CH1011 Tutorial 7 Answers

1. Define the term the **entropy** of a substance.

Entropy (S) is an *energetic term which is a measure of molecular disorder*. Entropy is an expression of the number of ways a substance can be arranged without changing the energy of the system. The importance of entropy is underscored by the second law of thermodynamics which says that all *processes occur spontaneously in the direction that increases the total entropy of the universe* (system + surroundings).
S +ve high disorder. S -ve ordered - low disorder
Entropy values are typically quoted in kJ/mol at a specified temperature in K.

State whether entropy increases of decreases in the following reactions.

$HgS(s) + O_2(g) \rightarrow Hg(g) + SO_2(g)$ increase 2 molecules **s+g** $\rightarrow$ 2 molecules **g+g**
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ decrease **3** moleculesg+g+g $\rightarrow$ **2** molecules g+g

2. Calculate the Gibbs free energy for the following reaction at 25°C and from this the value of K°.

$H_2O(l) \rightleftharpoons H_2O(g)$
$\Delta G^o = \Sigma \Delta G^o_f(\text{products}) - \Sigma \Delta G^o_f(\text{reactants})$
$= [\Delta G^o_f(H_2O(g))] - [\Delta G^o_f(H_2O(l))]$
$= [-228.6 \text{ kJ/mol}] - [-237.2 \text{ kJ/mol}]$
$= 8.6 \text{ kJ / mol}$

$T = 25 + 273 = 298K$
$\Delta G^o = -RT \ln K$

$K = e(-\Delta G^o / RT) = e(-8.6 \times 10^3 \text{ J / mol} / 8.31 \text{ J/mol K} \times 298 \text{ K}$
$= e(-3.47)$
$= 0.031$ - this means the equilibrium lies to the LHS at 25°C

3. Assign the oxidation state of sulphur in the following molecules:

SO_2	H_2SO_4	S_8
+IV	+VI	0

4. The electrode Ag(s) AgCl(s) Cl^-(aq), for which the half-reaction is $AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$ and $E^o = +0.223V$, can be used to measure chloride ion concentrations. The e.m.f. of the following cell is +1.059V at 298K.

- What is the cell reaction?
- What is the standard free energy change ΔG^o for the cell reaction?
- Calculate the concentration of chloride ion in the sea water sample.

Zn(s)	Zn^{2+}(aq) c = 0.01M	sea water (Cl^-)	AgCl(s)	Ag(s)

$Zn(s) \rightarrow Zn^{2+}_{(aq)} + 2e^-$
$2AgCl(s) + 2e^- \rightarrow 2Ag(s) + 2Cl^-_{(aq)}$

Cell Reaction: $Zn(s) + 2AgCl(s) \rightarrow Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} + 2Ag(s)$

$\Delta G^o = -n\,F\,E^o_{cell} = -n\,F\,(E^o_{cathode} - E^o_{anode})$

$= -2 \times 96500 \times (0.223 - -0.761)$

$= -2 \times 96500 \times 0.984J$

$= -190$ kJ

$$E_{cell} = E^o_{cell} - \frac{RT}{nxF}\ln\left(\frac{[Zn(aq)^{2+}]x[Cl(aq)^-]^2 x[Ag(s)]^2}{[Zn(s)]x[AgCl(s)]^2}\right)$$

$$\therefore 1.059 = E^o_{cell} - \frac{8.314 \times 298}{2x96500}\ln\left\{\frac{0.01 \times [Cl^-]^2 \times 1^2}{1 \times 1^2}\right\}$$

$$\therefore 1.059 = 0.984 - \frac{2477.572}{193000}\ln\{[0.01][Cl^-]^2\}$$

$\therefore$ 1.059 = 0.984 - {(0.01284) $ln[Cl^-]^2$ + 0.01284 $ln[0.01]$}

$\therefore$ 1.059 = 0.984 - (0.01284 x 2) $ln[Cl^-]$ + 0.059

(if you have problems with this see BLB Appendix A.2 Logarithms)

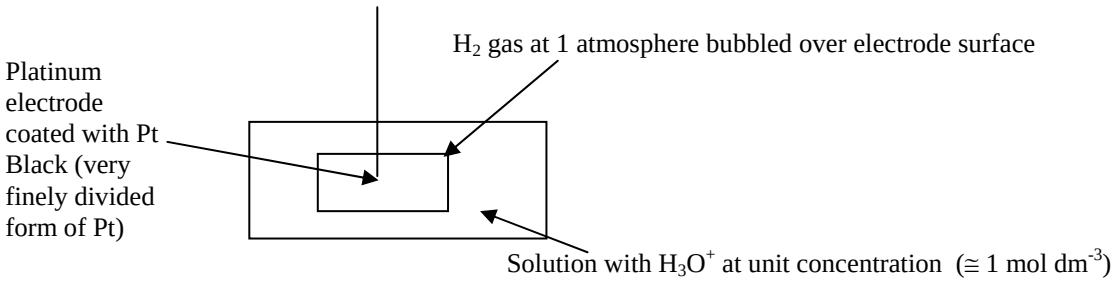
$\therefore$ 1.059 = 0.984 - 0.02567 $ln[Cl^-]$ + 0.059

$-(0.016/0.02567) = ln[Cl^-]$

Hence **$[Cl^-] = 0.536$ mol dm^{-3}**

5. Using an example illustrate the chief features of a **gas-ion electrode**.

Standard Hydrogen Electrode is an example of a typical gas/ion electrode.



Hydrogen gas at 1 atmosphere (unit pressure) is adsorbed at the surface of the electrode in contact with a solution containing H_3O^+ at unit concentration ($[H_3O^+] \cong 1$ mol dm^{-3}). This is the standard reference electrode against which all redox couples are measured, either directly or indirectly, it is used as the anode in standard reference cells.

6. (a) It has turned out after a recent legal battle that Duracell® alkaline batteries really do last longer than their competitors.

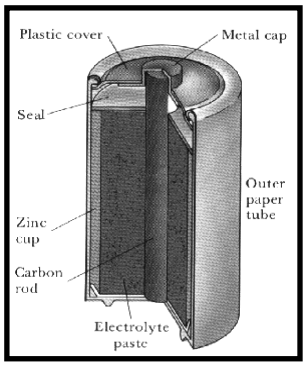
- Why do alkaline batteries outperform standard dry cell batteries?
- Sketch the essential features of a **primary battery**.

(4 marks)

Dry Cell

Anode : $Zn_{(s)} \rightarrow \quad Zn^{2+}_{(aq)} + 2e^-$

Cathode : $2NH_4^+{}_{(aq)} + 2MnO_{2(s)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$



Alkaline Cell

Anode : $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2e^-$

Cathode : $2MnO_{2(s} + H_2O + 2e^- \rightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$

The difference between the two batteries is in terms of the presence of a weak acid in the dry cell NH_4^+ and strong base in the alkaline battery (KOH). These materials are present in the electrolyte paste which fills the inside of the battery. The case is made of Zn and in the presence of weak acid this corrodes. This does not occur in the alkaline battery. The dry cell generates NH3 gas which diffuses only slowly away from the cathode and the equilibrium response is to limit the current drain from the dry cell.