

Dr. Dilip Kumar Verma.
Associate Prof,
PG Dept. of Chemistry
(PU)

SEMESTER -1V (Physical Chem)

UNIT-11

THE HAMMETT EQUATION

UNIT-1V

KINETICS OF ELECTRODE REACTION

The Hammett equation

The equilibrium constants and the rate of polar organic reactions are strongly affected by substituents on organic molecules. In 1937 Louis P. Hammett of Columbia University (U.S.A.) suggested that the effects of meta and para substituents on the ionization constants of benzoic acids could be general predictors of the electronic influences of the substituents in a variety of reactions.

Considering the effects of meta and para substituents on ionization constants, Hammett proposed an equation called Hammett equation. The equation is -

$$\log \left(\frac{K_a}{K_{a,0}} \right) = \rho \sigma \quad \text{--- (I)}$$

$$\text{or, } \log K_a - \log K_{a,0} = \rho \sigma \quad \text{--- (II)}$$

where K_a is the acidity constant for a substituted benzoic acid and $K_{a,0}$ is the acidity constant for benzoic acid. σ is the substituent constant. Hammett defined substituent constant as the logarithm of the ratio of ionization constant of a substituted benzoic acid to that of benzoic acid itself. ρ is called the reaction constant which is the slope of the line in a Hammett diagram { plot of $\log(K_a/K_{a,0})$ vs σ }

The Hammett equation is a linear free ~~and~~ energy relationship. This can be

demonstrated as follows for the case of equilibrium

Constants. For each reaction,

$$\Delta G^\circ = -RT \ln K_a$$

For unsubstituted case,

$$\Delta G_{0}^\circ = -RT \ln K_{a,0}$$

The Hammett equation is -

$$\log K_a - \log K_{a,0} = \rho f$$

$$\text{or, } \frac{-\Delta G^\circ}{2.303 RT} - \left(\frac{-\Delta G_0^\circ}{2.303 RT} \right) = \rho f$$

$$\text{or, } \frac{-\Delta G^\circ}{2.303 RT} + \frac{\Delta G_0^\circ}{2.303 RT} = \rho f$$

$$\text{or, } -\Delta G^\circ = \rho f 2.303 RT - \Delta G_0^\circ$$

For a given reaction, ρ , R , T and ΔG_0° are constants, so, σ is linear with ΔG° .

Sem-IV (Physical Chemistry)

Unit-IV Kinetics of electrode reactions

The faradic current, Non-faradic current,
Current density, Rate law in faradic processes

The Faradic Current:

The faradic current is the current generated by the reduction and oxidation of some chemical substance at an electrode. The net faradic current is the algebraic sum of all the faradic current

flowing through an indicator electrode or working electrode.

Non-Faradic current :-

The portion of the current observed in an electrochemical system that can not be attributed to any redox processes occurring at an electrode surface is called non-faradic current.

Current density, Rate law in faradic process

A metal electrode acts as a catalytic surface that facilitates transfer of electrons to and from chemical reactant molecules and ions. Thus, an electrode reaction can be viewed as a succession of following steps -

- (i) Diffusion of reactants to electrode
- (ii) Adsorption of reactants on electrode
- (iii) Transfer of electrons to or from adsorbed reactant species
- (iv) Desorption of products from electrode
- (v) Diffusion of products away from electrode

In an electrode reaction, the energy of an electric field acts on charged species, so as to help them surmount an activation energy barrier.

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For each ionic species, the rate of electron transfer occurs across an electrode in the cathodic direction or in anodic direction. Current flowed per unit area is called current density. Its unit is $A m^{-2}$.

At equilibrium, the rate of electron transfer across an electrode in the cathodic direction is exactly balanced by an equal rate of electron transfer in the anodic direction. So, the current density (i) is -

$$i_c = i_a = i_0$$

The current density at equilibrium is called exchange current density (i_0).

Rate Law :-

The rate (r) of a chemical reaction at the surface of an electrode is given by -

$$r = \frac{i}{zF}$$

where z is the charge on the ionic species and F is the Faraday. We see that in an electrochemical reaction, $r \propto i$. Thus, the rate law is - "the rate of reaction in faradic process is directly proportional to current density." The rate of chemical reaction at the electrode is expressed in units of $mol m^{-2} s^{-1}$, the rate of charge transfer at the electrode is expressed in units of $A m^{-2}$.

For a given electrochemical reaction, the electrodes are said to be

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~~nonpolarizable~~ if they have high exchange current density and polarizable if they have a low exchange current density. Application of potential difference across a nonpolarizable electrode results in an increased flow of charge between the electrode and the solution. The Calomel electrode is an example of a non-polarizable electrode.

If the applied potential difference across a polarizable electrode is increased, there is little flow of charge into the solution. The dropping mercury electrode is an example of a polarizable electrode.