Thermodynamics and Its Application on Corrosion

Thermodynamics can provide a basis for the understanding of the energy changes associated with the corrosion reaction. It can, in general, predict when corrosion is possible. Thermodynamics cannot predict corrosion rates. The rate at which the reaction proceeds is governed by kinetics.

Free Energy Change

The tendency for any chemical reaction to go, including the reaction of a metal with its environment, is measured by Gibbs free energy change (AG).

1- If the change in free energy accompanying the transition of a system from one state to another is negative, this indicates a loss in free energy and also the spontaneous reaction direction of the system.

AG = - spontaneous reaction direction

2- If the change in free energy is positive, this indicates that the transition represents an increase in energy, and this requires that additional energy be added to the system. These principle are illustrated in the figure

AG = + un spontaneous reaction direction

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The more negative the value of AG, the greater is the tendency for the reaction to go. For example:

1- $Mg + H_2O_{(L)} + 1/20_{2\,(g)} \rightarrow Mg(OH)_2$ AG°=-142600 cal

2- $Cu + H_2O_{(L)} + 1/2O, \rightarrow Cu(OH)_2$ AG°= -28000 cal

The free energy is positive, indicating that the reaction has no tendency to go at all,For example:

3- $Au + 3/2H_2O) + 3/2\ 02_{(g)} \rightarrow Au(OH)_3$ AG=+15700 cal

Cell Potential

Electrochemical cells generate electrical energy due to electrochemical reactions. The electrical energy available is:

$$\text{Electrical energy} = \text{volts} \times \text{current} \times \text{time}$$

$$= \text{volts} \times \text{coulombs}$$

$$= E\,Q$$

where:

$$Q = nF$$

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n is the number of electrons involved in the chemical reaction

F is Faraday's constant = 96 500 $Cmol^{-1}$

E is electromotive force (emf) of the cell (volts).

Any work performed can only be done through a a decrease in free energy of the cell reaction , hence

$$AG=-nFE$$

where:

AG = free energy change.

E = potential of the reaction.

n = number of electrons involved in the reaction.

F = Faraday's constant.

Nernst Equation

Consider the system in which metallic iron is immersed in a solution of copper sulfate. In course of time metallic copper begins to appear. This process is known as a cementation reaction.

Then, we may write the reactions occurring as:

$Fe \rightarrow Fe_2+ +2e$ Oxidation (anodic)

$Cu_2+ +2e- \rightarrow Cu°$ Reduction (cathodic

$Fe + Cu^2+ Fe_2+ + Cu°$

The equilibrium constant K and the free energy change in the overall cementation reaction may be written as:

$$AG = AG^{\circ} + RT\ In \frac{[Fe2+][Cu^{\circ}]}{[Fe^{\circ}]\ [Cu2+]}$$

Since the corrosion of iron in copper sulfate solution involves an oxidation and reduction reactions with exchange of electrons, the reaction must involve an electrochemical potential difference, related to the equilibrium constant. This relationship may be written as (Under standard state conditions):

$$AG^{o} = -nFE^{o}$$

Neglecting solids we may write, for the reaction of iron in copper sulfate solution:

$$-nFE = -nFE^{\circ} + RT\ In \frac{[Fe2+]}{[Cu2+]}$$

Division by -nF leads to:

$$E = E^{o} - \frac{RT}{nF}\ In \frac{[Fe2+]}{[Cu2+]}$$

In general terms

$$E = E^{o} - \frac{RT}{nF}\ In \frac{[Product]}{[Reactant]}$$

Converting to log and T = 298, and inserting numerical F; R values:

$$E = E^{o} - \frac{0.059}{2} \log \frac{[Product]}{[Reactant]}$$

This equation is known as the Nernst equation, and is extensively used in electrochemical measurements.

Example (1)

For the cell [$Cu/Cu^{2+}(1.0M)$]//[$Zn^{2+}(1.0M)/Zn$], and the cell reaction

$Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn$:

If $\Delta G^{\circ}_{298K} = -147.5$ kJ mol^{-1} for Zn^{2+}

and $\Delta G^{\circ}_{298K} = 63.35$ kJ mol^{-1} for Cu^{2+}

does the reaction take place simultaneously?

Solution:

AG Reaction = ∑ n AG(i)− ∑ n¡AG(j)

where

i = products

j = reactants

$\therefore \Delta G^{\circ}_{Reaction} = 2\ [63.35 + 0 - (-147.5 + 0)]$

$\Delta G^{\circ}_{Reaction} = 425.1$ kJ mol^{-1}

Since,

$\Delta G^{\circ}_{Reaction} = -\ n\ F\ E^{\circ}$

425.1 kJ mol^{-1} $= 2 \times 96500$ C mol$^{-1} \times E^{\circ}$

$E^{\circ} = -0.002$ V

Reaction does not take place simultaneously.

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Example (2)

Represent the cell in which the following reaction takes place. Calculate its $E_{(cell)}$ if $E_{(cell)}^{\circ} = 3.17$ V.

$Mg_{(s)} + 2Ag^{+}\,(0.0001M) \rightarrow Mg^{2+}\,(0.130M) + 2Ag^{(s)}$,

Solution:

$Mg_{(s)} \rightarrow Mg^{2+} + 2e^{-}$

$2Ag^{+} + 2\,e^{-} \rightarrow 2Ag_{(s)}$ n=2

$$E = E^{\circ} - \frac{0.059}{n}\log\frac{[\mathrm{Product}]}{[\mathrm{Reactant}]}$$

$$E_{cell} = E^{\circ}{}_{cell} - \frac{0.059}{2}\log\frac{[Mg^{2+}]}{[Ag^{+}]^{2}}$$

$$E_{cell} = 3.17 - \frac{0.059}{2}\log\frac{0.13}{(0.0001)^{2}}$$

$$E_{cell} = 2.96\,V$$

Example (3)

For Daniel cell, Calculate the standard Gibbs energy for the reaction:

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

$$E^{\circ}_{Zn/Zn2+} = -0.763\ V$$

$$E^{\circ}_{Cu/Cu2+} = 0.337\ V$$

Solution:

$Zn_{(s)} \rightarrow Zn^{2+} + 2e^{-}$ $\quad E^{\circ}_{Zn/Zn2+} = -0.763\ V$

$Cu^{2+} + 2\ e^{-} \rightarrow Cu_{(s)}$ $\quad E^{\circ}_{Cu/Cu2+} = 0.337\ V$ $\quad n= 2$

$$E^{\circ}_{cell} = E^{\circ}_{Cu/Cu^{2+}} - E^{\circ}_{Zn/Zn^{2+}}$$

$$E^{\circ}_{cell} = 0.337 - (-0.763)$$

$$E^{\circ}_{cell} = 1.1\ V$$

$$\Delta G^{\circ}_{cell} = -\ n\ F\ E^{\circ}_{cell}$$

$$= -\ 2 * (96500\ C/mol) * (1.1\ V)$$

$$= 212300\ J/mol = 212.3\ KJ/mol$$

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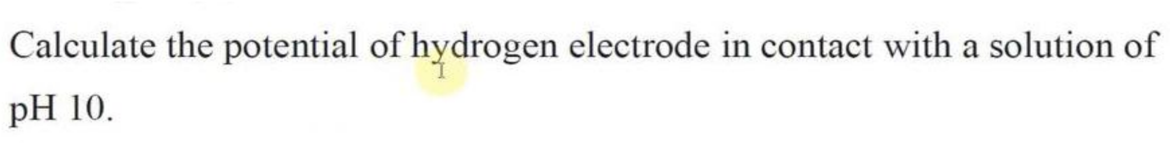
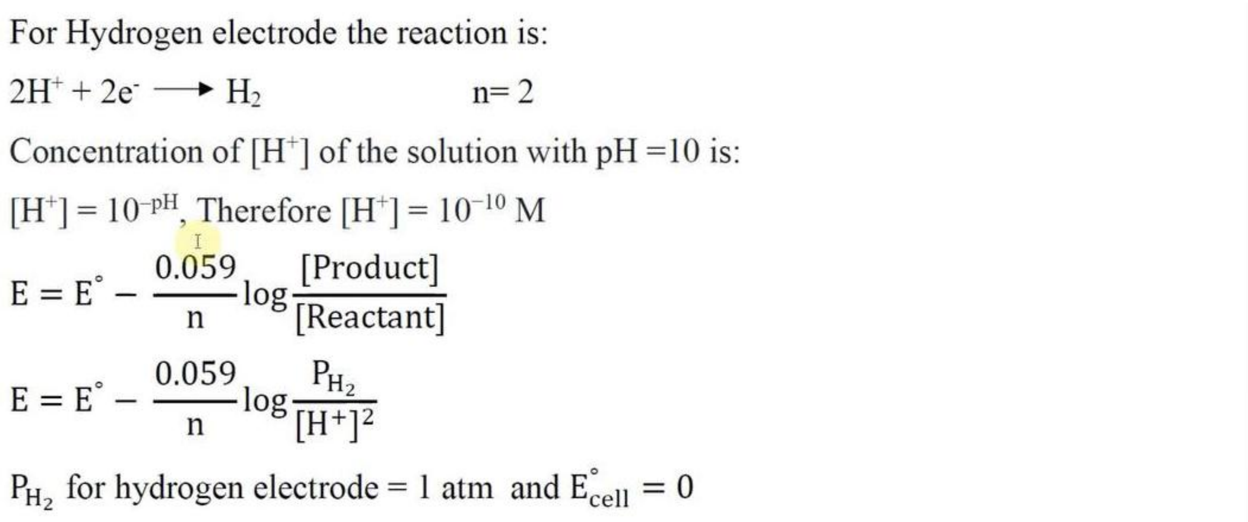
Example (4)



Calculate the potential of hydrogen electrode in contact with a solution of pH 10.

Solution:



For Hydrogen electrode the reaction is:

$2H^+ + 2e^- \longrightarrow H_2$ n= 2

Concentration of $[H^+]$ of the solution with pH =10 is:

$[H^+] = 10^{-pH}$, Therefore $[H^+] = 10^{-10}$ M

$$E = E^\circ - \frac{0.059}{n}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^\circ - \frac{0.059}{n}\log\frac{P_{H_2}}{[H^+]^2}$$

P_{H_2} for hydrogen electrode = 1 atm and $E^\circ_{cell} = 0$

$$E = 0 - \frac{0.059}{2}\log\frac{1}{(10^{-10})^2}$$

$$E = -0.59\ V$$

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Example (5)

Determine the thermodynamic tendency for silver to corrode in a deaerated acid solution of pH = 1.0 Assume $\alpha_{Ag^+} = 10^{-6}$ and $P_{H_2} = 1$atm.

$$Ag + H^+ \longrightarrow Ag^+ + 1/2\ H_2$$

$$E^\circ_{Ag/Ag+} = 0.799\ V$$

Solution:

$$Ag \longrightarrow Ag^+ + e^- \qquad E^\circ_{Ag/Ag+} = 0.799\ V$$

$$H^+ + e^- \longrightarrow 1/2H_2 \qquad E^\circ_{H2/H+} = 0\ V \qquad n = 1$$

$$E^\circ_{cell} = E^\circ_{H_2/H^+} - E^\circ_{Ag/Ag^+}$$

$$E^\circ_{cell} = 0 - 0.799$$

$$E^\circ_{cell} = -0799\ V$$

$$E = E^\circ - \frac{0.059}{n}\log\frac{[Product]}{[Reactant]}$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{[Ag^+].(P_{H_2})^{1/2}}{[H^+]}$$

$$[H^+] = 10^{-pH}$$

$$[H^+] = 10^{-1} = 0.1\ M$$

$$[H^+] = 10^{-1} = 0.1\ M$$

$$E_{cell} = -0.799 - \frac{0.059}{1}\log\frac{10^{-6} * 1}{0.1}$$

$$E_{cell} = -0.504\ V$$

$$\Delta G_{cell} = -n\ F\ E_{cell}$$

$$\Delta G_{cell} = -1 * 96500\ C/mol * -0.504\ V$$

$$\Delta G_{cell} = +48636\ J/mol \qquad \Delta G = +\ \text{silver will not corrode}$$

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