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Electrochemistry

The standard state is defined as the one corresponding to $25\,^{\circ}$C (298.15 K), unit activity for all the substances in an electrochemical zero-current cell under 1 bar of pressure (10^5 Pa). For a reaction in which H^+ ions participate, the standard state is pH = 0 (approximately 1 mol acid).

In the hydrogen electrode used as the standard of electrode potential, 1 atm of hydrogen gas (a_{H+} = 1) is slowly contacted with a platinum-black electrode immersed in a strong acid solution of activity a_{H2} = 1. The potential is expressed as

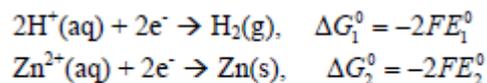$$E = E^0 + \frac{RT}{F} \ln \frac{a_{H^+}}{a_{H_2}}$$

A redox reaction takes place only when redox partners exist and a reactant can be either an oxidant or reductant depending on its reaction partner. The relative redox capability can be expressed numerically by introducing the reduction potentials E^0 of imaginary half-reactions. The free energy change ΔG^0 of a reaction is related to E^0,

$$\Delta G^0 = -nFE^0$$

Where n is the number of transferred electrons and F the Faraday constant 96500 $Cmol^{-1}$.

For example, the two reactions

$$2H^+(aq) + 2e^- \rightarrow H_2(g), \quad \Delta G_1^0 = -2FE_1^0$$
$$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s), \quad \Delta G_2^0 = -2FE_2^0$$

do not occur independently, but if both H^+(aq) and Zn (s) are present, the redox reaction takes place. The equation for the actual reaction is complete when the latter equation is subtracted from the former.

$$2H^+(aq) + Zn(s) \rightarrow H_2(g) + Zn^{2+}(aq)$$
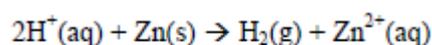
The free energy change of the whole redox reaction is the difference between for the respective half-reactions.

$$\Delta G^0 = \Delta G_1^0 - \Delta G_2^0$$
$$= -2F(E_1^0 - E_2^0)$$

Because half-reactions are not real and they are used in pairs, the free energy change of H_{01} $G\Delta^{+}$ is set to zero for convenience. Potential $E02G\Delta^{0}$ corresponding to ΔG^{0} of a half-reaction is called the **standard reduction potential**.

$$E^0 = -\frac{\Delta G^0}{nF}$$

Oxidation and reduction

Oxidation number

The oxidation number is the formal electrical charge of a component atom in a compound or in an ion allocated in such a way that the atom with smaller electronegativity has a positive charge.

Redox reactions

Originally, oxidation meant the formation of oxides from elements or the formation of compounds by the action of oxygen, and reduction is the reverse of oxidation. The present definition of **reduction** is a reaction which gives an electron, and **oxidation** is the reaction which takes an electron. Therefore, a reagent which gives an electron is a **reductant** and one which takes an electron is an **oxidant**. As a result of a redox reaction, a reductant is oxidized and an oxidant is reduced. For example, in the reaction of molybdenum metal and chlorine gas to form molybdenum pentachloride,

$$2\,Mo + 5\,Cl_2 \rightarrow Mo_2Cl_{10}$$
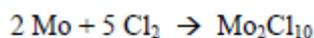
molybdencoum is a reductant and changes its oxidation state from 0 to +5 and chlorine is an oxidant and changes its oxidation state from 0 to -1.

Hydrogen bonding

One of the interesting factors critical to the understanding of chemistry and biochemistry is that of hydrogen bonding.

Hydrogen bonding is a phenomenon that arises from the properties of polar molecules. It occurs when the hydrogen center of apparent charge in a polar molecule is attracted to the negative center of apparent charge in another polar molecule.

Acid and Base

An acid–base reaction is a chemical reaction that occurs between an acid and a base, which can be used to determine pH. In 1884, Svante Arrhenius formulated the first of these definitions.

An Arrhenius acid is a source of H⊕ ion.

An Arrhenius base is a source of c- OH ion.

According to the Brønsted-Lowry definition, an acid is any molecule or ion that donates a proton to another molecule or ion, and a base is any molecule or ion that receives that proton. The following statements briefly summarize the Brønsted-Lowry definition.

A Brønsted-Lowry acid is a proton donor.

A Brønsted-Lowry base is a proton acceptor.

An example of the Brønsted-Lowry definition is the reaction between hydrogen chloride and sodium hydroxide:

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Proton   Proton
donor   acceptor
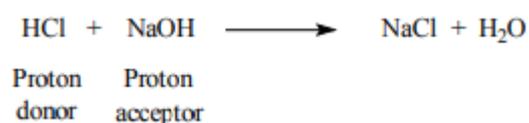
pH scale

pH is a unit of measure which describes the degree of acidity or alkalinity of a solution. It is measured on a scale of 0 to 14. The term pH is derived from "p," the mathematical symbol for negative logarithm, and "H," the chemical symbol for Hydrogen. The formal definition of pH is: the negative logarithm of Hydrogen ion activity.

$$pH = -\log[H+]$$

The pH Scale
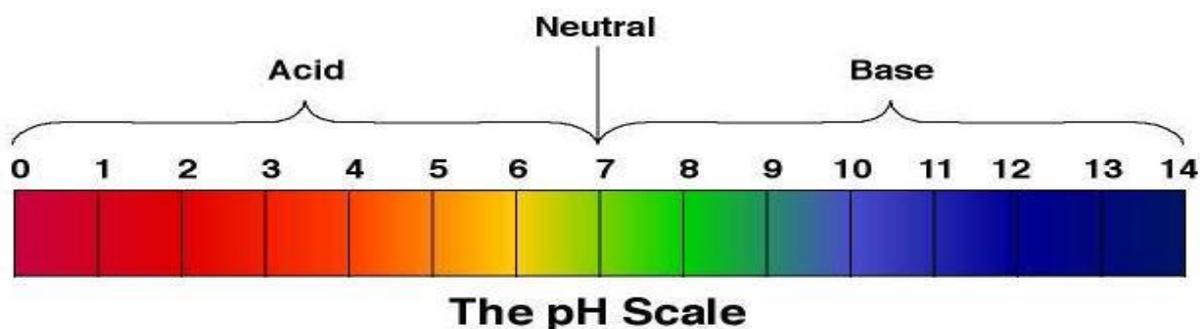
1. What is the pH of the buffer solution in which the concentration of acetic acid is 0.200 M and that of sodium acetate is 0.500 M?

$c_{acetic\ acid} = 0.200$ M
$c_{Na\text{-}acetate} = 0.500$ M

$K_a = 1.86 \times 10^{-5}$

$[H^+] = K_a \dfrac{c_{weak\ acid}}{c_{weak\ base}} = 1.86 \times 10^{-5} \times \dfrac{0.200}{0.500} = 7.44 \times 10^{-6}$ M

$pH = -\log [H^+]$

$pH = -\log 7.44 \times 10^{-6}$

$pH = 5.128$

2. What is the pH of the buffer solution in which the concentration of acetic acid is 0.200 M and that of sodium acetate is 0.100 M? (Assignment)

3. What is the pH of the buffer solution in which the concentration of ammonia is 0.250 M and that of ammonium chloride is 0.450 M?

$c_{ammonia} = 0.250$ M
$c_{ammonium\ chloride} = 0.450$ M

$[OH^-] = K_b \dfrac{n_{weak\ base}}{n_{salt}} = 1.75 \times 10^{-5} \times \dfrac{0.250}{0.450} = 9.72 \times 10^{-6}$ M

$pOH = -\log [OH^-]$

$pOH = -\log 9.72 \times 10^{-6}$
$pOH = 5.012$ $pH = 14.000 - 5.012 = 8.988$

5. Calculate the buffer capacity of a basic buffer in which c(NH3) = 1.2 mol/dm3 and c(NH4Cl) = 1.0 mol/dm3 ?

a) When we add acid to the system:

$$pH = 8.322$$
$$pOH = 5.678$$
$$[OH^-] = 2.0989 \times 10^{-6}\,M$$

$$2.0989 \times 10^{-6} = 1.75 \times 10^{-5} \times \frac{1.20 - X}{1.00 + X}$$

X = 0.965 mol of acid

b) When we add base to the system:
$$pH = 10.322$$
$$pOH = 3.678$$
$$[OH^-] = 2.0989 \times 10^{-4}\,M$$

$$2.0989 \times 10^{-4} = 1.75 \times 10^{-5} \times \frac{1.20 + Y}{1.00 - Y}$$

Y = 0.831 mol of base

6. Calculate the buffer capacity of an acidic buffer in which c(CH3COOH) = 0.5 mol/dm3 and c(CH3COONa) = 0.5 mol/dm3?

$$[H^+] = K_a \frac{c_{weak\ acid}}{c_{weak\ base}} = 1.86 \times 10^{-5} \times \frac{0.500}{0.500} = 1.86 \times 10^{-5}\,M$$

$$pH = -\log [H_3O^+]$$

$$pH = -\log 1.86 \times 10^{-5}$$

pH = 4.730

Buffer capacity:
a) When we add acid to the system:
$$pH = 3.730$$

$$[H^+] = 1.862 \times 10^{-4}\,M$$

$$1.862 \times 10^{-4} = 1.86 \times 10^{-5} \times \frac{0.50 + X}{0.50 - X}$$

X = 0.4092 mol of acid

c) When we add base to the system:

pH = 5.730

$[H^+] = 1.862 \times 10^{-6} M$

$1.862 \times 10^{-6} = 1.86 \times 10^{-5} \times \dfrac{0.50 - Y}{0.50 + Y}$

Y = 0.4092 mol of base