Chapter 3

Stoichiometric Calculations

- Stoichiometry deals with the ratios in which chemicals react.

3.1 Review of Fundamental Concepts

- gram-atomic weight:
  the weight of a specified number of atoms of that element.

  Avogadro's number:

  6.022×10^{23} atoms/g-at wt.

- gram-molecular weight (gmw):
  the sum of the atoms that make up a compound.

- gram-formula weight (gfw):
  molar mass; formula weight; for substances that don't exist as molecules but exist as ionic compounds.

- daltons:
  the mass of a single carbon-12 atom is equivalent to 12 daltons.
  $\Rightarrow$ 1 dalton=1.661×10^{-24} g

- moles:
  as Avogadro's number of atoms, molecules, ions…

$$\text{moles} = \frac{\text{grams}}{\text{formula weight (g/mol)}}$$

$$\text{millimoles} = \frac{\text{milligrams}}{\text{formula weight (mg/mmol)}}$$

$$\text{g}/\text{mol} = \text{mg}/\text{mmol}\ ,\ \ \text{g}/\text{L} = \text{mg}/\text{mL}\ ,$$

$$\text{mol}/\text{L} = \text{mmol}/\text{mL} = \text{molarity}$$

$$\text{milligrams} = \text{millimokes} \times \text{formula weight (mg/mmol)}$$

3.2 Concentrations of Solutions

- Molarity:
  moles per liter or millimoles per milliliter.

$$\text{moles} = \left(\text{moles}/\text{liter}\right) \times \text{liters}$$

$$= \text{molarity (M)} \times \text{liters}$$

$$\text{millimoles} = \text{molarity} \times \text{milliliters}$$

- Normality (N): the equivalent per liter

  equivalent:

  the mass of material providing Avogadro's number of reacting units.

  reacting unit:

  a proton or an electron.

  equivalent weight:

  the formula weight divided by the number of reacting units.

$$\text{number of equivalents (eq)} = \frac{\text{wt. (g)}}{\text{eq.wt. (g/eq)}}$$

$$= \text{normality } \left({}^{eq}\!/\!_{L}\right) \times \text{volume (L)}$$

$$\text{meq} = \frac{\text{mg}}{\text{eq.wt. (mg/meq)}}$$

$$= \text{normality } \left({}^{meq}\!/\!_{mL}\right) \times \text{mL}$$

$${}^{g}\!/\!_{eq} = {}^{mg}\!/\!_{meq} \;,\quad {}^{eq}\!/\!_{L} = {}^{meq}\!/\!_{mL} = \text{normality}$$

$$\text{stoichiometry factor, n (units of } {}^{eq}\!/_{mol})$$

$$\text{equivalents} = \text{moles} \times \text{n} \, ({}^{eq}\!/_{mol})$$

$$\text{N} \, ({}^{eq}\!/_{L}) = \text{M} \, ({}^{mol}\!/_{L}) \times \text{n} \, ({}^{eq}\!/_{mol})$$

$$\text{eq. wt.} \, ({}^{g}\!/_{eq}) = \frac{\text{f. wt.} \, ({}^{g}\!/_{mol})}{\text{n} \, ({}^{eq}\!/_{mol})}$$

The number of equivalents depends upon the specific reaction.

$$\text{Ex}: \quad CO_3^{2-} + H^+ \rightarrow HCO_3^- \qquad n = 1$$

$$CO_3^{2-} + 2H^+ \rightarrow H_2CO_3 \qquad n = 2$$

In clinical chemistry

equivalent:

the number of charges on an ion

- Formality (F):
  used for solution of ionic salts=molarity

- Molality (m):
  moles per 1000 grams of solvent

  Molal concentrations are not temperature dependent.

- Analytical concentration: the concentration of total dissolved substance.

  $$\text{Ex}: \ \text{HOAc} + H_2O \leftrightarrow H_3O^+ + \text{OAc}^-$$

  $$\text{HOAc}: 0.100 \,\text{mol}/0.100\text{L}$$

  $$\Rightarrow [\text{HOAc}] = 0.0987$$

  $$[\text{OAc}^-] = 0.0013 = [H^+] \quad \alpha = 1.3\%$$

- Density: the weight per unit volume at the specified temperature. g/mL or g/cm^3 at 20℃.

- Specific gravity: the ratio of the mass of a body (usually at 20℃) to the mass of an equal volume of water at 4℃.

  density=specific gravity at 4℃

  density=specific gravity×0.99823 at 20℃

  Ex: 3.10

- Dilutions: millimoles (stock sol'n)

  =millimoles (final sol'n)

3.3 Expressions of Analytical Results

- Results will be reported as concentration on either a weight or a volume basic: the quantity of analyte per unit weight or per volume of sample.

K=kilo=10^{3}	μ =micro=10^{-6}	p=pico=10^{-12}
m=milli=10^{-3}	n=nano=10^{-9}	f=femto=10^{-15}
a=atto=10^{-18}	M=mega=10^{6}	G=giga=10^{9}
T=tera=10^{12}	P=peta=10^{15}	E=exa=10^{18}

- Solid Sample:

$$\%\left({}^{wt}\!/\!_{wt}\right) = \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^2$$

$$\text{parts per thousand (ppt)}: \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^3$$

$$\text{parts per million (ppm)}: \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^6$$

$$\text{parts per billion (ppb)}: \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^9$$

$$\text{parts per trillion (ppt)}: \left[\frac{\text{wt solute (g)}}{\text{wt sample (g)}}\right] \times 10^{12}$$

See Table 3.2

$$\text{ppt} = \frac{\text{mg}}{\text{g}} = \frac{\text{g}}{\text{Kg}}$$

$$\text{ppm} = \frac{\mu\text{g}}{\text{g}} = \frac{\text{mg}}{\text{Kg}}$$

$$\text{ppb} = \frac{\text{ng}}{\text{g}} = \frac{\mu\text{g}}{\text{Kg}}$$

$$1\ \text{ppt} = 10^3\ \text{ppm} = 10^6\ \text{ppb},\quad 1\ \text{ppm} = 10^3\ \text{ppb}$$

$$\text{milligram percent (mg\%)}$$

$$= \text{mg of analyte per 100g of sample}$$

- Liquid Sample:

weight/weight basis ; weight/volume basis

$$\% \left({}^{wt}/_{vol}\right) = \left[\frac{\text{wt. solute (g)}}{\text{vol. sample (mL)}}\right] \times 10^2 = \frac{\text{g}}{\text{100 mL}}$$

$$\text{ppt} \left({}^{wt}/_{vol}\right) = \left[\frac{\text{wt. solute (g)}}{\text{vol. sample (mL)}}\right] \times 10^3$$

$$\text{ppm} \left({}^{wt}/_{vol}\right) = \left[\frac{\text{wt. solute (g)}}{\text{vol. sample (mL)}}\right] \times 10^6$$

$$\text{ppb} \left({}^{wt}/_{vol}\right) = \left[\frac{\text{wt. solute (g)}}{\text{vol. sample (mL)}}\right] \times 10^9$$

$$\text{ppt} = \frac{\text{mg}}{\text{mL}} = \frac{\text{g}}{\text{L}}$$

$$\text{ppm} = \frac{\mu\text{g}}{\text{mL}} = \frac{\text{mg}}{\text{L}}$$

$$\text{ppb} = \frac{\text{ng}}{\text{mL}} = \frac{\mu\text{g}}{\text{L}}$$

(wt/wt)=(wt/vol)

when aqueous solutions are dilute

volume/volume basis:

Ex: alcoholic beverage.

- Gas Sample:
  weight/weight , weight/volume , or volume/volume basis

- In general:
  - solid sample: wt/wt
  - concentrated liquids: wt/wt
  - dilute liquids: wt/vol
  - gas sample: vol/vol

For expressing the amount of major electrolytes in biological fluids: (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, $H_2PO_4^-$, etc…)

milliequivalent (meq): the number of millimoles of analyte multiplied by the charge on the analyte ion. ⇒ meq/L

$$\text{meq} = \frac{\text{mg}}{\text{eq. wt. (mg/meq)}}$$

$$= \frac{\text{mg}}{\text{f. wt. (mg/mmol)} \big/ \text{n (meq/mmol)}}$$

Table 3.3

- Expressing Concentrations as Equivalents of Substances

  Ex: % Fe $\leftrightarrow$ % Fe_2O_3

  % Ca^{2+} $\leftrightarrow$ % $CaCO_3$ $\leftrightarrow$ % CaO

  wet weight: the fresh, untreated sample

  dry weight: the sample has been dried by heating…

  ashed weight: the weight of the ash residue.

3.4 Volumetric Analysis: Stoichiometric Calculation

1) rapid
2) convenient
3) accurate
4) readily automated

3.4-2

- Titration Principles:
  1) Volumetric titrimetry $\Rightarrow$ volume
  2) Weight or gravimetry titrmetry $\Rightarrow$ weight
  3) Coulometric titrimetry $\Rightarrow$ electricity

- Standard solution:
  the reagent of known concentration.

  Titrant:
  the reagent (a standard solution) which is added from a buret to react with the analyte.

  Titration:
  the process of measuring the volume of titrant required to reach the equivalence point.

- The requirements of a titration:
  1. The reaction must be stoichiometric, there must be a well-defined and known reaction between the analyte and the titrant.
  2. The reaction should be rapid.
  3. There should be no side reactions, and the reaction should be specific.

4. There should be a marked change in some property of the solution when the reaction is complete.
   $\Rightarrow$ the equilibrium constant of the reaction should be large.
5. Equivalence point:

   the point in a titration where chemically equivalent amounts of analyte and titrant are present.

End point:

- the point in a titration where there is a sudden change in a physical property of the solution, such as the color of an indicator.

Titration error:

- difference between equivalence point and end point.

$\Rightarrow$ some method must be available for determining when the equivalence point is reached.

- The reaction should be quantitative

$\Rightarrow$ sharp change will occur at the end point to obtain the desired accuracy.

- Standard Solution:
  1) be sufficiently stable
  2) react rapidly with the analyte
  3) react more or less completely with the analyte
  4) undergo a selective reaction with the analyte

- Methods for establishing the concentration of standard solutions:
  1) direct method: from primary standard
  2) standardization:
     a) from primary standard
     b) from secondary standard
     c) from another standard solution

- Primary Standard:
  1. It should be 100.00% pure, or impurity < 0.01~0.02%.
  2. It should be stable to drying temperatures, and it should be stable indefinitely at room temperature.
  3. It should be readily available.
  4. It should have a high formula weight.
  5. It should possess the properties required for a titration.

- Classification of Volumetric Methods:

1. Acid-Base:

   $HA + OH^- \rightarrow A^- + H_2O$

   titrant: NaOH; HCl

   adding indicator, or by electrode

2. Precipitation:

   $Ag^+ + Cl^- \rightarrow AgCl_{(s)}$

   adding indicator, or by electrode

3. Complexometric:

   $Ag^{+} + 2CN^{-} \rightarrow Ag(CN)_2^{-}$

   titrant: chelating agent

   Ex: EDTA

   (Ethylenediaminetetraacetic acid)

4. Reduction-Oxidation (redox titration):

   $Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$

3.5 Molarity Volumetric Calculations

$$\text{moles} = \text{g} / \text{f.w.(g/mol)}$$

$$\text{millimoles} = \text{mg} / \text{f.w.(mg/mmol)}$$

$$\text{M} = \text{mol} / \text{L} \; ; \; \text{M} = \text{mmol} / \text{mL} \; ;$$

$$\text{M} \times \text{L} = \text{mol} \; ; \; \text{M} \times \text{mL} = \text{mmol}$$

$$\text{g} = \text{mol} \times \text{f.w.(g/mol)} \; ; \; \text{mg} = \text{mmol} \times \text{f.wt.(mg/mmol)}$$

$$\text{g} = \text{M} \times \text{L} \times \text{f.wt.(g/mol)} \; ; \; \text{mg} = \text{M} \times \text{mL} \times \text{f.w.(mg/mmol)}$$

$$\%\,\text{A} = \frac{\text{mg analyte}}{\text{mg sample}} \times 100\% = \frac{\text{M} \times \text{mL} \times \text{f.w.}}{\text{mg sample}} \times 100\%$$

- General Calculations with Molarity:

$$aA + tT \rightarrow P$$

$$mmol_A = mmol_T \times \frac{a}{t}\frac{mmol\ A}{mmol\ T}$$

$$\Rightarrow M_T \times mL_T \times \frac{a}{t}$$

$$mg_A = M_T \times mL_T \times \frac{a}{t} \times f.w._A$$

$$\%\ A = \frac{M_T \times mL_T \times {}^{a}\!/\!_{t} \times f.w._A}{mg\,(sample)} \times 100\%$$

- Standardization:

$$M_T = \frac{\frac{mg_{(s)}}{f.w._{(s)}} \times \frac{t}{s}}{mL_{(T)}}$$

t : titrant   s : standard

- Back-Titrations:

1) A reaction is show to go to completion

2) A sharp end point cannot be obtained

Ex: in the titration of antacid tablets with a strong acid such as HCl

mmol reagent reacted =mmol taken-mmol back-titrated

3.6 Normality Volumetric Calaulations

$$N = {}^{eq}\!/_{L} = {}^{meq}\!/_{mL}$$

$$eq = mol \times n \quad meq = mmpl \times n$$

- Equivalent weight:

  the weight of a substance that will furnish one mole of the reacting unit.

$$meq_A = meq_T \quad meq = N_T \times mL$$

$$mg_A = N_T \times mL_T \times eq.wt._A$$

$$\%\,A = \frac{N_T \times mL_T \times eq.wt._A}{mg\,(sample)} \times 100\,\%$$

- Reacting unit in normality calculation:
  1) Acid-Base $\Rightarrow$ reacting unit: H^+
     depends on reaction
  2) Reduction-Oxidation $\Rightarrow$ reacting unit: e^-

  Ex :

$$5Fe^{2+} + MnO_4^- + 8H^+ \leftrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$\%\,A = \frac{N_T \times mL_T \times eq.wt._A}{mg\,(sample)} \times 100\%$$

3.7 Titer

- Titer=milligrams analyte that react with 1mL of titrant

Ex: a potassium dichromate solution has a titer of 1.267mg Fe

$\Rightarrow$ w.t.$_A$=Titer$\times$mL

3.8 Weight Relationships: Gravimetric Analysis

$$\text{GF} = \text{gravimetric factor}$$

$$= \frac{\text{f.wt. of substance sought}}{\text{f.wt. of substance weight}} \times \frac{a\,(\text{mol sought})}{b\,(\text{mol weight})}$$

$$\text{mg of analyte} = (\text{mg of weight p.p.t}) \times \text{G.F.}$$

$$\text{Ex}: \quad \text{Fe} \longrightarrow \text{Fe}_2\text{O}_3$$

$$\text{GF} = \frac{\text{A.wt. of Fe}}{\text{F.wt. of Fe}_2\text{O}_3} \times \frac{2}{1}$$