13-4 Nernst Equation:

Nernst Equation:

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

ie the effect of concentration on electrode potential.

For the half reaction.

$$aA + ne^- \rightleftharpoons bB$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{[B]^b}{[A]^a}$$

$$E = E^0 - \frac{0.05916}{n} \log \frac{[B]^b}{[A]^a}.$$

Where

E^0 = Standard reduction potential (or) Standard electrode potential, which is characteristic constant for each half - reaction.

R = gas constant (8.314 J/k.mol)

T = Temperature in kelvin

n = number of moles of electrons that appear in the half - reaction for the electrode process as it has been written.

F = Faraday constant (9.649×10^4 C/mol)

A_i = activity of species i.

$\ln$ = The nature logarithm = 2.303 log.

Examples :

Typical half-cell reactions and their correspondi
Nernst expressions follow.

(1) $Zn^{2+} + 2e^- \rightleftharpoons Zn_{(s)}$

$$E = E^0 - \frac{0.05916}{2} \log \frac{1}{[Zn^{2+}]}$$

(2) $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$

$$E = E^0 - \frac{0.05916}{1} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

(3) $2H^+ + 2e^- \rightleftharpoons H_{2\,(g)}$

$$E = E^0 - \frac{0.05916}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

(4) $MnO_4^- + 5e^- + 8H^+ \rightleftharpoons Mn^{2+} + H_2O.$

$$E = E^0 - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$$

(5) $AgCl_{(s)} + e^- \rightleftharpoons Ag_{(s)} + Cl^-$

$$E = E^0 - \frac{0.05916}{1} \log [Cl^-].$$

(6) $\frac{1}{4} P_4 \text{ (s, white)} + 3H^+ + 3e^- \rightleftharpoons PH_{3(g)}$

Phosphine

$E^0 = -0.046\,V.$

$$E = -0.046 - \frac{0.05916}{3} \log \frac{P_{PH_3}}{[H^+]^3}$$

Example :

Calculate the potential of a zinc electrode in 0.0600 M $Zn(NO_3)_2$ at 25°C.

Soln

$Zn(NO_3)_2$ is a strong electrolyte and complete dissociate.

Hence: $[Zn^{2+}] = 0.0600M$

$Zn^{2+} + 2e^- \rightleftharpoons Zn \qquad E^0 = -0.763\ V$

$$E = E^0 - \frac{0.0592}{n} \log \frac{1}{[Zn^{2+}]}$$

$$= E^0 - \frac{0.0592}{2} \log \frac{1}{[Zn^{2+}]}$$

$$= -0.763 - \frac{0.0592}{2} \log \frac{1}{0.0600}$$

$$\boxed{E = -0.799V}$$

Example:

Calculate the potential of a zinc electrode immersed in 0.01000 M NaOH and saturated with $Zn(OH)_2$ at 25°C.

Soln

$Zn(OH)_2$ has very limited solubility

$$K_{sp} = 3.0 \times 10^{-16}$$

$$\therefore K_{sp} = [Zn^{2+}][OH^-]^2 = 3.0 \times 10^{-16}$$

$$= [Zn^{2+}][0.01000]^2 = 3.0 \times 10^{-16}$$

$$\therefore [Zn^{2+}] = 3.0 \times 10^{-12}$$

$$E = E^0 - \frac{0.05916}{n} \log \frac{1}{[Zn^{2+}]}$$

$$= E^0 - \frac{0.05916}{2} \log \frac{1}{[Zn^{2+}]}$$

$$= -0.763 - \frac{0.0592}{2} \log \frac{1}{3.0 \times 10^{-12}}$$

$\because E^0 = -0.763$

$$\boxed{E = -1.104\,V}$$

Example:

Calculate the electrode potential of a silver electrode immersed in a 0.0500M solution of NaCl using (a) $E^0_{Ag^+/Ag} = 0.799\,V$ at $25^\circ c$

(b) $E^0_{AgCl} = 0.222\,V.$

Solution

(a) $Ag^+ + e^- \longrightarrow Ag_{(s)}$ $\quad E^0_{Ag^+} = 0.799\,V.$

$$k_{sp} = [Ag^+][Cl^-] = 1.82 \times 10^{-10}$$

$$\therefore [Ag^+] = \frac{k_{sp}}{[Cl^-]} = \frac{1.82 \times 10^{-10}}{0.0500} = 3.64 \times 10^{-9}\,M$$

$$\therefore E = E^0_{Ag^+} - \frac{0.0592}{n} \log \frac{1}{[Ag^+]}$$

$$= 0.799 - \frac{0.0592}{1} \log \frac{1}{3.64 \times 10^{-9}} = 0.299\,V$$

$$\boxed{E = 0.299\,V}$$

(b) $AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-$

$E^{\circ}_{AgCl} = 0.222\,V.$

$[Cl^-] = 0.0500\,M.$

$$\therefore E = E^{\circ}_{AgCl} - \frac{0.0592}{n} \log \frac{[Cl^-]}{1}$$

$$= 0.222 - \frac{0.0592}{1} \log (0.0500)$$

$$\boxed{E = 0.299\,V}$$

Nernst Equation for a complete reaction:

Nernst equation for a complete cell

$$\boxed{E = E_+ - E_-}$$

where E_+ - is the potential of the electrode attached to the positive terminal of the potentiometer.

E_- - is the potential of the electrode attached to the -ve terminal.

The potential of each half-reaction (written as reduction) is governed by a Nernst equation.

The voltage for the complete reaction is the difference between the two half-cell potentials.

Procedure for writing a net cell reaction and finding voltage:

Step 1: Write reduction both half-cell, find E°

Multiply for same electron numbers, not E°.

Step 2: Write Nernst equation for right half cell, E_+

Step 3: Write Nernst equation for left half cell, E_-

Step 4: Net cell voltage: $E^\circ = E_+ - E_-$

Step 5: Balance net cell reaction.

$E > 0$: net cell reaction goes $\rightarrow$

$E < 0$: net cell reaction goes $\leftarrow$

Measuring cell voltage:

Calculating cell voltage.

$$\Delta E^0_{cell} = V_{cell} = E^0_{cathode} - E^0_{anode}.$$

$$\Delta E^0_{cell} = V_{cell} = E^0_{right} - E^0_{left}.$$

Ex $Cd_{(s)} + 2Ag^+ \rightleftharpoons Cd^{2+}_{(aq)} + 2Ag_{(s)}$

$Ag^+ + e^- \rightleftharpoons Ag_{(s)}$ $E^0 = +0.799V$

$Cd^{2+} + 2e^- \rightleftharpoons Cd_{(s)}$ $E^0 = -0.402V$

$2Ag^+ + 2e^- \rightleftharpoons 2Ag_{(s)}$ $E^0 = +0.799V$

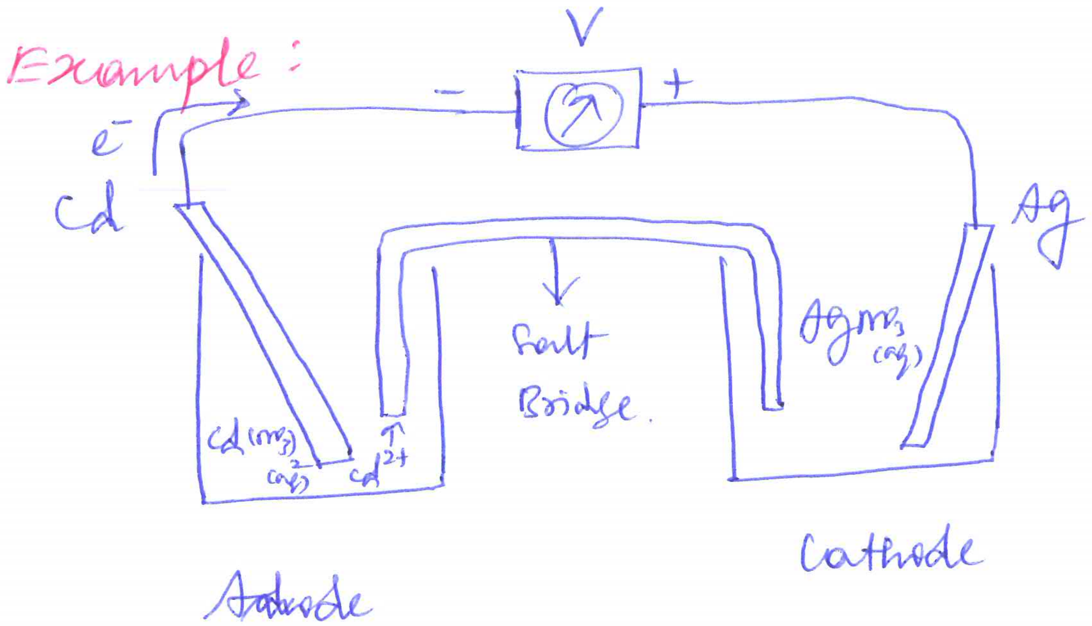
$-$ $Cd^{2+} + 2e^- \rightleftharpoons Cd_{(s)}$ $E^0 = -0.402V$

$Cd_{(s)} + 2Ag^+ \rightleftharpoons Cd^{2+}_{(aq)} + 2Ag_{(s)}$

$$E^0_{cell} = +0.799V - (-0.402V)$$

$$E^0_{cell.} = +1.201V$$

Example:



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

$$Cd_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2e^-$$

Find the ~~cell~~ voltage of the cell in the above figure if the right half-cell contains 0.50 M $AgNO_{3(aq)}$ and the left half-cell contains 0.010 M $Cd(NO_3)_{2(aq)}$. Write the net cell reaction and state whether it is spontaneous in the forward or reverse direction.

Soln

Soln

Step 1:

Right Electrode: $2Ag^+ + 2e^- \rightleftharpoons 2Ag_{(s)}$ $E_+^0 = 0.799V$

Left Electrod: $Cd^{2+} + 2e^- \rightleftharpoons Cd_{(s)}$ $E_-^0 = -0.402V$

Step 2: Nernst equation for right electrode:

∵ Pure solids, Pure liquids and solvents are omitted from Q

$$E_+ = E_+^0 - \frac{0.05916}{2} \log \frac{1}{[Ag^+]^2}$$

$$= 0.799 - \frac{0.05916}{2} \log \frac{1}{[0.50]^2} = 0.781V$$

Step 3: Nernst equation for left electrode:

$$E_- = E_-^0 - \frac{0.05916}{2} \log \frac{1}{[Cd^{2+}]}$$

$$= -0.402 - \frac{0.05916}{2} \log \frac{1}{[0.010]} = -0.461V$$

Step 4: cell voltage:

$$E = E_+ - E_-$$

$$= 0.781 - (-0.461) = +1.242V$$

Step 5: Net cell reaction:

$$2Ag^{+} + 2e^{-} \rightleftharpoons 2Ag_{(s)}$$
$$-\quad Cd^{2+} + 2e^{-} \rightleftharpoons Cd_{(s)}$$

$$Cd_{(s)} + 2Ag^{+} \rightleftharpoons Cd^{2+} + 2Ag_{(s)}$$

※ [**Note:** Subtracting a reaction is the same as reversing the reaction and adding.]

Because the voltage is +ve, the net reaction is spontaneous in the forward direction.
$Cd_{(s)}$ is oxidised and Ag^{+} is reduced.

Electrons flow from the left-hand electrode to the right hand electrode.