

Ch. 1: Introduction

Analytical chemistry - deals with the chemical characterization of matter; may involve use of chemical reactivity or instrumental methods.

Qualitative analysis - identification of elements, ions, or compounds present in a sample.

Quantitative analysis - determination of the relative amounts of different substances in a sample.

Analytical Process:

1. define the problem

type of sample → method (std method)

2. obtain representative sample***

homogeneous sample - "grab" sample

heterogeneous sample - combine several samples into gross sample, then get lab sample

handling and storage*
biological samples - special problems*

3. prepare sample for analysis

drying
weighing
dissolution

4. perform necessary chemical separations - remove interferences

5. perform the measurement

gravimetric analysis - analyte is isolated and weighed

volumetric analysis - titrations

instrumental analysis - use of chemical instrumentation

must be properly calibrated**

6. calculate and report results

accuracy vs. precision

sample analysis - complete or partial

major constituent ($X > 1\%$)

minor constituent ($1\% > X > 0.1\%$)

trace constituent ($0.1\% > X$)

Chapter 3: Data Handling

Accuracy - agreement between measured value and accepted true value.

Precision - degree of agreement between replicate measurements of the same quantity.

Significant figures - number of digits necessary to express the results of a measurement consistent with the measured precision; all known digits + first uncertain one.

multiplication and division - answer has same number of sig figs as least in the input values.

addition and subtraction - answer has same number of decimals as least in the input values.

logarithms - set by mantissa.

rounding - $n > 5 \rightarrow$ next larger number

errors - expression of accuracy

absolute error = [true value - exp. value]

relative error = (abs. error / true value) %

indeterminate error - random

- will have normal distribution

determinate (systematic) error - has bias

- instrumental
- operative
- method

deviation - expression of precision

d = [avg. - exp. value]

If N = number of determinations, the mean from N measurements is $N^{1/2}$ more reliable than a single measurement.

standard deviation (σ) if N is large.

est. standard deviation (s) if N is small.

small < 40 (use degrees of freedom)

RSD = s / mean (may be as %)

If no systematic error is present:

68% of results +/- s from mean

95% of results +/- 2 s from mean

99% of results +/- 2.5 s from mean

variance = s^2

**propagation of errors - may be relative (x / ÷)
or absolute (+ / -).**

**control charts - plot of known value (inner
and outer limits) vs time. Look for trends.**

confidence level:

confidence limit = mean +/- (ts / $N^{1/2}$)

see p. 90 for table of t values

**tests of significance - comparison of 2
methods**

rejection of value - Q test (table, p. 99)

small data sets - median vs mean

AD and RAD - for very small data sets

note: consider detection limits vs blank.

Chapter 4: Quality Assurance

QA – implementation of procedures to ensure and document that a method continues to perform as required.

“Good Laboratory Practice”

method hierarchy

- a. technique – scientific principle**
- b. method – selected adaptation**
- c. procedure – written directions**
- d. protocol – specific directions**

QA documentation required includes:
validation of method
documentation of procedures followed
sample custody chain

QC – Quality Control (quantitative procedures to implement QA)

- 1. control charts**
- 2. documentation and archiving
(may be electronic)**
- 3. proficiency testing**

Laboratory Accreditation: agencies

Chapter 5: Stoichiometric Calculations

Review:

atomic, molecular, formula weight (mass)
mole - formula wt expressed in grams

concentration of solutions:

M = molarity = moles solute / L soln

N = normality = eq solute / L soln

redox and acid/base - 1 eq is
amount which supplies 1 reacting
unit (e^- , H^+ , or OH^-)

N = M x eq/mole

F = formality (defunct concept)

m = molality = $\frac{\text{moles solute}}{\text{kg solvent}}$

d = density = mass/vol (at specific T)

sp. gravity = mass/same mass of H_2O

analytical conc (C_x) vs equilibrium conc [X]

dilution: $V_{\text{conc}}C_{\text{conc}} = V_{\text{dil}}C_{\text{dil}}$

expression of results:

solid samples - % by mass (ppm, ppb)

**liquid samples - % by mass or % by vol
(% mass/vol - ppt, ppm, ppb) - caution**

Volumetric Analysis

titration - test substance is reacted with a measured amount of a reagent solution of known concentration (standard solution), usually added from a buret.

requirements:

- 1. must be stoichiometric**
- 2. must be rapid reaction**
- 3. no side reactions**
- 4. some marked change at end point**
- 5. small endpoint error**
- 6. must be quantitative (complete rx)**

standard solutions:

primary standard - material is weighed out and diluted directly to known conc.

requirements for primary standard:

- 1. ultrapure substance**
- 2. stable in drying oven**
- 3. readily available and cheap**
- 4. high formula weight is good**
- 5. have req. properties for titration**

secondary standard - solution standardized by titration against a primary standard.

types of titrations:

- 1. acid/base (neutralization)**
- 2. precipitation**
- 3. complexiometric**
- 4. oxidation/reduction (redox)**

Volumetric Calculations:

M vs N

M = moles/vol, so moles = vol x M

If moles analyte = moles titrant, at eq pt,

$$M_{\text{anal}} V_{\text{anal}} = M_{\text{titrant}} V_{\text{titrant}}$$

**If moles analyte \neq moles titrant, at eq pt,
must incorporate correction factor.**

This is compensated for by N, so

$$N_{\text{anal}} V_{\text{anal}} = N_{\text{titrant}} V_{\text{titrant}}$$

**backtitrations - pass eq. pt., titrate
excess titrant, and correct volume.**

Gravimetric Analysis

GF = grav. factor = $\frac{\text{f wt substance sought}}{\text{f wt substance analzd}}$

% X = $\frac{\text{ppt wt} \times \text{GF}}{\text{sample wt}} \times 100\%$

Chapter 6: Chemical Equilibrium

equilibrium – state in which forward and reverse reaction rates become equal; concentrations will be constant.

$$K = k_f/k_r = [\text{products}] / [\text{reactants}]$$

note: expression is valid, but deriv. Is not for reaction $aA + bB = cC + dD$,

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ or (gas phase) } K_p$$

K is determined empirically by measuring eq. concentrations. K is T dependent; the value is not changed by changing concentrations (LeChatelier's Principle) or adding a catalyst.

$$\Delta G = - RT \ln K = - 2.303 RT \log K,$$

$$\text{or at eq, } E^0 = 0.0522/n \log K$$

Types of equilibria:

1. acid/base (dissoc. constants) - K_a , K_b
2. solubility (solubility prod. Cst) - K_{sp}
3. complex formation - K_f
4. redox - K
5. phase distribution (distrib. cst)- K_d

Types of calculations:

1. determination of K
2. dissociation – eq. concentrations
3. common ion

Calculation procedure:

1. examine problem
2. if quadratic, use assumptions?
 - successive approximations
 - neglect x in denominator if
 $C_x > 1\% K$, or $C_x/K > 100$

other considerations:

1. mass balance (stoichiometry)

$$\text{total } [\text{CO}_3^{2-}] = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

2. charge balance (total + = total -)

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-]$$

heterogeneous equilibria: solids and pure liquids (solvents in dilute solutions) do not appear in the K expression.

Example: K_{sp}

Activity (α_x) – “effective concentration” of a solute in solution

diverse salt effect – increase dissociation of weak electrolyte or solubility of a substance

$$\alpha_x = f_x[X] \quad f_x = \text{activity coefficient}$$

If $[X] < 10^{-4}$, $f_x \approx 1$. If $[X] > 10^{-4}$, look up in tables or calculate.

Debye-Huckel Eq:

$$-\log f_x =$$

μ = ionic strength (measure of total electrolyte concentration)

Ch. 9: Complexiometric Titrations

Coordination Compounds: contain central metal atom or ion surrounded by ligands

ligands - electron pair donating species

monodentate ligands - donate only one electron pair. Ex: H_2O , NH_3 , Cl^-

polydentate ligands - donate more than one electron pair. Ex: en, DMG, and $\text{C}_2\text{O}_4^{2-}$ - bidentate, EDTA - hexadentate

coordination number - number of metal-ligand bonds formed. 2 (linear), 4 (square planar or tetrahedral), and 6 (octahedral) most common

chelates - ring structures formed by bonding of polydentate ligands to a metal

formation constants (K_f) - sequential

monodentates - $K_1 > K_2 > K_3$, etc

chelates - reverse - **chelate effect**

**EDTA = ethylenediaminetetraacetic acid
= H₄Y**

see book, p. 255

used for titrimetric Ca

**primary standard (Na₂H₂Y)
several indicators available
need basic pH for Y⁴⁻**

Chapter 10: Gravimetric Analysis

gravimetric analysis - the desired component is separated from the sample, usually as a precipitate, and weighed.

Steps:

1. **preparation of solution** - must consider factors such as concentration, volume, pH, T, and removal of interfering substances

2. **precipitation** -

-precipitation process

- a. supersaturation - K_{sp} is exceeded
- b. nucleation - formation of seed crystals
- c. crystal growth - should be slow

factors to slow growth

- dilute solutions
- add reagents slowly with good mixing (ppt from homo. solution)
- use hot solutions
- low pH

3. **digestion** - allow solution to remain in contact with mother liquor. This aids in removal of several types of impurities.
4. **filtration** - types of media
5. **washing** - avoid peptization (breaking up of colloidal ppt) by adding electrolyte
6. **drying / igniting**
7. **weighing**
8. **calculation** - gravimetric factor (GF)

$$\text{GF} = \frac{\text{molar mass of substance sought}^*}{\text{molar mass of substance weighed}}$$

***remember stoichiometry!!**

Types of impurities:

1. inclusion and occlusion - occlusion is caused by rapid growth; can be removed by digestion. Inclusion is usually similar size and charge ions and requires prior removal.
2. surface adsorption - removed by washing
3. post precipitation - avoid by not delaying filtration

organic chelating agents - may be very specific. Ex: DMG - Ni

solubility equilibria - K_{sp}

common ion effect - decreases solubility

Ch. 11: Precipitation Rx and Titrations

- reaction involves formation of a slightly soluble precipitate

factors to consider:

1. pH - formation of a weak acid
example: BaF_2 and HF
2. complex formation
example: AgCl and NH_3
3. detection of end point - main problem in ppt titrations
 - indicators may react with titrant
examples: Volhard (SCN^-) and Mohr (CrO_4^{2-}) methods for Cl^-
 - adsorption indicators
example: Fajans method for Cl^-

Mohr method: based on differences in K_{sp} between AgCl and AgCrO_4

Fajans method: based on change in charge of adsorbed counter ion after eq point

Chapter 7: Acid-Base Equilibria

practical definitions of acids and bases

- acid - tastes sour
 - turns litmus red
- base - tastes bitter
 - slippery feel
 - turns litmus blue

Acid-Base Theories:

Arrhenius:

- acid - H^+ donor
(note: H^+ = proton; in aqueous soln, is H_3O^+ - hydronium ion)
- base - OH^- donor

Bronsted-Lowery:

- acid - H^+ donor
- base - H^+ acceptor

Lewis:

- acid - e^- pair acceptor
- base - e^- pair donor

Acid-base equilibria in water

water is amphoteric - can act as either acid or base

$$K_w = [\text{H}^+][\text{OH}^-] = \text{autoionization cst} \\ = 1 \times 10^{-14} \text{ at } 25^\circ \text{ C}$$

neutral solution: $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

acid solution: $[\text{H}^+] > [\text{OH}^-]$, $[\text{H}^+] > 1 \times 10^{-7} \text{ M}$

base solution: $[\text{H}^+] < [\text{OH}^-]$, $[\text{H}^+] < 1 \times 10^{-7} \text{ M}$

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

neutral solution: $[\text{H}^+] = 1 \times 10^{-7} \text{ M}$, $\text{pH} = 7$

acidic solution: $[\text{H}^+] > 1 \times 10^{-7} \text{ M}$, $\text{pH} < 7$

basic solution: $[\text{H}^+] < 1 \times 10^{-7} \text{ M}$, $\text{pH} > 7$

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

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

strong acid - completely dissociated



strong base - completely dissociated



weak acid - incompletely dissociated

(equilibrium - K_a)

HF, HC₂H₃O₂, organic acids (-CO₂H)

weak base - incompletely dissociated

(equilibrium - K_b)

NH₃, organic bases (amines)

conjugate acids and bases - determine strength of acids and bases (note: leveling effect)

pH of strong acids: complete ionization

[H⁺] = nominal conc. of acid

pH = -log [H⁺]

pH of strong bases: complete ionization

[OH⁻] = nominal conc. of base

pOH = -log [OH⁻]

pH = 14 - pOH

pH of weak acids: K_a (solve eq. problem)

% dissociation

if $[HA]/K_a > 10^2$, neglect $-x$ in denom

$$[H^+] = K_a M_a$$

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

if not, must solve quadratic equation

pH of weak bases: K_b (solve eq. problem)

if $[B]/K_b > 10^2$, neglect $-x$ in denom

$$[OH^-] = K_b M_b$$

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

$$pH = 14 - pOH$$

if not, must solve quadratic equation

Salts - pH controlled by strength of conjugate species

$$K_w = K_a K_b$$

Hydrolysis - pH affect of salt on water.

salt of strong acid + strong base = neutral

salt of strong acid + weak base = acidic

salt of weak acid + strong base = basic

salt of weak acid + weak base = ??

solve pH of salts like that of a weak base or weak acid, using conjugate species of "weak" component

Examples: NH_4Cl → acidic solution

KNO_2 → basic solution

Buffers:

buffer solution - solution which resists a drastic change in pH upon addition of small amounts of a strong acid or base.

These frequently consist of a weak acid and its salt or a weak base and its salt.

pH of a buffer solution:

a. weak acid and its salt:

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+][\text{salt}]}{[\text{acid}]}$$

$$[H^+] = K_a \times [\text{acid}]/[\text{salt}]$$

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

note: minimal dilution effects

b. weak base and its salt:

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{[OH^-][\text{salt}]}{[\text{base}]}$$

$$[OH^-] = K_b \times [\text{base}]/[\text{salt}]$$

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

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

b. Henderson-Hasselbach equation

Polyprotic acids:

polyprotic acids - more than one H⁺

If $K_{a1} / K_{a2} > 1000$, ignore 2nd ionization.

buffer solutions - fraction at pH

salts: $[H^+] = (K_1 K_2)^{1/2}$ for HA⁻

Ch. 8: Acid-base titrations

titration curve - plot of pH (y-axis) vs. volume of titrant (x-axis).

a. strong acid / strong base

b. weak acid / strong base (det. of K_a)

stronger acid → better pH break

c. strong acid / weak base

d. polyprotic acids

for successive eq. points, $\Delta K_a > 10^4$

indicators - usually dyes which are weak organic acids or bases which have different colors for the acidic and basic forms.

- change over range of 2 pH units
- must be appropriate to species used

nonaqueous titration - solvent not water

Chapter 16: Spectrometry

Spectroscopy - interaction of radiation with matter

Spectrometric methods - measurement of intensity of radiation with an electronic device.

Electromagnetic radiation - type of energy which has both electrical and magnetic components (ex - heat and light). However, usually only consider electrical component, because that is what interacts with matter.

- requires no supporting medium; is transmitted readily through a vacuum
- frequently described in terms of a wave

ν = frequency (cycles per second)

λ = wavelength (distance between two equivalent points)

$$v_i = \nu\lambda$$

note: in vacuum, $v_i = c = 3.00 \times 10^8$ m/sec
treat air as vacuum

electromagnetic spectrum - large range; divisions based on methods required to generate radiation.

optical methods - UV, vis, IR

Quantum Mechanical model of radiation describes light in terms of **photons**, or particles of energy.

photoelectric effect – non-additive property of energy below a threshold level.

$$E = h\nu = hc/\lambda$$

ground state – lower energy state = E_0 .

excited state – higher energy state = E^* .

A species can be excited by:

1. particle bombardment
2. exposure to heat or electricity
3. irradiation by electromagnetic radiation

Emission - $E^* \rightarrow E_0$ (radiation given off)

Absorption - $E_0 \rightarrow E^*$

spectrum - plot of intensity of radiation (y) vs. λ or ν (x).

line spectrum – radiation only at certain wavelengths; from isolated atoms, due to electronic energy changes.

continuous spectrum – some radiation at all wavelengths over a given range.

band spectrum – series of peaks caused by overlay of electronic and vibrational changes; characteristic of molecules.

Types of Absorption:

atomic absorption – electron transitions
valence electrons – UV and visible
core electrons – X-rays

molecular absorption –

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{vibration}} + E_{\text{rotation}}$$

UV, visible – broad bands

IR – sharper bands

magnetic field – NMR and ESR

Quantitative Aspects:

Absorbance: Beer's Law $A = abc$ ($c = \text{g/L}$)
 $A = \epsilon bc$

Transmittance: $T = I_t / I_0$ $I = \text{intensity}$

$$A = \log 1/T = -\log T$$

instrumentation – UV, vis, IR

components :

1. stable source
2. transparent sample container
3. device to isolate small λ range
4. detector to convert I to electrical signal
5. signal processor / readout

- many components in common ; different arrangement and materials

- single and double beam instruments
 - single beam - quantitative
 - double beam - qualitative

chromophore - absorbing species

Chapter 12: Electrochemical Cells and Electrode Potentials

oxidation - loss of electrons

reduction - gain of electrons

oxidation-reduction (redox) reactions:



reducing agent - substance reduced.

oxidizing agent - substance oxidized

galvanic cell - uses a spontaneous redox reaction to generate electricity

electrolytic cell - uses applied potential to drive a nonspontaneous chemical reaction.

anode - electrode where oxidation occurs

cathode - electrode where reduction occurs

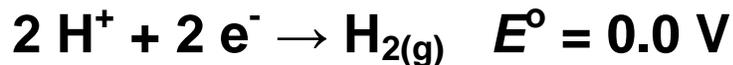
salt bridge - allows for passage of ions

line notation : $\text{Zn} / \text{Zn}^{2+}(\text{M}) // \text{Cu}^{2+}(\text{M}) / \text{Cu}$

cell potential - driving force for electron flow; measured in volts; also called emf or

electromotive force. This can't be measured absolutely, so must be measured relative to some standard.

standard reduction potential(E°) - potential of a half-reaction, written as a reduction, under standard conditions ($P = 1 \text{ atm}$, $[X] = 1 \text{ M}$), compared to the standard hydrogen electrode.



These can be found in tables (see p. 287)

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} + E^\circ_{\text{anode}}$$

If $E_{\text{cell}} > 0$, this is a spontaneous process and the cell is a galvanic cell.

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

n = moles e^- changed
 F = Faraday's cst
= 96,485 C/mole e^-
1 C = 1 amp x 1 sec

note: $\Delta G = - RT \ln K$, so this is one method of determining K

If $E_{cell} < 0$, this is a nonspontaneous process and the cell is an electrolytic cell.

dependence of cell potential on concentration is given by the Nernst equation:

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

At 25° C, this may be simplified to

$$E = E^{\circ} - \frac{0.0591}{n} \log Q,$$

so one can calculate E_{cell} if concentrations are known.

At equilibrium, $Q = K$ and $E_{cell} = 0.00 \text{ V}$,

so this becomes $E^{\circ} = \frac{0.0591}{n} \log K$,

$$\text{or } \log K = \frac{nE^{\circ}}{0.0591}.$$

note: may be affected by pH and / or complexation

Chapter 13: Potentiometry

based on measurement of potential of a solution by an electrode; measures activity directly rather than concentration.

Indicator Electrodes

1. electrodes of the first kind - metal in contact with its ions

Ex: $\text{Cu} / \text{Cu}^{2+}$

$$E = E^{\circ} - 2.303 RT / nF (\log 1/\alpha_{\text{Cu}^{2+}})$$

$\alpha_{\text{Cu}^{2+}} = \text{activity of Cu}^{2+}$

$$E_{\text{meas}} = E_{\text{cell}} = E_{\text{ind}} + E_{\text{ref}}$$

E_{ind} = potential of indicator electrode

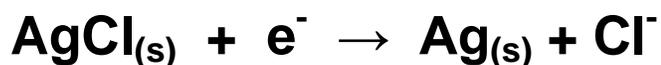
E_{ref} = potential of reference electrode

since reference electrode is std. H electrode,
 $E_{\text{ref}} = 0.00 \text{ V}$, and

$$E_{\text{cell}} = E_{\text{ind}}$$

2. electrodes of the second kind - metal in contact with an anion with which its ion forms a ppt or complex

Ex: Ag / AgCl electrode



$$E = E^\circ - 2.303 RT / nF (\log K_{sp})$$

This is often used as a reference electrode

3. redox electrodes - inert metal responsive in contact with soluble oxidized and reduced forms of a substance

Example: hydrogen electrode with Pt

To make potential measurements, must have two half-cells, or two electrodes, one of which has a constant potential (reference)

$$E_{cell} = E_{ind} + E_{ref}, \text{ if no liquid junction}$$

liquid junction - interface between two solutions containing different electrolytes or different concentrations of the same electrolyte; will cause a potential difference

$$E_{cell} = E_{ind} + E_{ref} + E_j$$

E_{ind} = potential of indicator electrode

E_{ref} = potential of reference electrode

E_j = liquid junction potential

Ideally, $E_j = 0.0$ V and E_{ref} is constant

Reference electrodes should

1. be easy to assemble
2. provide reproducible potential
3. remain unchanged in potential with passage of small amounts of current

Standard Hydrogen Electrode



Calomel Electrode



E° depends on KCl solution conc; for saturated calomel electrode @ 25° C = 0.2444 V

Indicator Electrodes:

glass pH electrode - potential forms across thin glass membrane separating two solutions of different pH. Potential is due to ion exchange processes on membrane surfaces

note: actually measures activity of H^+ directly

pH meter - measures potential between indicator and reference electrodes; must be standardized with buffers of known pH.

alkaline error - occurs at high pH due to high concentrations of Na^+ and K^+ .

acid error - at low pH activity of water is less than 1.

Chapter 14: Redox and Potentiometric Titrations

Balancing redox equations:

Method of half-reactions

1. Identify species being oxidized and reduced and write as half-reactions in the direction given.
2. Balance each half-reaction by first balancing the element undergoing oxidation or reaction, then balance oxygens by adding H_2O , then balance hydrogens by adding H^+ , then balance charge by adding e^- .
3. Multiply each balanced half-reaction by a common denominator to balance e^- loss and gain.
4. Add half-reactions back together to obtain balanced equation. Check for smallest coefficients.
5. If reaction is not in acidic solution, add OH^- to each side to neutralize all H^+ .

Redox Titrations:

1. $\text{K}_2\text{Cr}_2\text{O}_7$ as oxidizing agent

- is a primary standard
- requires indicator

2. KMnO_4 as oxidizing agent

- is not a primary standard
- requires elevated temperature
- must autocatalyze
- acts as own indicator
- must be acidic solution

3. Iodometric titrations