## A: SOLUBILITY REVISION QUESTIONS

- 1. The solubility products of BaCrO<sub>4</sub> and SrCrO<sub>4</sub> are  $1.2x10^{-10}$  and  $3.5x10^{-5}M^2$  respectively. If the K<sub>2</sub>CrO<sub>4</sub> solution is added to aqueous solution of 0.1M Ba<sup>2+</sup> and 0.1M of Sr<sup>2+</sup> ions
  - (i) Which salt will be the first to precipitate? [Ans. BaCrO<sub>4</sub> will be the first to precipitate]
  - (ii) Calculate the % of the first cation when the  $2^{nd}$  cation just begins to precipitate? [*Ans.* %*Ba*<sup>2+</sup>=0.0034%]
- 2. The solubility product of Aluninium iodate and barium iodate are  $1.0 \times 10^{-8}$  and  $6 \times 10^{-10}$  respectively. If  $8.6 \times 10^{-4}$ M chloride and  $3.74 \times 10^{-3}$ M of Aluminum chloride is added to solution iodate
  - (i) Which salt precipitate first? [Ans. Ba(IO<sub>3</sub>)<sub>2</sub> will be the first to precipitate]
  - (ii) Calculate the percentage of the first cation when the 2<sup>nd</sup> cation just begins to precipitate? [*Ans.* 0.3622%]
- 3.  $H_2S$  is passed to a solution containing  $Cu^{2+}$ ,  $Ag^+$  and  $Ca^{2+}$  ion at a concentration of  $1.0x10^-$  <sup>5</sup> each.
  - (*i*) Give the order at which the sulphides will be precipitated? [*Ans. AgS, CaS and CuS*]
  - (ii) Calculate the concentration of  $S^{2-}$  at which each sulphide is precipitated?

Given Ksp of CuS,  $Ag_2S$  and CaS respectively are  $1x10^{-17}$ ,  $1x10^{-80}$  and  $1x10^{-30}$ .

- **4.** An aqueous solution of Na<sub>2</sub>S is gradually added to solution containing Ca<sup>2+</sup>, Cu<sup>2+</sup> and Ag<sup>+</sup> each atconcentration of 10<sup>-3</sup>M. Determine [S<sup>2-</sup>] at which precipitation of each cations occurs. Ksp(CaS)=1x10<sup>-28</sup>M<sup>2</sup>, Ksp(CuS)=1x10<sup>-36</sup>M<sup>2</sup> and Ksp(Ag<sub>2</sub>S)=1x10<sup>-50</sup>M<sup>3</sup> hence give the order of precipitation of given compunds? [*Ans. Ag*<sub>2</sub>*S*>*CuS*>*CaS*, *CaS*([S<sup>2-</sup>]=10<sup>-25</sup>), *CuS*([S<sup>2-</sup>]=10<sup>-33</sup>), *Ag*<sub>2</sub>S([S<sup>2-</sup>]=10<sup>-44</sup>)]
- 5. To a solution containing  $0.1M \text{ Ca}^{2+}$  and  $0.1M \text{ Ba}^{2+}$ , BaSO<sub>4</sub> is added slowly. The solubility product of CaSO<sub>4</sub> and BaSO<sub>4</sub> are  $2.4 \times 10^{-5}$  and  $1.1 \times 10^{-10}$  respectively.
  - *i.* Which will precipitate first, CaSO<sub>4</sub> and BaSO<sub>4</sub>? Explain [*Ans. BaSO<sub>4</sub> will be the first to precipitate*]
  - *ii.* What is the  $[SO_4^{2-}]$  at instant the first solid precipitates?  $[Ans. [SO_4^{2-}] = 1.1 \times 10^{-9} M]$
  - *iii.* Neglect dilution and calculate the  $[Ba^{2+}]$  present when the first precipitate of CaSO<sub>4</sub> occurs? [*Ans.* [*Ba*<sup>2+</sup>]=4.58x10<sup>-7</sup>*M*]
- **6.** To a solution containing 0.1M chlorine ion and 0.01M  $CrO_4^{2-}$ , a solution of AgNO<sub>3</sub> is added slowly
  - i. Which salt will precipitate first between AgCl and Ag<sub>2</sub>CrO<sub>4</sub>? Show clearly how you answer [Ans. AgCl will precipitate first despite of large ksp value]
  - Find the concentration of ion that will precipitate first at the time the second ion will start precipitating. The Ksp values for AgCl 2.72x10<sup>-10</sup> and 2.4x10<sup>-12</sup> respectively. [Ans. 1.755x10<sup>-5</sup>M]

- 7. At  $25^{\circ}$ C the solubility product Ksp for SrSO<sub>4</sub> is 7.6x10<sup>-7</sup>. The Ksp for the SrF<sub>2</sub> is 7.9x10<sup>-10</sup>
  - i. What is the molar solubility of SrSO<sub>4</sub> and SrF<sub>2</sub> in pure water?
  - ii. An aqueous solution of  $Sr(NO_3)_2$  is added slowly to 1Liter of a well stirred solution containing 0.02mole of F<sup>-</sup> and 0.1mole  $SO_4^{2-}$  at  $25^0C$  (You may assume that the added  $Sr(NO_3)_2$  solution does not materially affect the total volume)
    - Which salt precipitates first? [Ans. SrF<sub>2</sub> precipitate first]
    - What is the concentration of strontium ion in the solution when the first precipitate begins to form?
  - iii. As more  $Sr (NO_3)_2$  is added to the mixture (ii) above a second precipitate begins to form. At that stage, what percentage of the anion of the first precipitate remains in the solution?
- 8. AgNO<sub>3(aq)</sub> is slowly added to a solution that has  $[CrO_4^{2-}]=0.01M$  and  $[Br^{-}]=0.01M$ . Given the Ksp:AgBr=5.0x10<sup>-13</sup>; Ag<sub>2</sub>CrO<sub>4</sub>=1.1x10<sup>-12</sup>
  - *i.* Show that  $AgBr_{(s)}$  should precipitate before the  $Ag_2CrO_{4(S)}$  does? ([ $Ag^+$ ] required to start precipitation of  $AgBr_{(s)}$  is less than that for  $Ag_2CrO_{4(S)}$ ,  $AgBr_{(s)}$  will precipitate first)
  - ii. When Ag<sub>2</sub>CrO<sub>4(S)</sub> begins to precipitate, what will be the [Br<sup>-</sup>] be remaining in the solution? (Ans.5.0x10<sup>-8</sup>M)
  - iii. Is the complete separation of Br<sup>-</sup> and CrO<sub>4</sub><sup>2-</sup> by fractional precipitation feasible? (*Before Ag<sub>2</sub>CrO<sub>4(S)</sub> begins to precipitate, [Br<sup>-</sup>] will be reduced from 1.0x10^{-2} to*  $5.0x10^{-8}$  (*Calculate the % [Br<sup>-</sup>] remaining*). Essentially all the Br<sup>-</sup> will have precipitated from the solution of AgBr whereas the CrO<sub>4</sub><sup>2-</sup> remains in solution. Fractional precipitation is feasible for separating mixtures of Br<sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>)
- **9.** The first step in a commercial process in which magnesium is obtained from sea water involves precipitating  $Mg^{2+}$  as  $Mg(OH)_2$ . The concentration of magnesium ion in the seawater is about 0.059M. If a seawater sample was treated so that its  $[OH^-]$  is maintained at  $2.0x10^{-3}$  M
  - i. Show that AgBr should precipitate before Ag<sub>2</sub>CrO<sub>4</sub> does?
  - ii. When  $Ag_2CrO_4$  begins to precipitate, what will the [Br<sup>-</sup>] be remaining in solution?
- iii. Is the complete separation of  $Br^{-}$  and  $CrO_4$  by fractional precipitation be feasible?
- **10.** Explain each of the following
  - (a). The solubility of silver chloride in water decreases when dilute hydrochloric is added but increases when concentrated hydrochloric acid is added?
  - (b). Aqueous ammonium carbonate can precipitate some metals as their metal carbonates but the presence of sodium hydroxide in the solution often prevents the precipitation?

(c). What will happen when KOH solution is added to a solution containing copper chloride and in excess KOH?

- **11.** Three drops of 0.2M KI are added to 100.0Ml of 0.010M Pb(NO<sub>3</sub>)<sub>2</sub>. Will a precipitate of lead(II)iodate form? (Assume 1drop = 0.05mL; Ksp=7.1x10<sup>-9</sup>)
- 12. Lead (II) sulphate (PbSO<sub>4</sub>) is a key component in lead-acid batteries. Its solubility in water at 25<sup>o</sup>C is found to be 4.25x10<sup>-3</sup>g/100cm<sup>3</sup> solution. Calculate the value of Ksp of PbSO<sub>4</sub>? (Ans. 1.96x10<sup>-8</sup>)

- **13.** A solution is prepared by mixing 150.0mL of  $1.0x10^{-2}$  Mg(NO<sub>3</sub>)<sub>2</sub> and 25 mL of  $1.0x10^{-1}$  NaF. Calculate the concentration of Mg<sup>2+</sup> and F<sup>-</sup> at equilibrium with solid MgF<sub>2</sub>. Given Ksp= $6.4x10^{-9}$  mol<sup>3</sup>/dm<sup>-6</sup> at 298K. (Ans. [Mg<sup>2+</sup>]= $2.12x10^{-6}$ )
- **14.** Solid sodium oxalate is gradually added to a solution containing 0.50M Ba<sup>2+</sup> and  $3.0 \times 10^{-5}$  M Ag<sup>+</sup>. Is it possible to achieve a complete separation of the two cations? Support your answer by calculations. Given Ksp (BaC<sub>2</sub>O<sub>4</sub>=2.x10<sup>-8</sup> and Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub>=1.6x10<sup>-11</sup>)
- 15. A sample of AgCl was treated with 5.0ml of 1.5M Na<sub>2</sub>CO<sub>3</sub> the remaining solution contains 0.0026g of Cl<sup>-</sup> per liter. Calculate the solubility product of AgCl [Ksp=8.2x10<sup>-12</sup>]? (Ans. 1.71x10<sup>-9</sup>)
- **16.** A solution consists of 0.2M MgCl<sub>2</sub> and 0.1M CuCl<sub>2</sub>. Calculate the [OH<sup>-</sup>] that would separate the metal ions as their hydroxides Ksp of Mg(OH)<sub>2</sub> is 6.3x10<sup>-10</sup> and Ksp of Cu(OH)<sub>2</sub> is 2.2x10<sup>-20</sup>? (Ans.5.6x10<sup>-5</sup>)
- 17. The solubility product of BaSO<sub>4</sub> in water at 25°C is 1x10<sup>-10</sup>. Calculate the mass precipitated when 20cm<sup>3</sup> of 0.01M BaCl<sub>2</sub> solution and 20cm<sup>3</sup> of 0.01M Na<sub>2</sub>SO<sub>4</sub> solution were mixed at 298K? [*Ans. Mass of BaSO<sub>4</sub>=0.0465g*]
- 18. The solubility of Sr(OH)<sub>2</sub> at 298K is 19.23g/l of solution. Calculate the concentration of strontium and hydroxyl ions and P<sup>H</sup> of the solution? [*Ans.* [Sr<sup>2+</sup>]=0.158M, [OH<sup>-</sup>]=0.316M and P<sup>H</sup>=13.5]
- **19.** Calculate hydroxide has a Ksp= $7.9 \times 10^{-6}$ , what is the P<sup>H</sup> of the solution made by equilibrating Ca(OH)<sub>2</sub> solid with water? [*Ans. P<sup>H</sup>*=*12.39*]
- 20. A mixture of H<sub>2</sub>O and solid AgCl shaken to obtain saturated solution. The solid is filtered to 100mL filtrate, 100mL of 0.03M NaBr is added will precipitate be formed? Provided with Ksp(AgCl)=10<sup>-10</sup> and Ksp(AgBr)=5x10<sup>-13</sup> [Ans. Qsp>Ksp ppt formed, Qsp=7.5x10<sup>-8</sup>]

## **B: ELECTROCHEMISTRY REVISION QUESTIONS**

## I: ELECTRODE POTENTIAL

- 1. Explain the following observation
  - *i.* No two electrodes can have the same standard electrode potential, why? [Ans. This is because no two electrodes have exactly the same structure and the tendency to gain or lose electrons is also different]
  - *ii.* If two of the same metal are dipped separately into two solutions of the same electrolyte at different concentration connected by salt bridge then whole arrangement acts as a Galvanic cell why?

# [Ans. This is because at different concertation of the electrolyte, the two cells half cells have different electrode potential]

*iii.* Predictions from E<sup>0</sup> values concerning the feasibility of a reaction are not always realized in practice. Suggest reasons for this

# [kinetic factors, non-standard conditions and very small difference in $E^0$ values]

2. Calculate the equilibrium constant for the reaction at  $25^{\circ}C$ 

 $Cu(s) + 2Ag^+_{(aq)} \rightleftharpoons Cu^{2+}_{(aq)} + 2Ag_{(s)}$ . Given the standard cell potential for the reaction at 25<sup>o</sup>C is 0.46V? [Ans. Kc=3.69x10<sup>15</sup>]

- 3. Draw a sketch of a cell formed by combining  $Zn^{2+}_{(aq)}/Zn_{(s)}$  and  $Cu^{2+}_{(aq)}/Cu_{(s)}$  half-cells. Indicate on sketch the following
  - i. The positive electrode?
  - ii. The direction of the electron flow in the external circuit
  - iii. The electrodes at which oxidation and reduction occurs
- 4. Calculate the emf of the cell operating under standard conditions given that,

 $Ag^{+}_{(aq)}/Ag_{(s)} E^{0}(V)=0.80V$ 

 $Cu^{2+}_{(aq)}/Cu_{(s)} E^{0}(V)=0.34V$ 

 $Zn^{2+}_{(aq)}/Zn_{(s)} E^{0}(V)=-0.76V$ 

- i. Explain how the emf of the cell would be affected by increase in  $[Cu^{2+}]$  and increase  $[Zn^{2+}]$ ?
- ii. If the  $Zn^{2+}_{(aq)}/Zn_{(s)}$  electrode system is replaced by the  $Ag^{+}_{(aq)}/Ag_{(s)}$  electrode system, what would be the emf of the cell be?
- 5. a. Use the data to explain why copper (I) ions disproportionate in aqueous solution but silver(I) ions do not

$E^{0}(V)$
+ 1.98
+0.80
+0.34
+0.52

[Ans. The cell diagram corresponding to disproportionation reaction is  $Cu^+_{(aq)}/Cu^+_{(aq)}/Cu^+_{(aq)}/Cu_{(s)} E0cell = E^0_R - E^0_L = +0.18$ , since Emf is positive, the reaction is spontaneous]

b. In this light of information in (a) suggest what you might observe when copper (I) oxide excess dilute sulphuric acid. Write an equation for the reaction?

[Ans. Blue solution of CuSO<sub>4</sub>, Cu<sub>2</sub>O<sub>(s)</sub> + H<sub>2</sub>SO<sub>4(aq)</sub>  $\rightarrow$  CuSO<sub>4(aq)</sub> + Cu<sub>(aq)</sub> + H<sub>2</sub>O<sub>(l)</sub>]

- 6. (a). Distinguish between galvanic from electrolytic cell?
  - (b). Why is it necessary to use a salt bridge in a galvanic cell?
  - (c). Explain the functions of moisture in the rusting process?
  - (d). Explain methods of rust prevention?
  - (e). Difference between passivation and cathodic protection as used in corrosion prevention
- 7. Sketch apparatus used to measure the standard electrode potential of  $Fe/Fe^{3+}$ . The electrochemical cell is made up of iron as anode  $(Fe_2(SO_4)_{3(1M)})$  and copper as cathode  $(CuSO_{4(1M)})$ .
  - i. Name the instrument that could be used to measure the emf of the cell?
  - ii. State the function of the salt bridge?
  - iii. What is the molarity of Fe<sup>3+</sup> ions in iron(III)sulphate solutions?
  - iv. Give the conventional representation of the cell?
  - v. Write equations to represent the cell reactions?
  - *vi.* If the emf of the cell is +0.38V, find the standard electrode potential of  $Fe^{3+}/Fe$  electrode given that the standard electrode potential of Cu<sup>2+</sup>/Cu electrode is 0.34V? [*Ans. 0.04V*]

8. Using the following half-reactions

Au<sup>3+</sup> + 3e  $\rightarrow$  Au NO<sub>3</sub><sup>-</sup> +4H<sup>+</sup>+3e $\rightarrow$  NO + 2H<sub>2</sub>O Predict whether 1M HNO<sub>3</sub> will dissolve gold metal to form 1M Au<sup>3+</sup> solution? [Reverse equation Au<sup>3+</sup> + 3e  $\rightarrow$  Au  $E^0$ =+1.50V  $Au \rightarrow Au^{3+} + 3e$   $E^0$ =-1.50V  $NO_3^- +4H^++3e \rightarrow NO + 2H_2O$   $E^0$ =+0.96V Overall equation Au + NO<sub>3</sub><sup>-</sup> +4H<sup>+</sup>  $\rightarrow$  NO + 2H<sub>2</sub>O + Au<sup>3+</sup>  $E^0$ =-0.54V Therefore, the reaction will not occur] 9. Calculate the emf of the following cell

 $\begin{array}{ll} Pb_{(s)} / Pb^{2+}{}_{(aq) (1X10}{}^{-3}{}_{M)} / / Cu^{2+}{}_{(aq)(1x10}{}^{-2}{}_{M)} / Cu_{(s)}. \ \ Given the following standard reduction potentials. Pb^{2+}{}_{(aq)} / Pb_{(s)} & E^{0}(V) = -0.250V \\ Cu^{2+}{}_{(aq)} / Cu_{(s)} & E^{0}(V) = -0.277V \end{array}$ 

10. Calculate the equilibrium constant of the reaction between cobalt and nickel from the following redox potentials at  $25^{0}$ C

11. (a). i.With the aid of a well labelled diagram, describe how Daniel cell is used to supply electricity?

ii. Write the equation for the reactions taking place at the electrodes and the overall equations?

(b) Compare the efficiency of Zinc and tin as rust protective covering materials in iron, given the following standard reduction potentials at  $25^{\circ}C$ 

$$E^{0}(Zn^{2+}/Zn) = -0.76V E^{0}(Fe^{2+}/Fe) = -0.44V E^{0}(Sn^{2+}/Sn) = -0.14V$$

- 12. For the electrochemical cell  $Zn/ZnSO_4//$  CuSO<sub>4</sub>// CuSO<sub>4</sub>// Cu.
  - i. Sketch a labelled diagram of such a cell to show the essential features?
  - ii. Write an expression for the emf of the cell in above operating under standard conditions?
  - iii. Calculate the emf of the cell, if [Cu2+] =1M and [Zn2+] =0.01M at standard conditions?
  - iv. Calculate the equilibrium constant for the electrochemical cell above?
  - v.
- 13. Given the following reduction potentials

Reduction half reactions	<b>Standard Electrode potential (V)</b>
$Cl_2 + 2e \rightarrow 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$	+1.33
$Ni^{2+} + 2e \rightarrow Ni$	-0.23
$Cr^{3+} + e \rightarrow Cr^{2+}$	-0.50
$Cr^{3+} + 3e \rightarrow Cr$	-0.73
$Br_2 + 2e \rightarrow 2Br$ -	+1.09
$2S_2O_3^{2-} + 2e \twoheadrightarrow S_4O_6^{2-}$	+0.17

- i. Determine the standard emf of the following cells Ni/Ni2+(1M) // 2Br(1M)/Br2, Pt  $Cr^{3+}_{(1M)}+Cl_2 \rightleftharpoons Cr_2O_7^{2-}+2Cl^{-}$
- ii. Sketch the galvanic cell based on the reactions above and show the directions of the electron flow?
- iii. Given the following equation for a cell reaction  $S_4O_6^{2-} + Cr^{2+} \rightarrow Cr^{3+} + S_2O_3^{2-}$ Calculate the standard potentials for the cell and equilibrium constant, Kc? [Ans. i. E=1.32V ii. E=0.03V iii. E<sup>0</sup>=+0.67V and Kc=5.151x10<sup>22</sup>]
- 14. Provided with a list of standard redox potentials below

 $\begin{array}{ll} Zn^{2+}{}_{(aq)}+2e\rightleftharpoons Zn_{(s).} & E^0\ Zn^{2+}/\ Zn=-0.76V\\ Fe^{2+}{}_{(aq)}+2e\rightleftharpoons Fe_{(s).} & E^0\ Fe^{2+}/\ Fe=-0.44V\\ Sn^{2+}{}_{(aq)}+2e\rightleftharpoons Sn_{(s).} & E^0\ Sn^{2+}/\ Sn=-0.14V\\ Cu^{2+}{}_{(aq)}+2e\rightleftharpoons Cu_{(s).} & E^0\ Cu^{2+}/\ Cu=+0.34V \end{array}$ 

- i. What will happen when a copper knife is dipped into an aqueous solution of FeSO<sub>4</sub>? Give reasons for your answer
- ii. Write down the symbols of the cell which can be constructed with a maximum emf from the list of redox potentials given above?
- iii. Write the cell reaction equation of the cell above?
- iv. Find the value of the equilibrium constant at  $25^{\circ}$ C for the cell constructed above when the cell reaction is at equilibrium. Is the cell reaction feasible? Explain [Ans i. nothing is observed since  $E^{\circ}$   $Fe^{2+}$ / Fe = -0.44V and  $E^{\circ}$   $Cu^{2+}$ / Cu =+0.34V, THUS Fe is more reactive than Cu as suggested by the electrode potential values ii. Maximum emf is obtained with electrode with large difference in potential ie.  $Zn^{2+}_{(aq)}$  and  $Sn^{2+}_{(aq)}$  iii.  $Zn/Zn^{2+}//Sn^{2+}/Sn$  $Zn+Sn^{2+} \rightarrow Zn^{2+}+Sn$ ]
- 15. Why do we apply paint on iron?

Paints cover the surface of the iron hence moist air cannot come directly in contact with iron. As a result, it cannot be attack iron and preventing rusting

16. Why the colour of copper solution changes when iron is dipped in it?

Iron is more reactive than copper, it displaces copper from copper sulphate and form iron sulphate. The blue colour of copper sulphate changes to green colour of iron sulphate

$$CuSO4 + Fe \rightarrow FeSO4 + Cu$$

Blue colour Green

17. Given the following reactions

 $Zn^{2+}{}_{(aq)} + 2e \rightleftharpoons Zn_{(s)}$ . E  $Zn^{2+}/Zn = -0.76V$ Ni $^{2+}{}_{(aq)} + 2e \rightleftharpoons Ni_{(s)}$ . E Ni $^{2+}/Ni = -0.25V$ 

- i. Which are the feasible reactions, reduction of  $Ni^{2+}by$  zinc or the reduction of  $Zn^{2+}_{by}$  nickel? Give reasons
- ii. Write a balanced redox equation for the feasible reaction?
- iii. Determine the cell diagram?
- iv. Calculate the emf of the cell?

[i. Reduction of nickel (II) by zinc is the feasible reaction since Zn is more reactive as suggested by the electrode potential values, hence Zn can supply electrons to reduce nickel ii.  $Zn(s) + Ni^+_{(aq)} \approx Zn^{2+}_{(aq)} + Ni_{(s)}$  iii.  $Zn(s) / Zn^{2+}_{(aq)} / Ni^+_{(aq)} / Ni_{(s)}$ ]

- 18. The emf of the cell M/M<sup>n+</sup>(0.02M)// H<sup>+</sup>(1M)/H<sub>2(g)</sub>(1atm) Pt at 25°C is 0.81V. Calculate the valence of metal if  $E^0$  M/M<sup>n+</sup> = 0.76V [Ans. 2]
- 19. The emf of a cell Ag/AgI, 0.05M KI // 0.05M AgNO<sub>3</sub>/Ag is 0.788V. Calculate the solubility product of AgI? [Ans.1.10x10<sup>-16</sup>]
- 20. Given the following standard electrode potnetials  $K^+/K = -2.93V Ag^+/Ag = 0.80V Hg^+/Hg = 0.79V Mg^{2+}/Mg = -2.73V and Cr^{2+}/Cr = -0.74V$ . Arrange these metals in their increasing order of reducing power [Ans. Ag<Hg<Cr< Mg< K]
- 21. Two metals A and B have E<sup>0</sup> =+0.76V and -0.80V respectively. Which will liberate H<sub>2</sub> from H<sub>2</sub>SO<sub>4</sub>? [Ans. B will liberate H<sub>2</sub> from H<sub>2</sub>SO<sub>4</sub>]
- 22. Calculate the standard cell potentials of galvanic cell in which the following reactions take place. Given  $E^{0}_{op}$  Cr, Cd, Fe<sup>2+</sup>, Ag are 0.74V, 0.40V, -0.77Vand -0.80V respectively.

a. 
$$2Cr_{(s)} + 3Cd^{2+}_{(aq)} \rightarrow 2Cr^{3+} + 3Cd$$

b.  $Fe^{2+}(aq) + Ag^{+}(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$ 

Calculate the  $\Delta_r G^0$  and equilibrium constant of the reactions [Ans. 3.17x10<sup>34</sup> and 3.22]

23.  $E^0$  of some oxidants are given as:

$I_2 + 2e \rightarrow 2I^-$	$E^0 = +0.54V$		
$MnO_{4} + 8H + +5e \rightarrow Mn^{2+} + 4H_2O$	$E^0 = +1.52V$		
$Fe^{3+} + e \rightarrow Fe^{2+}$	$E^0 = +0.77V$		
$\mathrm{Sn}^{4+} + e \rightarrow \mathrm{Sn}^{2+}$	$E^0 = +0.10V$		
i. Select the strongest reductant and	l oxidant in these		
[Ang Strongest reductont - Sn <sup>2+</sup> weakest eviden			

ii. Select the weakest reductant and oxidant in these

#### [Ans. Strongest oxidant = MnO4<sup>-</sup> weakest oxidant = Mn<sup>2+</sup>]

- iii. Select the spontaneous reaction from the changes given below
  - a.  $Sn^{4+} + 2Fe^{2+} \rightarrow Sn^{2+} + 2Fe^{3+}$  [Ans. non-spontaneous]
  - b.  $2Fe^{2+} + I_2 \rightarrow 2Fe^{3+} + 2I^{-}$  [Ans. non-spontaneous]
  - c.  $Sn^{4+} + 2I^- \rightarrow Sn^{2+} + I_2$  [Ans. non-spontaneous]
  - d.  $Sn^{2+} + I_2 \rightarrow Sn^{4+} + 2I^{-}$  [Ans. Spontaneous]

## **II: ELECTROLYTIC CONDUCTIVITY**

- 1. A 0.0015M sodium hydroxide solution has a conductivity of 155  $\Omega^{-1}$ m<sup>-1</sup>. Calculate its molar conductivity? [Ans. 103.33  $\Omega^{-1}m^2mol^{-1}$ ]
- 2. How many grams of sodium acetate must be dissolved in  $1 \text{dm}^3$  of water to make a solution of molar conductivity 97.5  $\Omega^{-1}\text{m}^2\text{mol}^{-1}$  and conductivity of 130  $\Omega^{-1}\text{m}^{-1}$ ? [Ans.0.109g]
- 3. The specific conductance of a 0.02M solution of KCl at 25°C is  $0.002765\Omega^{-1}$ cm<sup>-1</sup>. If the resistance of the cell containing this solution is 400°Ω, what is the cell constant? [*Ans.1.106cm*<sup>-1</sup>]

- The resistance of a conductivity cell containing 0.001M KCl solution at 298K is 1500<sup>Ω</sup>. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is 0.146x10<sup>-3</sup>Scm<sup>-1</sup>? [Ans.219x10<sup>-3</sup> cm<sup>-1</sup>]
- 5. The resistance of a 0.01M solution of an electrolyte is  $210^{\circ}\Omega$  at  $25^{\circ}C$ . Calculate the molar conductivity of the solution at the same temperature. The cell constant is  $0.88 \text{cm}^{-1}$ ? [Ans.419.04' $\Omega$ <sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>]
- 6. The resistance of 0.5M solution of an electrolyte in a cell was found to be  $45^{\circ}\Omega$ .Calculate the molar conductance of the solution if the electrodes of the cell are 2.2cm apart and have an area of  $3.8 \text{cm}^2$ ? [Ans.25.73 $\Omega^{-1}$ cm<sup>2</sup>mol<sup>-1</sup>]
- 7. 0.5N solution of a salt placed between two platinum electrodes, 20cm apart and the area  $4\text{cm}^2$  has a resistance of 25 $\Omega$ . Calculate the equivalent conductance of the solution? [Ans.400 $\Omega^{-1}$ cm<sup>2</sup>eq<sup>-1</sup>]
- 8. The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 1.80cm apart and 5.4cm<sup>2</sup> in area was found to be 32  $\Omega$ . Calculate equivalent conductance of the solution? [Ans.104.16 $\Omega^{-1}$ cm<sup>2</sup>eq<sup>-1</sup>]
- 9. The resistance of 0.1N solution is 2500  $\Omega$ . Calculate the equivalent conductance of the solution? Given the cell constant is  $1.15 \text{cm}^{-1}$  [Ans.4.6 $\Omega^{-1}$ cm<sup>2</sup>eq<sup>-1</sup>]
- 10. A conductivity cell is filled with 0.05M KCl. Its specific conductance and observed resistance is 0.00667 Ω-1cm-1 and 243 Ω respectively. When the cell is filled with 0.01M NaOH, observed resistance is 681 Ω. Calculate specific and molar conductivity of 0.01M NaOH? [Ans. 0.00238 Ώ<sup>-1</sup>cm<sup>-1</sup>, 238 Ώ<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>]
- 11. The specific conductance of water is 0.076 Sm<sup>-1</sup> and the specific conductance of 0.1M aqueous solution of KCl is 1.1639Sm<sup>-1</sup>. A cell has a resistance of  $33.20 \,\Omega$  when filled with 0.1M KCl solution and the 300  $\Omega$  when filled with 0.1M CH<sub>3</sub>COOH solution. Calculate the molar conductance of acetic acid? *[Ans. 0.528Scm<sup>2</sup>mol<sup>-1</sup>]*
- 12. (a). Mention atleast two applications of Kohlrausch's law (b). The conductivity of 0.001M CH<sub>3</sub>COOH is 4.95x10-5Scm-1. Calculate its dissociation constant given that  $\Lambda_{\infty}$  (CH<sub>3</sub>COOH) =390.5 Scm<sup>2</sup>mol<sup>-1</sup> [Ans. 1.84x10<sup>-5</sup>M]
- 13. Calculate the molar conductivity at infinite dilution of acetic acid from the following data;  $\lambda_{\infty(HCl)}=426 \ \Omega^{-1} \text{cm}^2 \text{mol}^{-1}, \lambda_{\infty(CH3COONa)}=91 \ \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \text{ and } \lambda_{\infty(NaOH)}=126 \ \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ [Ans. 391  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ]
- 14. (a). State Kohlrausch's law
  (b). Molar conductivity at infinite dilution for NH4Cl, NaOH and NaCl at 298K are 129.8, 218.4 and 108.95 Scm<sup>2</sup>mol<sup>-1</sup> respectively and molar conductivity of 0.01M NH<sub>4</sub>OH is 9.33 Scm<sup>2</sup>mol<sup>-1</sup>. Calculate the degree of dissociation of NH<sub>4</sub>OH at 298K? [*Ans.0.039*]
- 15. After making allowance for conductivity of water, the conductivity solution of silver chloride at 25°C is  $1.5 \times 10^{-4} \,\Omega^{-1} \text{m}^{-1}$ . If the molar conductivity at infinite dilution of Ag<sup>+</sup> is  $6.2 \times 10^{-3} \,\Omega^{-1} \text{m}^2 \text{mol}^{-1}$  and that of Cl<sup>-</sup> is  $7.6 \times 10^{-3} \,\Omega^{-1} \text{m}^2 \text{mol}^{-1}$ . Calculate the molar solubility of silver chloride? [Ans. 1.087x10<sup>-5</sup>M]
- 16. The resistivity of 0.02M KCl solution is 316 $\Omega$ cm and conductivity of the cell containing such a solution had a resistance of 550 $\Omega$ 
  - i. What is the cell constant?

ii. The same cell filled with  $0.1M ZnSO_4$  solution had a resistance of 72  $\Omega$ . What is the conductivity of  $0.1M ZnSO_4$  solution?

#### [Ans i. 1.5235cm<sup>-1</sup>, ii. 0.02116 Ω<sup>-1</sup> cm<sup>-1</sup>]

- 17. In a particular cell, 0.01M solution of KCl gave resistance of 15  $\Omega$  while 0.01M solution of HCl gave a resistance of 51.4  $\Omega$  at the same temperature. If the specific conductance of 0.01M KCl is 0.1409Scm<sup>-1</sup>, calculate
  - i. Cell constant
  - ii. Specific conductance of HCl solution
  - iii. Equivalent conductivity of HCl solution

## [Ans. 2.1135 m<sup>-1</sup>, 0.04112Sm<sup>-1</sup> and 0.004112 Sm<sup>2</sup>eq<sup>-1</sup> or 41.12Scm<sup>2</sup>eq<sup>-1</sup>]

- 18. A solution of 0.1M HCOOH has conductivity of 0.166  $\Omega^{-1}$ m<sup>-1</sup> at 25<sup>0</sup>C. The molar conductivity at infinite dilution is 4.04x10<sup>-2</sup>  $\Omega$ m2mol-1, calculate
  - i. The degree of dissociation
  - ii. The dissociation constant of HCOOH [Ans.0.041, 1.681x10<sup>-4</sup>M]
- 19. A solution of dichloroethanoic acid of concentration  $1.25 \times 10^{-4}$ M has conductivity at infinite dilution of  $3.85 \times 10^{-2} \Omega^{-1} m^2 mol^{-1}$ . Given the conductivity of dichloroethanoic acid is  $2.5 \times 10^{-3} \Omega^{-1} m^{-1}$ . Calculate the degree of dissociation and hence dissociation constant? *[Ans. 0.5195, 7.02x10<sup>-5</sup>M]*
- 20. The resistance of a 0.02N solution of an electrolyte MgCl<sub>2</sub> was found to be 210Ω at 298K using a conductivity cell with a cell constant of 0.88cm<sup>-1</sup>. Calculate conductivity, equivalent conductivity and molar conductivity? [Ans. 4.1905x10-3 Ώ<sup>-1</sup>cm<sup>-1</sup>, 209.52 Ώ<sup>-1</sup>cm<sup>2</sup>eq<sup>-1</sup> and 419.04 Ώ<sup>-1</sup>cm<sup>2</sup>mol<sup>-1</sup>]

#### **III: ELECTROLYSIS**

1. List two importance of the second law of electrolysis?

## Ans. Determination of chemical equivalent of elements

- **2.** Explain the electrolysis of dilute sulphuric acid using platinum electrodes? Show the equations of discharge process at the anode and cathode.
- **3.** A current of 0.5A were made to flow through silver voltameter for 30minutes. Calculate the mass of silver deposited and its equivalent weight?
- **4.** 298500C were required to deposit one mole of metallic element Q from its aqueous salt solution. Calculate the valence of Q?
- **5.** Calculate the number of electrons of Aluminum used to deposit 1mole of Al during electrolysis when Aluminum oxide used as electrolyte and 3 Faradays were needed to deposit one mole of Aluminum?
- 6. A steady current of 2A passed through a solution containing ions of divalent metal for nine minutes. The mass of the metal M liberated was 0.3552g. Calculate relative atomic mass of the metal? [Ans. 64g]
- 7. a. How much electricity is required in coulomb for the oxidation of the following
  - i. 1 mole of  $H_2O$  to  $O_2$  [Ans. 2F]
  - ii. 1 mole FeO to Fe2O3 [Ans. 1F]

**b.** Calculate the number of electrons lost or gained during electrolysis of

i. 2g Br<sup>-</sup> ions [Ans. 1.51x10<sup>22</sup> electrons lost]

ii. 1g Cu2+ ions [Ans. 1.89x10<sup>22</sup> electrons gained]

- **8.** A 4.0 molar aqueous solution of NaCl is prepared and 500mL of this solution is electrolyzed. This leads to the evolution of chlorine gas at one of the electrodes. Calculate
  - i. The total number of moles of chlorine gas evolved? [Ans. 1mole]
  - ii. If the cathode is Hg electrode, the maximum mass of amalgam formed from this solution? [Ans. 446g]
  - iii. Total charge required to complete electrolysis? [Ans. 193000C]
- **9.** (a). What is an electrolytic cell?
  - (b). List at least three differences between electrolytic cells and electrochemical cells?
  - (C). Calculate the quantity of electricity (Coulombs) necessary to deposit 100g of copper from a CuSO<sub>4</sub> solution? [Ans.  $3.0367 \times 10^5$ C]
- 10. In an electrolytic cell, a current of 0.25A is passed through a solution of chloride of iron, producing  $Fe_{(s)}$  and  $Cl_{2(g)}$ 
  - i. Write the equations for the reaction that occurs at the electrode?
  - ii. When the cell operates for 2.0hours, 0.521g of iron is deposited at one electrode. Determine the formula of the chloride of iron in the original solution?
  - iii. Write the balanced equation for the overall reaction at that occurs in the cell?
  - iv. How many liters of  $Cl_{2(g)}$  measured at 25<sup>o</sup>C and 750 mmHg are produced when the cell operates as described in part (b) above?
  - v. Calculate the current that would produce  $Cl_{2(g)}$  gas at a rate of 3.0g/hour? [Ans. (i).  $2Cl_{(aq)} \rightarrow Cl_{2(g)} + 2e$  (ii).  $FeCl_2$  (iii).  $Fe^{2+}_{(aq)} + 2Cl_{(aq)} \rightarrow Fe_{(s)} + Cl_{2(g)}$ (iv). 0.231L (v). 2.27A]
- 11. How many hours are required for a current of 3.0A to decompose 18g water? [Ans.17.87hours]
- 12. Three electrolytic cells A, B and C containing solution of ZnSO4, AgNO3 and CuSO4 respectively are connected in series. A steady current of 1.5 A was passed through them until 1.45g of silver deposited at the cathode of the cell B. How long did the current flow? What mass of copper and of zinc were deposited? [Ans. t=14.4min, mzn=0.437g and mcu=0.427g]
- 13. Calculate the volume of gases liberated at the anode and cathode at NTP from the electrolysis of  $Na_2SO_{4(aq)}$  solution by a current of 2A passed for 10minutes? [Ans.  $VO_2=0.0696$  liters and  $VH_2=0.139$  liters]
- 14. A current of 3.7A is passed for 6 hours between Ni electrodes in 0.5liters of 2M solution of Ni(NO<sub>3</sub>)<sub>2</sub>. What will be the molarity of the solution at the end of electrolysis? [Ans. reaction at the electrodes Anode Ni → Ni<sup>2+</sup>+2e and cathode Ni<sup>2+</sup>+2e →Ni, [Ni<sup>2+</sup>] formed is equal to [Ni<sup>2+</sup>] lost Thus there will be no change in concentration of Ni(NO<sub>3</sub>)<sub>2</sub> solution after electrolysis (it will remain 2M)]
- **15.** A 100watt, 110volt incandescent lamp is connected in series with an electrolytic cell containing CdSO<sub>4</sub> solution. What weight of Cd will be deposited by a current flowing for 10hour? Cd=112.4 [**Ans. 19.06g**]

- **16.** Calculate the volume of Cl<sub>2</sub> at 27<sup>o</sup>C and 2 atm produced during electrolysis of MgCl<sub>2</sub> which produce 6.50g Mg? Given Mg=24.3 [Ans. 3.29liters]
- 17. A metal is known to form fluoride MF<sub>2</sub>. When 10A electricity is passed through a molten salt for 330 sec, 1.95g metal is deposited Find out the atomic weight of metal. What will be the quantity of charge required to deposit the same mass of Cu from CuSO4(aq)? Given Cu=63.6 [Ans. Q=5917.45C]
- 18. Calculate the number of Kw-h of electricity is necessary to produce 1.0 metric ton (1000Kg) of aluminum by the Hall process in cell operating at 15.0V? [Ans. 4.47x104 Kw-h]
- 19. How long a current of 3A has to be passed through a solution of AgNO<sub>3</sub> to coat a metal surface of 80cm<sup>2</sup> with a thickness of 0.005mm. Density of silver is 10.5 g/cm<sup>3</sup> [Ans. 125.09sec]
- 20. Same quantity of charge is being used to liberate iodine (at anode) and a metal M (at the cathode). The mass of metal M liberated is 0.617g and the liberated iodine is completely reduced by 46.3 mL of 0.124 M sodium-thiosulphate. Calculate equivalent weight of metal. Also calculate the total time to bring this charge if 10A current passed through solution of metal iodide? [Ans. 107.47, 55.4 second]

#### **C: GENERAL CHEMISTRY**

#### I: Lewis structures

- 1. Determine the Lewis structures of  $SiH_4$ ,  $NO^+$ , and  $OF_2$ ,  $CHO_2^-$
- 2. Both carbon monoxide, CO, and carbon dioxide, CO<sub>2</sub>, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO<sub>2</sub> has been implicated in global climate change. What are the Lewis structures of these two molecules?
- 3. What is Octet rule? Discuss three exceptions to the octet rule with examples.

#### II: intermolecular forces

- 1. The attractive energy between two ions is proportional to 1/r, whereas the attractive energy between two dipoles is proportional to  $1/r^6$ . Explain
- 2. Arrange ethyl methyl ether ( $CH_3OCH_2CH_3$ ), 2-methylpropane [( $CH_3$ )<sub>2</sub>CHCH<sub>3</sub>], and acetone ( $CH_3COCH_3$ ) in order of increasing boiling points
- 3. Considering:
  - CH<sub>3</sub>OH, C<sub>2</sub>H<sub>6</sub>, Xe, & (CH<sub>3</sub>)<sub>3</sub> N,
  - CH<sub>3</sub>CO<sub>2</sub>H, (CH<sub>3</sub>)<sub>3</sub>N, NH<sub>3</sub>, & CH<sub>3</sub>F

Which can form hydrogen bonds with themselves? Draw the hydrogen-bonded structures

- 4. Neon and HF have approximately the same molecular masses.
- a) Explain why the boiling points of Neon and HF differ.
- b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass

#### **III:** Overlapping and hybridization of atomic orbitals

- 1. What's the relationship btn hybridization and geometrical shapes of molecules?
- 2. Identify the type of hybridization of the following cpds:

i.	$H_2O$	ii.	PCl <sub>5</sub>	iii.	BeCl <sub>2</sub>
iv.	NH <sub>3</sub>	v.	BF <sub>3</sub>	vi.	$SF_4$

- 3. Distinguish sigma bond from pi bond (6 pnts)
- 4. With the help of structures illustrate 3 ways of sigma bond formation and 1 way of pi bond formation
- 5. Explain the degree of saturation of aliphatic hydrocarbons interms of sigma and pi bonds in their structures

#### **D: STATES OF MATTER: LIQUIDS**

#### I: Colligative properties

#### These details might be useful:

Solvent	Boiling Point (°C at 1 atm)	$\frac{K_{\rm b}}{(Cm^{-1})}$	Freezing Point (°C at 1 atm)	$\frac{K_{f}}{(Cm^{-1})}$
water	100.0	0.512	0.0	1.86
hydrogen acetate	118.1	3.07	16.6	3.9
benzene	80.1	2.53	5.5	5.12
chloroform	61.26	3.63	-63.5	4.68
nitrobenzene	210.9	5.24	5.67	8.1

- 1. The triple point of air-free water is defined as 273.15 K. Why is it important that the water be free of air?
- 2. Meat can be classified as fresh (not frozen) even though it is stored at −1 °C. Why wouldn't meat freeze at this temperature?
- 3. An organic compound has a composition of 93.46% C and 6.54% H by mass. A solu- tion of 0.090 g of this compound in 1.10 g of camphor melts at 158.4 °C. The melting point of pure camphor is 178.4 °C. K for camphor is 37.7 °C/m. What is the molecu- lar formula of the solute? Show your calculations.
- 4. A sample of HgCl weighing 9.41 g is dissolved in 32.75 g of ethanol, C H OH (K = 1.20 °C/m). The boiling point elevation of the solution is 1.27 °C. Is HgCl an elec- trolyte in ethanol? Show your calculations.
- 5. A salt is known to be an alkali metal fluoride. A quick approximate determination of freezing point indicates that 4 g of the salt dissolved in 100 g of water produces a solution that freezes at about -1.4 °C. What is the formula of the salt? Show your calculations.
- 6. A sample of an organic compound (a nonelectrolyte) weighing 1.35 g lowered the freezing point of 10.0 g of benzene by 3.66 °C. Calculate the molar mass of the compound.
- 7. A 1.0 m solution of HCl in benzene has a freezing point of 0.4 °C. Is HCl an elec- trolyte in benzene? Explain.

- 8. A solution contains 5.00 g of urea, CO(NH2)2, a nonvolatile compound, dissolved in 0.100 kg of water. If the vapor pressure of pure water at 25 °C is 23.7 torr, what is the vapor pressure of the solution?
- 9. A 12.0-g sample of a nonelectrolyte is dissolved in 80.0 g of water. The solution freezes at -1.94 °C. Calculate the molar mass of the substance.
- 10. Arrange the following solutions in order by their decreasing freezing points: 0.1 m Na3PO4 , 0.1 m C2H5OH, 0.01 m CO2 , 0.15 m NaCl, and 0.2 m CaCl2
- 11. Explain these observations: Red blood cell membranes are water permeable and will
  - a) Swell and possibly rupture in a hypotonic solution;
  - b) maintain normal volume and shape in an isotonic solution; and
  - c) shrivel and possibly die in a hypertonic solution

#### II: Raoult's Law

1. Benzene and toluenen form nearly ideal solutions. At 300K pure pressure of toluene is 30mmHg and that of benzene is 100mmHg. A liquid mixture is composed of 3 mol of toluene and 2 mol of benzene.

(a) If the pressure over the mixture at 300K is reduced. At what pressure does the first vapor form ?

(b) What is the composition of the first trace of vapor formed ?

- (c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear ?
- (d) What is the composition of the last trace of liquid ?

#### **III:** Partition

- 1. Answer briefly:
  - **a**) State the distribution law
  - a) Mention the factors that control the distribution law and explain how each factor exerts its effect
  - **b**) How does the distribution law relate to solubility?
  - c) Explain the significance of the term distribution coefficient
  - **d**) Why are multiple extractions advantageous over a single extraction using the same volume of solvent

2.(a) (i) How is distribution law modified when the solute undergoes dissociation in one of the solvents

(ii) What would happen if the solute is completely dissociated in one of the solvents

(b) An organic acid is distributed between 500 ml each of the solvent A and water. In water it is dissociated. The amount of the acid in the aqueous layer was 6g and in solvent A it was 0.72g. if the dissociation coefficient of the acid between the solvent A and water is 0.16, calculate the degree of dissociation assuming the acid has normal molecular weight in A

Useful links:

- ✓ <u>https://opentextbc.ca/chemistry</u>
- ✓ https://chem.libretexts.org/Courses/Howard\_University

#### NOTE:

All students should come with hardcopy of this holiday package on the opening date.