How are single electrode potential and rates of oxidation and reduction related?

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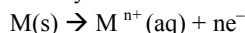**Email:** manjunath5496@gmail.com

Abstract: The Aim of this article is to establish the relationship between single electrode potential and the rates of oxidation and reduction.
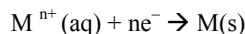
1. Single electrode potential or potential of the half cell:

Whenever a metal is in contact with a solution containing its own ions, the metal atoms have a tendency to lose electrons i.e. the metal atoms have a tendency for oxidation.

$$M(s) \rightarrow M^{n+}(aq) + ne^-$$

Metal ions of the solution have a tendency to deposit on the metal; by gaining electrons i.e. the metal ions have a tendency to undergo reduction.

$$M^{n+}(aq) + ne^- \rightarrow M(s)$$

As a result an electrical double layer is established with a corresponding potential difference between metal and solution, and is called the **single electrode potential** or **potential of the half cell**.

2. Relationship between single electrode potential and the rates of oxidation and reduction:

Considering a reversible reaction such as:

$$A+B \longleftrightarrow C+D$$
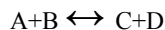
The change in free energy is given by the equation

$$\Delta G = \Delta G^0 + RT \ln Q$$

where R is the gas constant $(8.314 \text{ J K}^{-1}\text{mol}^{-1})$, T is the temperature in Kelvin scale, ln represents a logarithm to the base e, ΔG^0 is the Gibbs free energy change when all the reactants and products are in their standard state and Q is the reaction quotient or reaction function at any given time (Q = [C] [D] / [A] [B]).

We may resort to thermodynamics and write for ΔG^0

$$\Delta G^0 = - RT \ln K_{eq}$$

where K_{eq} is the equilibrium constant for the reaction.

"If K_{eq} is greater than 1, ln K_{eq} is positive, ΔG^0 is negative; so the forward reaction is favored. If K_{eq} is less than 1, ln K_{eq} is negative, ΔG^0 is positive; so the backward reaction is favored".

It can be shown that

$$\Delta G= - RT \ln K_{eq} + RT \ln Q \qquad \ldots (1.1)$$

The dependence of the reaction rate on the concentrations of reacting substances is given by the **Law of Mass Action**. This law states that the rate of a chemical reaction is directly proportional to the product of the molar concentrations of the reactants at any constant temperature at any given time.

Applying the law of mass action to the forward reaction
$$v_1 = k_1 [A] [B] \qquad \ldots (1.2)$$
where k_1 is the rate constant of the forward reaction.

Applying the law of mass action to the backward reaction
$$v_2 = k_2 [C] [D] \qquad \ldots (1.3)$$
where k_2 is the rate constant of the backward reaction.

Further, the ratio of Eq. (1.2) to Eq. (1.3) yields
$$v_1 / v_2 = k_1 / k_2 \; Q \qquad \dots (1.4)$$
But

"Equilibrium constant is the ratio of the rate constant of the forward reaction to the rate constant of the backward reaction".

and, consequently,
$$v_1 / v_2 = K_{eq} / Q \qquad \dots (1.5)$$

At equilibrium $v_1 = v_2$, hence $Q = K_{eq}$

On taking natural logarithms of Eq. (1.5) we get
$$\ln (v_1 / v_2) = \ln K_{eq} - \ln Q \qquad \dots (1.6)$$

On multiplying by $-RT$ on both sides, we obtain,
$$-RT \ln (v_1 / v_2) = - RT \ln K_{eq} + RT \ln Q \qquad \dots (1.7)$$

Comparing Eqs. (1.1) and (1.7), the Gibbs free energy change is seen to be
$$\Delta G = -RT \ln (v_1 / v_2) \qquad \dots (1.8)$$

"If the forward reaction is favored, (v_1 / v_2) is greater than 1, $\ln (v_1 / v_2)$ is positive; so the ΔG is negative. If the backward reaction is favored, (v_1 / v_2) is less than 1, $\ln (v_1 / v_2)$ is negative; so the ΔG is positive. At equilibrium $v_1 = v_2$, hence $\Delta G = 0$ ".

For the electrode reaction $M^{n+} (aq) + ne^- \longleftrightarrow M(s)$, where M^{n+} is the oxidized state and M is the reduced state. The change in Gibbs free energy (ΔG) is given by
$$\Delta G = - n F E \qquad \dots (1.9)$$
where n is the valency of the metal ion, F is the Faraday constant (96,500 coulombs) and E is the single electrode potential or potential of the half cell.

But ΔG is also related to the rates of oxidation and reduction by the equation
$$\Delta G = -RT \ln (v_{red} / v_{ox}) \qquad \dots (1.10)$$
where v_{red} and v_{ox} are, respectively, the reduction rate and oxidation rate.

If these two expressions for ΔG are equated, we obtain
$$RT \ln (v_{red} / v_{ox}) = n F E \qquad \dots (1.11)$$
and hence
$$E = (2.303RT / n F) \log (v_{red} / v_{ox}) \quad \dots (1.12)$$

At 298 K, $(2.303 \, RT / F) = (2.303 \times 8.314 \times 298) / 96,500 = 0.0591$
Hence,
$$E = (0.0591 / n) \log (v_{red} / v_{ox}) \text{ at 298 K}$$

Conclusion:

"We have thus related the single electrode potential and the rates of oxidation and reduction. If $v_{red} > v_{ox}$, $(v_{red} / v_{ox}) > 1$, $\log (v_{red} / v_{ox})$ is positive; so the electrode potential is positive. If $v_{red} < v_{ox}$, $(v_{red} / v_{ox}) < 1$, $\log (v_{red} / v_{ox})$ is negative; so the electrode potential is negative. At equilibrium $v_{red} = v_{ox}$, hence the electrode potential is zero".

Problem 1.1: Electrode potential of Zinc is – 0.831volt at 298 K. Calculate the value of (v_{red} / v_{ox}).

Solution: $E = (0.0591/ n) \log (v_{red} / v_{ox})$

           $– 0.831V = (0.0591/ 2) \log (v_{red} / v_{ox})$

                 $(v_{red} / v_{ox}) = \log^{-1} (– 28.12)$

Note: Since E is negative. Consequently, $v_{red} < v_{ox}$

Problem 1.2: Electrode potential of copper is 0.287volt at 298 K. Calculate the value of (v_{red} / v_{ox}).

Solution: $E = (0.0591/ n) \log (v_{red} / v_{ox})$

           $0.287V = (0.0591/ 2) \log (v_{red} / v_{ox})$

                 $(v_{red} / v_{ox}) = \log^{-1} (9.712)$

Note: Since E is positive. Consequently, $v_{red} > v_{ox}$

"Eq. (1.12) permits the calculation of the ratio of the reduction rate to the oxidation rate from the measured potential of the half cell".

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