Analytical chemistry

Analytical chemistry is a measurement science consisting of a set of powerful ideas and methods that are useful in all fields of science, engineering, and medicine.

Analytical chemistry is concerned with the chemical characterization of matter and the answer to two important questions: what is it (**qualitative analysis**) and how much is it (**quantitative analysis**).

Chemical Concentrations

Concentration of Solutions

Molar Concentration:

The **molar concentration** c_x of a solution of a solute species X is the number of moles of that species that is contained in 1 liter of the solution (*not 1 L of the solvent*). In terms of the number of moles of solute, n, and the volume, V, of solution, we write

$$c_x = \frac{n_X}{V}$$

$$\text{molar concentration} = \frac{\text{no. moles solute}}{\text{volume in liters}}$$

The unit of molar concentration is **molar**, symbolized by **M**, which has the dimensions of mol/L, or mol L^{-1}. Molar concentration is also the number of millimoles of solute per milliliter of solution.

$$1\ M = 1\ mol\ L^{-1} = 1\ \frac{mol}{L} = 1\ \frac{mmol}{mL}$$

Calculate the molar concentration of ethanol in an aqueous solution that contains 2.30 g of C_2H_5OH (46.07 g/mol) in 3.50 L of solution.

Solution

To calculate molar concentration, we must find both the amount of ethanol and the volume of the solution. The volume is given as 3.50 L, so all we need to do is convert the mass of ethanol to the corresponding amount of ethanol in moles.

$$\text{amount } C_2H_5OH = n_{C_2H_5OH} = 2.30 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH}$$

$$= 0.04992 \text{ mol } C_2H_5OH$$

To obtain the molar concentration, $c_{C_2H_5OH}$, we divide the amount by the volume. Thus,

$$c_{C_2H_5OH} = \frac{2.30 \text{ g } C_2H_5OH \times \frac{1 \text{ mol } C_2H_5OH}{46.07 \text{ g } C_2H_5OH}}{3.50 \text{ L}}$$

$$= 0.0143 \text{ mol } C_2H_5OH/L = 0.0143 \text{ M}$$

Describe the preparation of 2.00 L of 0.108 M $BaCl_2$ from $BaCl_2 \cdot 2H_2O$ (244.3 g/mol).

Solution

To determine the number of grams of solute to be dissolved and diluted to 2.00 L, we note that 1 mole of the dihydrate yields 1 mole of $BaCl_2$. Therefore, to produce this solution we will need

$$2.00 \text{ L} \times \frac{0.108 \text{ mol } BaCl_2 \cdot 2H_2O}{L} = 0.216 \text{ mol } BaCl_2 \cdot 2H_2O$$

The mass of $BaCl_2 \cdot 2H_2O$ is then

$$0.216 \text{ mol } BaCl_2 \cdot 2H_2O \times \frac{244.3 \text{ g } BaCl_2 \cdot 2H_2O}{\text{mol } BaCl_2 \cdot 2H_2O} = 52.8 \text{ g } BaCl_2 \cdot 2H_2O$$

Dissolve 52.8 g of $BaCl_2 \cdot 2H_2O$ in water and dilute to 2.00 L.

(a) Typical seawater contains 2.7 g of salt (sodium chloride, NaCl) per 100 mL (= 100 × 10^{-3} L). What is the molarity of NaCl in the ocean? (b) $MgCl_2$ has a concentration of 0.054 M in the ocean. How many grams of $MgCl_2$ are present in 25 mL of seawater?

Solution   (a) The molecular mass of NaCl is 22.99 g/mol (Na) + 35.45 g/mol (Cl) = 58.44 g/mol. The moles of salt in 2.7 g are (2.7 g̸)/(58.44 g̸/mol) = 0.046 mol, so the molarity is

$$\text{Molarity of NaCl} = \frac{\text{mol NaCl}}{\text{L of seawater}} = \frac{0.046 \text{ mol}}{100 \times 10^{-3} \text{ L}} = 0.46 \text{ M}$$

(b) The molecular mass of $MgCl_2$ is 24.30 g/mol (Mg) + 2 × 35.45 g/mol (Cl) = 95.20 g/mol. The number of grams in 25 mL is

$$\text{Grams of MgCl}_2 = \left(0.054 \frac{\text{mol̸}}{\text{L̸}}\right)\left(95.20 \frac{\text{g}}{\text{mol̸}}\right)(25 \times 10^{-3} \text{ L̸}) = 0.13 \text{ g}$$

What is the mass in grams of solute in
(a) 250 mL of 0.264 M H_2O_2?
(b) 37.0 mL of 5.75 × 10^{-4} M benzoic acid (122 g/mol)?
(c) 4.50 L of a solution that contains 31.7 ppm of $SnCl_2$?
(d) 11.7 mL of 0.0225 M $KBrO_3$?

Solution:

a) $M = \dfrac{mole}{volume} = \dfrac{n}{V}$ ∴ $mole = M \times volume = 0.264 \times \dfrac{250}{1000}$

$$n = 0.066 \ mole$$

$$mole = \frac{weight}{molecular \ weight} \qquad \therefore \qquad wt = 0.066 \times 34 = 2.244g$$

$$\therefore 2.244 \ g \ of \ H_2O_2 \ dissolved \ in \ 250 \ ml \ water \ to \ prepare \ 0.264M \ H_2O_2$$

What is the mass in milligrams of solute in

(a) 16.0 mL of 0.350 M sucrose (342 g/mol)?

(b) 1.92 L of 3.76×10^{-3} M H_2O_2?

(c) 356 mL of a solution that contains 2.96 ppm of $Pb(NO_3)_2$?

(d) 5.75 mL of 0.0819 M KNO_3?

Solution:

d) $M = \dfrac{wt(g) \times 1000}{Mwt\left(\frac{g}{mol}\right) \times V(ml)}$ $\qquad \therefore \quad wt = \dfrac{M \times M.wt \times V}{1000} = \dfrac{0.0819 \times 101 \times 5.75}{1000} = 0.0476g$

$$wt = 0.0476\ g = 47.6\ mg$$

Molarity for liquid substance

$$M = \frac{specific\ gravity \times \% \times 1000}{molecular\ weight} = \frac{sp.gr \times \% \times 1000}{M.wt}$$

$$specific\ gravity = \frac{density\ of\ a\ substnce}{density\ of\ water\ at\ 4^oC} = \frac{density\ of\ a\ substnce}{1}$$

Q: Find the molarity of 37.0 wt% HCl. The density of a substance is the mass per unit volume. The table inside the back cover of this book tells us that the density of the reagent is 1.19 g/ml.

$$M = \frac{sp.gr \times \% \times 1000}{M.wt} = \frac{1.19 \times 0.37 \times 1000}{36.5} = 12.1 \frac{mole}{l}$$

Dilution

Dilute solutions can be prepared from concentrated solutions. A volume of the concentrated solution is transferred to a fresh vessel and diluted to the desired final volume.

$$M_{conc} \cdot V_{conc} = M_{dil} \cdot V_{dil}$$

Moles taken from   Moles placed in
concentrated solution   dilute solution

Example Preparing 0.100 M HCl

The molarity of "concentrated" HCl purchased for laboratory use is approximately 12.1 M. How many milliliters of this reagent should be diluted to 1.000 L to make 0.100 M HCl?

Solution   The dilution formula handles this problem directly:

$$M_{conc} \cdot V_{conc} = M_{dil} \cdot V_{dil}$$

$$(12.1 \text{ M}) \cdot (x \text{ mL}) = (0.100 \text{ M}) \cdot (1\,000 \text{ mL}) \Rightarrow x = 8.26 \text{ mL}$$

To make 0.100 M HCl, we would dilute 8.26 mL of concentrated HCl up to 1.000 L.

Q:

The density of concentrated ammonium hydroxide, which contains 28.0 wt% NH_3, is 0.899 g/mL. What volume of this reagent should be diluted to 500.0 mL to make 0.250 M NH_3?

$$M = \frac{sp.\,gr \times \% \times 1000}{M.wt} = \frac{0.899 \times 0.28 \times 1000}{17} = 14.8 \frac{mole}{l}$$

$$M_{conc} \cdot V_{conc} = M_{dil} \cdot V_{dil}$$

$$14.8 \ M \times V_{conc} = 0.250 \ M \times 500.0 \ mL \Rightarrow V_{conc} = 8.45 \ mL$$

Now we find the volume of 14.8 M NH_3 required to prepare 500.0 mL of 0.250 M NH_3:

The procedure is to place 8.45 mL of concentrated reagent in a 500-mL volumetric flask, add about 400 mL of water, and swirl to mix. Then dilute to exactly 500 mL with water and invert the flask many times to mix well.

Calculate the molar concentration of HNO_3 (63.0 g/mol) in a solution that has a specific gravity of 1.42 and is 70.5% HNO_3 (w/w).

Solution:

$$M = \frac{sp.gr \times \% \times 1000}{M.wt} = \frac{1.42 \times 70.5 \times 10}{63} = 15.9 \frac{mol}{l}$$

How many milliliters of concentrated sulfuric acid, 94.0% (g/100 g solution), density 1.831 g/cm^3, are required to prepare 1 liter of a 0.100 M solution?

M.wt H_2SO_4=98 g/mol

Answer: 5.7ml

Describe the preparation of 100 mL of 6.0 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37% (w/w) HCl (36.5 g/mol).

Answer: 50ml of concentrated HCl diluted to 100ml by distilled water to give a solution of HCl with 6N HCl.

H.W.

You wish to prepare 500mL of a 0.100 M $K_2Cr_2O_7$ solution from a 0.250 M solution.

What volume of the 0.250 M solution must be diluted to 500 mL?

H.W.

Percent Concentration

Chemists frequently express concentrations in terms of percent (parts per hundred). Unfortunately, this practice can be a source of ambiguity because percent composition of a solution can be expressed in several ways. Three common methods are

$$\text{weight percent (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$$

$$\text{volume percent (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$$

$$\text{weight/volume percent (w/v)} = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$$

Q: Describe the preparation of 500 mL of 4.75% (w/v) aqueous ethanol (C_2H_5OH, 46.1 g/mol).

$$w/v = \frac{w(g)}{v(ml)} \times 100$$

$$4.75 = \frac{w}{500} \times 100$$

$w = 23.75g$ of ethanol added to a plenty of water and completed to 500ml by D.W.

Q: Describe the preparation of 2.50 L of 21.0% (w/v) aqueous glycerol ($C_3H_8O_3$, 92.1 g/mol).

<div align="center">H.W.</div>

Parts per Million and Parts per Billion

For very dilute solutions, **parts per million** (ppm) is a convenient way to express concentration:

$$c_{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \text{ ppm}$$

where c_{ppm} is the concentration in parts per million. The units of mass in the numerator and denominator must agree so that they cancel. For even more dilute solutions, 10^9 ppb rather than 10^6 ppm is used in the previous equation to give the results in **parts per billion** (ppb). The term **parts per thousand** (ppt) is also used, especially in oceanography.

Q: What is the mass in grams of solute in 4.50 L of a solution that contains 31.7 ppm of $SnCl_2$?

Solution:

$$M.wt\ SnCl_2 = 118.71 + (2 \times 35.45) = 189.6 \frac{g}{mol}$$

$$ppm = \frac{w(g)}{v(ml)} \times 10^6$$

$$w = \frac{ppm \times v}{10^6} = \frac{31.7 \times (4.5 \times 1000)}{1000000} = 0.1427g$$

p-Functions

Scientists frequently express the concentration of a species in terms of its p-function, or p-value. The p-value is the negative logarithm (to the base 10) of the molar concentration of that species. Thus, for the species X,

$$pX = -\log[X]$$

Calculate the p-value for each ion in a solution that is 2.00×10^{-3} M in NaCl and 5.4×10^{-4} M in HCl.

Solution

$$pH = -\log [H^+] = -\log (5.4 \times 10^{-4}) = 3.27$$

To obtain pNa, we write

$$pNa = -\log[Na^+] = -\log (2.00 \times 10^{-3}) = -\log (2.00 \times 10^{-3}) = 2.699$$

The total Cl^- concentration is given by the sum of the concentrations of the two solutes:

$$[Cl^-] = 2.00 \times 10^{-3} M + 5.4 \times 10^{-4} M$$

$$= 2.00 \times 10^{-3} M + 0.54 \times 10^{-3} M = 2.54 \times 10^{-3} M$$

$$pCl = -\log[Cl^-] = -\log 2.54 \times 10^{-3} = 2.595$$

Calculate the molar concentration of Ag^+ in a solution that has a pAg of 6.372.

Solution

$$pAg = -\log [Ag^+] = 6.372$$
$$\log [Ag^+] = -6.372$$
$$[Ag^+] = 4.246 \times 10^{-7} \approx 4.25 \times 10^{-7} M$$

Aqueous Solutions and Chemical Equilibria.

Classifying Solutions of Electrolytes

Most of the solutes we will discuss are electrolytes, which form ions when dissolved in water (or certain other solvents) and thus produce solutions that conduct electricity. Strong electrolytes ionize essentially completely in a solvent, but weak electrolytes ionize only partially.

| Classification of Electrolytes	
Strong	**Weak**
1. Inorganic acids such as HNO_3, $HClO_4$, $H_2SO_4^*$, HCl, HI, HBr, $HClO_3$, $HBrO_3$ 2. Alkali and alkaline-earth hydroxides 3. Most salts	1. Many inorganic acids, including H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3 2. Most organic acids 3. Ammonia and most organic bases 4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

Acids and Bases

In 1923, J. N. Brønsted in Denmark and J. M. Lowry in England proposed independently a theory of acid/base behavior that is especially useful in analytical chemistry.

According to the Brønsted-Lowry theory, an acid is a proton donor, and a base is a proton acceptor. For a molecule to behave as an acid, it must encounter a proton acceptor (or base). Likewise, a molecule that can accept a proton behaves as a base if it encounters an acid.

Conjugate Acids and Bases

An important feature of the Brønsted-Lowry concept is the idea that the product formed when an acid gives up a proton is a potential proton acceptor and is called the conjugate base of the parent acid.

For example, when the species acid1 gives up a proton, the species base1 is formed, as shown by the reaction
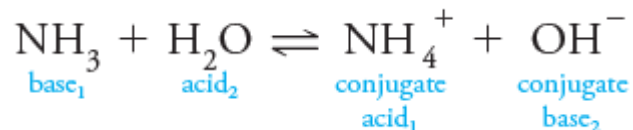
$$acid_1 \rightleftharpoons base_1 + proton$$
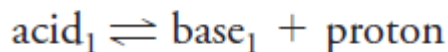
We refer to acid1 and base1 as a conjugate acid/base pair, or just a conjugate pair.

Similarly, every base accepts a proton to produce a conjugate acid. That is,

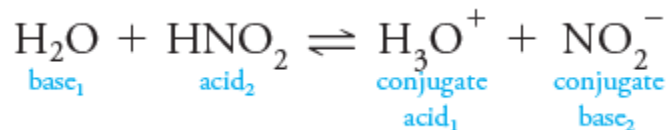$$base_2 + proton \rightleftharpoons acid_2$$
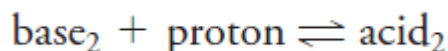
Many solvents are proton donors or proton acceptors and can thus induce basic or acidic behavior in solutes dissolved in them. For example, in an aqueous solution of ammonia, water can donate a proton and acts as an acid with respect to the solute NH_3:

$$\underset{base_1}{NH_3} + \underset{acid_2}{H_2O} \rightleftharpoons \underset{\substack{conjugate \\ acid_1}}{NH_4^+} + \underset{\substack{conjugate \\ base_2}}{OH^-}$$

In this reaction, ammonia (base1) reacts with water, which is labeled acid2, to give the conjugate acid ammonium ion (acid1) and hydroxide ion, which is the conjugate base (base2) of the acid water.

On the other hand, water acts as a proton acceptor, or base, in an aqueous solution of nitrous acid:

$$\underset{base_1}{H_2O} + \underset{acid_2}{HNO_2} \rightleftharpoons \underset{\substack{conjugate \\ acid_1}}{H_3O^+} + \underset{\substack{conjugate \\ base_2}}{NO_2^-}$$

The conjugate base of the acid HNO_2 is nitrite ion. The conjugate acid of water is the hydrated proton written as H_3O^+. This species is called the hydronium ion, and it consists of a proton covalently bonded to a single water molecule.
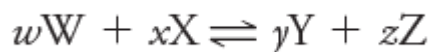
Chemical Equilibrium

Le Châtelier's principle

This principle states that the position of chemical equilibrium always shifts in a direction that tends to relieve the effect of an applied stress. For example, an increase in temperature of a system alters the concentration relationship in the direction that tends to absorb heat.

Equilibrium-Constant Expressions

Consider a generalized equation for a chemical equilibrium

$$wW + xX \rightleftharpoons yY + zZ$$

$$K = \frac{[Y]^y[Z]^z}{[W]^w[X]^x}$$

Types of Equilibrium Constants in Analytical Chemistry

Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, K_w	$2H_2O \rightleftharpoons H_3O^+ + OH^-$	$K_w = [H_3O^+][OH^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, K_{sp}	$BaSO_4(s) \rightleftharpoons Ba^{2+} + SO_4^{2-}$	$K_{sp} = [Ba^{2+}][SO_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, K_a or K_b	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$	$K_a = \dfrac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$
		$CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_b = \dfrac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$

Applying the Ion-Product Constant for Water

Aqueous solutions contain small concentrations of hydronium and hydroxide ions as a result of the dissociation reaction:

$$2H_2O \leftrightarrow OH^- + H_3O^+$$

An equilibrium constant for this reaction can be written as shown in

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K = [H_2O]^2 = K_w = [H_3O^+][OH^-]$$

Where the new constant K_w is given a special name, the ion-product constant for water.

At 25°C, the ion-product constant for water is 1.008×10^{-14}. For convenience, we use the approximation that at room temperature $K_w = 1 \times 10^{-14}$.

EXAMPLE

Calculate the hydronium and hydroxide ion concentrations and the pH andpOH of 0.200 M aqueous NaOH at 25°C.

Solution

Sodium hydroxide is a strong electrolyte, and its contribution to the hydroxide ion concentration in this solution is 0.200 mol/L. Hydroxide ions and hydronium ions are formed in equal amounts from the dissociation of water. Therefore, we write:

$$[OH^-] \approx 0.2\ M$$

$$pOH = -\log[OH^-] = -\log 0.2 = 0.699$$

$$K_w = [H_3O^+][OH^-] \qquad \therefore\ [H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{0.2} = 5 \times 10^{-14}$$
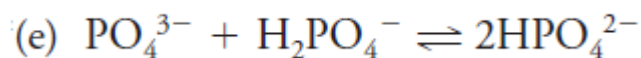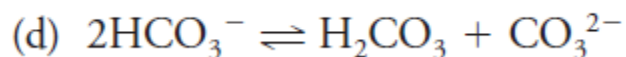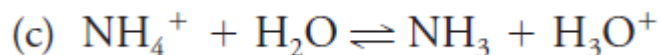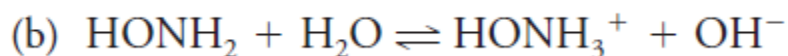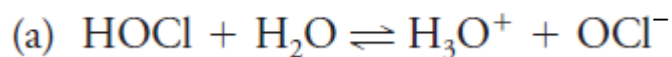
$$pH = -\log[H_3O^+] = -\log 5 \times 10^{-14} = 13.301$$

$$or\ pH + pOH = 14$$

$$pOH = 0.699$$

$$\therefore\ pH = 14 - 0.699 = 13.301$$

Q: Identify the acid on the left and its conjugate base on the right in the following equations:

(a) $HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$

(b) $HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$

(c) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

(d) $2HCO_3^- \rightleftharpoons H_2CO_3 + CO_3^{2-}$

(e) $PO_4^{3-} + H_2PO_4^- \rightleftharpoons 2HPO_4^{2-}$

Using Solubility-Product Constants

Most, but not all, sparingly soluble salts are essentially completely dissociated in saturated aqueous solution. For example, when an excess of barium iodate is equilibrated with water, the dissociation process is adequately described by the equation
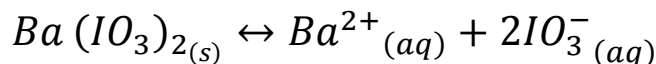
$$Ba\,(IO_3)_{2\,(s)} \leftrightarrow Ba^{2+}{}_{(aq)} + 2IO_3^-{}_{(aq)}$$
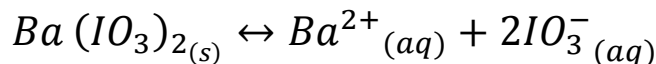
$$K = \frac{[Ba^{2+}][IO_3^-]^2}{[Ba\,(IO_3)_2]}$$

$$K[Ba\,(IO_3)_2] = K_{sp} = [Ba^{2+}][IO_3^-]^2$$

Where the new constant is called the solubility-product constant or the solubility product.

Example

What mass (in grams) of $Ba\,(IO_3)_2$ (487 g/mol) can be dissolved in 500 mL of water at 25°C? $K_{sp}[Ba\,(IO_3)_2] = 1.57 \times 10^{-9}$.

$$Ba\,(IO_3)_{2\,(s)} \leftrightarrow Ba^{2+}{}_{(aq)} + 2IO_3^-{}_{(aq)}$$

$$\qquad\qquad s \qquad\qquad 2s$$

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = s \times (2s)^2 = s \times 4s^2 = 4s^3$$

$$\therefore\ s = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{1.57 \times 10^{-9}}{4}} = 7.32 \times 10^{-4}\ \frac{mol}{l}$$

$$M_{Ba\,(IO_3)_2} = M_{Ba^{2+}} = 7.32 \times 10^{-4}\ \frac{mol}{l}$$

$$M_{Ba\,(IO_3)_2} = \frac{w \times 1000}{Mwt \times v}$$

$$w = \frac{M_{Ba\,(IO_3)_2} \times Mwt \times v}{1000} = \frac{7.32 \times 10^{-4} \times 487 \times 500}{1000}$$

$$w_{Ba\,(IO_3)_2} = 0.177\ g$$

Q: Calculate the solubility-product constant for each of the following substances, given that the molar concentrations of their saturated solutions are as indicated:

(a) AgSeCN $(2.0 \times 10^{-8}$ M; products are Ag^+ and $SeCN^-$).
(b) $RaSO_4$ $(6.6 \times 10^{-6}$ M).
(c) $Pb(BrO_3)_2$ $(1.7 \times 10^{-1}$ M).
(d) $Ce(IO_3)_3$ $(1.9 \times 10^{-3}$ M).

a) $K_{sp(AgSeCN)} = s^2 = [2 \times 10^{-8}]^2 = 4 \times 10^{-16}$

b) $K_{sp(RaSO_4)} = s^2 = [6.6 \times 10^{-6}]^2 = 4.356 \times 10^{-11}$

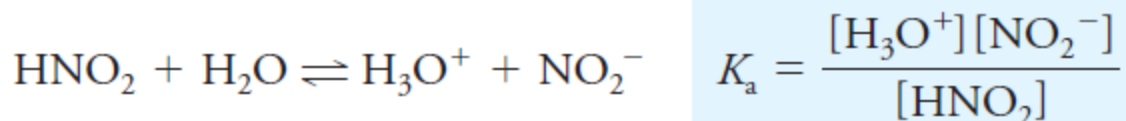c) $K_{sp[Pb(BrO_3)_2]} = 4s^3 = 4 \times [1.7 \times 10^{-1}]^3 = 0.0197$

d) $K_{sp[Ce(IO_3)_3]} = s \times (3s)^3 = 27s^4 = 27 \times (1.9 \times 10^{-3})^4 = 3.5 \times 10^{-10}$

Using Acid/Base Dissociation Constants

When a weak acid or a weak base is dissolved in water, partial dissociation occurs.
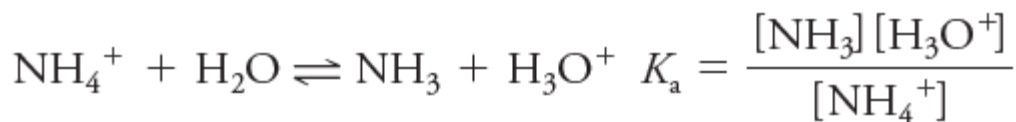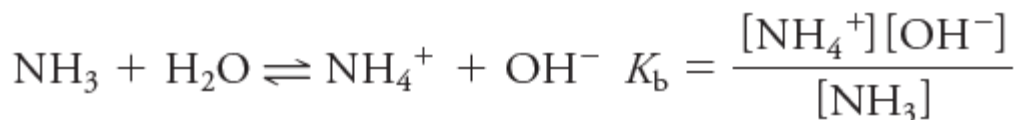
Thus, for nitrous acid, we can write

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^- \qquad K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

Where K_a is the acid dissociation constant for nitrous acid. In an analogous way, the base dissociation constant for ammonia is

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$
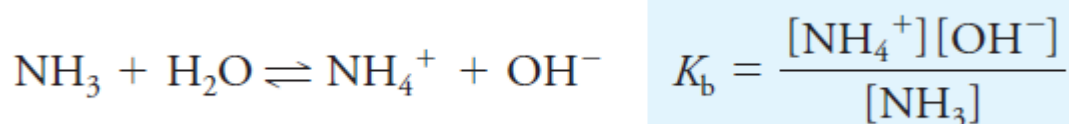
Dissociation Constants for Conjugate Acid/Base Pairs

Consider the base dissociation-constant expression for ammonia and the acid dissociation constant expression for its conjugate acid, ammonium ion:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \qquad K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

By multiplying one equilibrium-constant expression by the other, we have

$$K_aK_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-]$$

But $\qquad K_w = [H_3O^+][OH^-]$

and, therefore, $\qquad K_w = K_a K_b$

Example: What is K_b for the equilibrium:

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

K_a value of 6.2×10^{-10} for HCN.

$$K_b = \frac{K_w}{K_a} = \frac{[HCN][OH^-]}{[CN^-]}$$

$$K_b = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

Q: At 25°C, what are the molar H_3O^+ and OH^- concentrations in 0.0300 M C_6H_5COOH? ($K_a = 6.28 \times 10^{-5}$).

$$C_6H_5COOH + H_2O \leftrightarrow C_6H_5COO^- + H_3O^+$$

$$\qquad\qquad\qquad\qquad\qquad\qquad X \qquad\quad X$$

$$K_a = \frac{[C_6H_5COO^-][H_3O^+]}{[C_6H_5COOH]} = \frac{x^2}{[C_6H_5COOH]}$$

$$6.28 \times 10^{-5} = \frac{x^2}{0.03}$$

$$x = \sqrt{6.28 \times 10^{-5} \times 0.03} = 1.34 \times 10^{-3} M$$

$$\therefore \quad [H_3O^+] = 1.34 \times 10^{-3} M$$

$$[H_3O^+][OH^-] = K_w$$

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \times 10^{-14}}{1.34 \times 10^{-3}} = 7.46 \times 10^{-12} M$$

Buffer Solutions

A buffer solution resists changes in pH when it is diluted or when acids or bases are added to it. Generally, buffer solutions are prepared from a conjugate acid/base pair, such as acetic acid/sodium acetate or ammonium chloride/ammonia. Scientists and technologists in most areas of science and in many industries use buffers to maintain the pH of solutions at a relatively constant and predetermined level.

Calculating the pH of Buffer Solutions

The Henderson-Hasselbalch Equation

$$pH = pK_a + log \frac{[Salt]}{[Acid]}$$

$$pOH = pK_b + log \frac{[Salt]}{[Base]}$$

Example: What is the pH of a solution that is 0.400 M in formic acid and 1.00 M in sodium formate? $(K_a = 1.8 \times 10^{-4})$

$$pH = -\log(1.8 \times 10^{-4}) + log \frac{[1]}{[0.4]}$$

$$pH = 3.745 + 0.602 = 4.347$$

Q: Calculate the pH of a buffer that is 0.020 M in NH_3 and 0.030 M in NH_4Cl.

$(K_b = 1.8 \times 10^{-5})$

$$pOH = pK_b + log\frac{[Salt]}{[Base]}$$

$$pOH = -\log(1.8 \times 10^{-5}) + log\frac{0.03}{0.02} = 4.92$$

$$\therefore pH = 9.08$$

Classical Methods for Analysis

Titrations in Analytical Chemistry

Titrations are widely used in analytical chemistry to determine acids, bases, oxidants, reductants, metal ions, proteins, and many other species. Titrations are based on a reaction between the analyte and a standard reagent known as the titrant. The reaction is of known and reproducible stoichiometry.

The volume, or the mass, of the titrant needed to react completely with the analyte is determined and used to calculate the quantity of analyte.

A volume-based titration is shown in this figure in which

the standard solution is added from a burette, and the

reaction occurs in the Erlenmeyer

flask.
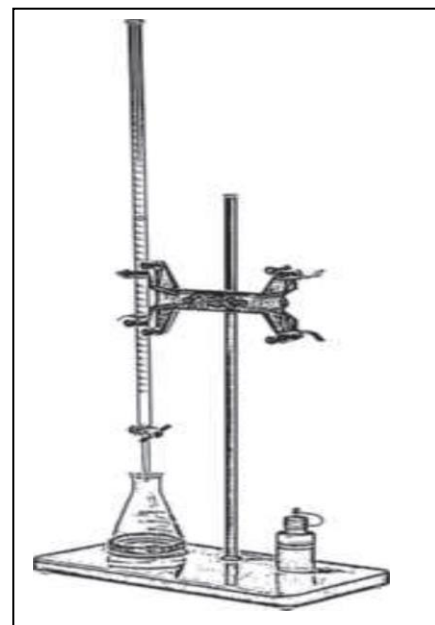
Volumetric titrations involve measuring the volume of a solution of known concentration that is needed to react completely with the analyte.

Some Terms Used in Volumetric Titrat ions

A standard solution is a reagent of known concentration that is used to carry out a volumetric titration.

The titration is performed by slowly adding a standard solution from a burette or other liquid-dispensing device to a solution of the analyte until the reaction between the two is judged complete.

The **equivalence point** in a titration is a theoretical point reached when the amount of added titrant is chemically equivalent to the amount of analyte in the sample.

We cannot determine the equivalence point of a titration experimentally. Instead, we can only estimate its position by observing some **physical change** associated with the condition of chemical equivalence. The position of **this change** is called the **end point** for the titration.

Indicators are often added to the analyte solution to produce an observable **physical change** (signaling the end point) at or near the **equivalence point**.

Typical indicator changes include the appearance or disappearance of a color, a change in color, or the appearance or disappearance of turbidity. As an example, the indicator used in the neutralization titration of hydrochloric acid with sodium hydroxide is phenolphthalein, which causes the solution to change from colorless to a pink color once excess sodium hydroxide has been added.

We often use instruments to detect end points. These instruments respond to properties of the solution that change in a characteristic way during the titration.

Among such instruments are colorimeters, turbidimeters, spectrophotometers, temperature monitors, refractometers, voltmeters, current meters, and conductivity meters.

A **primary standard** is a highly purified compound that serves as a reference material in titrations and in other analytical methods.

Important requirements for a primary standard are the following:

1. High purity.

2. Atmospheric stability.

3. Absence of hydrate water so that the composition of the solid does not change with variations in humidity.

4. Modest cost.

5. Reasonable solubility in the titration medium.

6. Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.

The ideal **standard solution** for a titrimetric method will

1. be sufficiently stable so that it is necessary to determine its concentration only once;

2. React rapidly with the analyte so that the time required between additions of reagent is minimized;

3. React more or less completely with the analyte so that satisfactory end points are realized;

4. Undergo a selective reaction with the analyte that can be described by a balanced equation.

The accuracy of a titration can be no better than the accuracy of the concentration of the standard solution used. Two basic methods are used to establish the

concentration of such solutions. The first is the direct method in which a carefully determined mass of a primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask. The second is by standardization in which the titrant to be standardized is used to titrate

(1) A known mass of a primary standard,

(2) A known mass of a secondary standard, or

 (3) A measured volume of another standard solution.

 A titrant that is standardized is sometimes referred to as a secondary standard solution.

Volumetric Calculations

For the standard solutions used in most titrations, either molar concentration, M, or normal concentration, N, is usually used.

Molar concentration is the number of moles of reagent contained in one liter of solution, and normal concentration is the number of equivalents of reagent in the same volume.

$$M = \frac{w(solute) \times 1000}{Molecular\ weight \left(\frac{g}{mol}\right) \times v(solution)}$$

$$N = \frac{w(solute) \times 1000}{Equivalent\ weight \left(\frac{g}{mol}\right) \times v(solution)}$$

$$Equivalent\ weight = \frac{Molecular\ weight}{number\ of\ equivalent}$$

$$\therefore N = number\ of\ equivalent \times M$$

Example: Describe the preparation of 2.000 L of 0.0500 M $AgNO_3$ (169.87 g/mol) from the primary-standard-grade solid.
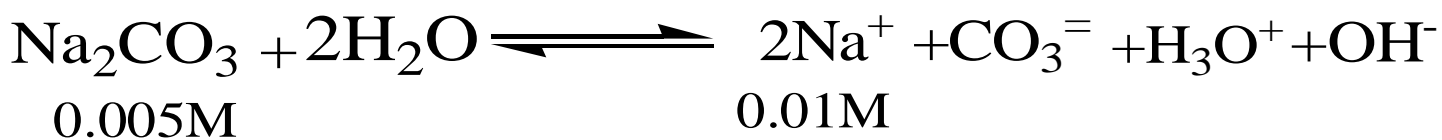
Solution:

$$M = \frac{w \times 1000}{M.wt \times v}$$

$$\therefore \quad w = \frac{M \times M.wt \times v}{1000} = \frac{0.05 \times 169.87 \times 2000}{1000} = 16.987 g$$

Therefore, the solution should be prepared by dissolving 16.987 g of $AgNO_3$ in water and diluting to the mark in a 2.000 L volumetric flask.

Example: Describe how 500 mL of 0.0100 M solution of Na^+ can be prepared from primary standard Na_2CO_3 (105.99 g/mL).

Solution:

$$Na_2CO_3 + 2H_2O \rightleftharpoons 2Na^+ + CO_3^= + H_3O^+ + OH^-$$
$$0.005M \qquad\qquad\qquad 0.01M$$

$$w = \frac{M \times M.wt \times v}{1000} = \frac{0.005 \times 105.99 \times 500}{1000} = 0.265 g$$

The solution should be prepared by dissolving 0.265 g of Na_2CO_3 in water and diluting to 500 mL.

Example: Describe the preparation of 0.5 L of 0.0200N $CaCO_3$ (100 g/mol) from the primary-standard-grade solid.

Solution:

$$w = \frac{N \times Eq.wt \times v}{1000} = \frac{0.02 \times \frac{100}{2} \times 500}{1000} = 0.5 \ g$$

The solution should be prepared by dissolving 0.5 g of $CaCO_3$ in water and diluting to 500 mL.

Working with Titration Data

Example: A 50.00-mL portion of an HCl solution required 29.71 mL of 0.04 N Ba(OH)$_2$ to reach an end point with bromocresol green indicator. Calculate the normality of the HCl.
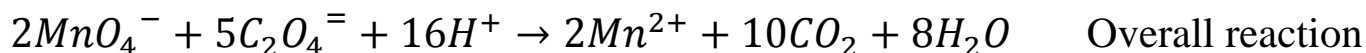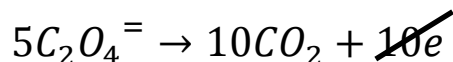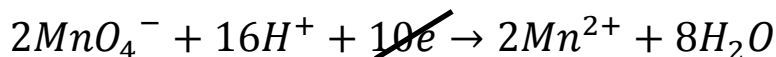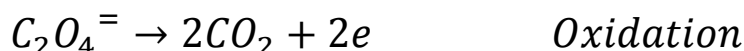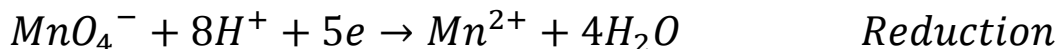
Solution:

$$(N \times V)_{Ba(OH)_2} \equiv (N \times V)_{HCl}$$

$$0.04 \times 29.71 = N \times 50$$

$$\therefore \quad N_{HCl} = 0.0237 \ g.eq/l$$

Example: Titration of 0.2121 g of pure $Na_2C_2O_4$ (134.00 g/mol) required 43.31 mL of $KMnO_4$. What is the molar concentration of the $KMnO_4$ solution? The chemical reaction is

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O \qquad Reduction$$

$$C_2O_4^= \rightarrow 2CO_2 + 2e \qquad Oxidation$$

$$2MnO_4^- + 16H^+ + 10e \rightarrow 2Mn^{2+} + 8H_2O$$

$$5C_2O_4^= \rightarrow 10CO_2 + 10e$$

$$2MnO_4^- + 5C_2O_4^= + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O \qquad \text{Overall reaction}$$

$$(N \times V)_{C_2O_4^=} = (N \times V)_{MnO_4^-}$$

$$\left(\frac{w \times 1000}{eq.wt}\right)_{C_2O_4^=} = (N \times V)_{MnO_4^-}$$

$$M.wt_{Na_2C_2O_4} = 2 \times 23 + 2 \times 12 + 4 \times 16 = 134\frac{g}{mol}$$

$$Eq.wt_{Na_2C_2O_4} = \frac{134}{2} = 67$$

$$\frac{0.2121 \times 1000}{67} = N \times 43.31$$

$$N_{KMnO_4} = 0.0731 \; g \; eq/l$$

$$M_{KMnO_4} = N_{KMnO_4} \div 5 = 0.0731 \div 5 = 0.01462 \; mol/l$$