

Fayoum university
Faculty of engineering

course: Engineering chemistry
Semester: 1st

*Final Engineering chemistry Exam for Pre-Engineering Students January
2010*

Answer of Q1

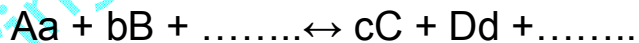
- | | | | |
|--------|---------|---------|----------|
| (1) b | (2) iii | (3) d | (4) c |
| (5) iv | (6) a | (7) a | (8) c |
| (9) c | (10) c | (11) b | (12) a&c |
| (13) b | (14) c | (15) ii | |

Answer of Q2

(a) If the reactant gases obey the ideal gas laws, the partial pressure of each gas involving in the reaction is given by

$$P = n/v RT$$

When n/v is equal to the molar conc. Thus, for the general reaction,



$$K_p = \frac{P_c^c P_D^d / P_A^a P_B^b}{(RT)^a \cdot [B]^b (RT)}$$

$$= [C]^c [D]^d \dots (RT) / [A]^a [B]^b \dots (RT)$$

$$= [C]^c [D]^d \dots / [A]^a [B]^b \dots (RT)$$

$$\text{But, since } K_c = [C]^c [D]^d / [A]^a [B]^b$$

$$\text{So } K_p = K_c (RT)^{\Delta n}$$

Where $\Delta n = [(c+d+\dots) - (a+b+\dots)]$ is equal to the difference in the total number of moles of gaseous products and reactants. Δn can be zero, positive or negative.

When $\Delta n = 0$, $K_p = K_c$
When $\Delta n = +Ve$, $K_p > K_c$
When $\Delta n = -Ve$, $K_p < K_c$

(b) The reaction



No of moles at eqm. $n(1-\alpha)$ $n\alpha/2$ $n\alpha/2$

$n = 2.40$ moles and $\alpha = 0.22$

No of moles of HI at eqm = $n(1-\alpha) = 2.40(1-0.22)$
= 1.872 moles

No of moles of H₂ at eqm = $n\alpha/2 = 2.40 \times 0.22/2$
= 0.264 moles

No of moles of I₂ at eqm = $2.40 \times 0.22/2$
= 0.264 moles

$$K_c = 0.0199$$

(c)

i- Forms of corrossions

1-General or Uniform Corrosion

In such corrosion there is a uniform decrease in the volume of a metal by chemical action. In such a reaction soluble corrosion products are formed. In this type of corrosion every exposed atom of the exposed surface of a metal reacts exactly in the **same manner with the** corrosive medium. In practice such an ideal case rarely occurs.

In such type of corrosion, metal is converted into soluble corrosion product at a constant rate. The rate of the corrosion is predictable and can be controlled to some extent. Example of such a type of corrosion is action of acids on some metals and action of amphoteric metals such as AL, Pb, and Zn on steel and iron and the tarnishing of silverware. When the surface or the environments are not uniform, the attack does not remain general but becomes concentrated at places causing pitting.

2- Pitting Corrosion

Sometimes corrosion may be concentrated at some places and at other places it may be less. Thus pits or holes are formed. Pitting is another form of very localized corrosion attack in which small pits or holes are formed. They ordinarily penetrate from the top of a horizontal surface down ward in a nearly vertical direction.

The reasons of pitting are the following:

- (I) Surfaces of metals are not uniform or not homogenous.
- (II) External environments are not homogenous.
- (III) Corrosion products may be insoluble

(IV) Films are not uniformly perfect.

Mechanism of Pitting

The mechanism for pitting is probably as the same as for crevice in that oxidation occurs within the pit itself, with complementary reduction at the surface. It is supposed that gravity causes the pits to grow downward, The solution at the pit tip becoming more concentrated and dense as pit growth progress. A pit may be initiated by a localized surface defect such as a scratch or a slight variation in composition. In fact, it has been observed that specimens having polished surfaces display a greater resistance to pitting corrosion. Pitting is neither uniform nor has it a constant rate. Pitting occurs mostly in chloride solutions containing a depolarizer either oxygen or oxidizing salts. Reduction of chloride ion concentration reduces pitting. Stainless steels are some what susceptible to this form of corrosion, however, alloying with about 2-4 % molybdenum, pitting can be decreased.

Velocity Factor

Pitting is usually associated with stagnant conditions such as a liquid in a tank or liquid trapped in a low part of an inactive pipe system. Velocity or increasing velocity, often decreases pitting attack, for example, a stainless steel pump would give good service handling seawater if it were run continuously, but would pit if it were shut down for extended periods.

PH

As PH is increased, the corrosion progress from general corrosion to highly localized pitting. Becoming at PH 4, the pits are covered by a cap of corrosion products. At PH 12, the corrosion products assume an unusual tubular shape and corrosion rates are 17,000 mpy at the bottom of the tube 1.

Prevention

Materials that show pitting, or tendencies to pit, during corrosion tests should not be used to build the plant or equipment under consideration. The best procedure is to use materials that are known not to pit in the environment under consideration.

3-Crevice Corrosion

Electrochemical corrosion may also occur as a consequence of concentration differences of ions or dissolved gases in the electrolyte solution, and between two regions of the same metal piece. For such a concentration cell, corrosion occurs in the local that has the lower concentration. A good example of this type of corrosion occurs in crevices and recesses or under deposits of dirt or corrosion products of dissolved oxygen. Corrosion preferentially occurring at these positions is called crevice corrosion. The crevice must be wide enough for the solution to penetrate, yet narrow enough for stagnancy, usually the width is several thousands of an inch.

The proposed mechanism for crevice corrosion is illustrated in fig. after oxygen has been depleted within the crevice, oxidation of the metal occur of this position to equation. Electrons from this electrochemical reaction are conducted through the metal to adjacent external regions, where they are consumed by reduction most probably reaction. In many aqueous environments, the solution within the crevice has been found to develop high concentration of H and CL ions.

Crevice corrosion may be prevented by using welded instead of riveted or bolted joints, using non absorbing gaskets when possible, removing accumulated deposits frequently, and designing containment vessels to avoid stagnant areas and ensure complete drainage.

ii-Cathodic Protection

The basis of Cathodic protection is shown in the polarization diagram for Cu-Zn cell. If polarization of the cathode is continued by use of an external current beyond the corrosion potential to the open-circuit potential of the anode, both electrodes reach the same potential and no corrosion of the zinc can take place. Cathodic protection is accomplished by supplying an external current to the corroding metal on the surface of which local action cells operates, as shown in the following figure. Current flows from the auxiliary anode and enters the anodic and Cathodic areas of the corrosion cell , returning to the source of the DC current. Current will cease to flow when all the

metal surface is at the same potential as a result of the cathodic areas being polarized by an external current to the open-circuit potential of the anodes. As long as this external current is maintained, the metal can't corrode.

The corrosion rate will remain at zero if the metal is polarized slightly beyond the open-circuit potential of the anode. However, this excess current has no value and may be injurious to amphoteric metals or coatings. Hence, in actual practice, the impressed current is maintained close to theoretical minimum.

If the current should fall below that required for complete protection, some protection will still be afforded.

iii- passivity

some normally active metals and alloys, under particular environmental conditions, lose their chemical reactivity and become externally inert. This phenomenon, termed passivity, is displayed by chromium, iron, nickel, titanium and many of their alloys. It is felt that this passive behavior results from the formation of a highly adherent and very thin oxide film on the metal surface, which serves as a protective barrier to further corrosion. Stainless steels are highly resistant to corrosion in a rather wide variety of atmospheres as a result of passivation. They contain at least 11% chromium which, as a solid-solution alloying element in iron, minimizes the formation of rust instead, a protective surface film forms in oxidizing atmospheres. Aluminum is highly corrosion resistant in many environments because it also passivates. If damaged, the protective film normally reforms very rapidly. However, a change in the character of the environment. Many cause a passivated material to revert to an active state. Subsequent damage to a preexisting passive film could result in a

substantial increase in corrosion rate, by as much as 100,000 times.

Question 3;

a) Define;

1-**Electrode potential:** Is the potential difference formed across the phase boundary or the double layer.

2-**Corrosion;** It is the destruction or deterioration of a material because of reaction with its environment—destruction of materials by means other than straight mechanical Or extractive metallurgy in reverse.

3-**Polarization;** The rate of an electrochemical reaction is limited by various physical and chemical factors. Hence; an electrochemical reaction is said to be polarized or retarded by these environmental factors. polarization can be divided into two different types, activation polarization and concentration polarization.

b) Consider an electrochemical cell in which one mole of M ion requires the passage of n faradays or nf coulombs to be reduced to M. according to the equation;



This charge nf is thus passed through a potential difference of E Volt. so that the electrical work done is the product of potential and charge is given by nFE. This work done at constant temperature and pressure's equal to the decrease in the free energy of the system dG, and is given by

$$dG = -nFE$$

Or $dG = -nFE$ (dG is the free energy change of the system when the activity is unity and is known as the standard free energy change) The activity is related to the free energy by the Vant Hoff reaction equation

$$dG = dG + RT \ln a_{M^+}/a_M$$

$$\text{Since } dG = -nFE \text{ and } dG = -nFE$$

$$= nFE = -nFE + RT \ln a_{M^+}/a_M$$

dividing by $-nF$ one obtains the Nernst equation

$$E = E - RT/nF \ln a_{M^+}/a_M$$

At $T=298K$, $R=8.31j$ mole/degree and $F=9600$ coul

Nernst equation becomes;

$$E = E + 0.0591/n \log a_{Mn^+}(\text{Oxid.})/a_M(\text{Red.})$$

C-Explain the

composition and mechanism of the following(illustrate your answer with equation whenever possible):-

I- Clark cell

This is quite similar to the Weston Cadmium cell but the Cd amalgam is replaced by a 10% Zn amalgam and the electrolyte is a saturated solution of $ZnSO_4$. Therefore Clark cell can be represented as follows:

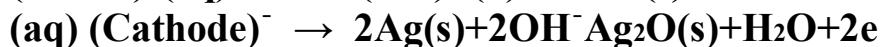
10%Zn amalgam / $ZnSO_4.H_2O(S)$ || $ZnSO_4$ Sat.

Solu| $HgSO_4(S)Hg$ The EMF of the cell is 1.4325V at $15^\circ C$ with temp coefficient of -11.4×10^{-4} V / degree.

ii-Alkaline Battery:

These tiny and rather expensive batteries have become popular as power sources in electronic wristwatches, auto exposure cameras, and electronic calculators. The cathode reactant is silver oxide, Ag_2O , and the anode once again is zinc .

The electrode reactions occur in a basic electrolyte.

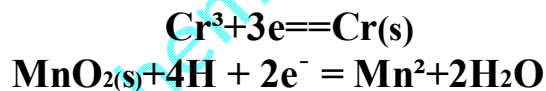


The emf of this battery is about 1.5V

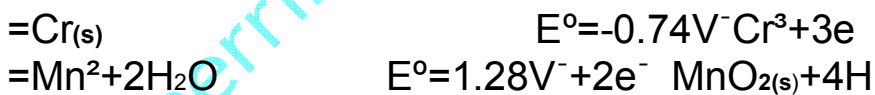
iii-Oxygen electrode:

$$\begin{aligned} \text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- &= 4 \text{OH}^- \\ E &= E^\circ + 0.059/4 \log P_{\text{O}_2} - a_{\text{H}^+}/a_{\text{OH}^-} \\ \text{If we consider that} \\ a_{\text{O}_2} = P_{\text{O}_2} &= 1 \text{ atm and } a_{\text{H}_2\text{O}} = 1 \\ E &= E^\circ + 0.059/4 \log 1/a_{\text{OH}^-} \\ &= +0.401 - \text{where } E^\circ_{\text{O}_2/\text{OH}^-} = 0.401 - 0.059 \log a_{\text{OH}^-} \\ &= 0.401 + 0.059 \text{pOH} \\ &= 0.401 + 0.059(14 - \text{pH}) \quad \text{where } \text{pH} + \text{pOH} = 14 \\ &= 1.23 - 0.059 \text{pH} \\ &= 1.23 - 0.059 \text{pH} \quad \text{At } 25^\circ \text{C } E_{\text{O}_2/\text{OH}^-} \end{aligned}$$

D-What will be the spontaneous reaction between the following two half-reaction ? what is the value of E°?



Answer



According to the value of E°

The anodic reaction :

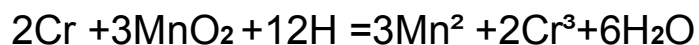


The cathodic reaction is:



The overall reaction :

Model Answer First year students Faculty of Engineering
Dr / Mohamed M. El Rabiei



$$E^\circ_{\text{cell}} = E^\circ_{\text{c}} + E^\circ_{\text{a}} \\ = 1.28 - (-0.74) = +2.02\text{V}$$

$$\text{Log}K = n E^\circ_{\text{cell}} / 0.0591 = 6 \times 2.02 / 0.0591 = 68.5$$

$$K = 10^{68.5}$$

So it is spontaneous reaction

With my best wishes

Dr. Mohamed M. El – Rabiei

Engineering chemistry Model Answer