

temperature in degrees Kelvin, °K, which is (273.16 + t°C). At 25°C

Subtracting equation (2.50) from equation (2.49), we get:

$$\Delta G - \Delta G^\circ = (G_{M_2} - G_{M_2}^\circ) + (G_{M_1^{n+}} - G_{M_1^{n+}}^\circ) - (G_{M_1} - G_{M_1}^\circ) - (G_{M_2^{n+}} - G_{M_2^{n+}}^\circ)$$

Substituting from equation (2.51), we obtain:

$$\begin{aligned} \Delta G - \Delta G^\circ &= RT \ln a_{M_2} + RT \ln a_{M_1} \\ &\quad - RT \ln a_{M_1} - RT \ln a_{M_2^{n+}}, \\ \Delta G - \Delta G^\circ &= RT \ln \left[\frac{a_{M_2} a_{M_1^{n+}}}{a_{M_1} a_{M_2^{n+}}} \right] \end{aligned} \quad (2.52)$$

where the 'a' values are any arbitrary activity values, for which ΔG is the corresponding free energy of that reaction. ΔG° is the free energy change for the reaction involving standard states (unit activities).

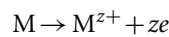
As ΔG = -nFE, and also ΔG° = -nFE°, from equations (2.44) and (2.45), respectively, the above equation (2.52) becomes:

$$E - E^\circ = \frac{RT}{nF} \ln \left[\frac{a_{M_1} a_{M_2^{n+}}}{a_{M_2} a_{M_1^{n+}}} \right] \quad (2.53)$$

whence

$$E - E^\circ = \frac{RT}{nF} \ln \left[\frac{a_{\text{product}}}{a_{\text{reactants}}} \right]$$

Suppose



$$\begin{aligned} E_M &= E_M^\circ - \frac{RT}{nF} \ln [a_M^{z+} \times z a_e^z] \\ &= E_M^\circ - \frac{RT}{nF} \ln [a_M^{z+}] \end{aligned}$$

because a_M and $a_e = 1$.

$$E_M = E_M^\circ - \frac{0.059}{2} \log [a_M^{z+}]$$

Equation (2.53) is a general form of the Nernst equation. It expresses the emf involved in an electrochemical reaction, such as equation (2.46) in terms of R, T, F, n activities of products and activities of reactants. However, the IUPAC sign convention requires the above minus sign to be replaced by a plus sign. The Nernst equation is re-written to comply with the IUPAC sign convention, as:

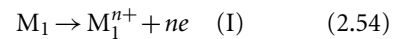
$$E = E^\circ + \frac{RT}{nF} \ln \frac{\text{oxidized state activities product}}{\text{reduced state activities product}}$$

which is written *regardless* of which way round the redox reaction is written. Hence, for Zn = Zn⁺⁺ + 2e⁻, and for Zn⁺⁺ + 2e⁻ = Zn,

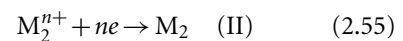
$$E = E^\circ + \frac{RT}{nF} \ln a_{Zn^{++}}.$$

2.11.1 APPLICATION OF NERNST EQUATION TO A CORROSION REACTION

A corrosion reaction can be considered as composed of two half cell reactions. One of the half cell reactions corresponds to 'oxidation reaction' taking place on the 'anode,' and the other half cell reaction corresponds to 'reduction reaction' taking place on the 'cathode' of the cell. The contribution of each half cell reaction to the Nernst expression can be derived as follows:



oxidation reaction at anode, and



reduction reaction at cathode.

Equation (2.53) can also be re-arranged into expressions to correspond to reactions (I) and (II):

$$E = E_1 + E_2 \quad (2.56)$$

$$E = \left[E_1^\circ + \frac{RT}{nF} \ln \left(\frac{a_{M_1}}{a_{M_1}^{n+}} \right) \right] + \left[E_2^\circ + \frac{RT}{nF} \ln \left(\frac{a_{M_2}^{n+}}{a_{M_2}} \right) \right] \quad (2.57)$$

where

E° = standard potential, and $E^\circ = E_1^\circ + E_2^\circ$

$$E_1 = E_1^\circ + \frac{RT}{nF} \ln \left[\frac{a_{M_1}}{a_{M_1}^{n+}} \right] \quad (2.58)$$

$$E_2 = E_2^\circ + \frac{RT}{nF} \ln \left[\frac{a_{M_2}^{n+}}{a_{M_2}} \right] \quad (2.59)$$

and

$$E = E^\circ + \frac{RT}{nF} \ln \left[\frac{a_{M_1} a_{M_2}^{n+}}{a_{M_1}^{n+} a_{M_2}} \right] \quad (2.60)$$

Equations (2.58) and (2.59) are Nernst equations for the half cell reactions and equation (2.60) is the Nernst equation for the complete cell reaction. Equation (2.60) can be put into a mathematical form:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{\text{activities of reactants}}{\text{activities of products}} \quad (2.61)$$

But, in addition to this statement (2.61), a sign convention is necessary as already mentioned and this will be discussed in the next section. Since

$$\frac{RT}{nF} \ln = \frac{2.303 \times 8.314 \times (273 + 25)}{96500} = 0.05915 \text{ at } 25^\circ\text{C} \quad (2.62)$$

Equation (2.60) is more commonly used in the form of

$$E = E^\circ + \frac{0.05915}{n} \times \log \frac{\text{product of activities of reactants}}{\text{product of activities of products}} \quad (2.63)$$

The expression (2.61) can also be written with the activities inverted, as

$$E = E^\circ - \frac{RT}{nF} \ln \frac{\text{product of activities of products}}{\text{product of activities of reactants}} \quad (2.64)$$

But this equation is incomplete without a sign convention.

Quite separate from the above considerations, standard Redox potentials are tabulated with reactive metals like Zn negative instead of positive, which accords with the experimental fact that Zn will *actually* become negative because when Zn^{++} ions leave it, then two electrons will appear in the Zn metal, to maintain a charge balance.

Such reduction potentials are given in Table 2.1. By convention the cell reaction is written as if the oxidation process is occurring at the electrode on the left and reduction on the right. This practice is in accordance with the International Union of Pure and Applied Chemistry (IUPAC) Convention held in 1953 and modified in 1960.

2.12 SIGN CONVENTION

The older American Convention has been to use oxidation potentials rather than reduction potentials. The present practice is to use reduction potentials instead of oxidation potentials in accordance with the recommendation of IUPAC (International Union of Pure and Applied Chemistry) and existing European practice – the general convention is that the cell emf is given by:

$$E_{\text{cell}}^\circ = E_{\text{Right}}^\circ - E_{\text{Left}}^\circ$$

The standard hydrogen electrode (SHE) is the reference point. The construction of hydrogen

electrode is shown in Fig. 2.10. By definition, SHE has zero potential at 25°C. It is assumed that oxidation occurs at the hydrogen electrode so that it is placed at the left-hand side of a cell diagram. If a cell is composed of SHE and some other electrode, then the measured voltage of the cell is the electrode potential of the second electrode:

$$E_{\text{cell}} = E_x - 0$$

$$E_{\text{cell}} = E_x$$

For example, in a galvanic cell made of a hydrogen electrode and a zinc electrode [Zn/Zn²⁺ (1.0 M)], the measured voltage is $E = -0.763$ volts.

$$E_{\text{cell}}^{\circ} = E_{\text{Zn}}^{\circ} - E_{\text{H}_2}^{\circ}$$

$$E_{\text{cell}}^{\circ} = -0.763 \text{ V}$$

In the older textbooks, *hydrogen electrode was placed on the right, and the cell potential becomes:*

$$E_{\text{cell}} = E_{\text{H}_2} - E_x$$

The reaction was made oxidation and the sign was changed. Thus the electrode potential $E_{\text{Zn/Zn}^{2+}}^{\circ}$ is +0.763 volts according to old convention.

$$E_{\text{cell}}^{\circ} = E_{\text{H}_2}^{\circ} - (E_{\text{Zn}}^{\circ}), \quad E_{\text{Zn}}^{\circ} = +0.763 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Zn}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = 0.763 \text{ volts}$$

which is opposite to that shown above. This should clarify the confusion caused in student's minds by different conventions. The simplest procedure avoids specifying 'right' and 'left' by just writing:

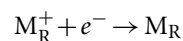
$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{\text{oxidized state activities product}}{\text{reduced state activities product}}$$

which is written regardless of which way round the chemical equation is written.

2.12.1 CELL EMF AND THE DIRECTION OF SPONTANEOUS REACTION

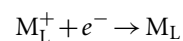
The following is a step-by-step procedure to apply the above sign convention to a cell reaction in order to determine cell emf and direction of spontaneous reaction correctly.

- (1) Write the right-hand electrode reaction. The right-hand electrode reaction is always *reduction* and the electron is always a reducing agent:



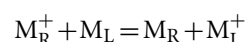
And reduction electrode potential is E_R° .

- (2) Write the left-hand electrode reaction. The left-hand electrode reaction is *oxidation*. However, we write it as reduction reaction because of the convention we are using:



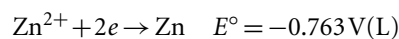
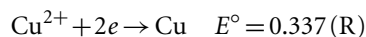
And the reduction electrode potential is E_L° .

- (3) Subtract the left-hand electrode reaction and potential from those of right-hand electrode to obtain cell reaction and cell potential:



$$\text{and } E_{\text{cell}}^{\circ} = E_R^{\circ} - E_L^{\circ}$$

For example, calculate E° for the Daniel cell. From the table of reduction potentials, write the corresponding reactions:



$$E_{\text{cell}} = E_R^{\circ} - E_L^{\circ}$$

$$= 0.337 - (-0.763 \text{ V})$$

$$= 1.100 \text{ V}$$

Another example: Using a cell of Pb^{2+}/Pb and Sn^{2+}/Sn , calculate E_{cell}° :

$$E_{cell}^{\circ} = E_R^{\circ} - E_L^{\circ}$$

$$L \rightarrow R$$

$$R \rightarrow L$$

$$= -0.126 - (-0.136)$$

$$= 0.10V$$

$$M^+ + e \rightarrow M$$

$$Zn \rightarrow Zn^{++} + 2e$$

$$Cu^{++} + 2e \rightarrow Cu$$

2.12.2 POSITIVE AND NEGATIVE EMF

A positive emf ($E > 0$) signifies a deficiency of electrons on the right-hand electrode because of the extraction of electrons from that electrode.

Therefore, the tendency of the right-hand electrode is reduction (acceptance of electron; $M_R + e = M_R$, if $E > 0$). At the same time, positive emf signifies an excess of electrons on the left-hand electrode. Therefore, the electrode reaction is oxidation ($M_L = M_L^+ + e$) on that electrode. Thus, if $E > 0$, the cell reaction has a tendency to proceed from left to right: that is, electrons are produced by the left-hand electrode and consumed by the right-hand electrode. It also indicates that the reaction is spontaneous.

Conversely, if $E < 0$, the reaction at the right-hand electrode is oxidation and the reaction at the left-hand electrode reduction. The tendency of the reaction would, therefore, be to proceed from right to left and the reaction would not be spontaneous. Figure 2.11 explains the flow of electrons in the two situations explained above. The same convention can also be understood in terms of flow of positive current (positive charged ions). It is to be noted that according to the convention, if a cell is short circuited, and the positive current flows through the electrolyte from left to right, the emf is positive. In this case the left-hand electrode is the anode and the right-hand electrode

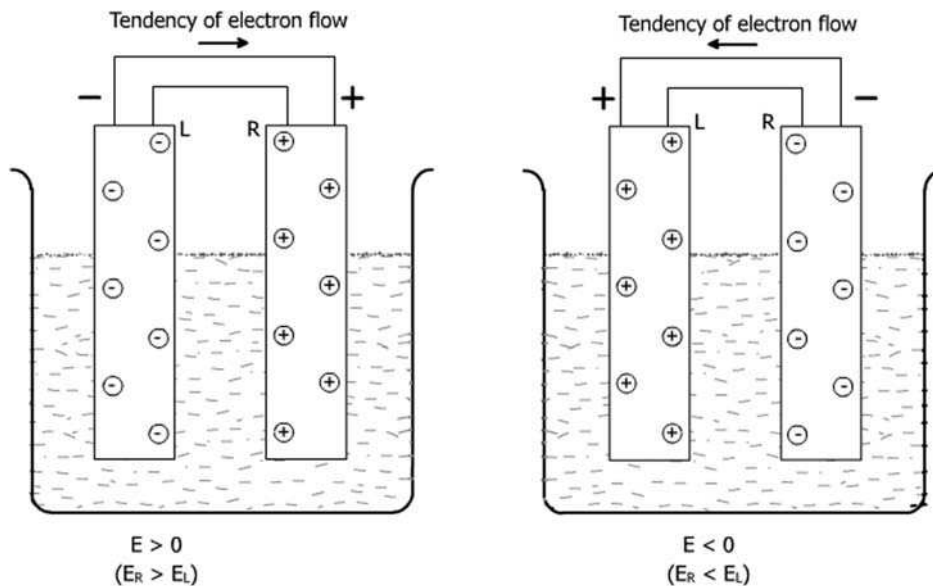


Figure 2.11 Implications of the sign convention

Table 2.2 Current flow conventions

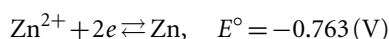
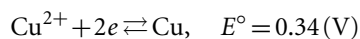
emf	Current flow	Anode	Cathode
+	L → R	L	R
-	R → L	R	L

the cathode. If the current flows from right to left, the emf is negative. Table 2.2 summarizes the current flow convention in a cell.

From knowledge of cell potential it is thus possible to predict whether a reaction would proceed spontaneously or not. From knowledge of potential of half cells, and the cell potentials, it is possible to predict whether a metal is an anode or cathode or whether a corrosion reaction is likely to take place or not. An understanding of electrode potential is of fundamental importance to the understanding of corrosion mechanism. This is illustrated in typical problems given below.

Illustrative Problem 2.4

Two half cell reactions are given below:



Their reduction potentials are given opposite to each reaction. Calculate:

- the emf of the cell and
- show the spontaneous cell reaction.

Solution:

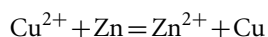
In Fig. 2.2, the left-hand electrode (Zn) is the anode and the right-hand electrode (Cu) is the cathode according to the convention we studied earlier on. Therefore, zinc will undergo oxidation and copper reduction as shown below. Hence:

- $E_{\text{cell}}^\circ = E_{\text{R}}^\circ - E_{\text{L}}^\circ$ (according to IUPAC convention)

$$E_{\text{cell}}^\circ = E_{\text{Cu}}^\circ - E_{\text{Zn}}^\circ \\ = 0.337 - (-0.763)$$

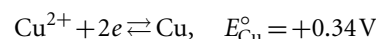
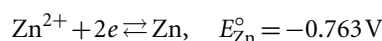
$$E_{\text{cell}}^\circ = +1.100 \text{ volts}$$

- Spontaneous cell reaction is given by:
cell reaction = cathodic reaction = anodic reaction

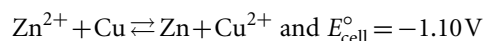


From the table of standard reduction potentials (Table 2.1), the reduction potential of Cu is +0.34 volts and that of Zn is -0.76 volts. The emf of the cell is positive. Hence the reduction is spontaneous and it should proceed from left to right.

If the position of the electrodes are now interchanged such that the copper electrode is placed on the left and the zinc electrode on the right, the sign of the cell emf will change. Here, zinc electrode being on the right is treated as cathode and the copper on the left as anode according to the convention discussed earlier in the chapter. Therefore:



Subtracting anodic reaction from cathodic reaction to obtain the cell reaction



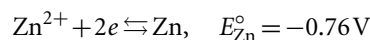
The emf obtained is now negative which indicates that the reaction is not spontaneous and the current flows from right to left. The left-hand electrode where the current originates is, therefore, the *anode*, and the right-hand electrode, the *cathode*. The polarity of the cell is, therefore, clearly established.

Illustrative Problem 2.5

Calculate the reversible potential for a zinc electrode in contact with ZnCl_2 when the activity of zinc is $a_{\text{Zn}^{2+}} = 10^{-3}$, Use IUPAC convention.

Solution:

We write the half cell reaction



Apply Nernst equation:

$$E_{\text{Zn}} = E_{\text{Zn}}^\circ + \frac{RT}{nF} \ln [a_{\text{Zn}^{2+}}]$$

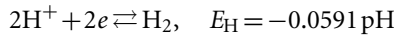
$$E_{\text{Zn}} = -0.76 + \frac{0.059}{2} \log [a_{\text{Zn}^{2+}}]$$

$$E_{\text{Zn}} = -0.76 + 0.03 \log [10^{-3}]$$

$$E_{\text{Zn}} = -0.85 \text{ V}$$

Illustrative Problem 2.6

Show that for the reduction reaction given below:



Solution:

The reaction is $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$. Using Nernst equation we obtain for the above reaction:

$$E_{(\text{H}^+/\text{H}_2)} = E_{(\text{H}^+/\text{H}_2)}^\circ + \frac{RT}{nF} \ln \frac{[\text{reactants}]}{[\text{products}]}$$

$$\text{or } E_{(\text{H}^+/\text{H}_2)} = E_{(\text{H}^+/\text{H}_2)}^\circ + \frac{RT}{nF} \ln \frac{[\text{oxidized state}]}{[\text{reduced state}]}$$

(IUPAC–Nernst)

Changing to 2.303 log and substituting for

$$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K}), \quad F = 96490 \text{ C},$$

$$T = 298^\circ \text{K}, \quad 2.303RT/F = 0.0591 \text{ V}.$$

The Nernst expression above can, therefore, be written as:

$$E_{(\text{H}^+/\text{H}_2)} = E_{(\text{H}^+/\text{H}_2)}^\circ + 0.059 \log[\text{H}^+]$$

Now substituting $\text{pH} = -\log(\text{H}^+)$ in the above expression we get:

$$E_{(\text{H}^+/\text{H}_2)} = -0.0591 \text{ pH}$$

Illustrative Problem 2.7

Show that for the reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightleftharpoons 4(\text{OH}^-)$,

$$E_{(\text{O}_2/\text{OH}^-)} = E_{(\text{O}_2/\text{OH}^-)}^\circ - 0.0591 \log a_{\text{OH}^-}$$

Solution:

The reaction is $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightleftharpoons 4(\text{OH}^-)$ (in a basic solution), and

$$E_{(\text{O}_2/\text{OH}^-)} = E_{(\text{O}_2/\text{OH}^-)}^\circ + \frac{RT}{nF} \ln \frac{a_{\text{O}_2}}{(a_{\text{OH}^-})^4}$$

Note that O_2 is the oxidized state and OH^- is the reduced state, for the above reaction (from IUPAC–Nernst expression).

The activity (a_i) of an ion is defined by $a_i = M_1 \gamma_i$, where $M_1 =$ molality (mol/kg) of

the ions in the solution, and a_i is the activity coefficient. The activity coefficient a_i for a given concentration can be found from a table of activity coefficients given at the end of the chapter. In dilute solutions, the activity coefficient is taken to be unity.

If we take $a_{\text{O}_2} = P_{\text{O}_2}/P^\circ = 1$, when $P_{\text{O}_2} = P^\circ = 1$ bar, standard state, and $R = 8.314 \text{ J}/\text{mol} \cdot \text{K}$, $F = 96485 \text{ C}/(\text{g equiv.})^{-1}$, $T = 298^\circ \text{K}$, and the term $2.303RT/F = 0.0591$, and substitute in the above expression, the oxygen electrode potential becomes:

$$E_{(\text{O}_2/\text{OH}^-)} = E_{(\text{O}_2/\text{OH}^-)}^\circ - 0.0591 \log a_{(\text{OH}^-)}$$

It can similarly be shown that in *acid solution* for a reaction, $\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 2\text{H}_2\text{O}$, the oxygen electrode potential becomes:

$$E_{(\text{O}_2)} = E_{(\text{O}_2)}^\circ + \frac{RT}{4nF} \ln \frac{a_{(\text{O}_2)} (a_{\text{H}^+})^4}{a_{\text{H}_2\text{O}}}$$

Substituting the values for the constants as above, we get:

$$E_{(\text{O}_2)} = E_{(\text{O}_2)}^\circ + 0.0592 \log a_{\text{H}^+}$$

or since $\text{pH} = -\log a_{\text{H}^+}$,

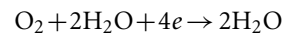
$$E_{(\text{O}_2)} = E_{(\text{O}_2)}^\circ - 0.0592 \text{ pH}$$

Illustrative Problem 2.8

Calculate the potential of oxygen electrode at $\text{pH} = 14.0$.

Solution:

Oxygen electrode reaction: in basic and neutral environment is expressed as:



Electrode potential equation for the electrode at 25°C is given by Illustrative Problem 2.7:

$$E_{\text{O}_2} = E_{\text{O}_2}^\circ - 0.0592 \log a_{(\text{OH}^-)}$$

where

$$\log a_{(\text{OH}^-)} = -14 - \log a_{(\text{H}^+)}$$

$$= -14 + \text{pH}$$

(from the knowledge of pH)

Therefore,

$$E_{O_2} = E_{O_2}^{\circ} - 0.0592(-14 + \text{pH})$$

Substitute $E_{O_2}^{\circ} = 0.401$ (from Table 2.1).
Therefore,

$$E_{O_2} = 0.401 + 14 \times 0.0592 - 0.0592 \text{pH}$$

$$E_{O_2} = 0.401 + 0.828 - 0.0592 \text{pH}$$

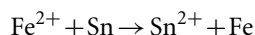
and so at $\text{pH} = 14$,

$$E_{O_2} = 0.401 + 0.828 - 0.828$$

and $E_{O_2} = 0.401$

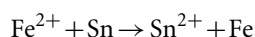
Illustrative Problem 2.9

In the cell reaction given below, what is the ratio of the activities of ionic species required to make the polarity reverse?



Solution:

Cell reaction:



Ratio of activities to make the polarity reverse at 25°C .

Standard cell potential:

$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} - E_{\text{Sn}^{2+}/\text{Sn}}^{\circ} \\ &= -0.441 - (-0.140) \\ &= -0.441 + 0.140 \\ &= -0.301 \text{ volts} \end{aligned}$$

The reaction in this case is non-spontaneous. That is, Fe^{2+}/Fe electrode will act as 'anode' and Sn^{2+}/Sn electrode will act as 'cathode,' the reverse case of what was assumed in the problem.

To reverse the polarity:

Overall cell potential is given by:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} + \frac{RT}{nf} \ln \frac{[a_{\text{Reactant}}]}{[a_{\text{Product}}]} \\ &= -0.301 + \frac{2.303RT}{nF} \log \frac{a_{\text{Fe}^{2+}} a_{\text{Sn}}}{a_{\text{Sn}^{2+}} a_{\text{Fe}}} \end{aligned}$$

where: $a_{\text{Sn}} = 1$ and $a_{\text{Fe}} = 1$.

$$E_{\text{cell}} = -0.301 + \frac{2.303RT}{nF} \log \frac{a_{\text{Fe}^{2+}}}{a_{\text{Sn}^{2+}}}$$

$$E_{\text{cell}} = 0, \quad \text{At the turn of polarity.}$$

Therefore,

$$0.301 = \frac{2.303RT}{nF} \log \frac{a_{\text{Fe}^{2+}}}{a_{\text{Sn}^{2+}}}$$

$$\log \left[\frac{a_{\text{Fe}^{2+}}}{a_{\text{Sn}^{2+}}} \right] = \frac{0.301 \times nF}{2.303RT}$$

Assuming the reaction is taking place at $t = 25^{\circ}\text{C}$, $n = 2$, $T = 298^{\circ}\text{K}$, $R = 8.315 \text{ J/mol}$ and $F = 96500 \text{ C (g equiv.)}^{-1}$

Then

$$\begin{aligned} \log \left[\frac{a_{\text{Fe}^{2+}}}{a_{\text{Sn}^{2+}}} \right] &= \frac{0.301 \times 2 \times 96500}{2.303 \times 8.314 \times 298} \\ &= 6.4 \times 10^{-11} \text{ at } 25^{\circ}\text{C} \end{aligned}$$

At $20^{\circ}\text{C} \cong 5 \times 10^{-11}$

Illustrative Problem 2.10

The emf of a cell made of Zn (anode) and H_2 electrode (cathode) immersed in 0.7 M ZnCl_2 is $+0.690$ volts. What is the pH of the solution?

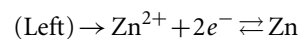
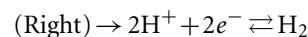
Solution:

Given:

$$[\text{Zn}^{2+}] = 0.7 \text{ M, For Zn}^{2+},$$

$$\text{activity coefficient, } \gamma = 0.6133$$

$$\therefore a_{\text{Zn}^{2+}} = 0.7 \times 0.6133 = 0.424$$



$$E_{\text{Zn}}^{\circ} = -0.762 \text{ V}$$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$\begin{aligned} &= E_{\text{H}_2}^{\circ} - \frac{0.0592}{2} [\log(\text{pH}_2) - \log(a_{\text{H}^+}^2)] \\ &- \left\{ E_{\text{Zn}}^{\circ} \frac{0.0592}{2} [\log[a_{\text{Zn}}] - \log[a_{\text{Zn}^{2+}}]] \right\} \end{aligned}$$

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$$\Rightarrow E_{\text{cell}} = -\frac{0.0592}{2}[2\text{pH}] + 0.762$$

$$+ \frac{0.0592}{2}[-\log(0.42)]$$

$$0.690 = -0.0296[2\text{pH}] + 0.762$$

$$+ 0.0296(0.376)$$

$$\Rightarrow 0.0296[2\text{pH}] = 0.762 - 0.690 + 0.011 = 0.083$$

$$\Rightarrow 2\text{pH} = \frac{0.083}{0.0296} \Rightarrow 2\text{pH} = 2.8$$

$$\Rightarrow \text{pH} = 1.4$$

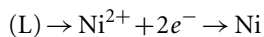
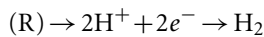
Illustrative Problem 2.11

Calculate the theoretical tendency of nickel to corrode in deaerated water of pH=8. Assume the corrosion products are H₂ and Ni(OH)₂ and the solubility product is 1.6×10^{-16} .

Solution:

Given: $K_{sp} = 1.6 \times 10^{-16}$, pH=8, $E_{\text{Ni}}^{\circ} = -0.25\text{V}$
 Since, pH+pOH=14 \Rightarrow pOH=14-8=6

$$[\text{Ni}^{2+}] = \frac{K_{sp}}{[\text{OH}^{-}]^2} = \frac{1.6 \times 10^{-16}}{10^{-12}} = 1.6 \times 10^{-4}$$



$$\Rightarrow E_{\text{cell}} = E_{\text{H}_2}^{\circ} - \frac{0.0592}{2} [\log(\text{pH}_2) - 2\log(a_{\text{H}^{+}})]$$

$$= - \left\{ \left[E_{\text{Ni}}^{\circ} - \frac{0.0592}{2} [\log(a_{\text{Ni}}) - \log(a_{\text{Ni}^{2+}})] \right] \right\}$$

$$\Rightarrow E_{\text{cell}} = -0.0296[2\text{pH}] + 0.25$$

$$+ 0.0296[-\log(1.6 \times 10^{-4})]$$

$$\Rightarrow E_{\text{cell}} = -0.0296[2 \times 8] + 0.25$$

$$+ 0.0296[4 - \log(1.6)]$$

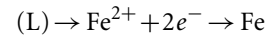
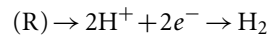
$$= -0.111 \text{ volts}$$

$$E_{\text{cell}} = -0.111 \text{ volts}$$

Illustrative Problem 2.12

Calculate the pressure of H₂ required to stop corrosion of iron immersed in 0.1 M FeCl₂, pH=4.

Solution:



$$E_{\text{Fe}}^{\circ} = +0.44$$

$$[a_{\text{Fe}^{2+}}] = \gamma \times [\text{Fe}^{2+}]$$

$$= 0.1 \times 0.75$$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}}$$

$$E_{\text{cell}} = E_{\text{H}_2}^{\circ} - 0.0296 [\log(\text{pH}_2) - \log(a_{\text{H}^{+}})^2]$$

$$- [E_{\text{Fe}}^{\circ} - 0.0296 (\log(a_{\text{Fe}}) - \log(a_{\text{Fe}^{2+}}))]$$

$$\text{Given: pH} = 4 \Rightarrow [a_{\text{H}_2}] = 10^{-4}$$

$$\Rightarrow E = E^{\circ} - 0.0296 \left[\frac{\log(\text{pH}_2) [a_{\text{Fe}^{2+}}]}{[\text{H}^{+}]^2} \right]$$

$$0 = 0.44 - 0.0296 [\log(7.5 \times 10^6) \text{pH}_2]$$

$$= \frac{0.44}{0.0296} = \log[7.5 \times 10^6] \text{pH}_2$$

$$= (7.5 \times 10^6) \text{pH}_2 = 7.32 \times 10^{14}$$

$$\text{pH}_2 = 9.7 \times 10^7 \text{ atm}$$

Illustrative Problem 2.13

Calculate if silver would corrode when immersed in 0.5 M CuCl₂ to form solid AgCl. What is the corrosion tendency?

Solution:

$$E_{\text{Cu}}^{\circ} = 0.337 \text{ V}, \quad \gamma_{\text{CuCl}_2} = 0.7$$

$$E_{\text{AgCl}}^{\circ} = 0.220$$

$$\Rightarrow a_{\text{Cu}^{2+}} = 0.47 \times 0.5 = 0.233$$

$$= 0.47 \times 2 \times 0.5 = 0.47$$