form the ideal binary solution, $AB$, in which the mole fraction of $A$ is $X_A$. The total vapour pressure of this solution is $P_{AB}$ when the partial vapour pressures of $A$ and $B$ are $P_A$ and $P_B$ respectively.

$R$ and $S$ are also two fully miscible volatile liquids. On mixing, $R$ and $S$ form the binary solution, $RS$ in which the mole fraction of $R$ is $X_R$. The forces of attraction between the molecules of $R$ and $S$ are slightly stronger than the forces of attraction between either $R$ molecules or $S$ molecules. The total vapour pressure of this solution is $P_{RS}$ when the partial vapour pressures of $R$ and $S$ are $P_R$ and $P_S$ respectively.

At a given temperature $T$, The saturation vapour pressures of the pure liquids $A$, $B$, $R$ and $S$ are respectively. $P_A^o$, $P_B^o$, $P_R^o$ and $P_S^o$
At all temperatures, $P_A^o = P_R^o$ ; $P_B^o = P_S^o$ ; $P_A^o > P_B^o$
Using the above data, answer all the parts i) - iii)

i) Prove below that at the temperature T,
$P_{AB} = P_B^o + X_A (P_A^o - P_B^o)$

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State below the important asumption you made in proving the above equation.

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ii) The diagrams given, sketch graphs to show clearly the following variations.

- I) The variation of each of the vapour pressures $P_A$, $P_B$ and $P_{AB}$ with $X_A$ at the given temperature T on diagram.
- II) The variation of each of the vapour pressures $P_R$, $P_S$ and $P_{RS}$ with $X_R$ at the given temperature T of diagram II.

N.B. Use identical scales for the vertical axes in diagrams I and II represent vapour pressure.

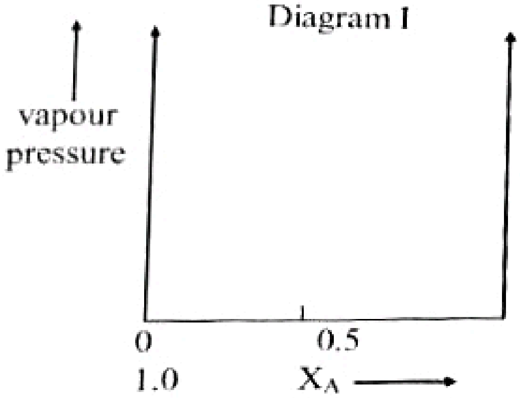
Diagram I

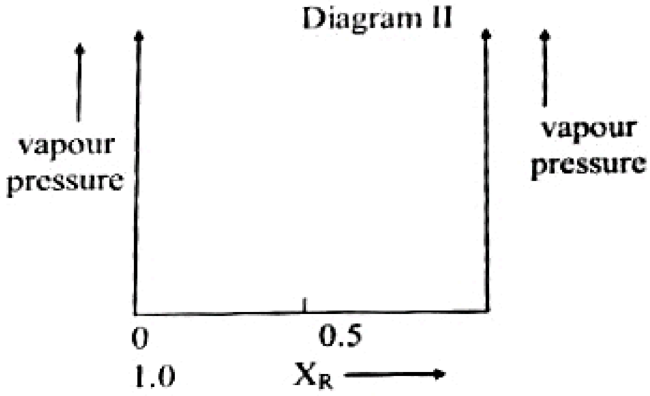
Diagram II

Label the graphs you drew in each diagram to the variations.
Mark on the relevant axes, the points corresponding to $P_A^o$, $P_B^o$, $P_R^o$ and $P_S^o$.

iii) Complete the passage given below by filling the blank correctly with appropriate words / letters:

When the temperature of a solution is increased, there is a / an .................. in its vapour pressure. We say that the solution boils when its total vapour pressure is equal to the ..................... pressure. At the normal boiling point, this pressure is equal to the ......................... pressure.

The normal boiling point of pure liquid ................. is equal to the normal boiling point of pure liquid *S*. The normal boiling points of each of the pure liquid ............... and .................... are less than that normal boiling point of pure liquid *B*.

The solution *RS* shows a .................... deviation from ideal behaviour. The total vapour pressure of an equimolar solution of *RS* is .................... than the total vapour pressure of an equimolar solution of *AB* at any given temperature. The normal boiling point of an equimolar solution of *RS* will therefore take a .................. value than that of an equimolar solution of *AB*.

(2) **2003 A/L**

c) Two pure liquids *A* and *B* mix together at temperature *T* to give a homogeneous solution *AB* in which

$f_{A\text{-}A} = f_{B\text{-}B} = f_{A\text{-}B}$

Where $f_{X\text{-}Y}$ for example refers to the force of attraction between two molecules *X* and *Y*.

Two pure liquids *B* and *C* mix together at the same temperature *T* to give a homogeneous solution *BC* in which the force of attraction $f_{B\text{-}C}$ is very slightly greater than $f_{B\text{-}B}$ and $f_{C\text{-}C}$. Some of the physical properties of liquids *A*, *B* and *C* together with the liquid quantities mixed to give the above mentioned solutions *AB* and *BC* are given in the table below.

| Liquid | Number of moles mixed | Number of molecules mixed | Vapour pressure at temperature T | Relative molecular mass | Boiling point |
|---|---|---|---|---|---|
| A | x | d | J | M | U |
| B | y | e | K | L | V |
| C | z | f | J | N | W |

The volume occupied by the vapour in equilibrium with each of the solutions *AB* and *BC* is S at the same temperature *T*. There are no intermolecular interactions between molecules in the vapour phase.

Universal gas constant = *R*

Using only symbols given above as may be necessary, (but using no other), answer the following.

i) Write down a mathematical expression for the Avogadro Constant.

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ii) Write down in respect of the vapour phase in equilibrium with the solution *AB*, mathematical expressions for,

I) the equilibrium vapour pressure of *A*.

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II) The total equilibrium vapour pressure

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III) The total number of molecules.

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IV) The ratio of the number of molecules of *A* and *B*.

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V) The number of molecules of $B$.

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VI) The mean square speed $\overline{C_B^2}$ of $B$ molecules.

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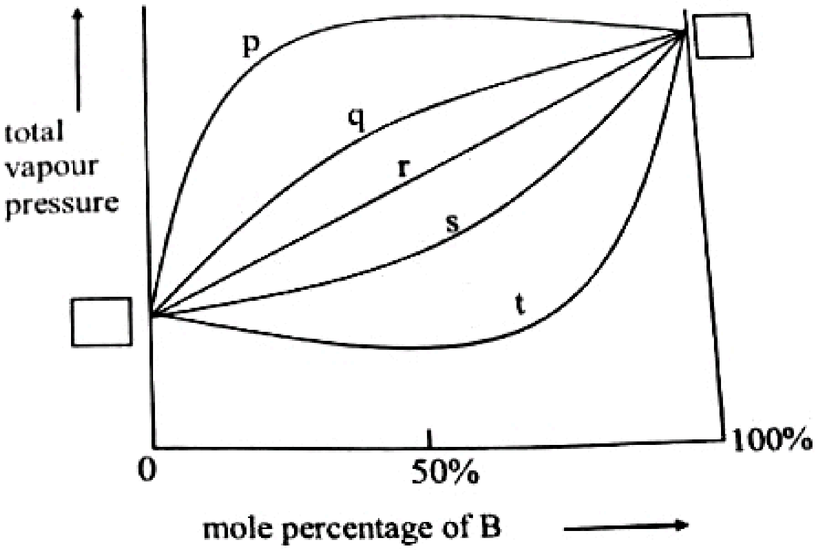
iii) Possible variations of the total vapour pressure of binary liquid solutions containing $B$ with the mole percentage of B in solution at temperature $T$ are indicated as $p$, $q$, $r$, $s$ and $t$ in the phase diagram below.



I) Identify the most appropriate variation $p$, $q$, $r$, $s$ and t in the above diagram relevant to each of the following solutions by writing same in the appropriate space below.

Solution $AB$ : ............................

Solution $BC$ : ............................

II) Mark in the two boxes of the above diagram, the appropriate symbols for the vapour pressures corresponding to 0% $B$ and 100% $B$ in both solutions $AB$ and $BC$.

(3) **2007 A/L**

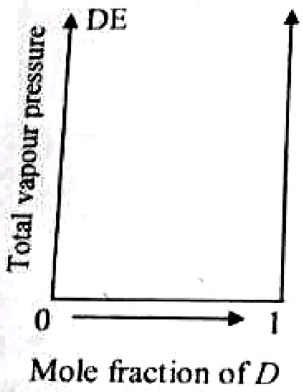
b) i) The pure liquids ***D*, *E*** and ***F*** form binary homogeneous solutions ***DE*, *EF*** and ***DF*** with each other at temperature *T*. The intermolecular forces between any two molecules of *D*, *E* and *F* are as indicated in the table below.

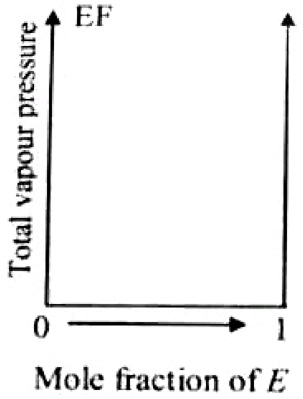
| Molecule | D | E | F |
|---|---|---|---|
| D | d | b | c |
| E | b | e | a |
| F | c | a | f |

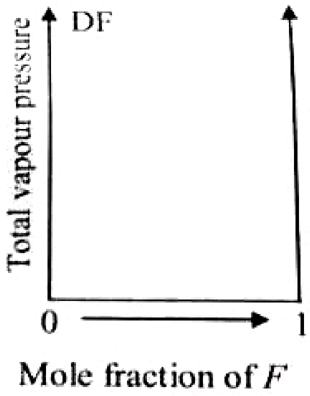
The following information is given :

- d = c = f
- *b* is **slightly smaller** than *d* and *e*.
- *a* is slightly greater than *e* and *f*.
- The vapour pressures of the three liquids ***D*, *E*** and ***F*** are $P_D$, $P_E$ and $P_F$ respectively, at the given temperature with $P_D > P_E$ and $P_F > P_D$.

I) Mark $P_D$, $P_E$ and $P_F$ as may be appropriate on each of the six vertical axes in the diagrams below.







II) Indicate in the relevant diagrams the likely variations of the total vapour pressure of each of the solutions *DE*, *EF* and *DF*.

ii) $\alpha$ mol of *D* and $\gamma$ mol of *F* are mixed to give a solution *DF*. The total equilibrium vapour pressure above *DF* at temperature *T* is P. Intermolecular forces in the vapour phase can be assumed to be absent.

Using the symbols given above in 2 b) i) and ii), but no other, write down mathematical expressions for the following.

I) The particle pressure of *D* in the vapour phase.

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II) The partical pressure of *F* in the vapour phase.

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III) The number of moles of *D* in the vapour phase.

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(4) 2008 A/L

b) $A$ and $B$ are pure liquids miscible in all proportions forming ideal solutions at temperature $T$. The boiling point of $A$ is higher than that of $B$. Mark / draw the following in figure 1.

i) $P_A^0$ and $P_B^0$ : Relative points representing vapour pressures of pure $A$ and Pure $B$ respectively.

ii) $P_A$ : Line / curve showing the variation of the vapour pressure of $A$ with composition.

iii) $P_B$ : Line / curve showing the variation of the vapour pressure of $B$ with composition.

iv) $P_T$ : Line / curve showing the variation of the vapour pressure with composition.

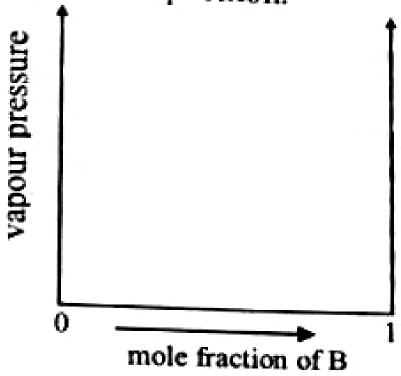

figure 1

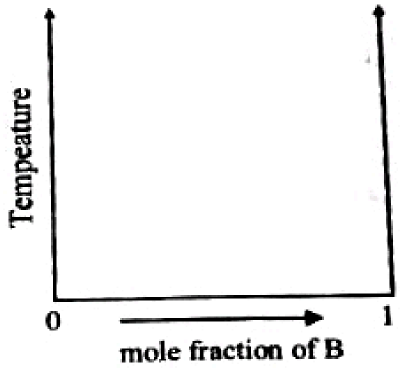

figure 2

v) Show that for an equimolar solution of $A$ and $B$ in equilibrium with its vapour, the mole fraction of $A$ in the vapour phase is $\dfrac{P_A^0}{P_A^0 + P_B^0}$

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iv) Draw the temperature – composition phase diagram for the solutions of $A$ and $B$ in figure 2. Mark in your diagram,

I) The boiling point, $T_A^0$ of pure $A$.

II) The boiling point, $T_B^0$ of pure $B$ and

III) The regions where the following phases exist. liquid, vapour and liquid + vapour together.

(5) **2011 A/L (Old)**

b) i) Non – volatile solute $A$ dissolves in solvent $B$ forming the ideal solution $C$. At a given temperature, the vapour pressure of the pure solvent and that of solution $C$ are $p°$ and $p$ respectively. The mole fraction of the solvent in solution $C$ is $X_B$.

I) Write the Raoult's law in the form of an equation for solution $C$, in terms of the symbols given above.

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II) The mole fraction of the solute in solution $C$ is $X_A$. Write an equation for the Raoult's law in terms of $p$, $p^{\circ}$ and $X_A$. Hence, derive a mathematical expression for $X_A$.

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ii) Calculate the mole fraction of the solute in each of the following solutions $P$, $Q$ and $R$.

P : 2.0 mol $dm^{-3}$ aqueous solution of glucose which has a density of **1.26 g $cm^{-3}$**

Q : Solution containing 180 g of glucose in 162 g of water.

R : Solution containing 171 g of sucrose in 171 $cm^3$ of water.
Consider that the density of water is 1.0 g $cm^{-3}$

Relative molar masses of water, glucose and sucrose are 18, 180 and 342 respectively.

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**iii) Arrange the solutions** $P$, $Q$ **and** $R$ **in the order of their increasing vapour pressure, according to** Raoult's **law.**

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**iv) Write the Raoult's** law as **an equation for a mixture consisting of glucose, sucrose and water** where the **masses of these are known.**

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(6) **2012 A/L**

b) i) Consider the following standard reduction potentials.

$E^{\theta}$ [$Br_2$(l) | $Br^-$ (aq) ] = 1.07V

$E^{\theta}$ [$I_2$(s) | $I^-$ (aq) ] = 0.54 V

I) What reaction would you expect to take place when liquid bromine is added to an aqueous solution of 1.0 mol $dm^{-3}$ KI.

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II) Write the colour changes you would expect in the above experiment.

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ii) Consider the following electrochemical reaction.

$Mg(s) + 2H^+ (aq) \rightarrow Mg^{2+} (aq) + H_2(g)$

I) Write the cathodic reaction of the Galvanic cell consistent with the above reaction.

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II) Write the conventional notation for representing the above cell, which includes a salt bridge.

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III) Does the entropy increase, decrease or remain constant when the above cell reaction proceeds?

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IV) What should be the relationship between enthalpy change (ΔH) and entropy change (ΔS) for the above reaction to be spontaneous at temperature *T*?

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(7) **2013 A/L**

Chlorine gas is used as an oxidizing agent to oxidize the metal ion. $M^{2+}$(aq) to $M^{3+}$(aq). The following data are given.

| Reaction | Standard enthalpy change $\Delta H^{\theta}$ at 25°C (kJ $mol^{-1}$) |
|---|---|
| $M(s) \rightarrow M^+(aq) + e$ | –32.5 |
| $M(s) \rightarrow M^{2+}(aq) + 2e$ | –48.5 |
| $M(s) \rightarrow M^{3+}(aq) + 3e$ | –82.5 |
| $Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$ | –334.0 |

$E^{\theta}_{M^{3+}/M^{2+}} = +0.27V$ $\qquad$ $E^{\theta}_{Cl_2/Cl^-} = +1.36\ V$

The above oxidation is carried out electrochemically.

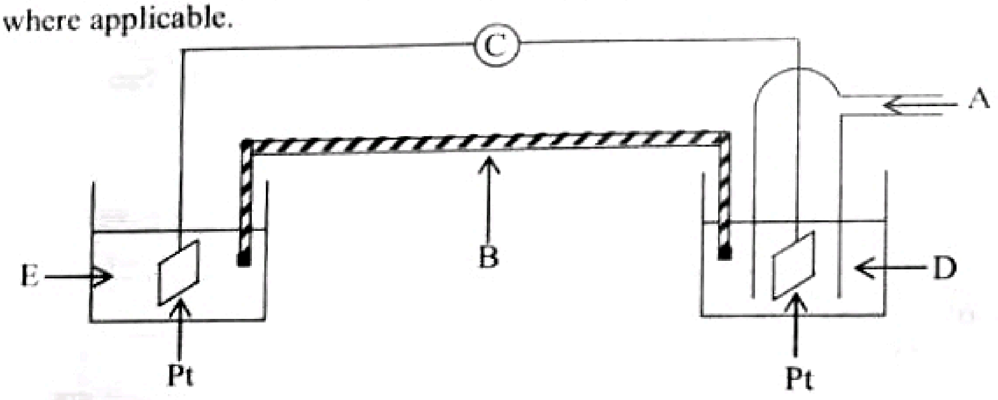
i) Write half reactions for oxidation and reduction processes and derive the cell reaction.

**Oxidation reaction** : ..........................................................................

**Reduction reaction** : ..........................................................................

**Cell reaction** : ..........................................................................

ii) The following diagram shows the experimental setup needed to measure $E^0_{cell}$ of the above reaction. Identify A – E giving physical state, concentration / pressure where applicable.



A : ..............................................  B : ..............................................

C : ..............................................  D : ..............................................

E : ..............................................................................

iii) Calculate $E^0_{cell}$ for the above cell.

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i) Calculate the standard enthalpy change ($\Delta H^\circ$) at 25°C for the cell reaction given in part i).

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iv) The relationship between standard Gibb's energy change, $\Delta G^\circ$ for the cell reaction and $E^0_{cell}$ is given by

$$\Delta G^\circ = -k\, E^0_{cell}$$

Where, $k = 1.93 \times 10^5\ J\ mol^{-1}\ V^{-1}$

Calculate the standard Gibbs energy change ($\Delta G^\circ$) at 25°C for the above cell reaction.

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v) Calculate the standard entropy change ($\Delta S^\circ$) at 25°C, for the above cell reaction.

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(8) **2014 A/L**

*Y* is a 1.00 *M* solution of a weak acid *HA* with a pH = 3.0 at 25 °C. *A* 100.0 $cm^3$ sample of this solution was placed in a shaking bottle and 100.0 $cm^3$ of organic solvent was added. After shaking the bottle it was placed in a water bath at 25°C for 30 minutes. There after, the two layers were separated and the aqueous layer was labelled as solution *Z*. A 25.00 $cm^3$ sample of solution *Z* was titrated with 0.50 *M* NaOH using phenolphthalein as the indicator. The volume of NaOH required was 40.00 $cm^3$.

i) Calculate the degree of dissociation α of the weak acid in solution *Y* at 25°C.

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ii) Calculate the dissociation constant ($K_a$) of the acid *HA* at 25°C.

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iii) Calculate the degree of dissociation α', of acid *HA* in solution *Z* at 25°C.

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iv) Using the values of $\alpha$ and $\alpha'$ calculated above, comment on the relationship between the degree of dissociation and concentration of the acid *HA* 25°C.

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v) Calculate the partition coefficient at 25°C of the acid *HA* between water and organic solvent. (The weak acid *HA*, does not associate or dissociate in an organic solvent. Disregard the dissolciation of *HA* in aqueous medium)

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**vi) Calculate the pH of a mixture containing 25.00 cm$^3$ of solution *Y* and 25.00 cm$^3$ of 0.50 M NaOH solution.**

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**(9) 2017 A/L**

**a)** Methylamine $CH_3NH_2$ is a weak base. The following equilibrium exists in a aqueous solution of methylamine.

$$CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$$

**i)** Write the expression for $K_b$ of methylamine.

$$K_b = \frac{[CH_3NH_3^+(aq)]\,[OH-(aq)]}{[CH_3NH_2(aq)]}$$

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ii) At 25°C, the pH value of a 0.20 mol dm$^{-3}$ aqueous solution of methylamine is 11.00. Calculate $K_b$.

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iii) A volume of 25.00 cm$^3$ of the solution in ii) above was titrated with 0.20 mol dm$^{-3}$ HCl at 25°C. Calculate the pH value of the solution at the equivalence point. ($K_w = 1.0 \times 10^{-14}$ mol$^2$ dm$^{-6}$ at 25°C)

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b) In an experiment, a limited volume of 1.00 mol dm$^{-3}$ $HNO_3$ was added to a precipitate MX(s) and the system was allowed to reach equilibrium at 25°C. This resulted in partial dissolution of the precipitate giving rise to a clear solution. The HX(aq) formed behaves as a weak acid.

i) Write chemical reactions for the equilibrium existing in the above solution.

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ii) **Calculate IX$^-$(aq) in the solution assuming that the dissociation of HX(aq) is negligiblo. (Solubility product of MX at 25°C, $K_{SP(MX)} = 3.6 \times 10^{-7}$ mol$^2$ dm$^{-6}$)**

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iii) **Giving reasons explain whether [IX$^-$(aq)] in a saturated aqueous solution of MX at 25°C is equal to, smaller than or greater than the value obtained in b) ii) above.**

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