ELECTROCHEMISTRY

PROBLEM 489 (a) When a current of 150 mA is used for 8.0 hr, what volume of fluorine gas at N.T.P. can be produced from a molten mixture of potassium and hydrogen fluoride?

(b) If the same current is passed for same interval of time, how many litre of oxygen gas could be produced from electrolysis of water?

PROBLEM 490 An aqueous solution of Na_2SO_4 was electrolysed for 30 min; 25 mL of O_2 was produced at the anode over water at 22°C at a total pressure of 722 torr. Determine the strength of current that was used to produce the oxygen gas. Vapour pressure of water at 22°C is 19.83 torr.

PROBLEM 491 A piece of copper metal is to be electroplated on all side with silver to a thickness of 1 micrometre. If the metal strip measures 50 mm × 10 mm × 1 mm, how long must the solution, which consists the $Ag(CN)_2^-$ ion, be electrolysed, using a current of 100 mA? The density of silver metal is 10.5 g/cc.

PROBLEM 492 19 g of fused $SnCl_2$ was electrolysed using inert electrode when 0.119 g of Sn was deposited at cathode. If nothing was given out during electrolysis, calculate the ratio of weight of $SnCl_2$ and $SnCl_4$ in fused state after electrolysis.

PROBLEM 493 Electrolysis of molten KBr generates bromine gas, which can be used in industrial bromination process. How long will it take to convert a 500 kg batch of phenol to monobromo phenol using a current of 20 kA?

PROBLEM 494 The cell $\text{Pt} \mid H_2(1\text{ bar}), H^+ \parallel \text{KCl}\,(1.0\text{ M } \textit{saturated}) \mid Hg_2Cl_2 \mid Hg$ was used to measure the pH of a solution of 0.01 M acetic acid in 0.0358 M sodium acetate. Calculate the cell potential expected at 25° C [$K_a = 1.81 \times 10^{-5}$ for acetic acid; $E° (Hg_2Cl_2/Hg, Cl^-) = 0.28$ V]

PROBLEM 495 The voltage required to electrolyse certain solutions changes as the electrolysis proceeds because the concentration in the solution is changing. In an experiment, 500 mL of a 0.1 M solution of copper (II) bromide was electrolysed until 2.827 g of Cu was deposited. Calculated the theoretical minimum voltage required to sustain the electrolysis reaction at the beginning and at the end of experiment. $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{Br_2/Br^-} = 1.07$ V.

PROBLEM 496 Calculate the concentration of I_3^- in a standard solution of iodine in 0.5 M KI, making use of the following standard electrode potentials: $E^\circ (I_2/I^- = 0.5355 \text{ V})$ and $E^\circ (I_3^-/I^- = 0.5365 \text{ V})$.. The molarity of I_2 in the standard solution can be assumed to be 0.5 M.

PROBLEM 497 Write both electrode reaction and overall cell reaction for the cell

$$\text{Tl} \,|\, \text{TlCl}(s) \,||\, \text{CdCl}_2\,(0.01\text{ M}) \,|\, \text{Cd}$$

and calculate *EMF* of the cell if $E^\circ (\text{Tl}^+/\text{Tl} = -0.34 \text{ V})$, $E^\circ (\text{Cd}^{2+}/\text{Cd} = -0.40 \text{ V})$ and the solubility product of TlCl is 1.6×10^{-3}.

PROBLEM 498 The meal *M* forms a soluble nitrate and a very slightly soluble chloride. The cell

$$M \,|\, M^+ (0.1\text{ M}),\ \text{HNO}_3\,(0.2\text{ M}) \,||\, \text{H}_2\,(1\text{ bar}),\ \text{Pt}$$

Has a measured $EMF = -0.4$ V. When sufficient solid KCl is added to make the solution of the cell 0.2 M in K^+, the *EMF* changes to – 0.05 V. Calculate the solubility product of *M*Cl.

PROBLEM 499 The voltage of the following cell is 0.987 V

$$\text{Pt(H}_2, 1.0\text{ atm)} \,|\, \text{HOCN}(1.4 \times 10^{-3}\text{ M}) \,||\, \text{Ag}^+ (0.8\text{ M}) \,|\, \text{Ag}(s)$$

Calculate K_a of HOCN, $E^\circ\, \text{Ag}^+/\text{Ag} = 0.8$ V

PROBLEM 500 For the galvanic cell:

$$\text{Ag} \,|\, \text{AgCl}(s),\ \text{KCl}(0.2\text{ M}) \,||\, \text{KBr}(0.001\text{ M}),\ \text{AgBr}(s) \,|\, \text{Ag}$$

Calculate the e.m.f. generated and assign correct polarity to each electrode for a spontaneous process after taking account of the cell reaction at 25°C. Given K_{sp} of $\text{AgCl} = 2.8 \times 10^{-10}$ and of $\text{AgBr} = 3.3 \times 10^{-13}$.

PROBLEM 501 Zinc granules are added in excess to 750 mL of 1.5 M $\text{Ni(NO}_3)_2$ solution at 30°C untill the equilibrium is reached. If emf of the cell

$\text{Zn}(s) \,|\, \text{Zn}^{2+} (1\text{ M}) \,||\, \text{H}^+ (1\text{ M}) \,|\, \text{H}_2 (g)\, 1.0\text{ atm}, \,|\, \text{Pt}$ is 0.76 V and that of cell

$\text{Ni} \,|\, \text{Ni}^{2+} (1\text{ M}) \,||\, \text{H}^+ (\text{pH} = 0) \,|\, \text{H}_2 (g, 1\text{ atm}) \,|\, \text{Pt}$ is 0.24 V, then calculate $[\text{Ni}^{2+}]$ at equilibrium. Also find the amount of zinc consumed.

PROBLEM 502 An electrochemical cell consist of a silver electrode in contact with 346 mL of 0.10 M AgNO_3 solution and a magnesium electrode in contact with 288 mL 0.1 M $\text{Mg(NO}_3)_2$ solution. (a) Calculate *E* for the cell at 25°C. (b) A current is drawn from the cell until 1.2 g of silver is deposited at the silver electrode. Calculate *E* for the cell at this stage of operation. $E^\circ(\text{Ag}^+/\text{Ag}) = 0.8$ V and $E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2.37$ V.

PROBLEM 503 An electrochemical cell is constructed by immersing a piece of copper wire in 25 mL of a 0.2 M $CuSO_4$ solution and a zinc strip in 25.0 mL of a 0.2 M $ZnSO_4$ solution. (a) Calculate the e.m.f. of the cell at 25°C and predict what would happen if a small amount of concentrated NH_3 solution were added to (i) the $CuSO_4$ solution and (ii) to $ZnSO_4$ solution? (b) In a separate experiment 25 mL of 3.0 M NH_3 are added to the $CuSO_4$ solution. If the e.m.f. of the cell is 0.68 V, calculate formation constant of $Cu(NH_3)_4^{2+}$. $E^\circ_{Cu^{2+}/Cu} = 0.34$ V, $E^\circ_{Zn^{2+}/Zn} = -0.76$ V

PROBLEM 504 The voltage of a certain cell at 25°C and 20°C are 0.3525 V and 0.3533 V respectively. If the number of electrons involved in the overall reactions are two, calculate ΔG°, ΔS° and ΔH° at 25°C.

PROBLEM 505 For the cell:

$$Pt \,|\, H_2(g) \,|\, \text{sol } X \,||\, KCl\,(sat) \,|\, Hg_2Cl_2(s) \,|\, Hg \,|\, Pt$$

the observed e.m.f. at 25°C was 612 mV. When solution *X* was replaced by a standard phosphate buffer whose assigned pH is 6.86, the e.m.f. was 741 mV. Find pH of the solution *X*.

PROBLEM 506 Use the following data to calculate solubility product of PbF_2. A galvanic cell consists of a hydrogen gas electrode ($p(H_2) = 1$ bar, $[H^+] = 1$ M) and a Pb electrode in a 1.0 M KF solution in equilibrium with $PbF_2(s)$. The cell potential is 0.348 V and $E^\circ_{(Pb^{2+}/Pb)} = -0.13$ V.

PROBLEM 507 A concentration cell has Zn electrodes. The electrolyte in each of the half-cells is a solution of $ZnCl_2$ dissolved in water. One has a freezing point of – 2.0°C and the other has a freezing point of – 0.9°C. What is the potential of the cell at 25°C?

PROBLEM 508 A lead storage battery is allowed to discharge until 23.92 g of PbO_2 have been reduced. Determine the mass of $PbSO_4$ formed and time required to recharge the battery to its original state using a current of strength 3.0 A.

PROBLEM 509 The chlorate ion ClO_3^- can disproportionate in basic solution according to the reaction

$$2ClO_3^-(aq) \rightleftharpoons ClO_2^-(aq) + ClO_4^-(aq)$$

What is the equilibrium concentration of the ions resulting from a solution initially at 0.1 M in chlorate ion? $E^\circ(ClO_4^-/ClO_3^-) = 0.36$ V and $E^\circ(ClO_3^-/ClO_2^-) = 0.33$ V.

PROBLEM 510 A platinum electrode is in contact with a solution containing Fe^{2+} and Fe^{3+} ions. The total concentration of iron ions is 0.033 M. What is the ratio of the concentrations if the potential difference between solution and metal surface is 35 mV and $E^\circ(Fe^{3+}/Fe^{2+}) = 0.77$ V?

PROBLEM 511 Calculate Gibb's free energy change and equilibrium constant for the reaction

$$Ni^{2+} + 2H_2O \longrightarrow Ni(OH)_2 + 2H^+$$

Given that $\quad NiO_2 + 4H^+ + 2e \longrightarrow Ni^{2+} + 2H_2O \quad E^\circ = 1.678$ V

and $\quad NiO_2 + 2H_2O + 2e \longrightarrow Ni(OH)_2 + 2OH^- \quad E^\circ = -0.49$ V

PROBLEM 512 The standard electromotive force of the cell:

$$Fe \,|\, Fe^{2+}(aq) \,||\, Cd^{2+} \,|\, Cd \text{ is } 0.0372 \text{ V}$$

The temperature coefficient of e.m.f. is -0.125 V K^{-1}. Calculate the quantities ΔG°, ΔH° and ΔS° at 25°C.

PROBLEM 513 The concentration of Ca^{2+} in sea water is determined using a Ca^{2+} selective electrode. A 10 mL sample of sea water is diluted to 100 mL and its 50 mL aliquot is placed in a beaker with Ca^{2+} ion selective electrode and a reference electrode. The e.m.f. was found to be – 0.053 V. A 1.0 mL aliquot of 0.05 M Ca^{2+} ion is added and emf was found to be – 0.0422 V. What is the concentration of Ca^{2+} in sea water? Ignore volume change due to addition of second aliquot.

PROBLEM 514 Use the van der Waals' equation of state to calculate the pressure at 35°C that would result if the chlorine produced from electrolysis of 10 kg molten NaCl is compressed into a tank with a volume of 75 L. Assume 96% efficiency of the electrolysis. $a = 6.5 \text{ atm L}^2 \text{ mol}^{-2}$, $b = 0.0562 \text{ L mol}^{-1}$.

PROBLEM 515 The pH of the solution in the cell

$Pt \mid H_2(g) \mid HCl(aq.) \parallel AgCl(s) \mid KCl(1M) \mid Ag$ is 0.65 and $E°(Ag^+ \mid Ag) = 0.8$ V. Calculate e.m.f. K_{sp} AgCl $= 1.6 \times 10^{-10}$.

PROBLEM 516 The e.m.f. of the following cell:

$Ag(s) \mid AgCl(saturated), KCl(M = 0.05) \mid KNO_3 \mid AgNO_3 \ (M = 0.1) \mid Ag(s)$ is 0.4312 V. Calculate solubility product of AgCl.

PROBLEM 517 The e.m.f. of cell: $H_2(g) \mid$ *Buffer* $\parallel$ *Normal calomal electrode* is 0.6885 V at 40°C when the barometric pressure is 725 mm of Hg. What is the pH of the solution. $E°_{\text{calomal}} = 0.28$.

PROBLEM 518 The cell :

$Ag(s) \mid AgCl(s), HCl(0.1\ N) \mid Glass \mid Buffer \parallel$ Saturated calomal electrode gave an e.m.f. of 0.112 V when the pH of the buffer used was 4.00. When a buffer of unknown pH was used, the potential was 0.3865 V. What is the pH of unknown buffer?

PROBLEM 519 One hundred mL of 0.01 N KCl are titrated with 0.1 N $AgNO_3$. Calculate potential of a silver electrode in the solution at equivalence point. The solubility product of AgCl is 1.56×10^{-10}? $[E°_{Ag^+/Ag} = 0.8 \text{ V}]$

PROBLEM 520 A 2.0 V battery is used in an electrolysis in which an e.m.f. of 1.45 V is developed. If the resistance of the entire circuit is 10 ohms, determine magnitude of current and quantity of heat produced by the current flow per faraday of electricity.

PROBLEM 521 A solution is made originally 0.1 M in Ag^+ ions and 0.25 M in KCN. If the dissociation constant of the complex $Ag(CN)_2^-$ is 3×10^{-19}, what will be the concentration of Ag^+ ions in this solution and what will be the deposition potential of Ag? $[E°(Ag^+/Ag) = 0.8 \text{ V}]$

PROBLEM 522 A solution is 0.1 M in Au^+ ions and 0.1 M in Ag^+ ions. The standard reduction potential of Au^+ is 1.68 V, while the dissociation constant of $Au(CN)_2^-$ is 5×10^{-39}. What concentration of NaCN will have to be maintained in the given solution in order to deposit Au and Ag simultaneously? $[E°_{Ag^+/Ag} = 0.8 \text{ V}]$.

PROBLEM 523 A Galvanic cell consist of Zn anode dipped into a 1.0 L 0.2 M $Zn(NO_3)_2$ solution and a silver cathode dipped into a 1.0 L 0.1 M $AgNO_3$ solution at 25°C and has e.m.f. $= 1.52$ V. Now, KCl(*s*) is added to the cathode chamber resulting in precipitation of AgCl and a change in e.m.f. After addition, e.m.f. was found to be 1.04 V and $[K^+] = 0.3$ M. Determine K_{sp} of AgCl.

PROBLEM 524 (a) Calculate $E°$ for:

$$Ag_2S + 2e \rightleftharpoons 2Ag(s) + S^{2-} \text{ if } K_{sp} \text{ of } Ag_2S = 6 \times 10^{-50} \text{ and } E°_{Ag^+/Ag} = 0.8 \text{ V}$$

(b) Consider an electrochemical cell having an indicator electrode Ag/Ag_2S coupled with a SCE ($E° = 0.244$ V) calculate $[S^{2-}]$ if the overall voltage of this cell is 0.766 V.

PROBLEM 525 An $I_2(s)/I^-$ (0.1 M) half cell is connected to a H^+/H_2(1.0 atm) half cell and e.m.f. found to be 0.755 V. If $E° I_2/I^-$ is 0.535 V, determine pH of H^+/H_2 half cell.

PROBLEM 526 To an aqueous solution of a weak acid (HA), 20 mL of a NaOH is added and connected to a reference electrode Ag/AgCl/Cl^- (0.1 M) electrode. E.m.f. of the cell was found to be 0.47 V. To the resulting solution, 30 mL of NaOH of the same strength was further added and new e.m.f. was found to be 0.5 V. Determine K_a of the weak acid. $E°$ (AgCl/Ag, Cl^-) = 0.23 V.

PROBLEM 527 A direct current of 1.25 A was passed through 200 mL of 0.25 M $Fe_2(SO_4)_3$ solution for a period of 1.1 hour. The resulting solution in cathode chamber was analyzed by titrating against acidic $KMnO_4$ solution. 25 mL permanganate solution was required to reach the end point. Determine molarity of $KMnO_4$ solution.

PROBLEM 528 A 80 mL sample solution of KI was electrolyzed for 3.0 minute, using a constant current. The I_2 produced required 0.25 M, 37.2 mL sodium thiosulphate solution and unreacted KI required 36.3 mL 0.02 M acidic solution of $KMnO_4$. Determine current strength and original molarity of KI solution.

PROBLEM 529 K_{sp} for AgBr $= 8 \times 10^{-13}$. What is the e.m.f. of the cell:

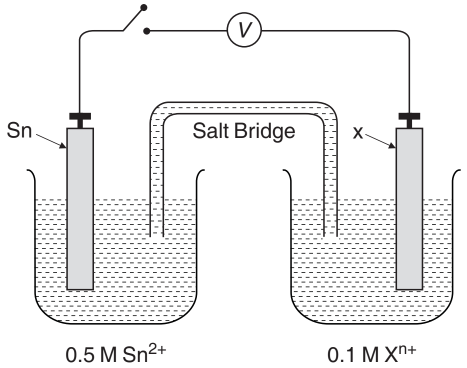
Ag, $AgNO_3$ (1.0 M) || KBr (1.0 M), AgBr, Ag

PROBLEM 530 E.m.f. of the cell:

Hg, Hg_2Cl_2, KCl(1.0 M) || $R_2NH_2^+Cl^-$ (0.1 M) | H_2, Pt is – 0.52 V

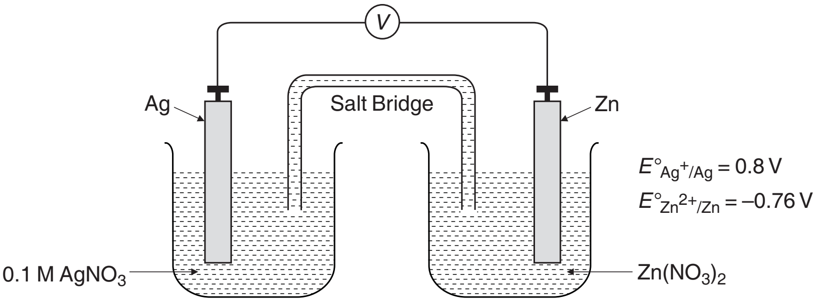
Calculate ionization constant of the base R_2NH · $E°(Hg_2Cl_2 \mid Cl^-) = 0.28$ V.

PROBLEM 531 An electrochemical cell is constructed with an open switch as shown below :



When the switch is closed, mass of tin-electrode increases. If $E°(Sn^{2+}/Sn) = -0.14$ V and for $E°(X^{n+}/X) = -0.78$ V and initial emf of the cell is 0.65 V, determine n and indicate the direction of electron flow in the external circuit.

PROBLEM 532 Consider the following electrochemical cell :



(a) Write a balanced net ionic equation for the spontaneous reaction that take place in the cell.
(b) Calculate the standard cell potential $E°$ for the cell reaction.
(c) If the cell emf is 1.6 V, what is the concentration of Zn^{2+}?
(d) How will the cell potential be affected if KI is added to Ag^+ half-cell?

PROBLEM 533 You have available a 0.001 M $Al(NO_3)_3$, 0.1 M $Cu(NO_3)_2$ and 1.0 M $Fe(NO_3)_2$ solutions, Al, Cu and Fe metal strips. Construct a galvanic cell that would have greatest cell potential at 25°C. $E^\circ_{Al^{3+}/Al} = -1.76$ V, $E^\circ_{Fe^{2+}/Fe} = -0.44$ V, and $E^\circ_{Cu^{2+}/Cu}$ is +0.34 V.

PROBLEM 534 Magnesium metal is produced commercially by isolation of $MgCl_2$ from seawater followed by electrolysis of molten salt.

$$MgCl_2 \longrightarrow Mg + Cl_2$$

(a) What mass of Mg can be produced if a current of 430 A is passed for 1.0 hour?
(b) If a current of 500 A is used, how many hours will be required to convert all the 1000 kg $MgCl_2$ into Mg metal?

PROBLEM 535 Commercial production of Al-metal involves electrolysis of Al_2O_3 obtained from bauxite ore. The balanced net equation is :

$$2Al_2O_3 + 3C \longrightarrow 4Al + 3CO_2$$

(a) How many moles of Al are produced if 12 moles of electrons are passed through this cell?
(b) How many kg of Al metal are produced if a current of 1250 A is passed for 1.25 hours?

PROBLEM 536 Consider the following redox reaction :

$$2IrCl_6^{3-} + 3HCOOH \longrightarrow 2Ir + 3CO_2 + 12Cl^- + 6H^+$$

Given : $CO_2 + 2H_3O^+ + 2e \longrightarrow HCOOH + 2H_2O$ $E° = -0.20$ V

$IrCl_6^{3-} + 3e \longrightarrow Ir + 6Cl^-$ $E° = 0.77$ V

(a) Determine standard state emf of cell.
(b) Is this reaction thermodynamically spontaneous as written? Briefly explain.

PROBLEM 537 An electrical source which might be used on a spacecraft should be light weight. Yet deliver high voltage and maximum useful energy. A galvanic cell using aluminium, one of the lightest metal, might be considered.

$$Al \mid Al^{3+} \parallel Ce^{4+} \mid Ce^{3+} \mid Pt$$

The cell is constructed with 2.0 L 4 M $Al_2(SO_4)_3$ and 2.0 L 6 M $Ce(SO_4)_2$. If $E°(Al^{3+}/Al) = -1.76$ V and $E°(Ce^{4+}/Ce^{3+}) = +1.443$ V.

(a) Determine standard state emf and emf of the cell in the given conditions, if the cathode compartment is initially 1.0 M in Ce^{3+} ion.

(b) What is the maximum amount of useful electrical energy which could be derived from this cell?

(c) The instruments on spacecraft require a reasonably steady voltage to operate correctly. What will be the cell voltage when the concentration of Ce^{4+} ion has dropped to half of its original concentration? Assume this galvanic cell operate under a reversible condition at 25°C.

PROBLEM 538 A Daniell cell was constructed from 2.00 L 4 M aqueous $CuSO_4$ solution and 2 Lit 4 M aqueous $ZnSO_4$ solution.

Also, given

$$Cu^+(aq) \xrightarrow{e} Cu(s) \qquad E° = +0.522 \text{ V}$$

$$Cu^{2+}(aq) + e \longrightarrow Cu^+(aq) \quad E° = 0.158 \text{ V}$$

$$Zn^{2+}(aq) + 2e \longrightarrow Zn(s) \qquad E° = -0.76 \text{ V}$$

(a) Calculate standard cell potential for this Daniell cell.

(b) Calculate the cell potential when the concentration of $Cu^{2+}(aq)$ dropped to 0.4 M. Assume current was drawn slowly, so that this galvanic cell operated under reversible conditions at 25°C.

PROBLEM 539 The half-reactions for a typical rechargable nickel-cadmium ("nicad") battery are :

$$Cd(OH)_2(s) + 2e \longrightarrow Cd(s) + 2OH^-(aq) \qquad E° = -0.81 \text{ V}$$

$$Ni(OH)_3(s) + e \longrightarrow Ni(OH)_2(s) + OH^-(aq) \quad E° = +0.49 \text{ V}$$

(a) Identify cathode and write a balanced equation that shows the reaction that occurs spontaneously as the cell discharges.

(b) If E° for electrolysis of molten $MgCl_2$ into Mg and $Cl_2(g)$ is –3.74 V, can this nicad battery be used to drive decomposition of molten $MgCl_2$ into Mg metal and Cl_2 gas?

(c) If the nicad battery can deliver 0.1 A for 12 hour, how many grams of Mg can be produced from $MgCl_2$ by electrolysis?

(d) The voltage delivered by a nicad battery doesnot change significantly as the battery discharges and the reaction reaches equilibrium. Using Nernst's equation, briefly explain, why this is true?

PROBLEM 540 Lead storage battery is used in automobiles. In order to reduce the amount of hazardous lead and compounds that end up in landfills when these batteries are dumped, it has been suggested that the lead be replaced with carbon monoxide. The unbalanced cell reaction when the battery discharge is :

$$PbO_2(s) + CO(g) + H_2SO_4(aq) \longrightarrow PbSO_4(s) + CO_2(g) + H_2O$$

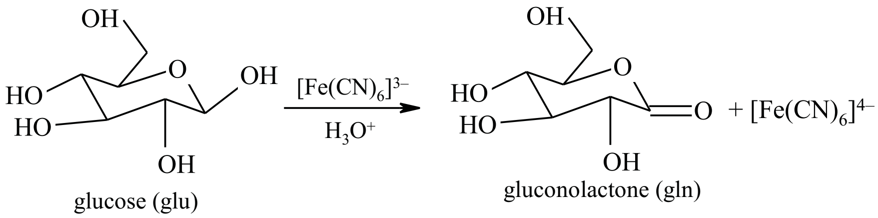
$$E°(PbO_2/PbSO_4) = +1.685 \text{ V} \quad \text{and} \quad E°(CO_2(g)/CO(g)) = -0.12 \text{ V}$$

(a) Calculate E° for this lead-storage battery.

(b) If density of sulphuric acid in battery decreases from 1.3 g/ml (40% H_2SO_4 by wt.) to 1.2 g/ml (20% H_2SO_4 by wt.) during its used, determine the ampere-hour for which battery has been used. Volume of battery is 3.0 Lit.

(c) Voltage of such battery is maintained constant during its used. Very briefly explain, why this is so?

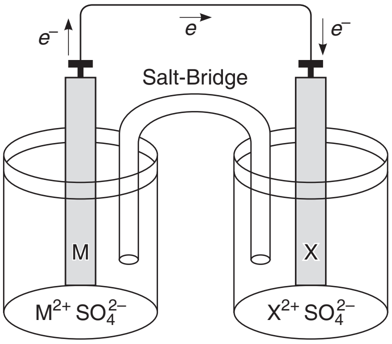
PROBLEM 541 Diabetic must monitor their levels of blood glucose to determine the proper insulin dose. An electronic device that does this uses the reaction below:



$$E^\circ\,(\text{gln/glu}) = +0.29\text{ V} \quad \text{and} \quad E^\circ\,\{[\text{Fe(CN)}_6]^{3-}/[\text{Fe(CN)}_6]^{4-}\} = +0.69\text{ V}$$

(a) Balance the cell reaction and determine standard state cell potential.
(b) Is this reaction spontaneous as written?
(c) When the concentration of glucose is increased, what happens to the cell voltage?

PROBLEM 542 The diagram below shows the experimental setup for a typical Zn–Ni galvanic cell :



$E^\circ\,(\text{Zn}^{2+}/\text{Zn}) = -0.76$ V

$E^\circ\,(\text{Ni}^{2+}/\text{Ni}) = -0.25$ V

$\text{MSO}_4 = 0.01$ M

$\text{XSO}_4 = 1.00$ M

(a) Identify M and X and determine cell potential at 25°C.
(b) If concentration of M^{2+} ion changes to 1.0 M during its uses, what would be the new cell voltage?
(c) Describe, what would happen to cell voltage if salt bridge was removed.

PROBLEM 543 At 25°C, H_2O_2 decomposes according to the following equation :

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(q) \qquad E^\circ = 0.55\text{ V}$$

(a) Determine the value of K_{eq} for decomposition reaction.

(b) If standard reduction potential for $O_2(g) + 4H^+ \xrightarrow{4e} 2H_2O$ is 1.23 V, using this information in addition to the information provided above, determine the value of E° for

$$O_2(g) + 2H^+ + 2e \longrightarrow H_2O_2$$

PROBLEM 544 In an electrolytic cell, Cu(s) is produced by electrolysis of $CuSO_4(aq)$. Calculate maximum mass of Cu(s) that can be deposited by a direct current of 100 A passed through 2 Lit 2 M $CuSO_4(aq)$ solution for a period of 1.5 hours. Also determine the final concentration of $CuSO_4$ in solution and volume of $O_2(g)$ measured at STP, produced at anode.

PROBLEM 545 (a) Using the following $E°$ values : $E^{\circ}_{\mathrm{Cu^+/Cu}} = 0.52$ V, $E^{\circ}_{\mathrm{Cu^{2+}/Cu^+}} = 0.16$ V, determine K for : $\mathrm{Cu}(s) + \mathrm{Cu}^{2+}(aq) \rightleftharpoons 2\mathrm{Cu}^{+}(aq)$.

(b) If $E°$ for the reaction $\mathrm{Cu}(s) + \mathrm{Cu}^{2+}(aq) + 2\mathrm{Br}^{-}(aq) \rightleftharpoons 2\mathrm{CuBr}(s)$ is 0.5147 V, determine K_{sp} of CuBr at 25°C.

PROBLEM 546 Consider the galvanic cell

$$\mathrm{Zn}(s)\,|\,\mathrm{Zn}^{2+}(0.04\ \mathrm{M})\,\|\,\mathrm{Cl}^-\ (5\times10^{-3}\ \mathrm{M})\,|\,\mathrm{Cl}_2\,(0.1\ \mathrm{atm})\,|\,\mathrm{Pt}(s)$$

(a) Determine emf of cell and equilibrium constant for the net cell reaction.

(b) Now, if $\mathrm{NH_3}$ is added to anode chamber at 1.0 M concentration, what would be the new emf. K_f for $[\mathrm{Zn(NH_3)_4}]^{2+} = 7.8\times10^{8}$, $E^{\circ}_{\mathrm{Zn^{2+}/Zn}} = -0.76$ V and $E^{\circ}_{\mathrm{Cl_2/Cl^-}} = 1.36$ V.

PROBLEM 547 A galvanic cell was constructed using Ag/Cu electrode as shown below :

$$\mathrm{Cu}\,|\,\mathrm{Cu}^{2+}(aq)\,\|\,\mathrm{Ag}^{+}(0.01\ \mathrm{M})\,|\,\mathrm{Ag}$$

The cell emf was measured to be 0.382 V. Now some $\mathrm{CaCl_2}$ was added to 250 ml electrolyte present in cathode chamber such that all Ag^+ precipitate out as AgCl and finally voltage drop to 0.01 V. If $[\mathrm{Cu}^{2+}]$ was 0.02 M, determine K_{sp} of AgCl.

PROBLEM 548 A solution of $\mathrm{M(NO_3)_2}$ is electrolyzed using a current of 2.5 A and 3.06 g metal was deposited in 35 minutes. Determine molar mass of the metal.

PROBLEM 549 Consider the galvanic cell :

$$\mathrm{Pt}\,|\,\mathrm{Sn}^{4+}(aq, 0.010\ \mathrm{M}), \mathrm{Sn}^{2+}(aq, 0.10\ \mathrm{M})\,\|\,\mathrm{O_2}\,(\mathrm{g}, 1.0\ \mathrm{atm});\ \mathrm{H}^{+}\,(\mathrm{pH} = 4)\,|\,\mathrm{C}(gr)$$

$E^{\circ}_{\mathrm{Sn^{4+}/Sn^{2+}}} = 0.15$ V and $E^{\circ}_{\mathrm{O_2,\ H^+/H_2O}} = 1.23$ V.

Assuming that the cathode chamber is buffered at constant pH = 4, determine (a) Cell-potential, (b) Concentrations of Sn^{4+} and Sn^{2+} when cell potential dropped to 0.8 V during its uses at 25°C.

PROBLEM 550 When a pH-meter was standardized with a basic-acid borate-buffer with a pH 9.4, the cell potential was 0.06 V. When the buffer was replaced by a solution of unknown hydronium ion, the cell potential was 0.22 V. Determine pH in this solution.

PROBLEM 551 A 200 ml $\mathrm{CuSO_4}$ solution was electrolyzed using a current of strength 4.0 A for 30 min. Determine pH of analyte at the end of electrolysis assuming initial pH = 7.

PROBLEM 552 A solution of $\mathrm{Mn(NO_3)_2}$ (0.15 M) and $\mathrm{Fe(NO_3)_2}$ (0.1 M) is placed in a beaker and buffered at pH = 5. Two platinum electrodes are inserted and current is passed through the solution in order to plate out the metals.

$$E^{\circ}_{\mathrm{Fe^{2+}/Fe}} = -0.44\ \mathrm{V},\ E^{\circ}_{\mathrm{Mn^{2+}/Mn}} = -1.18\ \mathrm{V},\quad \text{and}\quad E^{\circ}_{\mathrm{O_2,\ H^+/H_2O}} = 1.23\ \mathrm{V}$$

Which metal will be deposited first and what minimum voltage would be required for the onset of electrolysis?

PROBLEM 553 Consider the electroplating of a metal +1 cation from a solution of unknown concentration according to the half reaction : $\mathrm{M}^{+} + e \longrightarrow \mathrm{M}$ with a standard potential of $E°$. When the half-cell is connected to an appropriate oxidation half-cell and current is passed, M^{+} begins to plateout at a potential of E_1. To what value (E_2) must the applied potential be adjusted, relative to E_1, if 99.99% of the metal is to be removed from the solution?

PROBLEM 554 A steel pot containing acidic tomato sauce is covered with the aluminium foil; the foil is in contact with both the pot and sauce. Latter a large excess of aluminium foil has dissolved. It is believed that the following electrochemical reaction caused aluminium to dissolve :

$$3Fe^{2+}(aq) + 2Al \rightleftharpoons 3Fe(s) + 2Al^{3+}(aq)$$

At some instant, emf was found to be 1.2 V. Determine the area of holes created in the Al-foil at that instant. $E^\circ_{Al^{3+}/Al} = -1.66$ V and $E^\circ_{Fe^{2+}/Fe} = -0.44$ V. Density of Al metal is 2.7 g/cc, thickness of aluminium foil and volume of sauce was 100 ml and $[Fe^{2+}] = 5 \times 10^{-4}$ M.

PROBLEM 555 A balloon is being filled with hydrogen produced by the electrolysis of an aqueous solution of acid. How long will it take to generate enough hydrogen to lift 1.5 kg by using a current of 8.5 A. Average molar mass of air $= 28.8$ amu.

PROBLEM 556 A galvanic cell was constructed by dipping a zinc electrode in 0.1 M $Zn(NO_3)_2$ and a Pt electrode in 0.1 M HIO_3 solution and emf of this cell was found to be 0.72 V at 25°C. $E^\circ_{Zn^{2+}/Zn} = -0.76$ V. Determine acid dissociation constant (K_a) of HIO_3. Assume partial pressure of gaseous species to be 1.0 atm.

PROBLEM 557 A battery was used to supply a constant current of what was believed to be exactly 0.4 A as read on a meter in the external circuit. The cell was based on the electrolysis of a 100 ml 0.1 M aqueous copper sulphate solution. After a 30 minute duration, concentration of electrolyte dropped to 0.0528 M. Determine the extent to which meter was incorrect?

PROBLEM 558 A galvanic cell with a measured potential of 0.11 V at 25°C, contain a Pt electrode in a solution which is 0.0135 M in Cr^{+2} and 2.16×10^{-4} M in Cr^{+3}. In second compartment a Ni electrode dips into a solution of $Ni(NO_3)_2$. Determine concentration of Ni^{2+} second compartment. $E^\circ(Cr^{3+}/Cr^{2+}) = -0.41$ V and $E^\circ(Ni^{2+}/Ni) = -0.25$ V.

PROBLEM 559 The electrolysis of $Na_2SO_4(aq)$ is conducted into two separate half-cells joined by a salt bridge, also containing Na_2SO_4. The cell diagram for the electrolysis is

$$Pt \mid Na_2SO_4(aq) \parallel Na_2SO_4(aq) \mid Pt$$

Phenolphthalein indicator is added to each half-cells.

(a) Describe any colour-change occurring in half-cells as electrolysis progresses.

(b) After electrolysis is stopped, the solution of the two half-cells are mixed. Describe and explain any colour change that occur.

(c) In an experiment 10 ml HCl is added to cathode chamber alongwith phenolphthalein. Electrolysis is carried out with a 25 mA current and the solution colour becomes pink after 8.00 minutes. What is the molarity of HCl?

PROBLEM 560 Determine formation constant of complex HgI_4^{2-}. $E^\circ(Hg^{2+}/Hg) = 0.85$ V and $E^\circ(HgI_4^{2-}/Hg, I^-) = -0.04$ V.

Solutions

ELECTROCHEMISTRY

489. (a) $$Q = It = \frac{0.15 \times 8 \times 3600}{96500} \text{ faraday}$$

$$\text{Volume of } F_2(g) \text{ produced} = 11.2 \text{ F} = \mathbf{0.5\ L}$$

(b) $$\text{Volume of } O_2(g) \text{ produced} = 5.6 \text{ F} = \mathbf{0.25\ L}$$

490. Partial pressure of $O_2 = 722 - 19.83 = 702.17$ torr.

$$\Rightarrow \text{ Moles of } O_2(g) \text{ produced} = \frac{702.17}{760} \times \frac{25 \times 10^{-3}}{0.082 \times 295} = 9.548 \times 10^{-4}$$

$$\text{Gram equivalents of } O_2 = 3.82 \times 10^{-3} = \frac{I \times 30 \times 60}{96500} \quad \Rightarrow \quad I = \mathbf{0.2\ ampere}$$

491. Total surface area $= 11.2\,\text{cm}^2 \quad \Rightarrow \quad V = 11.2 \times 10^{-4}\ \text{cm}^3$

Mass of Ag $= 11.76 \times 10^{-3}$ g $\quad \Rightarrow \quad$ g eq. of Ag $= 1.088 \times 10^{-4} = \dfrac{It}{96500}$

$\Rightarrow$ $\qquad t = 105$ seconds.

492. The cell reaction is : $\quad 2\text{Sn}^{2+} \longrightarrow \text{Sn}^{4+} + \text{Sn}$

$$\text{Initial moles of } \text{SnCl}_2 = \frac{19}{190} = 0.1$$

$$\text{Moles of Sn deposited} = \frac{0.119}{119} = 0.001 = \text{moles of SnCl}_4 \text{ produced.}$$

$$\text{Moles of SnCl}_2 \text{ left unelectrolysed} = 0.1 - 0.002 = 0.098$$

$$\Rightarrow \quad \frac{m(\text{SnCl}_2)}{m(\text{SnCl}_4)} = \frac{0.098 \times 190}{0.001 \times 261} = \mathbf{71.34.}$$

493.

$$\text{Moles of } Br_2 \text{ required} = \frac{5\times10^5}{94}$$

$$\text{Gram equivalent of } Br_2 \text{ required} = \frac{10^6}{94} = \frac{It}{F} = \frac{20\times10^3}{96500}\,t$$

$$t = \mathbf{14.258\ hr.}$$

494. $E^\circ_{\text{cell}} = 0.28$, pH (from Henderson equation) $= 4.188$

$$E = E^\circ - 0.059 \log[H^+][Cl^-] = E^\circ + 0.059\,\text{pH} = 0.527\ \text{V}$$

495. The spontaneous cell reaction is $Cu + Br_2 \qquad Cu^{2+} + 2Br^- \quad E^\circ = 0.73\ \text{V}$

At the beginning : $E_{\text{cell}} = 0.73 - \dfrac{0.059}{2}\log(0.05)(0.1)^2 = 0.827\ \text{V}$

In order to reverse the cell reaction, minimum voltage requirement $= 0.827$ V

After deposition of 2.827 g Cu :

$$m \text{ mol of } CuBr_2 \text{ left} = 50 - 44.87 = 5.13 \quad \Rightarrow \quad [CuBr_2] = 0.01026\ \text{M}$$

$$\Rightarrow \qquad E_{\text{cell}} = 0.73 - \frac{0.059}{2}\log(0.01026)(0.02052)^2 = \mathbf{0.888\ V}$$

Thus, at this stage, minimum voltage required to reverse the reaction is 0.888 V.

496. For $\quad I_2 + I^- \rightleftharpoons I_3^- \quad E^\circ = -0.001\ \text{V} \quad \Rightarrow \quad \ln K = \dfrac{nE^\circ F}{RT} \quad \Rightarrow \quad K_c = 0.925$

$$\Rightarrow \qquad 0.925 = \frac{[I_3^-]}{0.25[I^-]} \quad \Rightarrow \quad 0.925 = \frac{x}{0.25(0.25-x)}$$

Solving, $\ x = 0.158$ M.

497.

$$Tl \longrightarrow Tl^+ + e \qquad 0.34$$

$$Cd^{2+} + 2e \longrightarrow Cd \quad -0.40$$

Cell reaction : $\quad 2Tl + Cd^{2+} \longrightarrow 2Tl^+ + Cd \quad E^\circ = -0.06$

$$E = -0.06 - \frac{0.059}{2}\log\frac{[Tl^+]^2}{[Cd^{2+}]} = \mathbf{-0.036\ V}$$

498. The cell reaction before adding KCl is :

$$M + H^+ \longrightarrow M^+ + \frac{1}{2}H_2$$

$$E = -0.4 = E^\circ - 0.059\log\frac{[M^+]}{[H^+]}$$

$$\Rightarrow \qquad E^\circ_{(\mathrm{M^+/M})} = +0.4177\ \mathrm{V}$$

After adding KCl, $\qquad [\mathrm{Cl^-}] = 0.1\ \mathrm{M}$

Cell reaction : $\qquad M + \mathrm{Cl^-} \longrightarrow M\mathrm{Cl} + e$

$$\mathrm{H^+} + e \longrightarrow \tfrac{1}{2}\mathrm{H_2}$$

$$M + \mathrm{Cl^-} + \mathrm{H^+} \longrightarrow M\mathrm{Cl} + \tfrac{1}{2}\mathrm{H_2}$$

$$\Rightarrow \qquad -0.05 = E^\circ - 0.059 \log \frac{1}{[\mathrm{Cl^-}][\mathrm{H^+}]}$$

$$\Rightarrow \qquad E^\circ = 0.05 \quad \Rightarrow \quad E^\circ_{(M\mathrm{Cl}/M,\mathrm{Cl^-})} = -0.05$$

$$\Rightarrow E^\circ \text{ for } M\mathrm{Cl} \rightleftharpoons M^+ + \mathrm{Cl^-} = -0.05 - 0.4177 = -0.4677\ \mathrm{V} = 0.059 \log K_{sp}$$

$$\Rightarrow \qquad K_{sp} = 1.18 \times 10^{-8}.$$

499.
$$0.987 = 0.8 - 0.059 \log \frac{[\mathrm{H^+}]}{0.8}$$

$$\Rightarrow \qquad [\mathrm{H^+}] = 5.4 \times 10^{-4}\ \mathrm{M}$$

$$K_a = \frac{[\mathrm{H^+}]^2}{[\mathrm{HOCN}]} = \mathbf{2.09 \times 10^{-4}}$$

500. $[\mathrm{Ag^+}]$ in a saturated solution of $\mathrm{AgCl} = 1.4 \times 10^{-9}$

$[\mathrm{Ag^+}]$ in a saturated solution of $\mathrm{AgBr} = 3.3 \times 10^{-10}$

The spontaneous direction of reaction will increase concentration of $\mathrm{Ag^+}$ in AgBr/KBr solution and decrease $\mathrm{Ag^+}$ in AgCl/KCl solution.

Therefore, spontaneous cell reaction is

$$\mathrm{Ag} \longrightarrow \mathrm{Ag^+}(R)$$

$$\mathrm{Ag^+}(L) \longrightarrow \mathrm{Ag}$$

$$\mathrm{Ag^+}(L) \longrightarrow \mathrm{Ag^+}(R)$$

$$E = 0 - 0.059 \log \frac{[\mathrm{Ag^+}]_R}{[\mathrm{Ag^+}]_L} = \mathbf{0.037\ V}$$

501.
$$0.76 = -E^\circ_{\mathrm{Zn^{2+}/Zn}} - \frac{0.059}{2} \log \frac{[\mathrm{Zn^{2+}}]}{[\mathrm{H^+}]^2}$$

$$\Rightarrow \qquad E^\circ_{\mathrm{Zn^{2+}/Zn}} = -0.76\ \mathrm{V}$$

$$0.24 = -E^\circ_{\mathrm{Ni^{2+}/Ni}} - \frac{0.059}{2} \log \frac{[\mathrm{Ni^{2+}}]}{[\mathrm{H^+}]^2}$$

$$\Rightarrow \qquad E^\circ_{\mathrm{Ni^{2+}/Ni}} = \mathbf{-\,0.24\ V}$$

⇒ For $$\mathrm{Zn} + \underset{1.5-x}{\mathrm{Ni}^{2+}} \rightleftharpoons \underset{x}{\mathrm{Zn}^{2+}} + \mathrm{Ni}$$

$$E^\circ = 0.52\ \mathrm{V} = \frac{2.303RT}{2F}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Ni}^{2+}]} \quad\Rightarrow\quad \frac{x}{1.5-x} = 1.99\times10^{17}$$

Such a large value of equilibrium constant indicate that all Ni^{2+} has been quantitatively reduced to Ni.

$$\text{Amount of Zn consumed} = 1.5\times0.75 = \mathbf{1.125\ moles}$$

502. (a) $$E = E^\circ - \frac{0.059}{2}\log\frac{[\mathrm{Mg}^{2+}]}{[\mathrm{Ag}^+]^2} = 3.17 - \frac{0.059}{2}\log = \mathbf{3.14\ V}$$

(b) As the reaction proceed, $[Ag^+]$ will decrease and $[Mg^{2+}]$ will increase.

$$m\ \text{mol of}\ \mathrm{Ag}^+\ \text{initially present} = 34.6$$

$$m\ \text{mol of}\ \mathrm{Ag}^+\ \text{present finally} = 34.6 - 11.11 = 23.48$$

⇒ $$[\mathrm{Ag}^+] = 0.0678\ \mathrm{M}$$

$$m\ \text{mol of}\ \mathrm{Mg}^+\ \text{produced} = 5.55$$

⇒ $$[\mathrm{Mg}^+] = 0.119\ \mathrm{M}$$

$$E = 3.17 - \frac{0.059}{2}\log\frac{0.119}{(0.0678)^2} = \mathbf{3.128\ V}$$

503. (a) $$E = E^\circ - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]} = 1.1 - \frac{0.059}{2}\log\frac{0.2}{0.2} = 1.1\ \mathrm{V}$$

(i) On adding $NH_3\,(aq)$ to Cu^{2+} solution, complex $Cu(NH_3)_4^{2+}$ will be formed reducing $[Cu^{2+}]$, E_{cell} will decrease (ii) On adding $NH_3\,(aq)$ to Zn^{2+} solution, complex $Zn(NH_3)_4^{2+}$ will be formed reducing $[Zn^{2+}]$, E_{cell} will increase.

(b) After adding NH_3, following equilibrium will establish:

$$\mathrm{Cu}^{2+} + 4\mathrm{NH}_3 \rightleftharpoons \mathrm{Cu(NH_3)_4^{2+}}$$

Now, $$0.68 = 1.1 - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]}$$

Solving, $$[\mathrm{Cu}^{2+}] = 1.16\times10^{-15}\ \mathrm{M}$$

Such low concentration of Cu^{2+} indicate that almost all Cu^{2+} has been consumed in complex formation.

⇒ $$[\mathrm{Cu(NH_3)_4^{2+}}] = 0.1\ \mathrm{M}, \quad [\mathrm{NH_3}] = 1.1\ \mathrm{M}$$

$$K_f = \frac{0.1}{(1.1)^4\times1.16\times10^{-15}} = \mathbf{5.88\times10^{13}}.$$

504. $E^\circ = \dfrac{\Delta S^\circ}{nF}T - \dfrac{\Delta H^\circ}{nF}$ Solving for E° at 25°C and 20° gives

$$\Delta S^\circ = \mathbf{-30.88\ JK^{-1}} \quad \text{and} \quad \Delta H^\circ = \mathbf{-77.23\ kJ} \quad \text{and} \quad \Delta G^\circ = \mathbf{-68.03\ kJ}$$

505. For the given cell, Nernst equation can be written as :

$E = C + 0.059$ pH, where C is a constant

$$\Rightarrow \qquad 0.129 = 0.059(6.86 - \text{pH}_1) \quad \Rightarrow \quad \text{pH}_1 = \mathbf{4.68}$$

506.
$$0.348 = 0.13 - \frac{0.059}{2} \log [\text{Pb}^{2+}] \quad \Rightarrow \quad [\text{Pb}^{2+}] = 4.075 \times 10^{-8}$$

$$K_{sp} = [\text{Pb}^{2+}][\text{F}^-]^2 = \mathbf{4.075 \times 10^{-8}}$$

507. The spontaneous cell reaction will be :

$$\text{Zn}^{2+}(T_f = -2) \rightleftharpoons \text{Zn}^{2+}(T_f = -0.9)$$

$$E = 0 - \frac{0.059}{2} \log \frac{0.9}{2} = \mathbf{0.01\ V}$$

508. The discharging reaction is :

$$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$$

$$\Rightarrow \qquad m(\text{PbSO}_4) \text{ produced} = \frac{23.92}{238} \times 2 \times 302 = \mathbf{60.7\ g}$$

$$\text{g eq. of PbO}_2 \text{ reduced} = \frac{23.92}{238} \times 2 = \mathbf{0.201}$$

$$\Rightarrow \qquad 0.201 \times 96500 = 3 \times t \quad \Rightarrow \quad t = 6465.5 \text{ second} = \mathbf{1.8\ hour}$$

509. $E°$ for
$$\underset{0.1-2x}{2\text{ClO}_3^-} \rightleftharpoons \underset{x}{\text{ClO}_4^-} + \underset{x}{\text{ClO}_2^-} = -0.03 \text{ V}$$

$$\Rightarrow \qquad K = 9.66 \times 10^{-2}$$

Therefore, $$9.66 \times 10^{-2} = \left(\frac{x}{0.1 - 2x}\right)^2; \quad \text{Solving } x = \mathbf{0.019\ M}$$

510.
$$0.035 = 0.77 - 0.059 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

$$\Rightarrow \qquad \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \mathbf{2.87 \times 10^{12}}$$

511.
$$\text{Ni}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{NiO}_2 + 4\text{H}^+ + 2e \qquad E° = -1.678 \text{ V}$$

$$2e + \text{NiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni(OH)}_2 + 2\text{OH}^- \qquad E° = -0.49 \text{ V}$$

Adding $$\text{Ni}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Ni(OH)}_2 + 4\text{H}^+ + 2\text{OH}^- \quad E° = -2.168 \text{ V} \quad K_1 = 4.5 \times 10^{-74}$$

$$2\text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + 2\text{OH}^- \qquad K_2 = 10^{-28}$$

Subtracting : $$\text{Ni}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Ni(OH)}_2 + 2\text{H}^+ \quad K = K_1/K_2 = 4.5 \times 10^{-46}$$

512. $\because$
$$\frac{dE°}{dT} = \frac{\Delta S°}{nF} \quad \Rightarrow \quad \Delta S° = -0.125 \times 2 \times 96500 = \mathbf{-24.125\ kJ\ K^{-1}}$$

$$\Delta G° = -nE°F = -2 \times 0.0372 \times 96500 = -7179.6 \text{ J} \quad \Rightarrow \quad \Delta H° = \mathbf{-7196.43\ kJ}$$

513. Let x be the concentration of Ca^{2+} ion in diluted sea water.

$$-0.053 = E^\circ - \frac{0.059}{2}\log\frac{1}{x}$$

and $$-0.0422 = E^\circ - \frac{0.059}{2}\log\frac{50}{50x+0.05}$$

$\Rightarrow$ $$0.0108 = \frac{0.059}{2}\log\frac{50x+0.05}{50x} \Rightarrow x = 7.55\times10^{-4}$$

$\Rightarrow$ $$[Ca^{2+}]\text{ in sea water} = 10x = \mathbf{7.55\times10^{-3}\ M}$$

514. Moles of $Cl_2(g)$ produced $= \dfrac{9.6\times10^3}{58.5\times2} = 82.05$

$$P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} = \mathbf{21.66\ atm.}$$

515. $E = E^\circ - 0.059\log\dfrac{[H^+]}{[Ag^+]} = 0.8 - 0.059\log\dfrac{0.22}{1.6\times10^{-10}} = \mathbf{0.26\ V}$

516. $E = 0 - 0.059\log\dfrac{[Ag^+]_L}{[Ag^+]_R} \Rightarrow 0.4312 = -0.059\log\dfrac{[Ag^+]_L}{0.1}$

$$[Ag^+]_L = 4.9\times10^{-9} \Rightarrow K_{sp} = [Ag^+][Cl^-] = 4.9\times10^{-9}\times0.05$$

$$= \mathbf{2.4\times10^{-10}}$$

517. $$E = 0.28 - \frac{RT}{2F}\ln\frac{[H^+]^2}{p_{H_2}} = 0.6885 \Rightarrow [H^+] = 2.57\times10^{-7} \quad\text{or}\quad pH = \mathbf{6.6}$$

518. For the given cell :

$$E = E^\circ + 0.059\ pH \Rightarrow 0.112 = E^\circ + 0.059\times4 \quad \text{...(i)}$$

$$0.3865 = E^\circ + 0.059\ pH \quad \text{...(ii)}$$

Solving, Eqs. (i) and (ii) gives $pH = \mathbf{8.65}$

519. $E = E^\circ - 0.059\log\dfrac{1}{[Ag^+]} = 0.8 + 0.059\log\sqrt{K_{sp}} = \mathbf{0.51\ V}$

520. Voltage drop due to resistance by the circuit $= 0.55$ V

$\Rightarrow$ $$I = \frac{\Delta V}{R} = \mathbf{0.055\ A}$$

$$Q = 0.55\times96500 = \mathbf{53.075\ kJ}$$

521. $$\underset{0.1-x}{Ag(CN)_2^-} \rightleftharpoons \underset{x}{Ag^+} + \underset{0.05+2x}{2CN^-}$$

$$3\times10^{-19} = \frac{x(0.05+2x)}{0.1-x} \approx \frac{0.05x}{0.1} \Rightarrow x = \mathbf{6\times10^{-19}}$$

$$E = 0.8 - 0.059 \log \frac{1}{[\text{Ag}^+]} = \mathbf{-\,0.27\ V}$$

522. $E^\circ_{\text{Au}^+/\text{Au}} - 0.059 \log \frac{1}{[\text{Au}^+]} = E^\circ_{\text{Ag}^+/\text{Ag}} - 0.059 \log \frac{1}{[\text{Ag}^+]}$

Substituting values of E° and $[\text{Ag}^+] = 0.1$ M gives $[\text{Au}^+] = 1.21 \times 10^{-16}$

Now,
$$\underset{0.1-x}{\text{Au(CN)}_2^-} \rightleftharpoons \text{Au}^+ + \underset{2x}{2\text{CN}^-}$$

$$K = 5 \times 10^{-39} = \frac{1.21 \times 10^{-16}\,[\text{CN}^-]^2}{0.1} \quad \Rightarrow \quad [\text{CN}^-] = 2.02 \times 10^{-12}\ \text{M.}$$

523. The cell reaction is
$$\text{Zn} + 2\text{Ag}^+ \rightleftharpoons \text{Zn}^{2+} + 2\text{Ag.}$$

$$E_1 = 1.52 = E^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]_1^2}$$

$$E_2 = 1.04 = E^\circ - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]_2^2}$$

$$\Rightarrow \qquad 0.48 = \frac{0.059}{2} \log \frac{[\text{Ag}^+]_1^2}{[\text{Ag}^+]_2^2} \quad \Rightarrow \quad [\text{Ag}^+]_2 = 7.31 \times 10^{-10}$$

$$[\text{Cl}^-] = 0.2\ \text{M} \quad \Rightarrow \quad K_{sp} = \mathbf{1.46 \times 10^{-10}}$$

524. (a) For
$$\text{Ag}_2\text{S} \rightleftharpoons 2\text{Ag}^+ + \text{S}^{2-}$$

$$E^\circ = \frac{0.059}{2} \log K_{sp} = \mathbf{-\,1.425\ V} \qquad \ldots\text{(i)}$$

$$2\text{Ag}^+ + 2e \rightleftharpoons 2\text{Ag}$$

$$E^\circ = 0.8\ \text{V} \qquad \ldots\text{(ii)}$$

Adding, Eqs. (i) and (ii) gives :

$$\text{Ag}_2\text{S} + 2e \rightleftharpoons 2\text{Ag} + \text{S}^{2-} \quad E^\circ = \mathbf{-\,0.652\ V}$$

(b)
$$0.766 = 0.896 - \frac{0.059}{2} \log \frac{1}{[\text{S}^{2-}]}$$

$$\Rightarrow \qquad [\text{S}^{2-}] = \mathbf{3.92 \times 10^{-5}\ M}$$

525. Cell reaction is : $\text{H}_2(g) + \text{I}_2(s) \rightleftharpoons 2\text{H}^+ + 2\text{I}^- \quad E^\circ = 0.535$

$$\Rightarrow \qquad 0.755 = 0.535 - 0.059 \log [\text{H}^+][\text{I}^-] \quad \Rightarrow \quad \text{pH} = \mathbf{2.72}$$

526. For the cell reaction :

$$\tfrac{1}{2}\text{H}_2 + \text{AgCl} \rightleftharpoons \text{Ag} + \text{H}^+ + \text{Cl}^-$$

$$0.47 = 0.23 - 0.059 \log [\text{H}^+][\text{Cl}^-]; \quad \text{pH} = 3.07$$

$$0.5 = 0.23 - 0.059 \log [\text{H}^+][\text{Cl}^-]; \quad \text{pH} = 3.58$$

If there is x mol of acid and y mol of NaOH in its 20 mL, then

$$3.07 = \mathrm{p}K_a + \log \frac{y}{x-y} \quad \text{and} \quad 3.58 = \mathrm{p}K_a + \log \frac{2.5y}{x-2.5y}$$

$$\Rightarrow \qquad 0.51 = \log \frac{2.5(x-y)}{x-2.5y} \quad \Rightarrow \quad x = 7.6\ y$$

$$\text{and} \qquad \mathrm{p}K_a = 3.07 - \log \frac{y}{6.6y} = 3.89 \quad \Rightarrow \quad K_a = \mathbf{1.3 \times 10^{-4}}$$

527. Faraday of electricity passed $= \dfrac{1.25 \times 1.1 \times 3600}{96500} = 0.0513$

$$\Rightarrow \qquad \text{meq of KMnO}_4 \text{ required } = 51.3 \quad \Rightarrow \quad M(\mathrm{KMnO_4}) = \frac{51.3}{25} \times \frac{1}{5} = \mathbf{0.41\ M}$$

528. $2\mathrm{I}^- \rightleftharpoons \mathrm{I}_2 + 2e \quad F = \dfrac{It}{96500} = \dfrac{I \times 3 \times 60}{96500} = 9.3 \times 10^{-3} \quad \Rightarrow \quad I = \mathbf{4.98\ A}$

$$\text{Total meq of I}^- = 9.3 + 36.3 \times 0.1 = 19.93 \quad \Rightarrow \quad M(\mathrm{KI}) = \mathbf{0.16}$$

529. $[\mathrm{Ag}^+]_R = 8 \times 10^{-13} \quad \Rightarrow \quad E = 0 - 0.059 \log \dfrac{[\mathrm{Ag}^+]_L}{[\mathrm{Ag}^+]_R} = \mathbf{-\ 0.71\ V}$

530. For the cell reaction $\quad 2\mathrm{Hg} + 2\mathrm{Cl}^- + 2\mathrm{H}^+ \rightleftharpoons \mathrm{Hg_2Cl_2} + \mathrm{H_2}$

$$-0.52\ \mathrm{V} = -0.28 - 0.059 \log \frac{1}{[\mathrm{H}^+][\mathrm{Cl}^-]} \quad \Rightarrow \quad [\mathrm{H}^+] = 8.5 \times 10^{-5}\ \mathrm{M}$$

For salt $R_2\mathrm{NH_2Cl}$: $\quad K_h = \dfrac{K_w}{K_b} = \dfrac{[\mathrm{H}^+]^2}{[R_2\mathrm{NH_2Cl}]} \quad \Rightarrow \quad K_b = \mathbf{1.36 \times 10^{-7}}$

531. Since mass of Sn increasing, Sn-electrode is working as cathode and X-metal electrode as anode and electrons are flowing from X-electrode to Sn-electrode in the external circuit. The half cell reactions are :

$$\mathrm{Sn}^{2+} + 2e \rightleftharpoons \mathrm{Sn} \qquad E^\circ = -0.14\ \mathrm{V}$$

$$X^{n+} + ne \rightleftharpoons X \qquad E^\circ = -0.78\ \mathrm{V}$$

Cell reaction : $\quad n\mathrm{S}_n^{2+} + 2X \rightleftharpoons n\mathrm{S}_n + 2X^{n+} \qquad E^\circ_{\text{cell}} = 0.64\ \mathrm{V}$

Now applying the Nernst equation:

$$E = \frac{E^\circ - 0.0591}{2n} \log \frac{[X^{n+}]^2}{[\mathrm{Sn}^{2+}]^n}$$

$$\Rightarrow \qquad 0.65 = \frac{0.64 - 0.0591}{2n} \left(\log 10^{-2} - n \log \frac{1}{2} \right)$$

$$\Rightarrow \qquad 0.01 = \frac{0.0591}{2n} (2 - 0.3\ n) \qquad \text{Solving :}$$

$$\Rightarrow \qquad n = 3$$

532. (a) The spontaneous cell reaction is :

$$\mathrm{Zn} + 2\mathrm{Ag}^{+}(aq) \rightleftharpoons \mathrm{Zn}^{2+}(aq) + 2\mathrm{Ag}(s)$$

(b) $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 0.8 - (-0.76) = 1.56\ \text{V}$

(c) Applying Nernst's equation:

$$1.6 = 1.56 - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Ag}^{+}]^{2}} \qquad \ldots\text{(i)}$$

$$\Rightarrow \qquad \log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Ag}^{+}]^{2}} = -1.356 \quad \Rightarrow \quad \frac{[\mathrm{Zn}^{2+}]}{10^{-2}} = 4\times10^{-2}$$

$$\Rightarrow \qquad [\mathrm{Zn}^{2+}] = 4\times10^{-4}\ \mathrm{M}$$

(d) As we add KI to cathode chamber, some Ag^{+} will precipitate out as:

$$\mathrm{Ag}^{+} + \mathrm{I}^{-} \longrightarrow \mathrm{AgI}$$

The above reaction reducing $[\mathrm{Ag}^{+}]$ from cathode chamber. This will reduce E_{cell} according to Nernst's equation (i).

533. In the above conditions, two Galvanic cell can be constructed as:
(i) Al/Cu and (ii) Fe/Cu.

$$E^{\circ}_{\text{Al/Cu}} = +0.34 + 1.76 = 2.1\ \text{V} \quad \text{and} \quad E^{\circ}_{\text{Fe/Cu}} = +0.34 + 0.44 = +0.78\ \text{V}$$

$\because$ E_{cell} depends predominantly on E°_{cell}, cell (i) is more likely to produce higher voltage.

$$E_{\text{cell (i)}} = 2.1 - \frac{0.059}{6}\log\frac{[\mathrm{Al}^{3+}]^{2}}{[\mathrm{Cu}^{2+}]^{3}} = 2.1 - \frac{0.059}{6}\log\frac{10^{-6}}{10^{-3}} = 2.1295\ \text{V}$$

$$E_{\text{cell (ii)}} = 0.78 - \frac{0.059}{2}\log\frac{[\mathrm{Fe}^{2+}]^{2}}{[\mathrm{Cu}^{2+}]} = 0.78 - \frac{0.059}{2}\log\frac{1}{0.1} = 0.75\ \text{V}$$

$\Rightarrow$ Cell : $\mathrm{Al}\,|\,\mathrm{Al}^{3+}(aq)\,\|\,\mathrm{Cu}^{2+}(aq)\,|\,\mathrm{Cu}$ will produce greater voltage.

534. $Q = It = 430\times60\times60 = 1.548\times10^{6}\,\mathrm{C}$

$\Rightarrow$ number of faraday passed $= \dfrac{Q}{96500} = 16.04 =$ number of equivalents of Mg deposited.

$$\Rightarrow \qquad \text{mass of Mg deposited} = 16.04\times\frac{24}{2} = 192.5\ \text{g}$$

(d) Number of gram equivalents of $\mathrm{MgCl_2}$ required to be electrolyzed $= \dfrac{10^{6}}{47.5}$.

$$\Rightarrow \qquad Q = \frac{10^{6}}{47.5}\times96500 = It = 500\,t$$

$$\Rightarrow \qquad t = 4.063\times10^{6}\ \text{sec} = 1128.6\ \text{hours.}$$

535. (a) $2\mathrm{Al}_2^{+6} + 12e \longrightarrow 4\mathrm{Al}$ $\Rightarrow$ 12 moles of electron will produce 4 moles of Al.

(b) $$\text{Number of faradays passed} = \frac{1250\times1.25\times3600}{96500} = 58.29$$

⇒ Mass of aluminium metal deposited $= 58.29 \times \frac{27}{3} = 524.6 \text{ g} = 0.5246 \text{ kg}$.

536. (a) $E^{\circ}_{\text{cell}} = E^{\circ}(\text{IrCl}_6^{3-}/\text{Ir}, \text{Cl}^-) - E^{\circ}(\text{CO}_2, \text{H}_3\text{O}^+/\text{HCOOH}) = +0.97 \text{ V}$

(b) For thermodynamic spontaneity of a cell reaction, $\Delta G^{\circ} < 0$.

Also $\Delta G^{\circ} = -nE^{\circ}F < 0$ since, $E^{\circ} > 0$

⇒ Reaction is thermodynamically spontaneous.

537. (a) The cell reaction is :

$$\text{Al} + 3\text{Ce}^{4+} \longrightarrow \text{Al}^{3+} + 3\text{Ce}^{3+} \qquad \ldots\text{(i)}$$

$$E^{\circ}_{\text{cell}} = E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) = +1.443 + 1.76 = 3.203 \text{ V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{3} \log \frac{[\text{Ce}^{3+}]^3[\text{Al}^{3+}]}{[\text{Ce}^{4+}]^3} = 3.203 - \frac{0.059}{3} \log \frac{8}{(6)^3} = 3.23 \text{ V}$$

(b) Since, Ce^{+4} is in limited quantity.

$$\Delta G^{\circ} = -nE^{\circ}F = -(1 \text{ mol } e \text{ per mol Ce}^{4+})(3.203) \times 96500 = -309 \text{ kJ/mol Ce}^{4+}$$

⇒ $$\Delta G^{\circ}(\text{total}) = -309 \times 12 = -3708 \text{ kJ}$$

(c) Initially $[\text{Al}^{3+}] = 8 \text{ M}, \quad [\text{Ce}^{4+}] = 6 \text{ M}, \quad [\text{Ce}^{3+}] = 1 \text{ M}$

Also total mole of Ce^{4+} present initially $= 6 \times 2 = 12$

total mole of Al^{3+} present initially $= 8 \times 2 = 16$

total mol of Ce^{3+} present initially $= 2$

As the concentration of Ce^{4+} drop to half, 6 mol of Ce^{4+} will be converted to Ce^{3+}.

⇒ $$[\text{Ce}^{4+}] = 3 \text{ M}, \quad [\text{Ce}^{3+}] = \tfrac{8}{2} \text{ M} = 4 \text{ M}$$

Also, for 3 mol Ce^{4+} reduction one mol Al^{3+} comes in solution.

⇒ for 6 mol Ce^{4+} reduction, two mol Al^{3+} comes in solution.

⇒ $$[\text{Al}^{3+}]_{\text{final}} = 9 \text{ M}$$

⇒ $$E_{\text{cell}} = 3.203 - \frac{0.059}{3} \log \frac{(4)^3(9)}{(3)^3} = \mathbf{3.177 \text{ V}}$$

538. (a) First of all, we need to determine E° for Cu^{2+}/Cu half-cell.

		E°	ΔG°
Given:	$e + \text{Cu}^+(aq) \longrightarrow \text{Cu}(s)$	$+0.522 \text{ V}$	-0.522 F
	$\text{Cu}^{2+}(aq) + e \longrightarrow \text{Cu}^+(aq)$	$+0.158 \text{ V}$	-0.158 V
Add:	$\text{Cu}^{2+}(aq) + 2e \longrightarrow \text{Cu}(s)$		$\Delta G^{\circ} = -2E^{\circ}_{\text{cell}} = -0.68 \text{ F}$

⇒ $$E^{\circ}_{\text{cell}} = +0.34 \text{ V}$$

Note : Here E° is determined using $\Delta G^{\circ} = -nE^{\circ}F$ relationship since, E° is an intensive property and can't be manipulated algebraically.

Now, for the Daniell cell:

$$\mathrm{Zn} + \mathrm{Cu}^{2+}(aq) \rightleftharpoons \mathrm{Zn}^{2+}(aq) + \mathrm{Cu}(s)$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.34 + 0.76 = 1.1\ \text{V}$$

(b) Initial moles of $\mathrm{Cu}^{2+} = 2 \times 4 = 8$

$\Rightarrow$ moles of Cu^{2+} finally $= 2 \times 0.4 = 0.8$

$\Rightarrow$ moles of Cu^{2+} deposited $= 8 - 0.8 = 7.2$

$\Rightarrow$ moles of Zn^{2+} produced during deposition of $\mathrm{Cu}^{2+} = 7.2$

$\Rightarrow$ final moles of Zn^{2+} in anode chamber $= 2 \times 4 + 7.2 = 15.2$

$\Rightarrow$ finally $[\mathrm{Zn}^{2+}] = \dfrac{15.2}{2} = 7.6$ M

$$\Rightarrow \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{2}\log\frac{[\mathrm{Zn}^{2+}]}{[\mathrm{Cu}^{2+}]} = 1.1 - \frac{0.059}{2}\log\frac{7.6}{0.4} = 1.062\ \text{V}.$$

539. (a) $\mathrm{Ni(OH)_3}(s)$ is cathode:

$$\mathrm{Ni(OH)_3}(s) + e \longrightarrow \mathrm{Ni(OH)_2} + \mathrm{OH^-} \quad \ldots\text{(i)}$$

$$\mathrm{Cd(OH)_2} + 2e \longrightarrow \mathrm{Cd} + 2\mathrm{OH^-} \quad \ldots\text{(ii)}$$

2 (i) – (ii) $\quad 2\mathrm{Ni(OH)_3}(s) + \mathrm{Cd} \longrightarrow 2\mathrm{Ni(OH)_2} + \mathrm{Cd(OH)_2}$

(b) $E^\circ\,(\text{Nicad}) = 0.49 + 0.81 = 1.3$ V

E° for $\mathrm{MgCl_2} \longrightarrow \mathrm{Mg} + \mathrm{Cl_2}$ is -3.74 V, –ve because the reaction is being driven in a thermodynamically non-spontaneous direction. To make the reaction proceed as written, the nicad would have to supply atleast 3.74 V. The voltage calculated for nicad battery is 1.3 V, so that nicad battery can't drive this electrolysis. It would take 3 nicad batteries in series to have enough voltage to do this:

$$3 \times 1.3 = 3.9\ \text{V} > 3.74\ \text{V}.$$

(c) $Q = 0.1 \times 12 \times 3600\ \text{C} = 4320\ \text{C}$

$\Rightarrow$ number of faradays $= Q/96500 = 0.0447$ F

$\Rightarrow$ mass of Mg deposited $= 0.0447 \times 12 = 0.54$ gram.

(d) Nernst equation is: $\quad E = E^\circ - \dfrac{0.059}{2}\log Q.$

All the reactant in nicad battery is solid and the products are also solid and not part of Q. Therefore, as the cell approach equilibrium, there is no change in Q and no change in voltage. This is a fundamental idea on the design of most modern batteries.

540. (a) The balanced cell reaction is:

$$\mathrm{PbO_2} + \mathrm{H_2SO_4} + \mathrm{CO} \longrightarrow \mathrm{PbSO_4} + \mathrm{H_2O} + \mathrm{CO_2}$$

$$E^\circ = E^\circ\,(\mathrm{PbO_2/PbSO_4}) - E^\circ\,(\mathrm{CO_2/CO}) = 1.685 + 0.12 = 1.905\ \text{V}$$

(b) Initial moles of $\mathrm{H_2SO_4}$

$$= 1.3 \times 3000 \times \frac{40}{100} \times \frac{1}{98} = 15.918$$

$$\text{Initial moles of } H_2SO_4 = 1.2 \times 3000 \times \frac{20}{100} \times \frac{1}{98} = 7.347$$

$$\Rightarrow \qquad \text{moles of } H_2SO_4 \text{ consumed} = 8.571$$

$\because$ It is evident from the given cell reaction that per mole of H_2SO_4 consumed involves transfer of two moles of electrons, total electron transferred $= 17.142$.

$$\Rightarrow \qquad Q(\text{withdrawn}) = 17.142 \times 96500\,\text{C}$$

$$\text{Ampere-hour} = Q/3600 = 459.5$$

(c) The Nernst equation tells us that voltage depends on Q(reaction quotient).

$$\text{In the given cell } Q = \frac{P_{CO_2}}{[H_2SO_4]\,P_{CO}}.$$

541. (a) $\text{Glu} \longrightarrow \text{Gln} + 2e + 2H^+ \ (>\!CH(OH) \longrightarrow\ >\!C{=}O + 2H^+ + 2e) \quad E° = -0.29\text{ V} \ldots\text{(i)}$

$$Fe(CN)_6^{3-} + e \longrightarrow Fe(CN)_6^{4-} \qquad E° = +0.69\text{ V} \quad \ldots\text{(ii)}$$

Cell-reaction: (i) + 2 (ii) $\text{Glu} + 2[Fe(CN)_6]^{3-} \longrightarrow \text{Gln} + 2H^+ + 2[Fe(CN)_6]^{4-} \quad E° = +0.40\text{ V}$

(b) $\because\ E° = 0.40 > 0,\ \Delta G° < 0$, cell is spontaneous.

(c) Nernst equation is:

$$E = E° - \frac{0.059}{2}\log\frac{[\text{Gln}][H^+]^2\{[Fe(CN)_6]^{4-}\}^2}{[\text{Glu}]\{[Fe(CN)_6]^{3-}\}^2}$$

Increasing concentration of glucose will increase cell-potential.

542. (a) For spontaneous cell reaction, $E^{\circ}_{\text{cell}} > 0 \Rightarrow M \rightarrow Zn$ and $X \rightarrow Ni$ and net cell reaction is:

$$Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni \qquad E^{\circ}_{\text{cell}} = +0.51\text{ V}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Ni^{2+}]} = 0.51 - \frac{0.059}{2}\log 0.01 = +0.569\text{ V}$$

(b) During use, $[Zn^{2+}]$ increases and $[Ni^{2+}]$ decreases by the same factor. Therefore, when $[Zn^{2+}] = 1.0\text{ M},\ [Ni^{2+}] = 0.01\text{ M}$

$$E_{\text{cell}} = 0.51 - \frac{0.059}{2}\log\frac{1}{0.01} = +0.451\text{ V}$$

Note : Equal volume of electrolytes have been considered in the two half-cells.

(c) If salt bridge is removed, electrolysis will stop immediately due to accumulation of Zn^{2+} ion around Zn-electrode making solution positively charged. This will prevent further oxidation of Zn into Zn^{2+} ion. Hence, cell voltage will become zero.

543. (a) $\Delta G° = -nE°F = -RT\ln K \ \Rightarrow\ \ln K = \dfrac{nE°F}{RT} = \dfrac{2 \times 0.55 \times 96500}{8.314 \times 298} = 42.84$

$$\Rightarrow \qquad K = 4.046 \times 10^{18}.$$

$$\begin{array}{llcc}
 & & E^\circ & \Delta G^\circ \\
\text{(b) Given:} & \tfrac{1}{2}O_2(g) + 2H^+ + 2e \longrightarrow H_2O & +1.23\text{ V} & -2\times 1.23\text{ F} \\
 & \tfrac{1}{2}O_2(g) + H_2O \longrightarrow H_2O_2 & -0.55\text{ V} & +0.55\text{ F} \\
\hline
\text{Adding:} & O_2(g) + 2H^+ + 2e \longrightarrow H_2O_2 & \multicolumn{2}{c}{\Delta G^\circ = -2E^\circ F = -1.91\text{ F}}
\end{array}$$

$$\Rightarrow \quad E^\circ = 1.91/2 = 0.955\text{ V.}$$

544. $$Q = It = 100\times 1.5\times 3600 = 5.4\times 10^5\text{C}$$

$$\Rightarrow \quad \text{number of faradays} = \frac{Q}{96500} = 5.596 = \text{number of gram equivalent of } Cu^{2+} \text{ deposited mass of}$$

$$Cu^{2+} \text{ deposited as Cu} = 5.596\times\frac{63.5}{2} = 177.673\text{ g}$$

Also, vol. of $O_2(g)$ produced at anode at STP = $5.596\times 5.6 = 31.34$ L.

Also; $$\text{initial moles of } Cu^{2+} = 4.0$$

$$\text{final moles of } Cu^{2+} = 4.0 - \frac{5.596}{2} = 1.2$$

$$\Rightarrow \quad \text{molarity of } CuSO_4 \text{ in final solution} = \frac{1.2}{2} = 0.6\text{ M}$$

545. (a)

$$\begin{array}{lcr}
 & Cu(s) \longrightarrow Cu^+(aq) + e & E^\circ = -0.52\text{ V} \\
 & Cu^{2+}(aq) + e \longrightarrow Cu^+(aq) & E^\circ = 0.16\text{ V} \\
\hline
\text{adding} & Cu(s) + Cu^{2+}(aq) \rightleftharpoons 2Cu^+(aq) & E^\circ = -0.36\text{ V}
\end{array}$$

Negative E° value indicates that the above reaction is non-spontaneous.

Also $$\Delta G^\circ = -nE^\circ F = -RT\ln K$$

$$\Rightarrow \quad \ln K = \frac{nE^\circ F}{RT} = \frac{-0.36\times 96500}{8.314\times 298} = -14.02 \quad \Rightarrow \quad K = 8.14\times 10^{-7}$$

(b) The reaction is combination of:

$$\begin{array}{lcl}
 & Cu(s) + Cu^{2+}(aq) \rightleftharpoons 2Cu^+(aq) & K = 8.14\times 10^{-7} \\
 & 2Cu^+(aq) + 2Br^-(aq) \rightleftharpoons 2CuBr(s) & K = \dfrac{1}{K_{sp^2}} \\
\hline
\text{Adding :} & Cu(s) + Cu^{2+}(aq) + 2Br^-(aq) \rightleftharpoons 2CuBr(s) & K = \dfrac{8.14\times 10^{-7}}{k_{sp^2}}
\end{array}$$

Now, E° for the given cell is 0.5147 V.

$$\Rightarrow \quad E^\circ F = RT\ln K \quad \Rightarrow \quad \ln K = \frac{0.5147\times 96500}{8.314\times 298} = 20.04$$

$$\Rightarrow \quad K = 5.086\times 10^8 = \frac{8.14\times 10^{-7}}{K_{sp^2}} \quad \Rightarrow \quad K_{sp} = \sqrt{\frac{8.14\times 10^{-7}}{5.086\times 10^8}} = \mathbf{4\times 10^{-8}}.$$

546. (a)

$$E^\circ_{\text{cell}} = 1.36 + 0.76 = 2.12\ \text{V}$$

$$\Rightarrow \quad E_{\text{cell}} = 2.12 - \frac{0.059}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cl}^-]^2} = 2.12 - \frac{0.059}{2}\log\frac{(0.04)}{(5\times10^{-3})^2} = 2.025\ \text{V}$$

(b) On adding ammonia, following reaction will go to right quantitatively:

$$\text{Zn}^{2+}(aq) + 4\text{NH}_3 \rightleftharpoons \text{Zn(NH}_3)_4^{2+} \qquad K_f = 7.8\times10^8$$

Initial	0.04	1 M	0
Eqn.	x	1 – 0.16	0.04

$$\Rightarrow \quad K_f = 7.8\times10^8 = \frac{[\text{Zn(NH}_3)_4^{2+}]}{[\text{Zn}^{2+}][\text{NH}_3]^4} = \frac{(0.04)}{x(0.84)^4} \quad \Rightarrow \quad x = [\text{Zn}^{2+}] = 10^{-10}\ \text{M}$$

Now :

$$E = E^\circ - \frac{0.059}{2}\log\frac{[\text{Zn}^{2+}]}{[\text{Cl}^-]^2} = 2.12 - \frac{0.059}{2}\log\frac{10^{-10}}{(5\times10^{-3})^2} = \mathbf{2.28\ V}$$

547. The galvanic cell reaction is :

$$2\text{Ag}^+ + \text{Cu} \rightleftharpoons 2\text{Ag}(s) + \text{Cu}^{2+}$$

and

$$E = E^\circ - \frac{0.059}{2}\log\frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2} = E^\circ - \frac{0.059}{2}\log[\text{Cu}^{2+}] + 0.059\log[\text{Ag}^+]$$

$$\Rightarrow \quad E = K + 0.059\log[\text{Ag}^+]$$

where

$$K = E^\circ - \frac{0.059}{2}\log[\text{Cu}^+] = \text{constant in the given problem.}$$

$$\Rightarrow \quad 0.382 = K + 0.059\log[\text{Ag}^+]_1 \quad \text{and} \quad 0.01 = K + 0.059\log[\text{Ag}^+]_2$$

$$\Rightarrow \quad 0.372 = 0.059\log\frac{[\text{Ag}^+]_1}{[\text{Ag}^+]_2} \quad \Rightarrow \quad \frac{0.01}{[\text{Ag}^+]_2} = 2.0187\times10^6$$

$$\Rightarrow \quad [\text{Ag}^+]_2\ (\text{final}) = 4.95\times10^{-9}\ \text{M}$$

Also, initial mmol of Cl^- (added) $= 2 \times$ mmol of $\text{Ca}^{2+} = 2\times0.02\times250 = 10$

Initial mmol of $\text{Ag}^+ = 250\times0.01 = 2.5$

$\Rightarrow$ mmol of Cl^- left after precipitation = 7.5 $\Rightarrow$ $[\text{Cl}^-]_{\text{final}} = 0.03$ M

$$\Rightarrow \quad K_{sp}(\text{AgCl}) = [\text{Ag}^+]_2(0.03) = 4.95\times10^{-9}\times0.03 = \mathbf{1.485\times10^{-10}}.$$

548.

$$Q = It = 2.5\times35\times60 = 5250\ \text{C}$$

$$\Rightarrow \quad \text{Number of faradays} = \frac{Q}{96500} = 0.0544 = \text{number of equivalent of metal deposited.}$$

$$\Rightarrow \quad \text{Equivalent mass of metal} = \frac{3.06}{0.0544} = 56.25 \Rightarrow \text{Molar mass} = 112.5\ \text{amu.}$$

549. (a) The spontaneous cell reaction is:

$$2\text{Sn}^{2+}(aq) + \text{O}_2 + 4\text{H}^+ \rightleftharpoons 2\text{Sn}^{4+}(aq) + 2\text{H}_2\text{O} \qquad E^\circ_{\text{cell}} = 1.08\ \text{V}$$

Applying Nernst equation :

$$E = 1.08 - \frac{0.059}{4}\log\left(\frac{0.01}{0.10}\right)^2\left(\frac{1}{10^{-4}}\right)^4 = 0.8735\text{ V}$$

(b) At any instant of uses, if x M Sn^{2+} concentration is decreased, $[Sn^{4+}]$ will increase by the same amount.

$$\Rightarrow \qquad 0.8 = 1.08 - \frac{0.059}{4}\log\left[\left(\frac{0.01+x}{0.10-x}\right)^2 \times 10^{16}\right]$$

Solving $\quad x = 0.0966\text{ M} \;\Rightarrow\; [Sn^{4+}] = 0.1066\text{ M}; \quad [Sn^{2+}] = 0.0034\text{ M}$

550. $$E_1 = E^\circ + 0.059\,\text{pH}_1 \quad \text{and} \quad E_2 = E^\circ + 0.059\,\text{pH}_2$$

$$\Rightarrow \qquad E_2 - E_1 = 0.16 = 0.059\,(\text{pH}_2 - \text{pH}_1) \;\Rightarrow\; \text{pH}_2 = 12.11$$

551. The electrolysis reaction is :

$$2Cu^{2+} + 2H_2O \longrightarrow 2Cu + 4H^+ + O_2$$

$$\text{Number of faradays of electricity passed} = \frac{4\times 30\times 60}{96500}$$

$$= 0.0746 = \text{number of gram equivalent of } H^+ \text{ produced.}$$

$$\Rightarrow \qquad \text{molarity of } H^+ = \frac{0.0746}{0.20} = 0.373 \;\Rightarrow\; \text{pH} = \mathbf{0.43}$$

552. Iron will be deposited first. The cell reaction would be :

$$Fe^{2+} + H_2O \longrightarrow Fe + 2H^+ + \tfrac{1}{2}O_2$$

$$E^\circ = -0.44 - 1.23 = -1.67\text{ V}$$

$$\Rightarrow \qquad E = -1.67 - \frac{0.059}{2}\log\frac{[H^+]^2}{[Fe^{2+}]} = -1.4\text{ V}$$

⇒ A minimum of 1.4 V would be required for the onset of electrolysis.

553. Reduction half-reaction is :

$$M^+_{(aq)} + e \longrightarrow M(s)$$

$$E_1 = E^\circ - 0.059\log\frac{1}{[M^+]_1} = E^\circ + 0.059\log[M^+]_1$$

$$\Rightarrow \qquad E_2 = E^\circ + 0.059\log[M^+]_2 = E^\circ + 0.059\log 10^{-2}[M]_1^+$$

$$= E_1 + 0.059\log 10^{-2} = E_1 - 0.118\text{ V}$$

i.e., lowering applied potential by **0.118 V**.

554. $$E^\circ_{\text{cell}} = 1.66 - 0.44 = 1.22\text{ V}$$

$$E_{\text{cell}} = 1.2 = 1.22 - \frac{0.059}{6}\log\frac{[Al^{3+}]^2}{[Fe^{2+}]^3}$$

$$\Rightarrow \qquad \log\left\{\frac{[Al^{3+}]^2}{[Fe^{2+}]^3}\right\} = 2.033$$

$$\Rightarrow \qquad \frac{[\mathrm{Al}^{3+}]^2}{1.25\times 10^{-10}} = 108 \quad \Rightarrow \quad [\mathrm{Al}^{3+}] = 1.16\times 10^{-4}\,\mathrm{M}$$

$\Rightarrow$ moles of Al^{3+} in sauce $= 1.16\times 10^{-4}\times 0.1 = 1.16\times 10^{-5}$

$\Rightarrow$ mass of Al dissolved $= 1.16\times 10^{-5}\times 27 = 3.132\times 10^{-4}\,\mathrm{g}$

$\Rightarrow$ vol. of of Al-foil dissolved $= \dfrac{3.132\times 10^{-4}}{2.7} = 1.16\times 10^{-4}\,\mathrm{cm}^3$

$\Rightarrow$ area of holes $= \dfrac{V}{\text{thickness}} = \dfrac{1.16\times 10^{-4}}{0.1} = 1.16\times 10^{-3}\,\mathrm{cm}^2.$

555. $$1500 = n(28.8-2) = 26.8\,n \quad \Rightarrow \quad n = \frac{1500}{26.8}\,\text{mol } \mathrm{H_2} \text{ required}$$

$\Rightarrow$ $2n$ faraday of electric current would be required

$$\Rightarrow \qquad Q = 2\times \frac{1500}{26.8}\times 96500 = 8.5\,t. \quad \Rightarrow \quad t = 353 \text{ hours.}$$

556. The electrodes reaction are :

$$\begin{array}{rlr}
\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e & & 0.76\ \mathrm{V} \\
2\mathrm{H}^+ + 2e \longrightarrow \mathrm{H_2} & & 0.00\ \mathrm{V} \\
\hline
\text{Cell reaction:}\quad \mathrm{Zn} + 2\mathrm{H}^+ \longrightarrow \mathrm{Zn}^{2+} + \mathrm{H_2} & & E^\circ = +0.76\ \mathrm{V}
\end{array}$$

Now, applying Nernst equation :

$$E = 0.72 = 0.76 - \frac{0.059}{2}\log\frac{0.1}{[\mathrm{H}^+]^2} \quad \Rightarrow \quad [\mathrm{H}^+] = 0.0664\ \mathrm{M}$$

For $\mathrm{HIO_3}$:
$$\begin{array}{ccc}
\mathrm{HIO_3} \rightleftharpoons & \mathrm{H}^+ + & \mathrm{IO_3^-} \\
0.1-x & x & x
\end{array}$$

$$K_a = \frac{x^2}{0.1-x} = \frac{(0.0664)^2}{0.1-0.0664} = \mathbf{0.13}$$

557. mmol of Cu^{2+} electrolyzed in 30 min $= (0.1-0.0528)\,100 = 4.72$
meq of Cu^{2+} deposited $= 9.44 =$ number of mF. $\because\ Q = It$

$$\Rightarrow \qquad 9.44\times 10^{-3}\times 96500 = \mathrm{I}\times 30\times 60 \quad \Rightarrow \quad I = 0.5\ \mathrm{A}$$

i.e., meter is showing only 80% of the actual current.

558. The spontaneous cell reaction is :

$$2\mathrm{Cr}^{2+} + \mathrm{Ni}^{2+} \rightleftharpoons 2\mathrm{Cr}^{3+} + \mathrm{Ni} \qquad E^\circ = +0.16\ \mathrm{V}$$

$$E = 0.11\ \mathrm{V} = 0.16 - \frac{0.059}{2}\log\frac{[\mathrm{Cr}^{+3}]^2}{[\mathrm{Cr}^{+2}]^2[\mathrm{Ni}^{+2}]} = 0.16 - \frac{0.059}{2}\log\frac{2.56\times 10^{-4}}{[\mathrm{Ni}^{+2}]}$$

$$\Rightarrow \qquad [\mathrm{Ni}^{2+}] = \mathbf{5.16\times 10^{-6}\ M}.$$

559. (a) The electrode reactions occurring are:

$$2H_2O + 2e \longrightarrow H_2 + 2OH^- \quad : \text{ at cathode}$$

$$2H_2O \longrightarrow 4H^+ + O_2 + 4e \ : \text{ at anode}$$

Since, phenolphthalein is colourless below a pH value of 8 and pink above a pH values of 10. At the start of electrolysis, both the solutions will be colourless. As electrolysis proceeds, cathode compartment will become basic and will acquire pink colouration while anode compartment will become more and more acidic and remains colourless.

(b) If electrolysis is stopped at any stage, the two compartments, cathode and anode compartment, will have same number of gram equivalent of hydroxide and hydronium ions. Therefore, if the content of two compartments are mixed, the net result will be formation of a neutral solution and it will be colourless.

(c) As electrolysis proceed, HO^- will be produced and will be neutralized with HCl added from out side. At end point when the whole HCl is neutralized, solution will acquire alkaline nature if electrolysis is carried on further and will become pink coloured.

$$\Rightarrow \qquad Q = \frac{25 \times 10^{-3} \times 8 \times 60}{96500} \text{ F} = 1.24 \times 10^{-4} = \text{equivalents of HCl in 10 mL.}$$

$$\Rightarrow \qquad \text{Molarity of HCl} = \frac{1.24 \times 10^{-4}}{0.01} = \mathbf{0.0124\ M}$$

560. Given :

$$\begin{array}{rlr} HgI_4^{2-} + 2e & \rightleftharpoons Hg + 4I^- & E^\circ = -0.04\text{ V} \\ Hg & \rightleftharpoons Hg^{2+} + 2e & E^\circ = -0.85\text{ V} \\ \hline \text{Adding : } HgI_4^{2-} & \rightleftharpoons Hg^{2+} + 4I^- & E^\circ = -0.89\text{ V} \end{array}$$

Writing Nernst equation :

$$E = -0.89 - \frac{0.059}{2} \log \frac{[Hg^{2+}][I^-]^4}{[HgI_4^{2-}]}$$

At equilibrium

$$E = 0 = -0.89 - \frac{0.059}{2} \log K_d$$

$$\Rightarrow \qquad K_d = 6.768 \times 10^{-3} = \frac{1}{K_f} \quad \Rightarrow \quad \boldsymbol{K_f = 1.47 \times 10^{30}}.$$