COVENANT UNIVERSITY NIGERIA

TUTORIAL KIT OMEGA SEMESTER

PROGRAMME: CHEMISTRY

COURSE: CHM 421

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1. Devise and describe a cell in which the reaction is $Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$
2. What is the potential of the half-cell consisting of Zn electrode in 0.01M ZnSO4 at 25^oC, E^o= 0.763V
3. Calculate the emf of the cell, $Zn_{(s)}$ - Zn^{2+}(0.001M) - - Ag^+(0.1M) - Ag

   Standard Reduction Potential of Ag - Ag^+ = 0.80V, $Zn_{(s)}$ - Zn^{2+} = -0.76V
4. Balance the following equation for a redox reaction in an alkaline medium:

   $CrI_{3(s)} + H_2O_2 + OH^- \rightarrow CrO_4^{2-} + IO_4^- + H_2O$
5. Differentiate between galvanic and electrolytic cells.

In an experiment designed to study the electrochemistry of the element Q, it was decided to examine the oxidation: $Q_{(s)} \rightarrow Q^{2+}_{(aq)} + 2e$, E^o = 0.5.

This oxidation may be brought about by constructing a cell using the electrode $Q_{(s)}$ - $Q^{2+}_{(aq)}$ and one of the following electrodes:

6. $A^{2+}_{(aq)}$ - $A_{(s)}$, E^o_{Red} = -0.76V
7. $B^{2+}_{(aq)}$ - $B_{(s)}$, E^o_{Red} = 0.80V

Explain which of these should be used in the construction.

8. Calculate the free energy change of the following cell at 25^oC:

   $Sn_{(s)}$ - Sn^{2+}(0.5M) - - Pb^{2+}(0.3M) - Pb

The standard EMF of the cell is 0.14 V.

Define or explain the following:

9. Standard hydrogen electrode (SHE)
10. Standard reduction potential of $Q_{(s)}$ - $Q^{2+}_{(aq)}$ Electrode

EVEN QUESTIONS

1. Differentiate between absorption and adsorption.

2. State the Freundlich adsorption isotherm.

3. Comment on why many adsorptions do not fit the Langmuir adsorption isotherm.

4. State the Langmuir adsorption isotherm equation and define the terms.

5. State the assumptions on which the Langmuir adsorption isotherm equation was derived.

6. Distinguish between physisorption and chemisorptions.

7. Under what conditions can (i) physisorption and (ii) chemisorption be reversed?

8. In chemisorption, (i) sometimes the gas desorbed may not be the same as the gas adsorbed; (ii) sometimes the gas desorbed is the same as the gas adsorbed. Give an example in each case.

9. Give an example of a case in which the same system displays physisorption at one temperature and chemisorption at another.

10. $As_2S_3 + H^+ + NO_3^- + H_2O \rightarrow H_3AsO_4 + NO_{(g)} + S_{(s)}$

ANSWERS

1. This cell is the Daniel cell. It is a simple voltaic cell which is constructed by placing a bar of zinc metal (anode) in zinc sulphate solution in a left container. A bar of copper (cathode) is immersed in copper sulphate solution in the right container. The zinc and copper electrodes are joined by a copper wire. When the cell is set up, electrons flow from zinc electrode through the wire to the copper cathode.

The standard cell can be represented as $Zn|Zn^{2+}(aq) || Cu^{2+}(aq) | Cu$

and the electrode reactions are:

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

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

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2. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Using the Nernst equation: $E = E^0 - \dfrac{2.303RT}{nF}\log K$

Calculation of half cell potential for an oxidation half cell rxn, $M \rightarrow M^{n+} + ne^-$

$$E = E^0 - \frac{2.303RT}{nF}\log\frac{[M^{n+}]}{[M]}$$

The concemtration of a solid metal is zero

Therefore, $E = E^0 - \frac{2.303RT}{nF}\log[M^{n+}]$

$$E = 0.763 - \frac{0.0591}{2}\log[0.01]$$

E = 0.822 V

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

Using Nernst equation, $E = E^0_{cell} - \frac{0.0591}{n}\log K$

$$K = \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.80 - (-0.76) = 1.56$ V

$$E_{cell} = 1.56 - \frac{0.0591}{2}\log\frac{[10^{-3}]}{[10^{-1}]^2}$$

E_{cell} = 1.59 V [4 marks]

4. The balance equation is as follows:
   I. The two half reactions are: Oxidation: $CrI_3 \rightarrow IO_4^- + CrO_4^{2-}$; Reduction: $H_2O_2 \rightarrow H_2O$
   II. Balance other atoms apart from H and O.

   $CrI_3 \rightarrow 3IO_4^- + CrO_4^{2-}$

   $H_2O_2 \rightarrow H_2O$

   III. Balance H and O

   $32OH^- + CrI_3 \rightarrow 3IO_4^- + CrO_4^{2-} + 16H_2O$

   $H_2O_2 + H_2O \rightarrow H_2O + 2OH^-$

   IV. Balance charge: In the first equation, there are 32 negative charges on the left and 5 negative charges on the right. So we add 27 electrons to the right. In the second equation, there are 2 negatives on the right and zero on the left we therefore add 2 electrons to the left.

   $32OH^- + CrI_3 \rightarrow 3IO_4^- + CrO_4^{2-} + 16H_2O + 27e$

   $2e + H_2O_2 + H_2O \rightarrow H_2O + 2OH^-$

   V. To ensure that the number of electrons lost is equal to the number of electrons gained, we multiply the first equation by 2 and the second equation by 27.

   VI. We combine the equations to obtain

$2CrI_3 + 10OH^- + 27H_2O_2 \rightarrow 6IO_4^- + 2CrO_4^{2-} + 32H_2O$ [7 marks]

5. Electrolytic cells are those in which electrical energy from an external source causes *non-spontaneous* chemical reactions to occur while Galvanic (or Voltaic) cells are those in which spontaneous chemical reactions produce electricity and supply it to an external circuit.

6. To know the electrode to be used in the construction, we will check the feasibility of the reactionofthe two electrodes combined with $Q_{(s)}$- $Q^{2+}_{(aq)}$ electrode. The net emf of the reaction, E_{cell}, can be calculated from the expression: $E^o_{cell} = E^o_{cathode} - E^o_{anode}$

In general, if E^o_{cell} = +ve, the reaction is feasible

E^o_{cell} = -ve, the reaction is not feasible

E^o_{anode} is the standard reduction potential of $Q_{(s)} \rightarrow Q^{2+}_{(aq)} + 2e$, $E^o = 0.5$ V

$A^{2+}_{(aq)}$- $A_{(s)}$, $E^o_{Red} = -0.76$V

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = -0.76 \text{ V} – 0.5 \text{ V}$

$E^o_{cell} = -1.26$ V.

E^o_{cell} = -ve, the given reaction is not feasible hence the oxidation of $Q_{(s)} \rightarrow Q^{2+}_{(aq)}$ cannot be brought about by constructing a cell using the electrode $Q_{(s)}$- $Q^{2+}_{(aq)}$ with $A^{2+}_{(aq)}$- $A_{(s)}$. [3 marks]

7. $B^{2+}_{(aq)}$- $B_{(s)}$, $E^o_{Red} = 0.80$ V

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.80 \text{ V} – 0.5 \text{ V}$

$E^o_{cell} = 0.30$ V.

E^o_{cell} = +ve, the given reaction is feasible hence the oxidation of $Q_{(s)} \rightarrow Q^{2+}_{(aq)}$ can be brought about by constructing a cell using the electrode $Q_{(s)}$- $Q^{2+}_{(aq)}$ with $B^{2+}_{(aq)}$- $B_{(s)}$.

8. $\Delta G = -nFE$

$Sn(s) + Pb^{2+} \rightarrow Sn^{2+}(aq) + Pb$

Using Nernst equation, $E = E^0_{cell} - \frac{0.0591}{n}\log K$

$K = Sn^{2+} / Pb^{2+}$

$\Delta G = -27.020$ Kj

9. The **standard hydrogen electrode** (abbreviated **SHE**), is a redox electrode which forms the basis of the thermodynamic scale of oxidation-reduction potentials. Its absolute electrode potential

is estimated to be 4.44 ± 0.02 V at 25 °C, but to form a basis for comparison with all other electrode reactions, hydrogen's standard electrode potential (E^0) is declared to be zero at all temperatures. Potentials of any other electrodes are compared with that of the standard hydrogen electrode at the same temperature.

Hydrogen electrode is based on the redox half cell:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

This redox reaction occurs at platinized platinum electrode. The electrode is dipped in an acidic solution and pure hydrogen gas is bubbled through it. The concentration of both the reduced form and oxidised form is maintained at unity. That implies that the pressure of hydrogen gas is 1 bar and the activity of hydrogen ions in the solution is unity. The activity of hydrogen ions is their effective concentration, which is equal to the formal concentration times the activity coefficient. These unit-less activity coefficients are close to 1.00 for very dilute water solutions, but are usually lower for more concentrated solutions.

10. The standard reduction potential is the likelihood that a species will be reduced. It is written in the form of a reduction half reaction. The standard reduction potential for $Q_{(s)}$- $Q^{2+}_{(aq)}$ electrode can be determined when it is connected to a reference electrode like SHE and it gains electrons (reduction). The half cell reaction is: $Q^{2+}_{(aq)} + 2e^- \rightarrow Q_{(s)}$