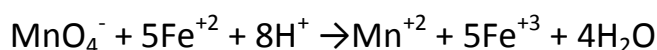


Calculation of Oxidation – Reduction titration

EX/A 0.8040 gm sample of an iron ore is dissolved in acid. The iron is then reduced to Fe^{+2} and titrated with 47.22 ml of 0.022242 M KMnO_4 solution. Calculate the results of this analysis in terms of (a) % Fe (55.847 gm/mol) and (b) % Fe_3O_4 (231.51 gm/mol). The reaction of the analyte with the reagent is described by the equation:



Solution/

(a) Stoichiometric ratio = 5 mmol Fe^{+2} / 1mmol KMnO_4

$$\text{Amount } \text{KMnO}_4 = 47.22 \text{ ml } \text{KMnO}_4 \times 0.022242 \text{ mmol } \text{KMnO}_4 / \text{ml } \text{KMnO}_4$$

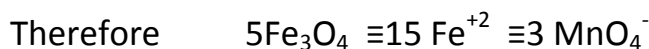
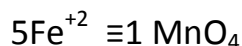
$$= 1.0587 \text{ mmol } \text{KMnO}_4$$

$$\text{Amount } \text{Fe}^{+2} = 1.0587 \text{ mmol } \text{KMnO}_4 \times 5 \text{ mmol } \text{Fe}^{+2} / 1 \text{ mmol } \text{KMnO}_4$$
$$= 5.2935 \text{ mmol } \text{Fe}^{+2}$$

$$\text{Mass } \text{Fe}^{+2} = 5.2935 \text{ mmol } \text{Fe}^{+2} \times 0.055847 \text{ gm } \text{Fe}^{+2} / \text{mmol } \text{Fe}^{+2}$$
$$= 0.2956 \text{ gm } \text{Fe}^{+2}$$

$$\% \text{Fe}^{+2} = 0.2956 \text{ gm } \text{Fe}^{+2} / 0.8040 \text{ gm sample} \times 100$$
$$= 36.77 \%$$

(b) in order to derive a stoichiometric ratio, we note that



$$\text{Stoichiometric ratio} = 5 \text{ mmol } \text{Fe}_3\text{O}_4 / 3 \text{ mmol } \text{KMnO}_4$$

$$\text{Amount } \text{KMnO}_4 = 47.22 \text{ ml } \text{KMnO}_4 \times 0.022242 \text{ mmol } \text{KMnO}_4 / \text{ml } \text{KMnO}_4$$

$$= 1.0587 \text{ mmol } \text{KMnO}_4$$

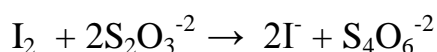
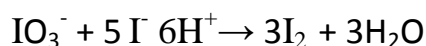
$$\text{Amount } \text{Fe}_3\text{O}_4 = 1.0587 \text{ mmol } \text{KMnO}_4 \times 5 \text{ mmol } \text{Fe}_3\text{O}_4 / 3 \text{ mmol } \text{KMnO}_4$$
$$= 1.7644 \text{ mmol } \text{Fe}_3\text{O}_4$$

$$\text{Mass Fe}_3\text{O}_4 = 1.7644 \text{ mmol} \times 0.23154 \text{ gm / mmol}$$

$$= 0.4086 \text{ gm}$$

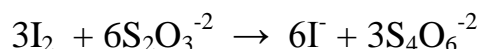
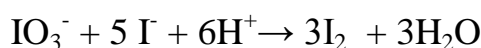
$$\% \text{Fe}_3\text{O}_4 = 0.4086 \text{ gm} / 0.8040 \text{ gm} \times 100 = 50.81 \%$$

Ex/ Titration of the I_2 produced from 0.1238 gm of primary – standard KIO_3 required 41.27ml of sodium thiosulfate :



Calculate the concentration of the $\text{Na}_2\text{S}_2\text{O}_3$.

Solution /



$$\text{No. mol KIO}_3 = 0.1238 \text{ gm} \times 1 \text{ mol} / 214.00 \text{ gm}$$

$$= 5.785 \times 10^{-4} \text{ mol} \times 10^3 \text{ mmol / mol}$$

$$= 0.5785 \text{ mmol KIO}_3$$

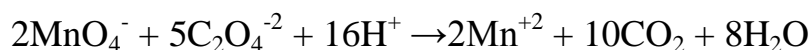
$$\text{No. mmol Na}_2\text{S}_2\text{O}_3 = 0.5785 \text{ mmol KIO}_3 \times 6 \text{ mmol Na}_2\text{S}_2\text{O}_3 / 1 \text{ mmol KIO}_3$$

$$= 3.471 \text{ mmol Na}_2\text{S}_2\text{O}_3$$

$$M = 3.471 \text{ mmol} / 41.27 \text{ ml} = 0.0841 \text{ M}$$

Ex / Titration of 0.2121 gm of pure $\text{Na}_2\text{C}_2\text{O}_4$ (134.00 gm / mol) required 43.31ml of KMnO_4 . What is the molarity of the KMnO_4 solution?

The chemical reaction is :



Solution /

$$\text{stoichiometric ratio} = 2 \text{ mmol KMnO}_4 / 5 \text{ mmol Na}_2\text{C}_2\text{O}_4$$

$$\text{Amount Na}_2\text{C}_2\text{O}_4 = 0.2121 \text{ gm} \times 1 \text{ mmol} / 134.00 \text{ gm}$$

$$= 1.5828 \text{ mmol}$$

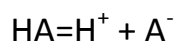
$$\text{Amount KMnO}_4 = 1.5828 \text{ mmol Na}_2\text{C}_2\text{O}_4 \times 2 \text{ mmol KMnO}_4 / 5 \text{ mmol Na}_2\text{C}_2\text{O}_4$$

$$= 0.6332 \text{ mmol KMnO}_4$$

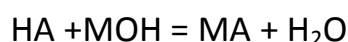
$$M = 0.6332 \text{ mmol KMnO}_4 / 43.31 \text{ ml KMnO}_4 = 0.01462 \text{ mmol/ml} = 0.01462 \text{ M}$$

Acid – base equilibria and PH of solutions

An acid is a substance that furnishes protons or H^+ ions and a base a substance that accepts protons. In classical terminology the acid HA dissociates in aqueous solution according to the equation



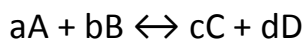
And a base MOH dissociates to give $\text{M}^+ + \text{OH}^-$ ions. The reaction of HA with MOH is



This reaction goes more or less to completion because the H_2O molecule is only slightly dissociated. To understand the limitations of acid-base titrations and the selection of proper indicators for such titrations, the student must understand the equilibrium relations involved in neutralization reactions.

Equilibrium constant :

A chemical reaction is at equilibrium when the rates of the forward and the concentrations of the reacting components are related by the equilibrium constant equation. For the reaction



We have the relation

$$K_e = [\text{D}]^d [\text{E}]^e / [\text{A}]^a [\text{B}]^b$$

In which the square brackets indicate the molar concentrations of the reacting species, and each molar concentration is raised to a power that is the coefficient of that substance in the chemical equation. The constant K_e is known as the equilibrium constant. Conventionally the products of the reaction are written in the numerator of the expression.

The equilibrium constant is experimentally determined for every reaction by measuring the concentrations of the reacting species after a condition of equilibrium has been attained. The constant is valid only at the temperature at which the determination is made, a change in temperature will change the equilibrium concentrations, there by changing the numerical value of K_e .

Factors effecting the equilibrium state:

Temperature , Pressure , Concentration, Time, Volume and Catalyst.

pH and Hydrogen ion concentration

Pure water dissociates slightly, forming equivalent amounts of hydronium and hydroxide ions , according to the equation



The H^+ ion formed by dissociation of one H_2O molecule unites with another H_2O molecule to form an hydronium ion. At room temperature the concentration of H_3O^+ and OH^- ions in pure water are each 1×10^{-7} molar.

The equilibrium expression for dissociation of water is :

$$K_e = [\text{H}_3\text{O}^+] [\text{OH}^-] / [\text{H}_2\text{O}]^2$$

Since $[\text{H}_2\text{O}]$ is constant, we have

$$[\text{H}_3\text{O}^+] [\text{OH}^-] = K_w$$

The constant K_w is evaluated by substituting known numerical values for the concentrations of the ions and solving this gives

$$K_w = (1 \times 10^{-7}) (1 \times 10^{-7}) = 1 \times 10^{-14}$$

This is the value for the constant at 25 °C .

The obvious simple solution is to use a related function , known as pH, to express hydronium ion concentrations .The function pH is defined by the equation

$$\text{pH} = - \log [\text{H}_3\text{O}^+]$$

which also gives corresponding values for the concentration of OH^- ion
pOH, defined by

$$\text{pOH} = -\log [\text{OH}^-]$$

It will be noted that the sum pH + pOH is always 14 when the solution is at room temperature

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

Ex/ What is the pH of a solution in which the hydronium ion concentration is 0.0002 M ?

Solution / $[\text{H}_3\text{O}^+] = \text{M} = 2 \times 10^{-4}$

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] \\ &= -\log (2 \times 10^{-4}) = -\log 2 + 4 \log 10 \\ &= -0.30 + 4 \\ &= 3.7\end{aligned}$$

Ex/ The pH of a solution is 5.40. What is the concentration hydronium ion?

Solution /

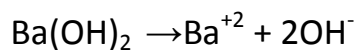
$$\begin{aligned}\text{pH} &= 5.40 \\ \text{pH} &= -\log [\text{H}_3\text{O}^+] \\ [\text{H}_3\text{O}^+] &= 10^{-\text{pH}} = 10^{-5.4} = 10^{-6} \times 10^{+0.6} \\ &= 3.98 \times 10^{-6} \approx 4 \times 10^{-6}\end{aligned}$$

Ex/ What is the OH^- concentration in 0.001 M of HCl solution? What is the H^+ concentration derived from the dissociates of the solvent ?

Solution /

$$\begin{aligned}K_w &= [\text{H}^+] [\text{OH}^-] \\ 1 \times 10^{-14} &= (0.001)[\text{OH}^-] \\ [\text{OH}^-] &= 1 \times 10^{-14} / 1 \times 10^{-3} = 1 \times 10^{-11} \text{M} \\ \text{H}_2\text{O} &\leftrightarrow \text{H}^+ + \text{OH}^- \\ [\text{OH}^-] &= [\text{H}^+] = 1 \times 10^{-11}\end{aligned}$$

Ex/ What are the concentration of H^+ and OH^- in 0.0030 M solution of $\text{Ba}(\text{OH})_2$?

Solution /

$$K_w = [\text{OH}^-] [\text{H}^+]$$

$$1 \times 10^{-14} = (2 \times 0.003) [\text{H}^+]$$

$$[\text{H}^+] = 1 \times 10^{-14} / 6 \times 10^{-3} = 1.6 \times 10^{-12}$$

$$[\text{OH}^-] 2 \times 0.003 = 6 \times 10^{-3}$$

Ex / A sample of blood found to have a pH 3.80. What were the H^+ and OH^- concentration in the blood?

Solution /

$$\text{pH} = -\log [\text{H}^+]$$

$$3.8 = -\log [\text{H}^+]$$

$$[\text{H}^+] = 10^{-3.8}$$

$$= 10^{-4} \times 10^{+0.2} = 1.58 \times 10^{-4}$$

$$= 1.6 \times 10^{-4}$$

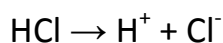
$$[\text{H}^+] [\text{OH}^-] = 1 \times 10^{-14}$$

$$[\text{OH}^-] = 1 \times 10^{-14} / 1.6 \times 10^{-4} = 6.25 \times 10^{-11}$$

Expression of equilibrium constant in acidic medium

For strong acid, such as HCl, we never need to write law of chemical equilibrium because the dissociation almost completely. However, is a weak acid and its reaction with water is an equilibrium law.

Ex / What is the pH of a 0.005 M solution of HCl at 25°C ?

Solution /

$$[\text{H}^+] = 0.005 \text{ M} = 5 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 5 \times 10^{-3}$$

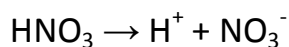
$$\text{pH} = -[\log 5 + \log 10^{-3}]$$

$$= -0.7 + 3$$

$$\text{pH} = 2.7$$

Ex / What is the pOH of a 2×10^{-4} M solution of HNO_3 ?

Solution /



$$[\text{H}^+] = 2 \times 10^{-4} \text{M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log 2 \times 10^{-4}$$

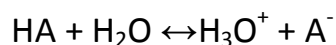
$$= -[\log 2 + \log 10^{-4}]$$

$$= -0.3 + 4 = 3.7$$

$$\text{pH} + \text{pOH} = \text{pK}_w = 14$$

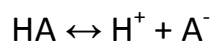
$$\text{pOH} = 14 - \text{pH} = 14 - 3.7 = 10.3$$

Expression of equilibrium constant for a weak acid in aqueous solution in the general equation:



$$\text{K}_a = [\text{H}_3\text{O}^+] [\text{A}^-] / [\text{HA}] [\text{H}_2\text{O}]$$

$[\text{H}_2\text{O}] = \text{constant}$

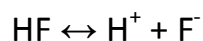


$$\text{K}_a = [\text{H}^+] [\text{A}^-] / [\text{HA}]$$

K_a = acid dissociation constant for weak acid

Ex / Express the acid dissociation constant for weak acid HF is dissolved in water ?

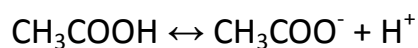
Solution /



$$\text{K}_a = [\text{H}^+] [\text{F}^-] / [\text{HF}]$$

Ex / / What is the pH of 0.02M solution of acetic acid ? $\text{K}_a = 1.8 \times 10^{-5}$

Solution /



$$\begin{array}{ccc} 0.02 & 0 & 0 \end{array}$$

$$0.02 - X \quad X \quad X$$

$$K_a = [\text{CH}_3\text{COO}^-] [\text{H}^+] / [\text{CH}_3\text{COOH}]$$

$$1.8 \times 10^{-5} = (X)(X) / (0.02 - X)$$

Neglects

$$X^2 = 36 \times 10^{-8}$$

$$X = 6 \times 10^{-4} \text{ M} = [\text{H}^+]$$

$$\text{pH} - \log [\text{H}^+] = -\log 6 \times 10^{-4} = -0.78 + 4 = 3.22$$

ملاحظة : يهمل (x) في الحالة التي يكون فيها ثابت تفكك الحامض الضعيف (K_a) يساوي

10⁻⁵ , 10⁻⁶.....فما دون

طريقة اخرى للحل

$$\text{pH} = 1/2 (\text{pK}_a - \log M_a)$$

$$\text{pK}_a = -\log K_a \quad , \quad M_a = [\text{H}^+] = [\text{Acid}]$$

$$\text{pH} = 1/2 (-\log K_a - \log M_a)$$

$$= 1/2 (-\log 1.8 \times 10^{-5} - \log 0.02)$$

$$= 1/2(4.47 + 1.7) = 3.22$$