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Analytical Chemistry (0303211)

Course Information

Text Book: **Fundamentals of Analytical Chemistry by Skoog, West, Holler and Crouch; 9th Edition (2004)**

Grading System:

First exam	**20 marks**	**(To be announced later)**
Second exam	**30 marks**	**(To be announced later)**
Final Exam:	**50 marks**	**(To be announced later)**
Total	**100**	

Course Outline

[1] Based on 1-hour lectures

No. of lectures	Topics
2	**The Nature of Analytical Chemistry (Chapter 1)**
5	**Calculations Used in Analytical Chemistry (Chapter 4)**
3	**Errors in Chemical Analysis (Chapter 5):** Some important terms, systematic errors,
3	**Random Errors in Chemical Analysis (Chapter 6):** The nature of random errors, statistical treatment of random errors, standard deviation of calculated results, reporting computed data,
2	**Statistical Data Treatment and Evaluation (Chapter 7)**: confidence intervals, detection of gross errors

No. of lectures	Topics
5	**Aqueous Solutions and Chemical Equilibria (Chapter 9):** classifying solutions of electrolytes, chemical equilibrium, buffer solutions
3	**Effect of Electrolytes on Chemical Equilibria (chapter 10)**: The effect of electrolytes on chemical equilibria, activity coefficients,
3	**Solving equilibrium Problems for complex systems (Chapter 11):** solving equilibrium problems by a systematic method, the solubility of metal hydroxides, separation of ions by control of the concentration of the precipitating agent

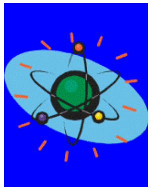
	Topics
6	**Gravimetric Methods of Analysis (Chapter 12):** Precipitation gravimetry, calculation of results from gravimetric data, applications of gravimetric methods
5	**Titrimetric methods; Precipitation Titrimetry (Chapter 13):** Some terms used in volumetric titrimetry, standard solutions, volumetric calculations, gravimetric titimetry, precipitation titrimetry
4	**Principles of Neutralization Titrations (Chapter 14):** Solutions and indicators for acid/base titrations, titration of strong acids and strong bases, titration curves for weak acids, titration curves for week bases, the composition of solutions during acid/base titrations.
3	**Complexation Reactions and Titrations (Chapter 17):** The formation of complexes, titrations with inorganic complexing agents, organic complexing agents, aminocarboxylic acid titrations

Chapter 1

The Nature of Analytical Chemistry?

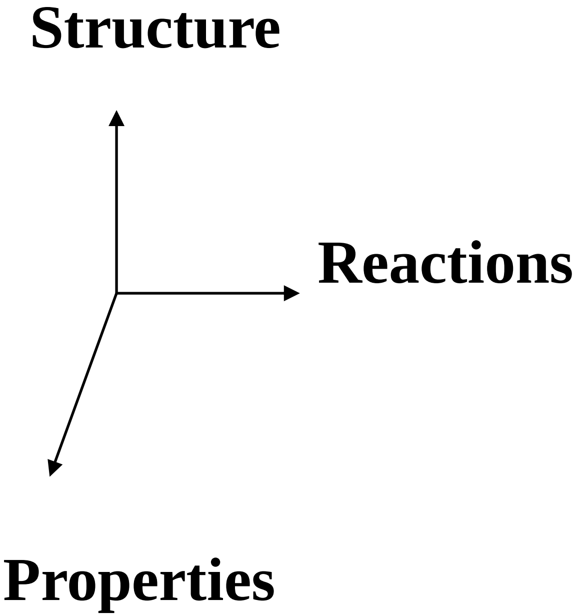
Modified by

Dr. Mohammed Rasheed



Introduction

What is chemistry ?



Structure

Reactions

Properties

Chemistry (kem'is tree): noun.

The science in which substances are examined to find out **what they are made of, how they act under different conditions, and how they are combined or separated to/from other substances**.

To paraphrase that, chemistry deals with finding what different substances are made of, what kind of transformations take place, and different chemically related facts about a certain organism or substance.

Introduction

Fields of chemistry

Physical chemistry

Analytical chemistry

Organic chemistry

Inorganic chemistry

Biological chemistry

What is Analytical Chemistry ?

- Analytical chemistry deals with separating, identifying, and quantifying the relative amounts of the components of an analyte.
- Analyte = the thing to analyzed; the component(s) of a sample that are to be determined.

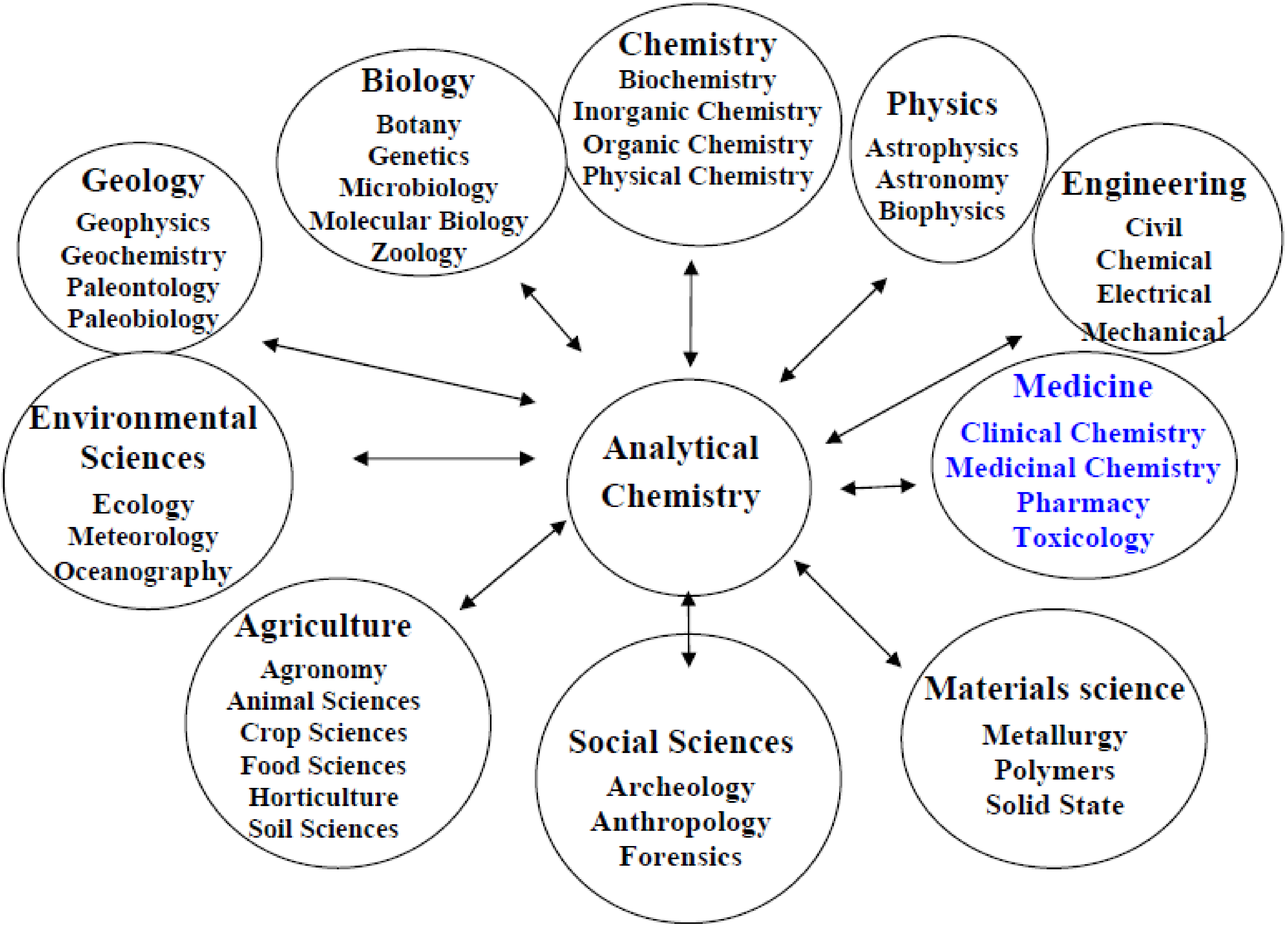


Figure 1-1 The relationship between analytical chemistry, other branches of chemistry and the other sciences. The central location of analytical chemistry in the diagram signifies its importance and the breadth of its interactions with many other disciplines.

What is analytical chemistry ?

- **Qualitative analysis :**

What is present ?

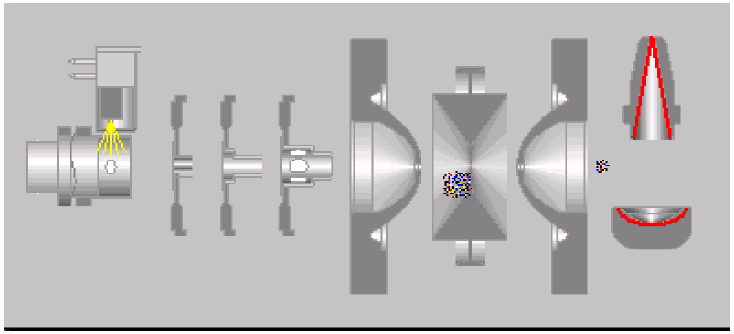
Determination of **chemical identity** of the species in the sample.

- **Quantitative analysis :**

How much present ?

determination of **the amount** of species or analytes, in **numerical** terms. Hence, math is heavily involved. In order to perform quantitative analysis, typically one needs to complete qualitative analysis. One needs to know what it is and then select the means to determine the amount.

- **Instrumental analysis**



Several different areas of analytical chemistry:

1. **Clinical** analysis - blood, urine, feces, cellular fluids, etc., for use in diagnosis.

2. **Pharmaceutical** analysis - establish the physical properties, toxicity, metabolites, quality control, etc.

3. **Environmental** analysis - pollutants, soil and water analysis, pesticides.

4. **Forensic** analysis - analysis related to criminology; DNA finger printing, finger print detection; blood analysis.

5. Industrial **quality control** - required by most companies to control product quality.

6. **Bioanalytical** chemistry and analysis - detection and/or analysis of biological components (i.e., proteins, DNA, RNA, carbohydrates, metabolites, etc.).
   This often overlaps many areas.
   Develop new tools for basic and clinical research.

Classification of Quantitative Methods of Analysis

1) Gravimetric Method: mass is measured.

2) **Volumetric** Method: volume is measured or used to determine amount of sample via concentration.

3) **Instrumental** Method: use an instrumental technique to assay the amount of sample:

Such as: **Electroanalytical** based upon electron-transfer
Spectroscopy including mass spectrometry
Separation: GC, HPLC, CE

Miscellaneous analytical methods

1. Mass spectrometry - mass-to-charge ratio of an analyte's decomposition products.
2. Radiochemical methods - measuring rates of radioactive decay by an analyte.
3. Kinetics - measuring reaction rates.
4. Thermal conductivity.
5. Optical activity - measuring the interactions of an analyte with plane-polarized light.
6. Refractometry / Refractive index.

ANALYTICAL CHEMISTRY

Analytical Methods

- Gravimetry (based on weight)

- Titrimetry (based on volume)

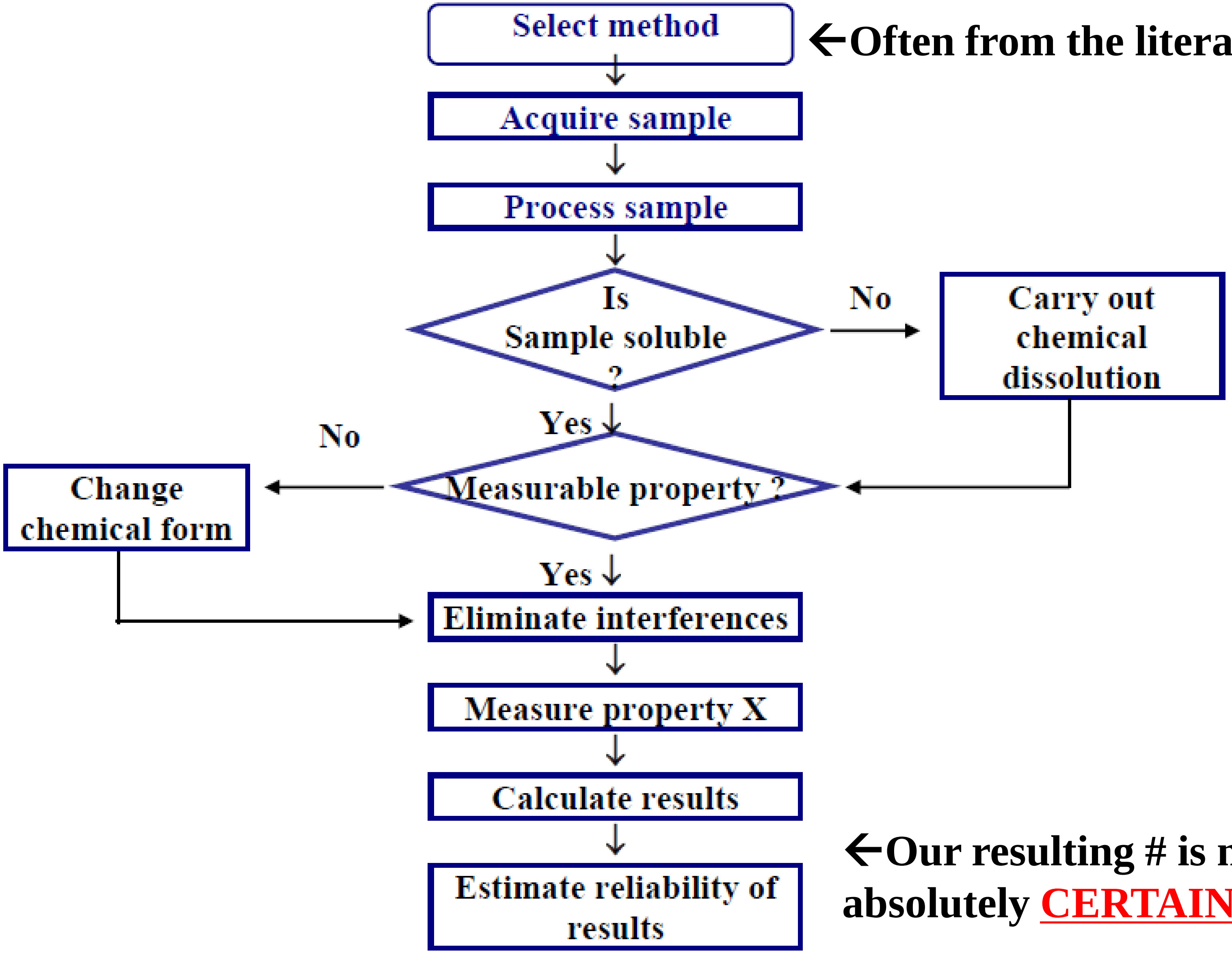
- Electrochemical (measurement of potential, current, charge, etc)

- Spectral (the use of electromagnetic radiation)

- Chromatography (separation of materials)

- Chemometrics (statistical treatment of data)

1C A Typical Quantitative Analysis



←**Often from the literature**

←**Our resulting # is never absolutely CERTAIN.**

An example of an analysis problem

Steps in a Typical Quantitative Analysis

1. Select a method: accuracy, reliability, time and cost, complexity of sample

   e.g., blood samples, pharmaceutical products.

2. Sampling: obtaining "a representative sample", especially important for mass products.

Select a small sample of composition that accurately represents the bulk

3. Sample preparation and handling
   a) Dissolution or digestion of samples
      Avoiding decomposition conditions. This is especially troublesome for biological samples.
   b) Preparation of solid samples :
      Solids are usually ground to a suitable particulate size to get a homogeneous sample.

4. Define replicate sample: accuracy, reliability and cost

5. Eliminating interferences: blank control

Interferences: species other than the analyte that affect the measurement

6. Calibration and measurement $C_A = kX$ $y = mX + b$

Calibration: process of determining the exact relationship between the property measured and the property sought for (Determination of k)

7. Calculation and data reduction

8. Evaluating results and estimating their reliability

   This requires appropriate use of statistics.
   An analytical result without an estimate of reliability is of no value.

Specificity and Selectivity

- Techniques or reactions that work for only one analyte are said to be **specific**.
- Techniques or reactions that apply for only a few analytes are **selective**.

Matrix

The **matrix** or **sample matrix** is all of the components in the sample containing an analyte.

Chapter 4

Calculations used in analytical chemistry

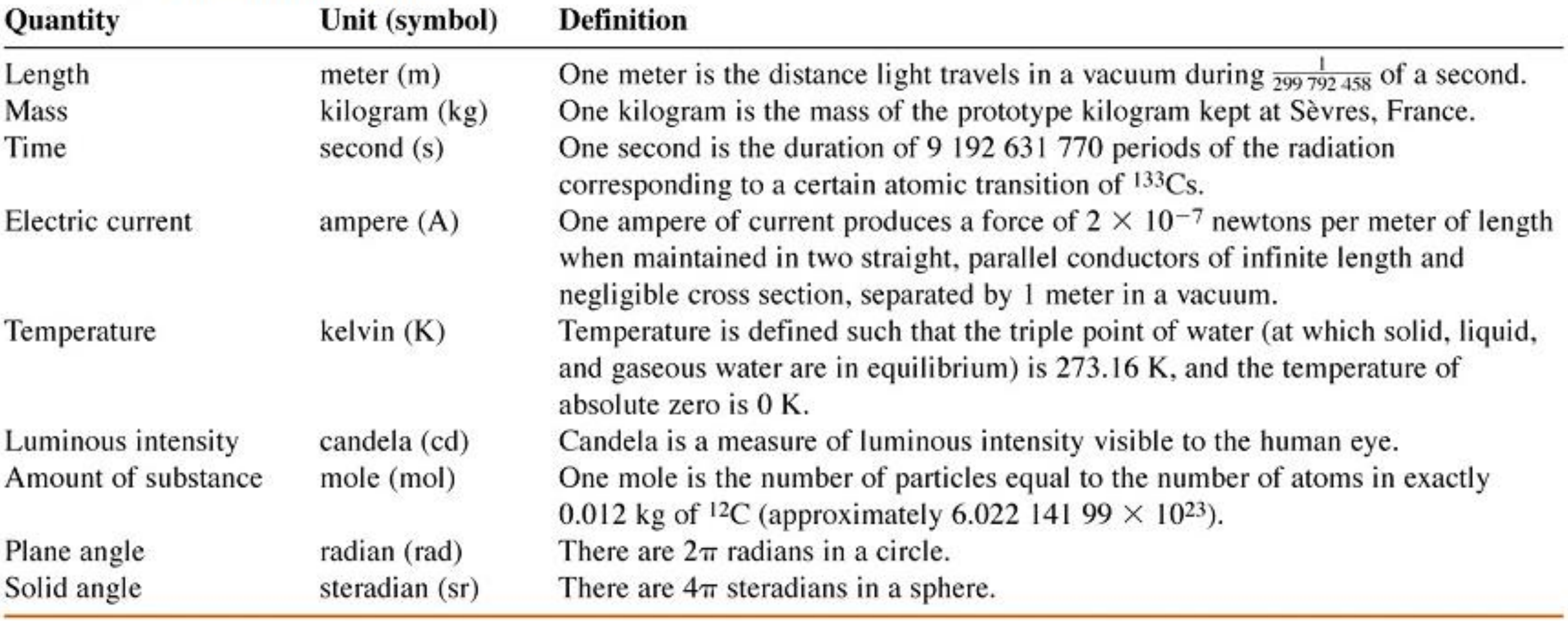
Modified by: Dr. Mohammed Rasheed

- The SI unit of mass, the kilogram, is defined as the mass of a specific **platinum-iridium alloy cylinder** (International Prototype Kilogram: IPK: K) kept at the International Bureau of Weights and Measures (Bureau International des Poids et Mesures) at Sevres, France. This mass standard was established in 1901, and there has been no change since that time because platinum iridium is an unusually stable alloy. The Sevres cylinder is 3.9 centimeters in diameter and 3.9 centimeters in height. A duplicate is kept at the National Bureau of Standards in Gaithersburg, Md.

Fig. 1. The official kilogram reference cylinder (left) and its copy (right) at the International Bureau of Weights and Measures in Sevres, France.

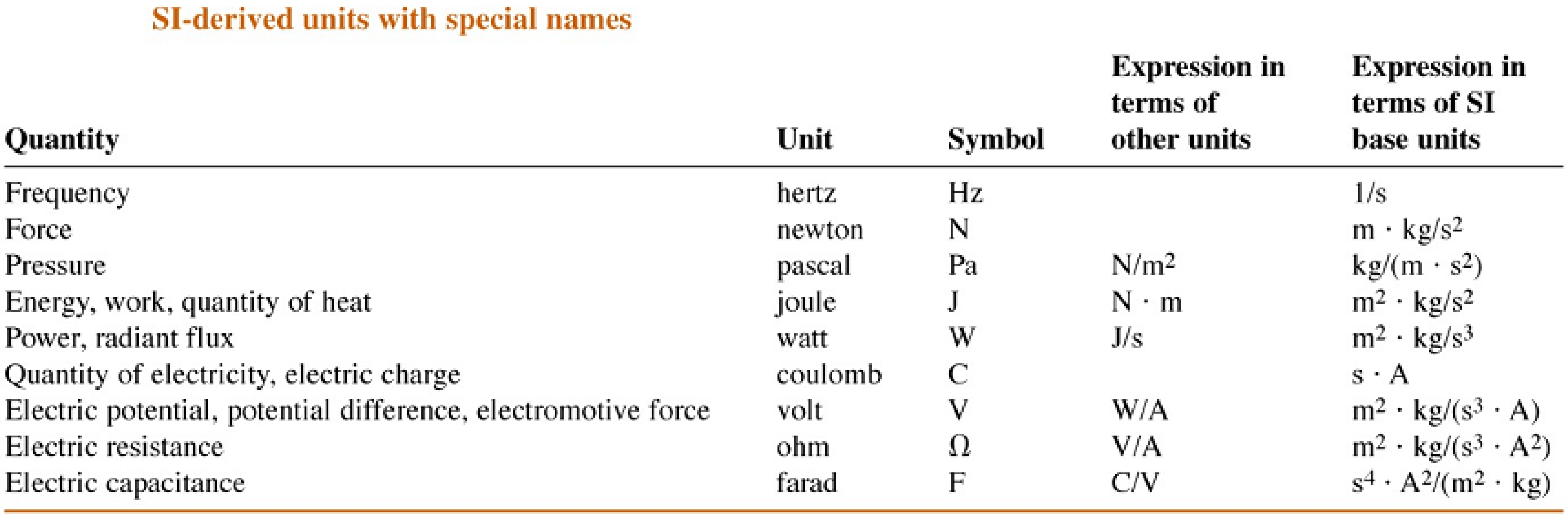
International system of unit (*Systeme International d'Unites*), 1960

Fundamental SI units



Quantity	Unit (symbol)	Definition
Length	meter (m)	One meter is the distance light travels in a vacuum during $\frac{1}{299\,792\,458}$ of a second.
Mass	kilogram (kg)	One kilogram is the mass of the prototype kilogram kept at Sèvres, France.
Time	second (s)	One second is the duration of 9 192 631 770 periods of the radiation corresponding to a certain atomic transition of ^{133}Cs.
Electric current	ampere (A)	One ampere of current produces a force of 2×10^{-7} newtons per meter of length when maintained in two straight, parallel conductors of infinite length and negligible cross section, separated by 1 meter in a vacuum.
Temperature	kelvin (K)	Temperature is defined such that the triple point of water (at which solid, liquid, and gaseous water are in equilibrium) is 273.16 K, and the temperature of absolute zero is 0 K.
Luminous intensity	candela (cd)	Candela is a measure of luminous intensity visible to the human eye.
Amount of substance	mole (mol)	One mole is the number of particles equal to the number of atoms in exactly 0.012 kg of ^{12}C (approximately $6.022\,141\,99 \times 10^{23}$).
Plane angle	radian (rad)	There are 2π radians in a circle.
Solid angle	steradian (sr)	There are 4π steradians in a sphere.

SI-derived units with special names



Quantity	Unit	Symbol	Expression in terms of other units	Expression in terms of SI base units
Frequency	hertz	Hz		$1/s$
Force	newton	N		$m \cdot kg/s^2$
Pressure	pascal	Pa	N/m^2	$kg/(m \cdot s^2)$
Energy, work, quantity of heat	joule	J	$N \cdot m$	$m^2 \cdot kg/s^2$
Power, radiant flux	watt	W	J/s	$m^2 \cdot kg/s^3$
Quantity of electricity, electric charge	coulomb	C		$s \cdot A$
Electric potential, potential difference, electromotive force	volt	V	W/A	$m^2 \cdot kg/(s^3 \cdot A)$
Electric resistance	ohm	Ω	V/A	$m^2 \cdot kg/(s^3 \cdot A^2)$
Electric capacitance	farad	F	C/V	$s^4 \cdot A^2/(m^2 \cdot kg)$

Conversion factors

Quantity	Unit	Symbol	SI equivalent[a]
Volume	liter	L	$*10^{-3}\ \mathrm{m}^3$
	milliliter	mL	$*10^{-6}\ \mathrm{m}^3$
Length	angstrom	Å	$*10^{-10}\ \mathrm{m}$
	inch	in.	*0.025 4 m
Mass	pound	lb	*0.453 592 37 kg
	metric ton		*1 000 kg
Force	dyne	dyn	$*10^{-5}\ \mathrm{N}$
Pressure	bar	bar	$*10^{5}\ \mathrm{Pa}$
	atmosphere	atm	*101 325 Pa
	torr (= 1 mm Hg)	Torr	133.322 Pa
	pound/in.^{2}	psi	6 894.76 Pa
Energy	erg	erg	$*10^{-7}\ \mathrm{J}$
	electron volt	eV	$1.602\ 176\ 462 \times 10^{-19}\ \mathrm{J}$
	calorie, thermochemical	cal	*4.184 J
	Calorie (with a capital C)	Cal	*1 000 cal = 4.184 kJ
	British thermal unit	Btu	1 055.06 J
Power	horsepower		745.700 W
Temperature	centigrade (= Celsius)	°C	*K − 273.15
	Fahrenheit	°F	*1.8(K − 273.15) + 32

[a] An asterisk (*) indicates that the conversion is exact (by definition).

Prefix of unit

Prefix	Symbol	Factor	Prefix	Symbol	Factor
Yotta	Y	10^{24}	Deci	d	10^{-1}
Zetta	Z	10^{21}	Centi	c	10^{-2}
Exa	E	10^{18}	Milli	m	10^{-3}
Peta	P	10^{15}	Micro	μ	10^{-6}
Tera	T	10^{12}	Nano	n	10^{-9}
Giga	G	10^{9}	Pico	p	10^{-12}
Mega	M	10^{6}	Femto	f	10^{-15}
Kilo	k	10^{3}	Atto	a	10^{-18}
Hecto	h	10^{2}	Zepto	z	10^{-21}
Deca	da	10	Yocto	y	10^{-24}

The Mole: The mole is **the SI unit** for the amount of chemical species. The mole is associated with a chemical formula and Avogadro's number (6.022×10^{23}) of particles. **The molar mass (M) of a substance is the mass in grams of one mole of the substance**. Molar masses are calculated by summing the atomic masses of all the elements appearing in a chemical formula.

- ➢ **Atomic mass unit (amu) = mass of 1 atom**
- ➢ **molar mass (g) = mass of 6.022×10^{23} atoms**

Approximately 1 mole of each of several different elements.

Clockwise from the upper left:

64 g of copper beads,

27 g of crumpled aluminum foil,

207g of lead shot,

24 g of magnesium chips,

52 g of chromium chunks, and

32 g of sulfur powder:

The beakers in the photo have a volume of 50 mL.

Ex: Molar Mass of formaldehyde CH_2O

12 g C/mol + 2g H/mole + 16g O/mole = 30 g/mole

From Periodic Table

Ex: Molar Mass of glucose $C_6H_{12}O_6$

6(12) + 12(1) + 6 (16) = 180 g/mole

Q4-1Calculate the mass of 2.4 moles of $NaNO_3$ (85.00 g/mol)?

Ans: 204 g

- **Mass and Weight:** **Mass** is an invariant measure of the amount of matter in an object. **Weight** is the force of attraction between an object and earth. The weight of an object depends on the location because gravitational attraction varies with geographic location. The mass of an object remains constant regardless of locations. A chemical analysis is always based on mass so that the results will not depend on locality.

- The mass of the Moon is only 1/81 that of Earth and the acceleration due to gravity is only 1/6 that on Earth.
- The weight of the object on the Moon is only 1/6 of their weight on Earth.

Ex. An object weighs less in Denver than in Atlantic City (both cities are at approximately the same latitude) because the attractive force between the object and the earth is smaller at the higher altitude of Denver.

Similarly, the object weighs more in Seattle than in Panama (both cities are at same sea level) because the earth is somewhat flattened at the poles, and the force of attraction increases measurably with latitude.

The mass of the object, however, remains constant regardless of where you measure it.

- **The Millimole:** The millimole (mmol) is 1/1000 of a mole. Sometimes it is more convenient to make calculations with millimoles (mmol) rather than mole. The mass in grams of a millimole of a substance is known as the **millimolar mass which is 1/1000 of the molar mass;** $1\ \text{mmol} = 10^{-3}\ \text{mol}$

Q4-2: Determine the number of moles and millimoles of benzoic acid (C_6H_5COOH) (122.1 g/mol) in 2.00 g of the pure acid.

Ans: 16.4 mmole

Q4-3: Determine the mass in grams of Na^+ (22.99 g/mol) in 25.0 g of Na_2SO_4(142.0 g/mol).

Ans: 8.10 g Na^+

CONCENTRATION OF SOLUTIONS

- The amount of solute dissolved in a given quantity of solvent or solution

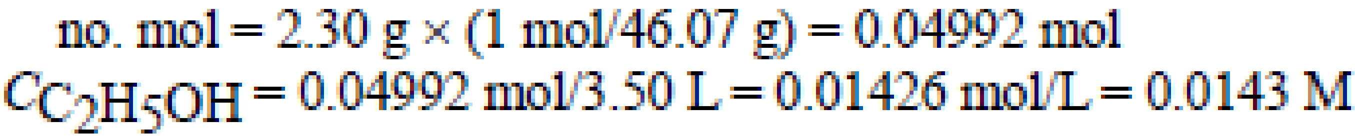
Molar concentration (Molarity M)

- The number of moles of solute per liter of solution

$$\text{Molarity} = \frac{\text{molessolute}}{\text{volume of solution}\left(\text{L}\right)} = \frac{\text{mmolessolute}}{\text{volume of solution}\left(\text{mL}\right)}$$

- A solution of 1.00 M (read as 1.00 molar) contains 1.00 mole of solute per liter of solution

Q 4-4: 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.



no. mol = 2.30 g × (1 mol/46.07 g) = 0.04992 mol

$c_{C_2H_5OH} = 0.04992 \text{ mol}/3.50 \text{ L} = 0.01426 \text{ mol/L} = 0.0143 \text{ M}$

Q4-5: After dissolving 1.56 g of NaOH in a certain volume of water, the resulting solution had a concentration of 1.60 M. Calculate the volume of the resulting NaOH solution?

Ans: 0.038 mol NaOH; 0.0237 L

CONCENTRATION OF IONS

- 1.00 M NaCl: 1.00 M Na^+ and 1.00 M Cl^-
- 1.00 M $ZnCl_2$: 1.00 M Zn^{2+} and 2.00 M Cl^-
- 1.00 M Na_2SO_4: 2.00 Na^+ and 1.00 M SO_4^{2-}

Q4-6: Calculate the number of moles of Na^+ and SO_4^{2-} ions in 1.50 L of 0.0150 M Na_2SO_4 solution

Ans: = 0.0450 mol Na^+ ; 0.0225 mol SO_4^{2-}

- **Analytical Molarity:** The analytical molarity of a solution gives the total number of moles of a solute in 1L of the solution (or total number of millimoles in 1 mL). A 1.0 M H_2SO_4 can be prepared by dissolving 1.0 mol or 98 g of H_2SO_4 in water and diluting to exactly 1.0 L.

- **Equilibrium Molarity:** The equilibrium molarity or species molarity express the molar concentration of a particular species in a solution at equilibrium. The equilibrium molarity of H_2SO_4 in a solution with an analytical concentration of 1.0 M is 0.0 M because H_2SO_4 is entirely dissociated, there are no H_2SO_4 molecules as such in this solution.

Analytical concentration

- **Strong electrolyte : completely dissociated**

Ex. NaCl MM: 58.44 g/mole

then if we dissolve 58.44 g/L, this will be equal to 1 M

2.7g NaCl /100 mL sea water = *x* M; *x* = 0.46 M

- Weak electrolyte : partially dissociated

Ex. HAC 0.1 M (1.3% dissociated)

Q4-7: Calculate the analytical and equilibrium molar concentrations of the solute species in an aqueous solution that contains 285 mg of trichloroacetic acid Cl_3CCOOH (HA) (163.4 g/mol) dissolve in 10.0 mL; Trichloroacetic acid is 73% ionized in water.

Ans: = 1.744 x 10^{-3} mol HA ; 0.174 M (Analytical); 0.047 M (Equilibrium Molarity)

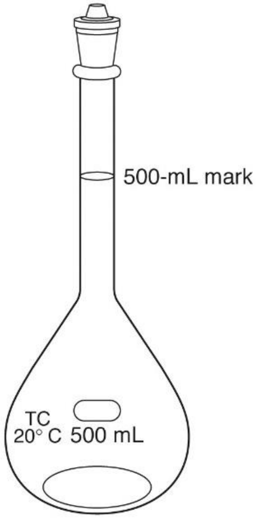
Q4-8

Describe the preparation of 2.00 L of 0.108 M $BaCl_2$ from $BaCl_2 \cdot 2H_2O$ (244 g/mol).

Ans: **dissolve 52.8 g in water and dilute to 2L**

Ex: Describe the preparation of 500 mL of 0.074 M Cl^- from solid $BaCl_2 \cdot 2H_2O$ (244 g/mol).

Ans: **dissolve 4.52 g in water and dilute to 500 ml**



DILUTION

- Consider a stock solution of concentration M_1 and volume V_1
- If water is added to dilute to a new concentration M_2 and volume V_2
- moles before dilution = moles after dilution
- Implies that $M_1V_1 = M_2V_2$

Example: Calculate the volume of 3.50 M HCl needed to prepare 500.0 mL of 0.100 M HCl

Concentration Units:

Percent concentration: Concentration can be expressed in terms of percent (parts per hundred). Percent composition can be expressed in three different methods:

$\text{weight \% (w/w)} = \frac{\text{weight solute}}{\text{weight solution}} \times 100\%$	37 % HCl (w/w) soln: 37 g HCl per 100 g soln. 70 % HNO_3 (w/w) soln
$\text{Volume \% (v/v)} = \frac{\text{volume solute}}{\text{volume solution}} \times 100\%$	5 % CH_3OH (v/v) soln: diluting 5.0mL CH_3OH with H_2O to 100mL.
$\text{weight/volume \% (w/v)} = \frac{\text{weight solute, g}}{\text{volume solution, mL}} \times 100\%$	5 %$AgNO_3$(w/v) soln: dissolving 5 g $AgNO_3$ in H_2O to 100 mL.

Concentration Units:

Parts Per Million and Parts Per Billion:

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

- C_{ppm} = (mass of solute)/(mass of solution) x 10^6

  ppm = (mg/kg) or mg/L for water when density is 1.00 g/ml

- For even more dilute solution **parts per billion (ppb)** is used

  C_{ppb} =(mass of solute)/(mass of solution) x 10^9

  ppb = (μg/Kg) μ g/L for water when density is 1.00 g/ml

Q4-9: A sugar solution is made by dissolving 5.8 g of sugar in 82.5 g of water. Calculate the percent by mass concentration of sugar.

Ans: 6.6 % m/m

Q4-10: Calculate the volume percent of solute if 345 mL of ethyl alcohol is dissolved in enough water to produce 1257 mL of solution

Ans: 27.4 % v/v

Q4-11: If 0.250 L of aqueous solution with a density of 1.00 g/mL contains 13.7 µg of pesticide, express the concentration of pesticide in ppm

Ans: 0.0548 ppm

Q4-12: What is the molarity of K^+ in a solution that contains 63.3 ppm of $K_3Fe(CN)_6$ (329.3 g/mol)?

Ans: 1.922 x 10^{-4} M $K_3Fe(CN)_6$; 5.77 x 10^{-4} M K^+

p-Function or p-value

For chemical species X: $\boxed{pX = -\log [X]}$ $pH = -\log [H^+]$

Ex: 4-8. **2.00 × 10^{-3} M NaCl and 5.4 × 10^{-4} M HCl solution**

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

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

$$pCl = -\log (2.00 \times 10^{-3} + 5.4 \times 10^{-4}) = -\log (2.54 \times 10^{-3}) = 2.595$$

Ex: 4-9. Calculate the molar conc. of Ag^+ in a solution that has a pAg of 6.372.

$$[Ag^+] = \text{antilog} (-6.372) = 4.25 \times 10^{-7}$$

Density: The density of a substance is its mass per unit volume. Density is expressed in units of kg/L or g/mL.

Specific Gravity: is the ratio of its mass to the mass of an equal volume of water at 4^{o}C. Specific gravity is dimensionless.

- Simply **specific gravity** is **the ratio of a material's density with that of water at 4oC (1g/ml)**

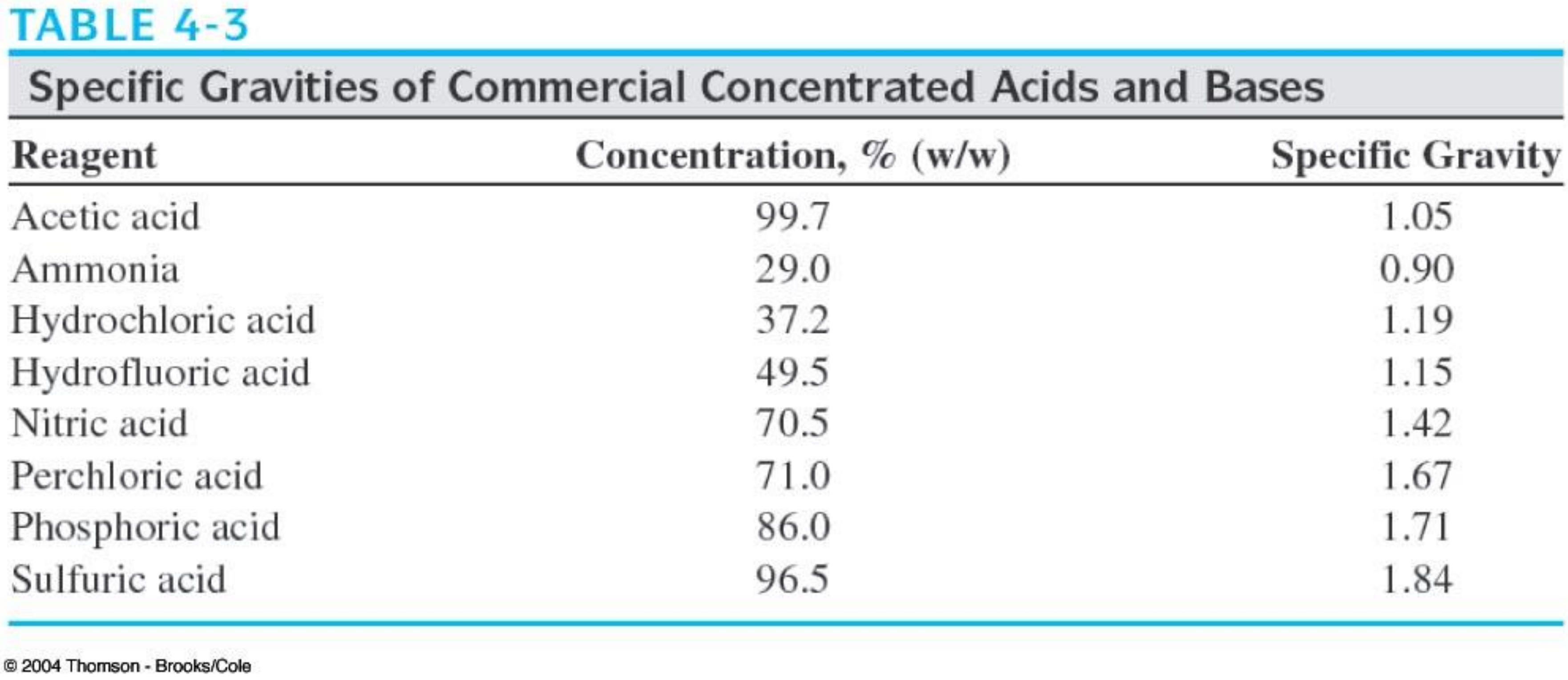


TABLE 4-3

Specific Gravities of Commercial Concentrated Acids and Bases

Reagent	Concentration, % (w/w)	Specific Gravity
Acetic acid	99.7	1.05
Ammonia	29.0	0.90
Hydrochloric acid	37.2	1.19
Hydrofluoric acid	49.5	1.15
Nitric acid	70.5	1.42
Perchloric acid	71.0	1.67
Phosphoric acid	86.0	1.71
Sulfuric acid	96.5	1.84

Q4-13: Calculate the molar concentration of HNO_3 (63.01 g/mol) in a solution that has a specific gravity of 1.42 and is 70% HNO_3 (w/w).

Density= 1.42 g/ml

We have 70g HNO_3/100g (Soln) We want mole HNO_3/L (Soln)

70 g/(63 g/mole) = 1.11 mole HNO_3

100 g soln / 1.42g/ml = 70.42 ml == 0.07042 L

Then M = 1.11 mole/0.07042L = 15.8 M

(Or conc. In M = (Sp.grav x % (m/m) / molar mass) x 10

(1.42 x 70/ 63) x 10 = 15.8 M

Q4-14

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

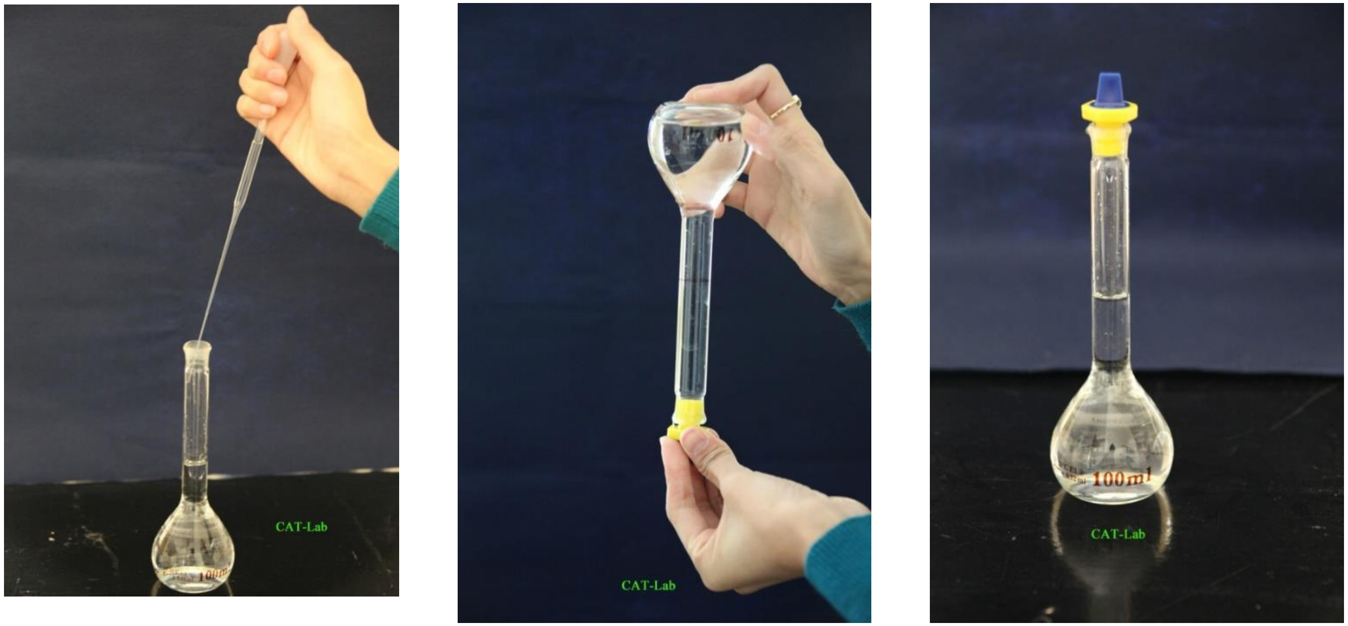
conc. In M = (Sp.grav x % (m/m) / molar mass) x 10

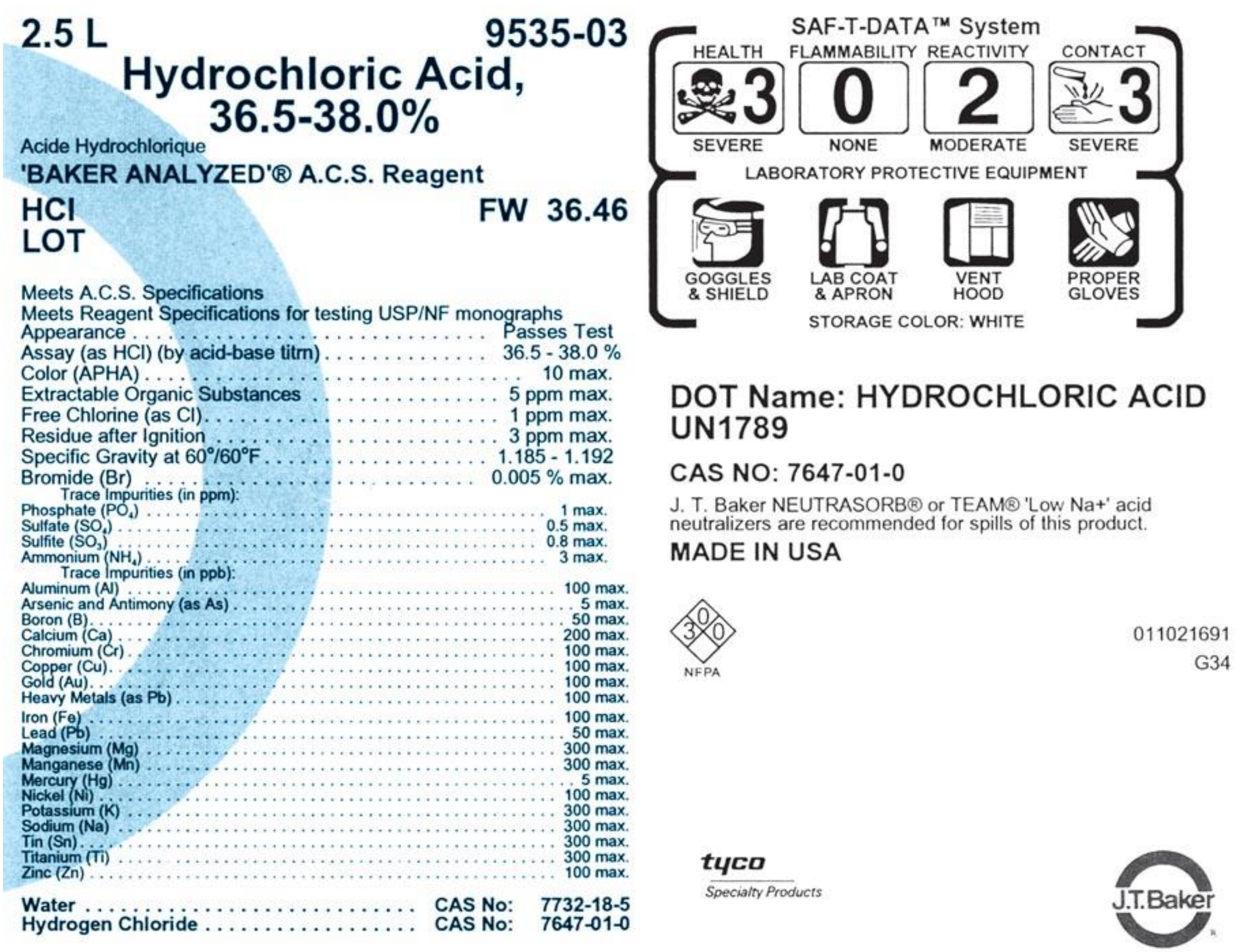
$C_{HCl} = 1.18 \times 10^3$ g/L × 37 g/100 g × (1 mol/36.5 g) = 12.0 M

amount HCl = 100 mL × (1 L/1000 mL) × 6.0 mol/L = 0.600 mol

vol conc. reagent = 0.600 mol × (1 L/12.0 mol) = 0.0500 L

Dilute 50 mL of the conc. reagent to 100 mL.





2.5 L **9535-03**

Hydrochloric Acid, 36.5-38.0%

Acide Hydrochlorique

'BAKER ANALYZED'® A.C.S. Reagent

HCl **FW 36.46**

LOT

Meets A.C.S. Specifications
Meets Reagent Specifications for testing USP/NF monographs

Appearance	Passes Test
Assay (as HCl) (by acid-base titrn)	36.5 - 38.0 %
Color (APHA)	10 max.
Extractable Organic Substances	5 ppm max.
Free Chlorine (as Cl)	1 ppm max.
Residue after Ignition	3 ppm max.
Specific Gravity at 60°/60°F	1.185 - 1.192
Bromide (Br)	0.005 % max.
Trace Impurities (in ppm):	
Phosphate (PO_4)	1 max.
Sulfate (SO_4)	0.5 max.
Sulfite (SO_3)	0.8 max.
Ammonium (NH_4)	3 max.
Trace Impurities (in ppb):	
Aluminum (Al)	100 max.
Arsenic and Antimony (as As)	5 max.
Boron (B)	50 max.
Calcium (Ca)	200 max.
Chromium (Cr)	100 max.
Copper (Cu)	100 max.
Gold (Au)	100 max.
Heavy Metals (as Pb)	100 max.
Iron (Fe)	100 max.
Lead (Pb)	50 max.
Magnesium (Mg)	300 max.
Manganese (Mn)	300 max.
Mercury (Hg)	5 max.
Nickel (Ni)	100 max.
Potassium (K)	300 max.
Sodium (Na)	300 max.
Tin (Sn)	300 max.
Titanium (Ti)	300 max.
Zinc (Zn)	100 max.

Water	**CAS No:**	**7732-18-5**
Hydrogen Chloride	**CAS No:**	**7647-01-0**

SAF-T-DATA™ System

HEALTH	FLAMMABILITY	REACTIVITY	CONTACT
3	0	2	3
SEVERE	NONE	MODERATE	SEVERE

LABORATORY PROTECTIVE EQUIPMENT

GOGGLES & SHIELD
LAB COAT & APRON
VENT HOOD
PROPER GLOVES

STORAGE COLOR: WHITE

DOT Name: HYDROCHLORIC ACID
UN1789

CAS NO: 7647-01-0

J. T. Baker NEUTRASORB® or TEAM® 'Low Na+' acid neutralizers are recommended for spills of this product.

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CHEMICAL FORMULA

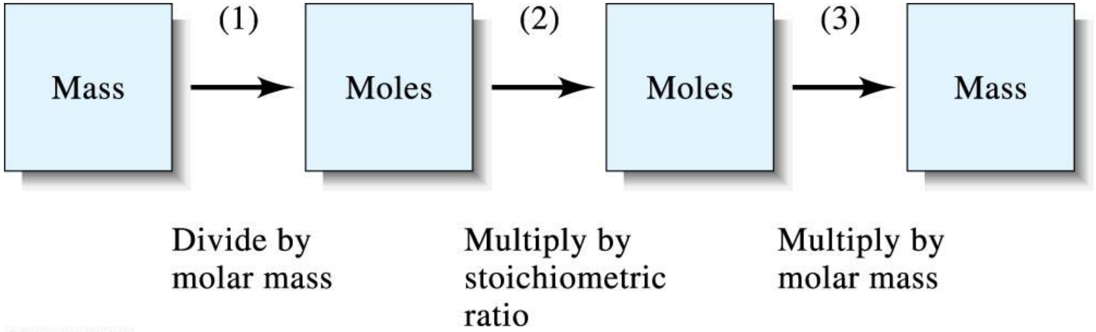
Consider $Na_2S_2O_3$:

- Two atoms of sodium, two atoms of sulfur, and three atoms ofoxygen are present in one molecule of $Na_2S_2O_3$
- Two moles of sodium, two moles of sulfur, and three moles of oxygen are present in one mole of $Na_2S_2O_3$

Ex: How many moles of sodium atoms, sulfur atoms, and oxygen atoms are present in 1.8 moles of a sample of $Na_2S_2O_3$?

I mole of $Na_2S_2O_3$ contains 2 moles of Na, 2 moles of S, and 3 moles of O

CHEMICAL EQUATIONS: (STOICHIOMETRIC CALCULATIONS)



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$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$$

- 1 molecule or mole of C_3H_8 reacts with 5 molecules ore mole of O_2 to produce 3 molecules or mole of CO_2 and 4 molecules or mole of H_2O

Ex: $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

a) What mass of oxygen will react with 96.1 g of propane (44.11 g/mol)?

Ans: 349g O_2

- make sure the equation is balanced
- calculate moles of propane from given mass and molar mass
- determine moles of oxygen from mole ratio (stoichiometry)
- calculate mass of oxygen

b) What mass of CO_2 will be produced from 96.1 g of propane?

Ans: 288g CO_2

Q4-15

What Mass of $AgNO_3$ (169.9 g/mol) is needed to convert 2.33 g of Na_2CO_3 (106.0 g/mol) to Ag_2CO_3? (b) What mass of Ag_2CO_3 (275.7 g/mol) will be formed?

$$Na_2CO_3\ (aq) + 2\ AgNO_3\ (aq) \rightarrow Ag_2CO_3\ (s) + 2\ NaNO_3\ (aq)$$

Ans: 7.47g $AgNO_3$; 6.06g Ag_2CO_3

Q4-16-a

What mass of Ag_2CO_3 (275.7 g/mol) is formed when 25.0 mL of 0.200M $AgNO_3$ are mixed with 50.0 mL of 0.0800M Na_2CO_3 ?

5mmol/2 < 4mmol/1 then Limiting Reactant is AgNO3

$n_{AgNO_3} = 25.0\text{ mL} \times 0.200\text{ M } AgNO_3 = 5.00\text{ mmol } AgNO_3$

$n_{Na_2CO_3} = 50.0\text{ mL} \times 0.0800\text{ M } Na_2CO_3 = 4.00\text{ mmol } Na_2CO_3$

Ans: 0.689 g Ag_2CO_3

Q4-16-b

What will be the molar analytical Na_2CO_3 conc. in the soln produced when 25.0 mL of 0.200 M $AgNO_3$ is mixed with 50.0 mL of 0.0800 M Na_2CO_3?

Ans: 0.0200 M Na_2CO_3

CHEMICAL CALCULATIONS

Ex: Calculate the number of molecules present in 0.075 g of urea, $(NH_2)_2CO$

Given mass of urea:

- convert to moles of urea using molar mass
- convert to molecules of urea using Avogadro's number (6.022×10^{23})

Ans: 7.5×10^{20} molecules $(NH_2)_2CO$

Ex: How many grams of carbon are present in a 0.125 g of vitamin C, $C_6H_8O_6$ (176.14 g/mol)

Given mass of vitamin C:

- convert to moles of vitamin C using molar mass
- convert to moles of C (1 mole $C_6H_8O_6$ contains 6 moles C)
- convert moles carbon to g carbon using atomic mass

Ans: 0.0511 g carbon

CONCENTRATION OF SOLUTIONS

Mole Fraction (χ): Fraction of moles of a component of solution

$$\chi = \frac{\text{moles of component}}{\text{total moles of all components}}$$

❖ The sum of mole fractions of all components = 1

EX: Given that the total moles of an aqueous solution of NaCl and other solutes is 1.75 mol. Calculate the mole fraction of NaCl if the solution contains 4.56 g NaCl (58.44 g/mol).

Ans: 0.0446

EX: Calculate the mole fraction of a 6.75 %(m/m) solution of ethanol (46.08 g/mol) in water

Mass water = 100 g solution – 6.75 g ethanol = 93.25 g water

Ans: 0.0257

Chapter 5

Errors in Chemical Analysis

Modified by Dr. Mohammed Rasheed

Data quality

- Measurements invariably involve errors and uncertainties.
  - **Uncertainties can never be completely eliminated**, measurement data can give us only an estimate of the “true” value.
- Reliability can be assessed in several ways:
  - ❖ Experiments designed to reveal the presence of errors
  - ❖ Compared with the known compositions
  - ❖ Consult to the chemical literature
  - ❖ Equipment Calibration
  - ❖ **Statistical tests**

Representative Data

- Chemists usually carry two to five portions **(replicates)** of a sample through an entire analytical procedure.
  - **Replicates are samples of about the same size that are carried through an analysis in *exactly* the same way.**
- One usually considers the “best” estimate to be the central value for the set:
  - Usually, the mean or the median is used as the central value for a set of replicate measurements.
  - The variation in data allows us to estimate the uncertainty associated with the central result

The Mean and Median

- The most widely used measure of central value is the **mean,** . The mean, also called the **arithmetic mean**, or the **average**,

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

❖ where x_i represents the individual values of x making up the set of N replicate measurements.

- The **median** is the middle result when replicate data are arranged according to increasing or decreasing value.

❖ Median can be **preferred** when there is an "***outlier***" - one reading very different from rest. Median less affected by outlier than is mean.

Ex: Calculate the mean and median for the data: 19.4, 19.5, 19.6, 19.8, 20.1 and 20.3

$$\text{mean} = \bar{x} = \frac{19.4 + 19.5 + 19.6 + 19.8 + 20.1 + 20.3}{6}$$

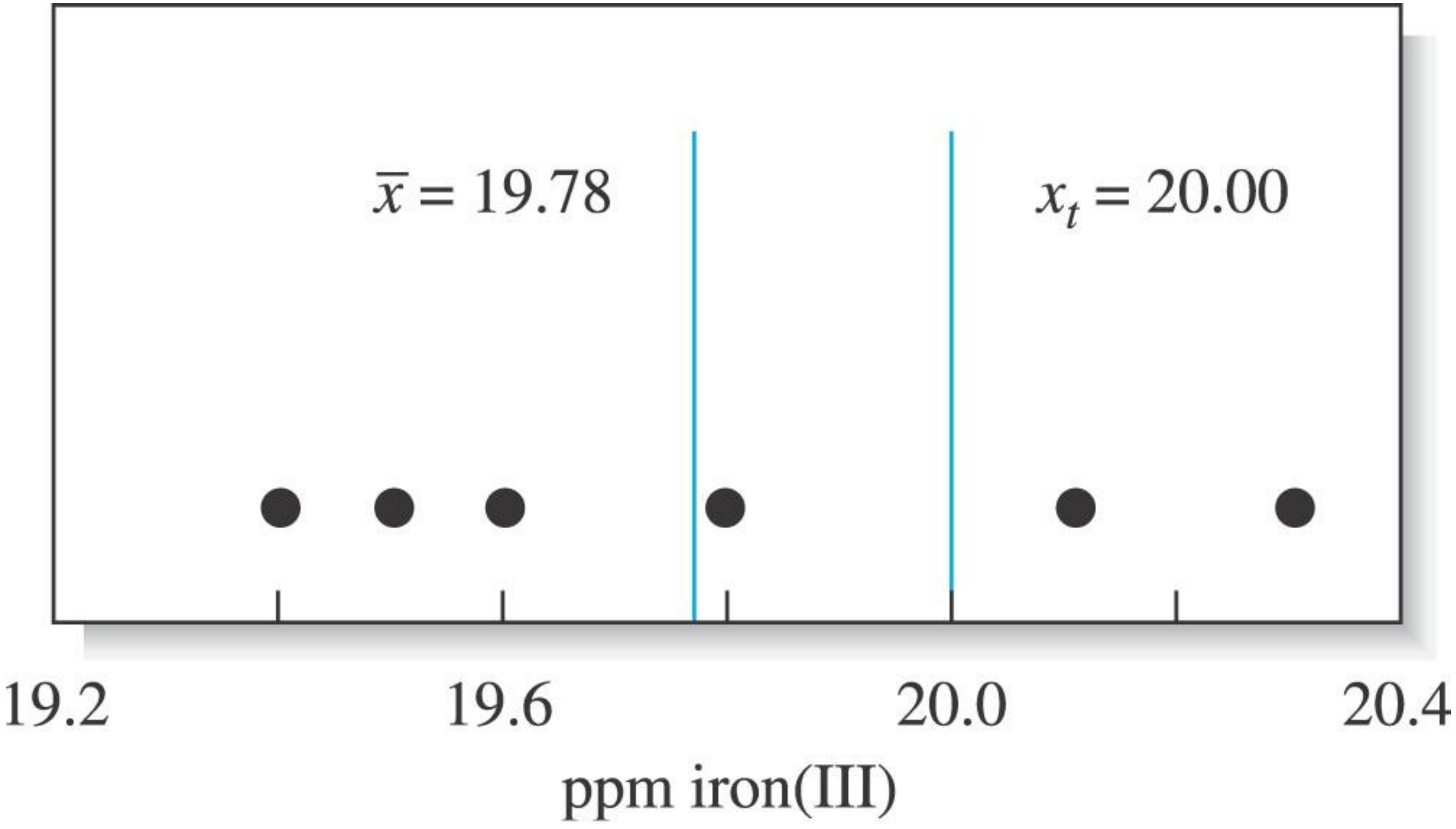
$$= 19.78 \approx 19.8 \text{ ppm Fe}$$

- Because the set contains an even number of measurements, the median is the average of the central pair:

$$\text{median} = \frac{19.6 + 19.8}{2} = 19.7 \text{ ppm Fe}$$

Illustration of “Mean” and “Median”

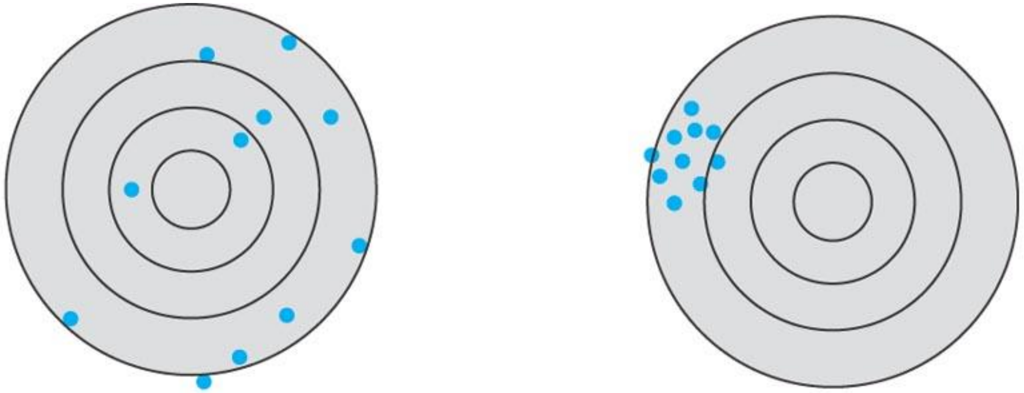
Results of 6 determinations of the Fe(III) content of a solution, known to contain 20 ppm:



Note: The **mean** value is 19.78 ppm (i.e. **19.8ppm**) –
The **median** value is **19.7 ppm**

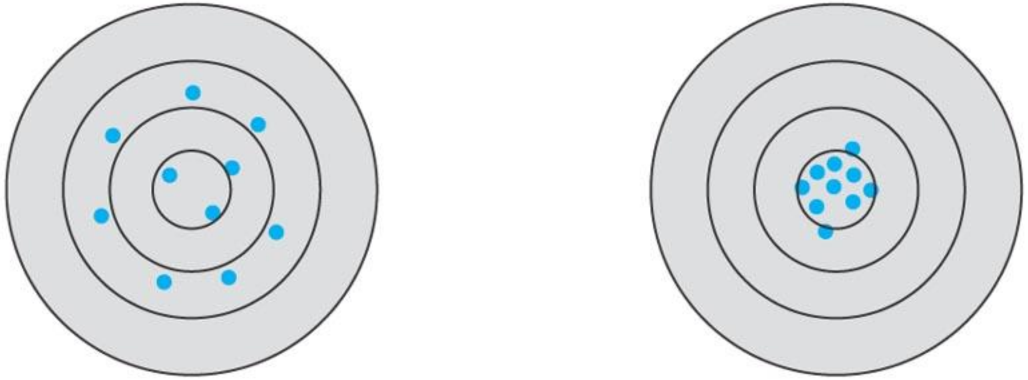
Some Important Terms

- *Precision – A measure of the **REPRODUCIBILITY** of measurement.*
- *Accuracy – A measure of how CLOSE a measured value is to the "TRUE" value.*



Low accuracy, low precision

Low accuracy, high precision



High accuracy, low precision

High accuracy, high precision

Figure 5-2 Note that we can have very precise results (upper right) with a mean that is not accurate and an accurate mean (lower left) with data points that are imprecise.

Precision

- Describes the **reproducibility** of measurements
- Or, the **closeness of results that have been obtained *in exactly the same way.***
- Three terms are widely used to describe the precision of a set of replicate data:
  - standard deviation; *later*
  - variance; *later*
  - coefficient of variation; *later*
- Deviation from the mean:

$$d_i = |x_i - \bar{x}|$$

Accuracy

- Indicates the closeness of the measurement to the true or accepted value
- Expressed in terms of either absolute or relative error.
- Absolute error:
  - where x_t is the true or accepted value of the quantity
  - We retain the sign in stating the absolute error.
- Relative error

Accuracy

Absolute Error

* The absolute error of a measurement is the difference between the measured value and the true value. If the measurement result is low, the sign is negative; if the measurement result is high, the sign is positive.

$$E = x_i - x_t$$

Relative Error

The relative error of a measurement is the absolute error divided by the true value. Relative error may be expressed in percent, parts per thousand, or parts per million, depending on the magnitude of the result.

$$E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

- Results can be precise without being accurate and accurate without being precise.
- Each dot represents the error associated with a single determination.
- Each vertical line labeled (xi - xt) is the absolute average deviation of the set from the true value.

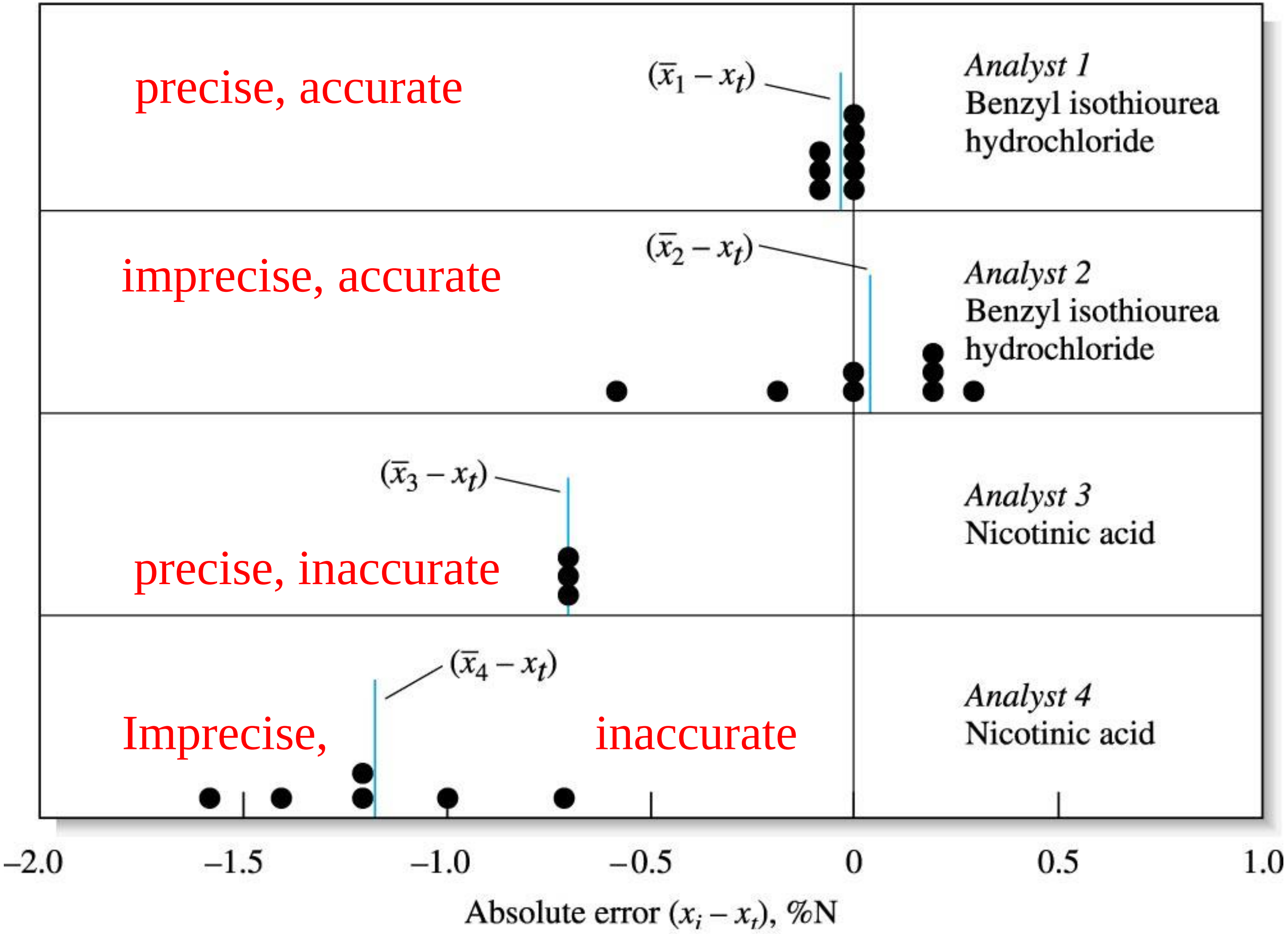


Figure 5-3 Absolute error in the micro-Kjeldahl determination of nitrogen

Types of Error in Experimental Data

(1) **Random (indeterminate) Error**

Data scattered approx. symmetrically about a mean value.
Affects precision - dealt with statistically (see later).

(2) **Systematic (determinate) Error**

Several possible sources - later. Readings all too high or too low. Affects accuracy.

(3) **Gross Errors; lead to "Outlier"**

These differ from indeterminate and determinate errors.

- They usually occur only **occasionally,** are often **large**, and may cause a result to be either **high or low**.
- They are often the product of human errors.
- Gross errors lead to outliers, results that appear to **differ markedly** from all other data in a set of replicate measurements.

5B Systematic errors

- ➢ have a definite value,
- ➢ an assignable (one definite) cause, and
- ➢ are of the **same magnitude** for replicate measurements made in the same way.
- ➢ They lead to **bias** in measurement results. Bias affects all of the data in a set in the same way and that bears a sign

There are three types of systematic errors:

- Instrumental errors.
- Method errors
- Personal errors

Instrumental Errors

✓are caused by nonideal instrument behavior, by faulty calibrations, or by use under inappropriate conditions

✓Pipets, burets, and volumetric flasks may hold or deliver volumes slightly different from those indicated by their graduations.

✓**Calibration eliminates most systematic errors of this type**.

✓Electronic instruments can be influenced by noise, temperature, pH and are also subject to systematic errors.

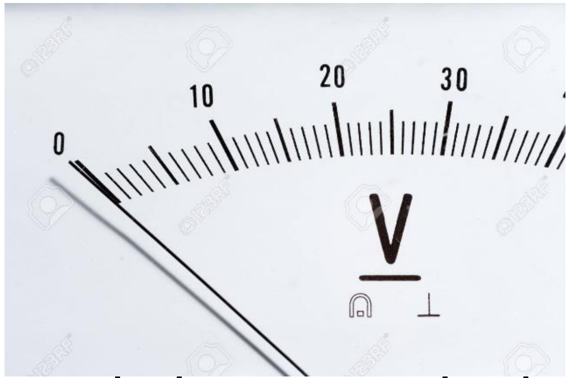
✓ **Errors of these types usually are detectable and correctable**.

Method Errors

- The nonideal chemical or physical behavior of the **reagents and reactions** on which an analysis is based often introduce systematic method errors.
- Such sources of nonideality include the **slowness of some reactions**, the **incompleteness of others**, the **instability of some species**, the **lack of specificity of most reagents**, and the **possible occurrence of side reactions that interfere with the measurement process**.
- Errors inherent in a method are often **difficult to detect** and hence, these errors are usually the most difficult to identify and correct.

Personal Errors

- result from the **carelessness**, **inattention**, or **personal limitations** of the experimenter.
- Many measurements require **personal judgments**.
- Examples include estimating *the position* of a pointer between two scale divisions, *the color* of a solution at the end point in a titration, or the *level of a liquid* with respect to a graduation in a pipet or buret.
- Judgments of this type are often subject to systematic, unidirectional errors.
- A universal source of personal error is **bias**.
- **Number bias** is another source of personal error that varies considerably from person to person.
- The most frequent number bias encountered in estimating the position of a needle on a scale involves a preference for the digits 0 and 5.



- Digital and computer displays on pH meters, laboratory balances, and other electronic instruments eliminate number bias because no judgment is involved in taking a reading.

5B-2 The effects of systematic errors on analytical results

- **Systematic errors may be either *constant or proportional***

Constant errors:

- The magnitude of a constant error stays essentially the same even if the size or the quantity of the sample is changed.
- With constant errors, **the absolute error is constant** with different sample size, **but the relative error varies when the sample size is changed;** the relative error from this source becomes more serious as the total volume decreases.

5-2. Suppose that 0.50 mg of precipitate (unknown) is lost as a result of being washed with 200 mL of wash liquid. (0.5 mg loss (constant error) regardless the sample quantity or size)

- If the ppt weights 500 mg, the relative error due to solubility loss is

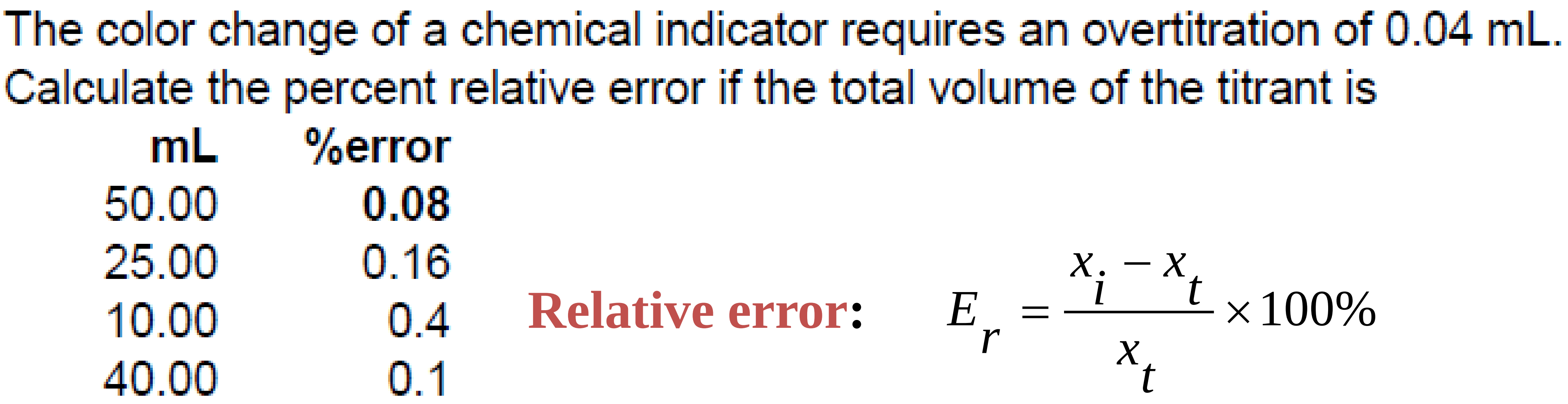
$$(499.5 - 500)/500 \times 100\% = -0.1\%$$

- **If the ppt weights 50 mg, the relative error due to solubility loss is**

$$(49.5 - 50)/50 \times 100\% = -1.0\%$$

- **The sample size changed (500 and 50mg) then the relative error is changed. While the absolute error is always 0.5mg)**
- One way of reducing the effect of constant error is to increase the sample size until the relative error is acceptable.

Example- Constant Error



The color change of a chemical indicator requires an overtitration of 0.04 mL. Calculate the percent relative error if the total volume of the titrant is

mL	%error
50.00	**0.08**
25.00	0.16
10.00	0.4
40.00	0.1

Relative error:

$$E_r = \frac{x_i - x_t}{x_t} \times 100\%$$

(50.04-50.00)/50.00 x 100% = 0.08%

(10.04-10.00)/10.00) x 100% = 0.4%

- Although a constant error of 0.04 ml regardless the total volume of titrant, the relative error is great for the less amount of the titarnt

- **Or Proportional errors: measured quantity** decrease or increase in proportion to the size or quantity of the sample but the relative error is independent on the sample size.
- A common cause of proportional errors is the presence of interfering contaminants in the sample.

Example:

- Determination of **Cu^{+2}** is based on it's reaction with **KI** to give **I_2** The quantity of iodine is then measured and is proportional to the amount of **Cu^{+2}**.
- if **Fe^{+3}** present, it gives also **I_2** from **KI.** high results are observed for the %**Cu^{+2}** because the iodine produced will be a measure of **Cu^{+2}** and **Fe^{+3}** in the sample.
- The size of this error is **fixed** by the **fraction** of **Fe^{+3}** contamination, which is dependent of the size of sample taken.
- If the sample size is doubled, the amount **of iodine liberated by both the copper and the iron contaminant is also doubled**.
- **Thus, the magnitude of the reported percentage of copper is independent of sample size. Then the absolute error is the same**

e.g:
If 1g sample gives 0.1 g of I_2 then for example the % of Cu in the sample increased by 10%
If 2g sample gives 0.2 g of I_2 then for example the % of Cu in the sample increased by 10%

5B-3 Detection and Elimination of Systematic (Instrumental and Personal) Errors

1. Periodic calibration of equipment is always desirable because the response of most instruments changes with time as a result of component aging, corrosion, or mistreatment.
2. Most personal errors can be minimized by careful, disciplined laboratory work.
3. It is a good habit to check instrument readings, notebook entries, and calculations systematically.
4. Errors due to limitations of the experimenter can usually be avoided by carefully choosing the analytical method or using an automated procedure.

5B-4 Detection of Systematic (Method) Errors

- Bias in an analytical method is particularly difficult to detect.
- Estimate the bias of an analytical method by
    - Independent Analysis: using different method to determine the analyte
    - Blank Determinations
    - Variation in sample size: can be used if there is constant error
    - Best by analyzing **Standard reference materials (SRMs).**

Analysis of Standard Samples using standard reference material

- **The best way of estimating the bias of an analytical method is by the analysis of standard reference materials:**
- ✓ Materials that contain one or more analytes at known concentration levels.
- ✓ Can sometimes be prepared by synthesis.
- ✓ Can be purchased from a number of governmental and industrial sources. Ex: National Institute of Standards and Technology (NIST); Sigma Chemical Co.

Independent Analysis & Variation in Sample Size

- A second independent and reliable analytical method can be used in parallel with the method being evaluated.
- A statistical test must be used to determine whether any difference is a result of random errors in the two methods or due to bias in the method under study.

Variation in Sample Size

As the size of a measurement increases, the effect of a constant error decreases. Constant errors can often be detected by varying the sample size.

Blank Determinations

❖ **The air for the balance is a blank**

- A blank contains the reagents and solvents used in a determination, but no analyte.
- Many of the sample constituents are added to simulate the analyte environment, often called the sample matrix.
- In a blank determination:
  - All steps of the analysis are performed on the blank material.
  - Blank determinations reveal errors due to interfering contaminants from the reagents and vessels used in the analysis.

Chapter 6

Random Errors in Chemical Analysis

Modified by Dr. Mohammed Rasheed

The Nature of Random Errors

- **Random errors are present in every measurement no matter how careful the experimenter.**

- Random, or **indeterminate**, errors can never be totally eliminated and are often the major source of uncertainty in a determination.

- Random errors are caused by the many uncontrollable variables that accompany every measurement.

- The accumulated effect of the individual uncertainties causes replicate results to fluctuate randomly around the mean of the set.

Random Error Sources

- ➢ Small undetectable uncertainties produce a detectable random error in the following way.
- ➢ Imagine a situation in which just **four small random errors combine to give an overall error.** We will assume that each error has an equal probability of occurring and that each can cause the final result to be **high or low** by a fixed amount **±*U*.**

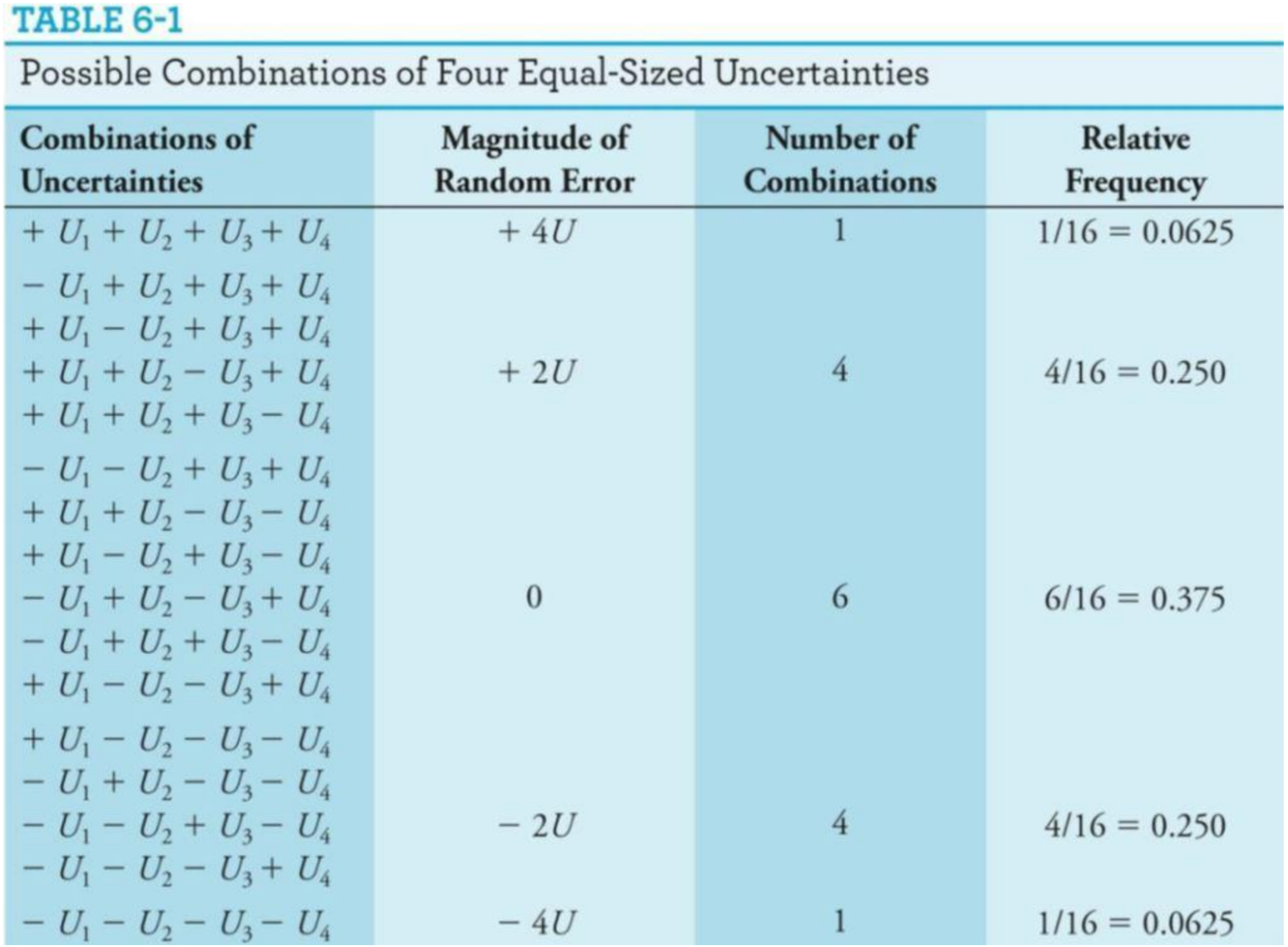


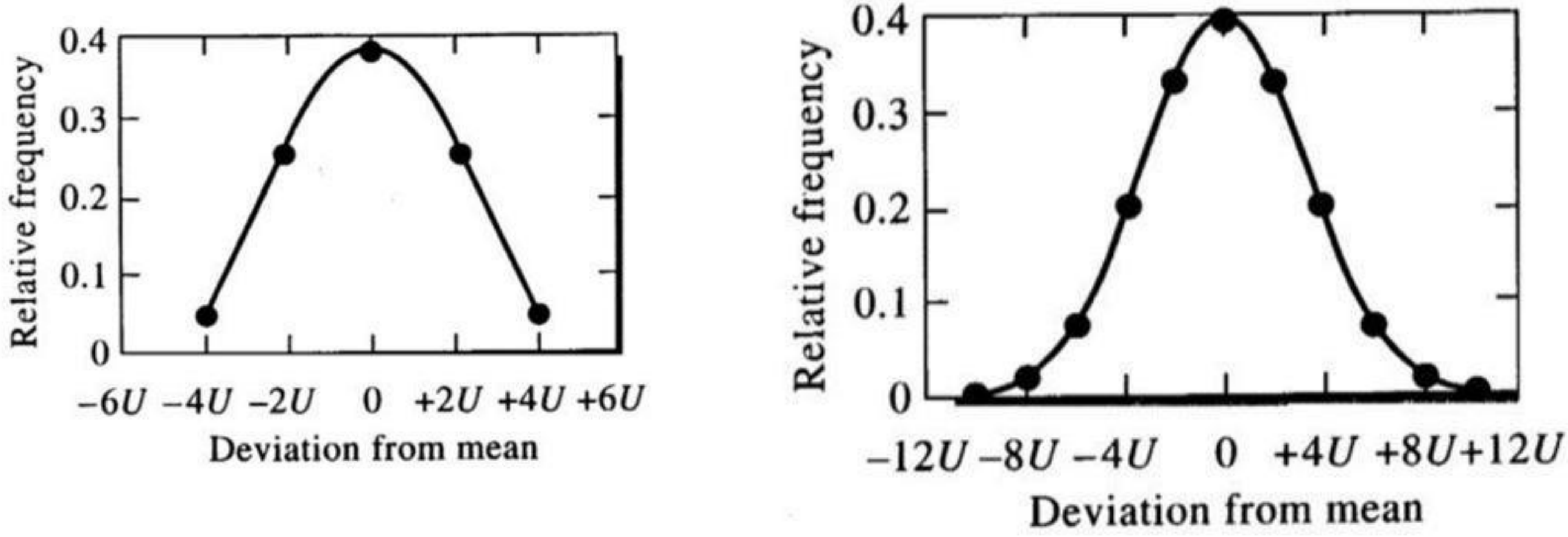
TABLE 6-1

Possible Combinations of Four Equal-Sized Uncertainties

Combinations of Uncertainties	Magnitude of Random Error	Number of Combinations	Relative Frequency
$+U_1+U_2+U_3+U_4$	$+4U$	1	$1/16 = 0.0625$
$-U_1+U_2+U_3+U_4$ $+U_1-U_2+U_3+U_4$ $+U_1+U_2-U_3+U_4$ $+U_1+U_2+U_3-U_4$	$+2U$	4	$4/16 = 0.250$
$-U_1-U_2+U_3+U_4$ $+U_1+U_2-U_3-U_4$ $+U_1-U_2+U_3-U_4$ $-U_1+U_2-U_3+U_4$ $-U_1+U_2+U_3-U_4$ $+U_1-U_2-U_3+U_4$	0	6	$6/16 = 0.375$
$+U_1-U_2-U_3-U_4$ $-U_1+U_2-U_3-U_4$ $-U_1-U_2+U_3-U_4$ $-U_1-U_2-U_3+U_4$	$-2U$	4	$4/16 = 0.250$
$-U_1-U_2-U_3-U_4$	$-4U$	1	$1/16 = 0.0625$

- ❖ **Note that only 1 combination leads to a deviation of +4 *U, 4 combinations give a deviation of + 2 U, and 6 give a* deviation of 0 *U*.**
- ❖ **This ratio of 1:4:6:4:1 is a measure of the probability for a deviation of each magnitude**

- If we make a sufficiently large number of measurements, we can expect a frequency distribution like that shown in Figure below.



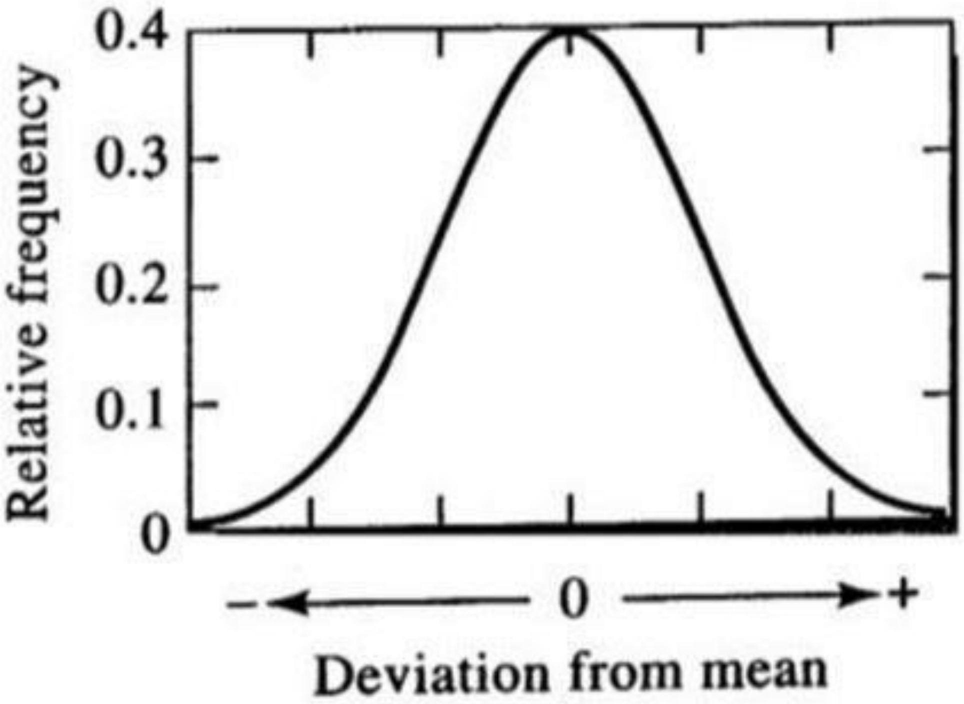
U: Uncertainty

Figure 6-2 Frequency distribution for measurements containing (a) Four random uncertainties, (b) ten random uncertainties;

- The most frequent occurrence is zero deviation from the mean. At the other extreme, a maximum deviation of 10 U occurs only about once in 500 results.

- When the same procedure is applied to a very large number of random uncertainties, a bell-shaped curve results. Such a plot is called a Gaussian curve or a normal error curve.

A very large number of random uncertainties



This is a Gaussian or normal error curve. Symmetrical about the mean.

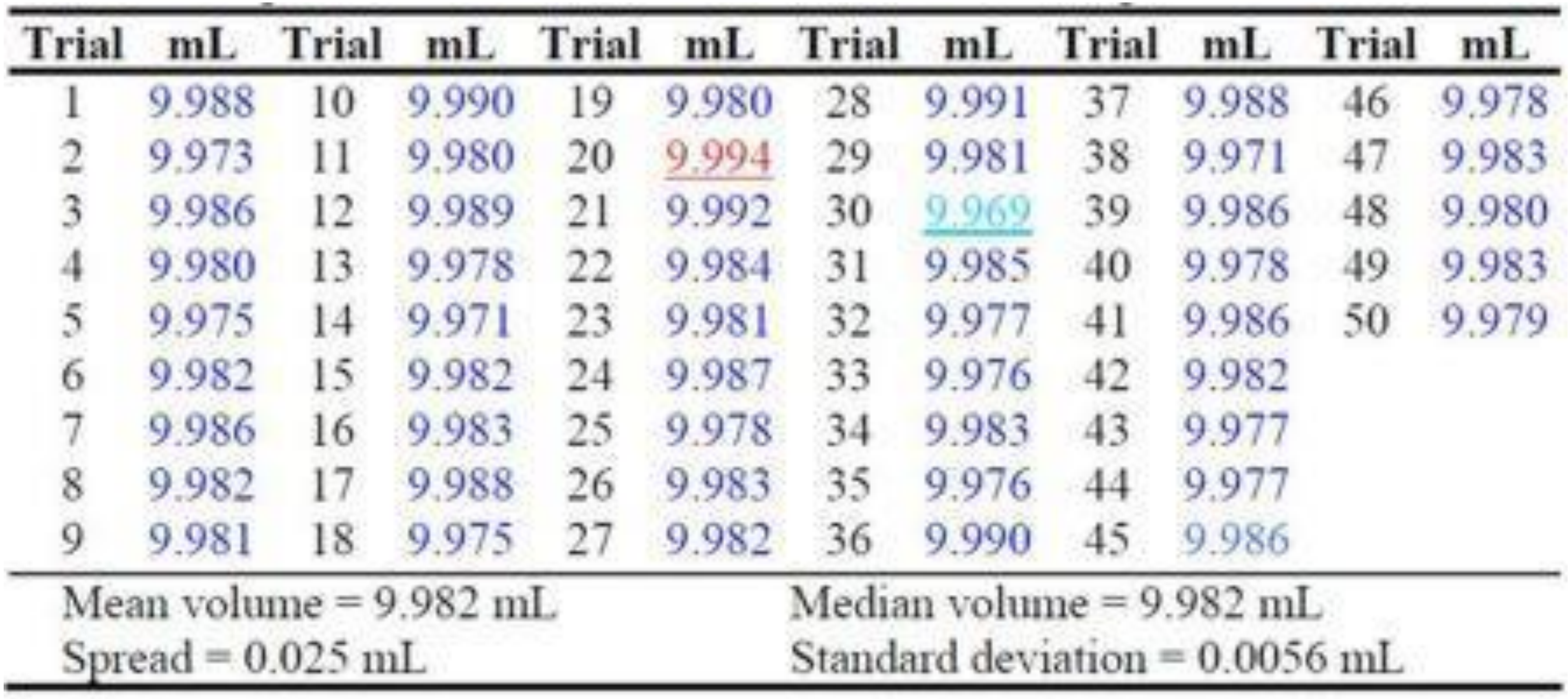
Distribution of Experimental Results

- ➢ The distribution of replicate data from most quantitative analytical experiments approaches that of the Gaussian curve.

Exp: Calibration of a 10-mL pipet.

1. In this experiment a small flask and stopper were weighed.
2. Ten milliliters of water were transferred to the flask with the pipet, and the flask was stoppered. The flask, the stopper, and the water were then weighed again.
3. The mass of the water was then calculated by taking the difference between the two masses.
4. The mass of water divided by its density is the volume delivered by the pipet. The experiment was repeated 50 times.

Table 6-2



Trial	mL	Trial	mL	Trial	mL	Trial	mL	Trial	mL	Trial	mL
1	9.988	10	9.990	19	9.980	28	9.991	37	9.988	46	9.978
2	9.973	11	9.980	20	9.994	29	9.981	38	9.971	47	9.983
3	9.986	12	9.989	21	9.992	30	9.969	39	9.986	48	9.980
4	9.980	13	9.978	22	9.984	31	9.985	40	9.978	49	9.983
5	9.975	14	9.971	23	9.981	32	9.977	41	9.986	50	9.979
6	9.982	15	9.982	24	9.987	33	9.976	42	9.982		
7	9.986	16	9.983	25	9.978	34	9.983	43	9.977		
8	9.982	17	9.988	26	9.983	35	9.976	44	9.977		
9	9.981	18	9.975	27	9.982	36	9.990	45	9.986		

Mean volume = 9.982 mL
Median volume = 9.982 mL
Spread = 0.025 mL
Standard deviation = 0.0056 mL

Consider the data in the table for the **calibration of a 10-mL pipet.**
The results vary from a low of 9.969 mL to a high of 9.994 mL.
This 0.025-mL spread of data results directly from an accumulation of all random uncertainties in the experiment. **The spread in a set of replicate measurements can be defined as the difference between the highest and lowest result**.

- The frequency distribution data in table 6-2 is shown in the table 6-3

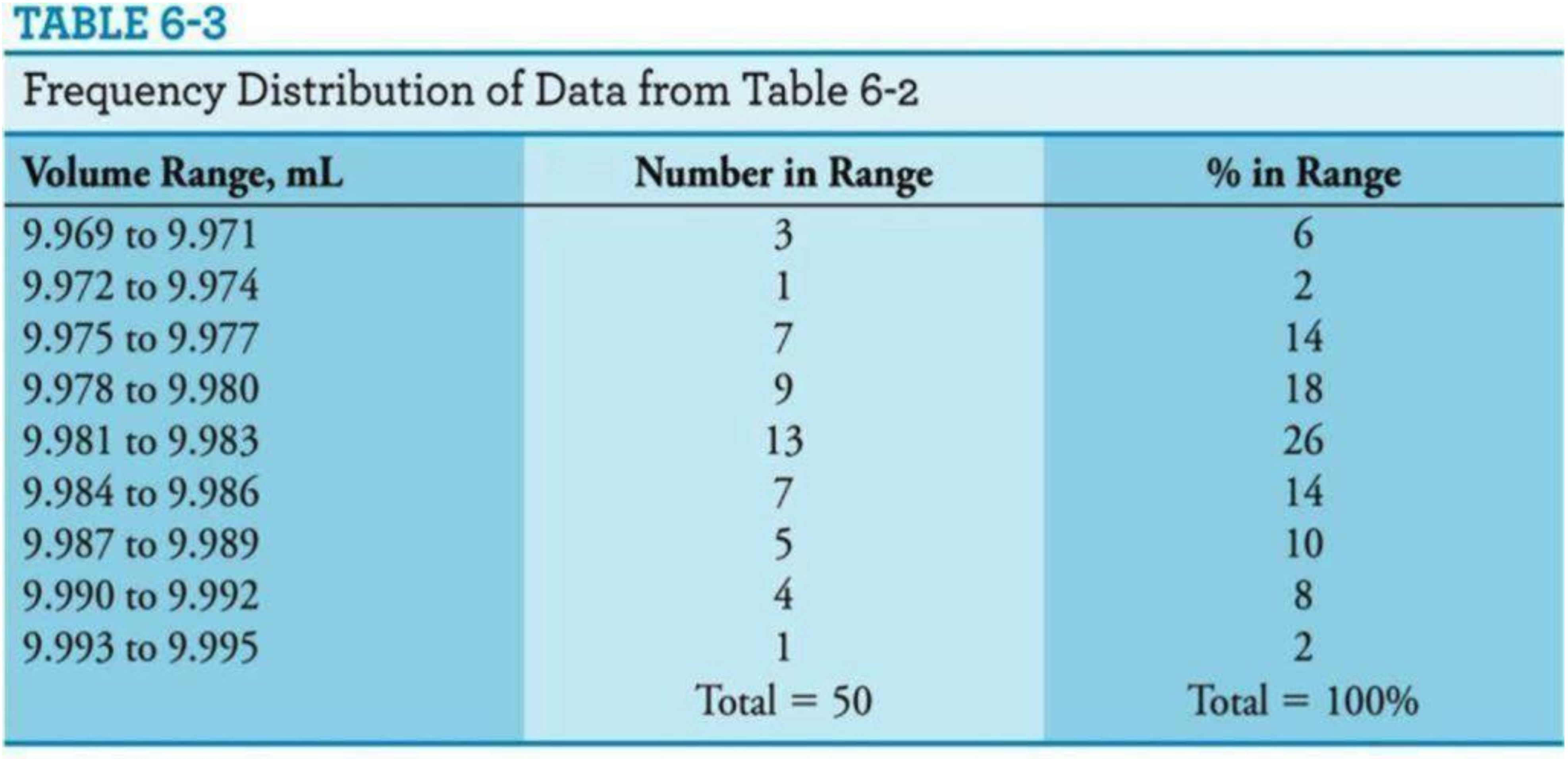


TABLE 6-3

Frequency Distribution of Data from Table 6-2

Volume Range, mL	Number in Range	% in Range
9.969 to 9.971	3	6
9.972 to 9.974	1	2
9.975 to 9.977	7	14
9.978 to 9.980	9	18
9.981 to 9.983	13	26
9.984 to 9.986	7	14
9.987 to 9.989	5	10
9.990 to 9.992	4	8
9.993 to 9.995	1	2
	Total = 50	Total = 100%

- The frequency distribution data are plotted as a bar graph, or histogram.
- As the number of measurements increases, the histogram approaches the shape of the continuous Gaussian curve.

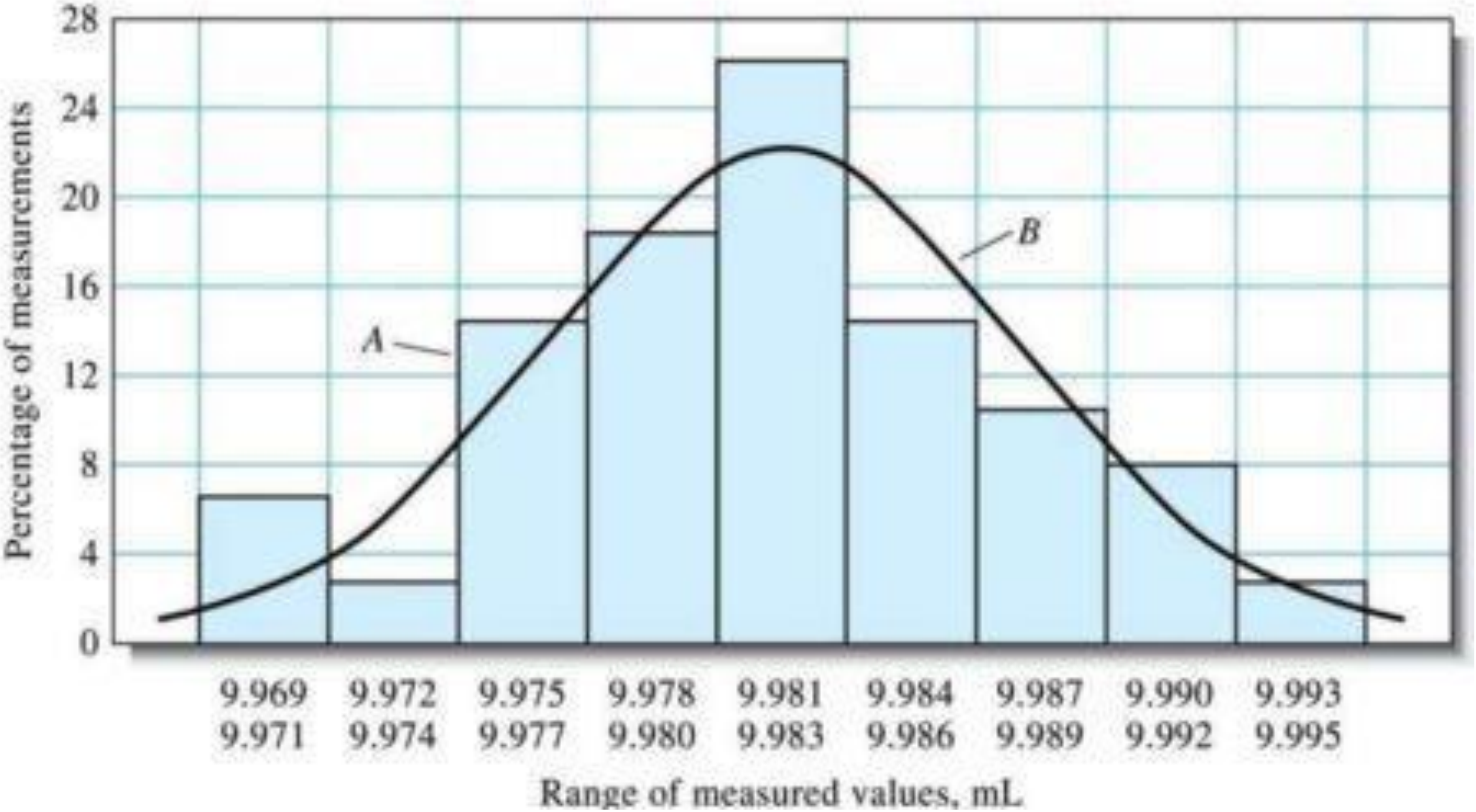


Figure 6-3: A histogram (A) showing distribution of the 50 results in Table 6-3 and a Gaussian curve (B) for data having the same mean and standard deviation as the data in the histogram.

Distribution of Experimental Results

- Variations in replicate measurements result from numerous small and individually undetectable random errors that are attributable to uncontrollable variables in the experiment.
- Such small errors ordinarily tend to cancel one another and thus have a minimal effect on the mean value.
- Ex:
  - Sources of random uncertainties in the calibration of a pipet:
    - Visual judgments
    - Variations in the drainage time and in the angle of the pipet as it drains
    - Temperature fluctuations
    - Vibrations and drafts that cause small variations in the balance readings

6B Statistical treatment of random errors

- Statistical analysis only reveals information that is already present in a data set.
- Statistical methods, do allow us to categorize and characterize data and to make objective and intelligent decisions about data quality and interpretation.

SAMPLE = finite number of observations

POPULATION = = total (infinite) number of observations

Properties of Gaussian curve defined in terms of population.
Then see where modifications needed for small samples of data

Main properties of Gaussian curve:

Population mean (μ) : defined as earlier (N → ∞). In absence of systematic error, μ is the ***true value*** (maximum on Gaussian curve).

Remember, **sample mean** ($\bar{x}$) defined for small values of N.

(Sample mean ≈ population mean when N ≥ 20)

Population Standard Deviation (σ) - defined on next overhead

- The MEAN defines the center of the Gaussian distribution.

- The STANDARD DEVIATION defines the WIDTH of the GAUSSIAN distribution.

$$\bar{x} = \frac{\sum_i x_i}{n}$$

- ***Alternative Expression for s (suitable for calculators)***

$$s = \sqrt{\frac{\left(\sum_{i=1}^{N} x_i^2\right) - \frac{\left(\sum_{i=1}^{N} x_i\right)^2}{N}}{N-1}}$$

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$

- The population mean μ is expressed as:
- where N is the total number of measurements in the population.

$$\mu = \frac{\sum_{i=1}^{N} x_i}{N}$$

The Population Standard Deviation σ

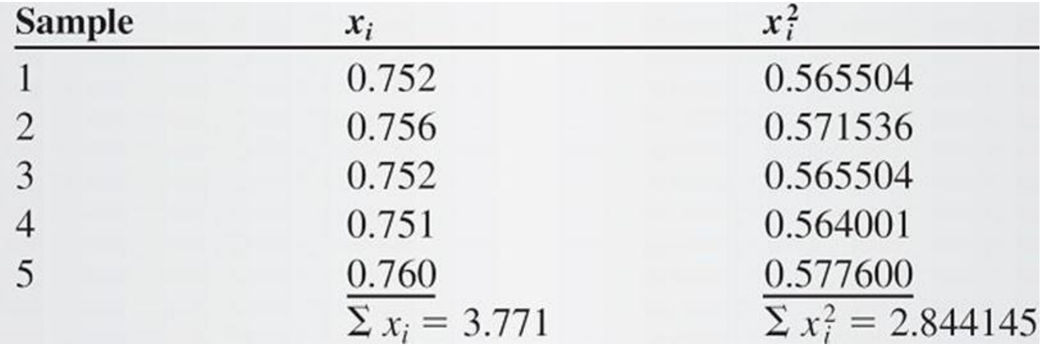
$$\sigma = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \mu)^2}{N}}$$

Some More Statistical Terms

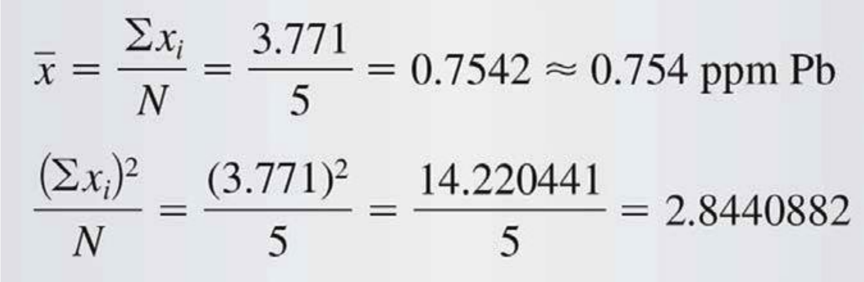
- Degree of Freedom = $n - 1$
- Variance = s^2
- Relative Standard Deviation (RSD) $$RSD = \left(\frac{s}{\bar{x}}\right)$$
- Coefficient of Variation (CV): $$CV = \left(\frac{s}{\bar{x}}\right) \times 100\%$$
- Standard Error of the Mean: $$s_m = {}^{s}\!/_{\sqrt{N}}$$
- Spread or Range = maximum value- minimum value

Q6-1: The following results were obtained in the replicate determination of the lead content of a blood sample: 0.752, 0.756, 0.752, 0.751 and 0.760 ppm Pb.

1. Calculate the mean
2. Standard deviation of this set of data.
3. Calculate the (a) variance, (b) relative standard deviation (c) coefficient of variation and (d) spread

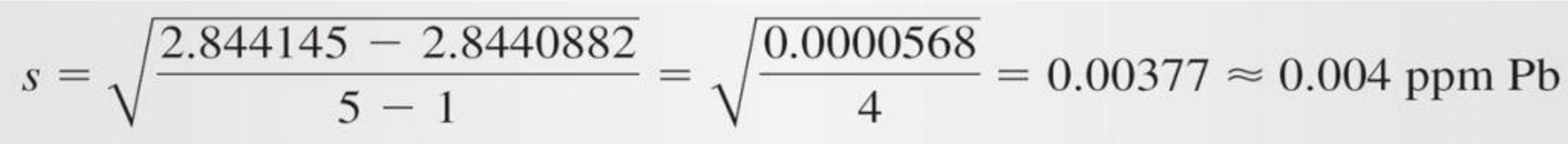


Sample	x_i	x_i^2
1	0.752	0.565504
2	0.756	0.571536
3	0.752	0.565504
4	0.751	0.564001
5	0.760	0.577600
	$\Sigma x_i = 3.771$	$\Sigma x_i^2 = 2.844145$

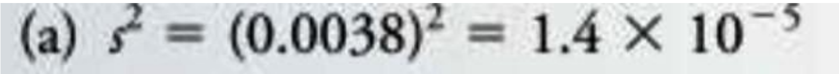


$$\bar{x} = \frac{\Sigma x_i}{N} = \frac{3.771}{5} = 0.7542 \approx 0.754 \text{ ppm Pb}$$

$$\frac{(\Sigma x_i)^2}{N} = \frac{(3.771)^2}{5} = \frac{14.220441}{5} = 2.8440882$$

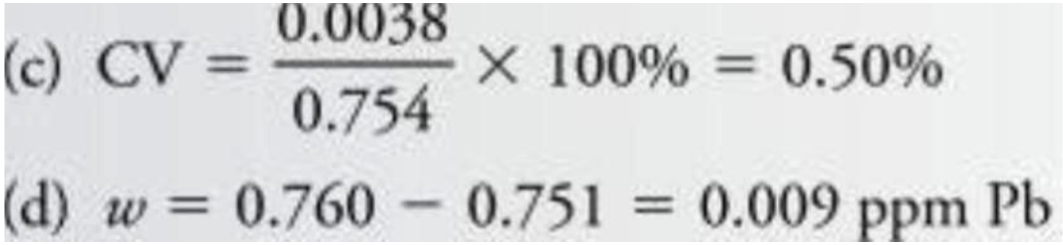


$$s = \sqrt{\frac{2.844145 - 2.8440882}{5 - 1}} = \sqrt{\frac{0.0000568}{4}} = 0.00377 \approx 0.004 \text{ ppm Pb}$$



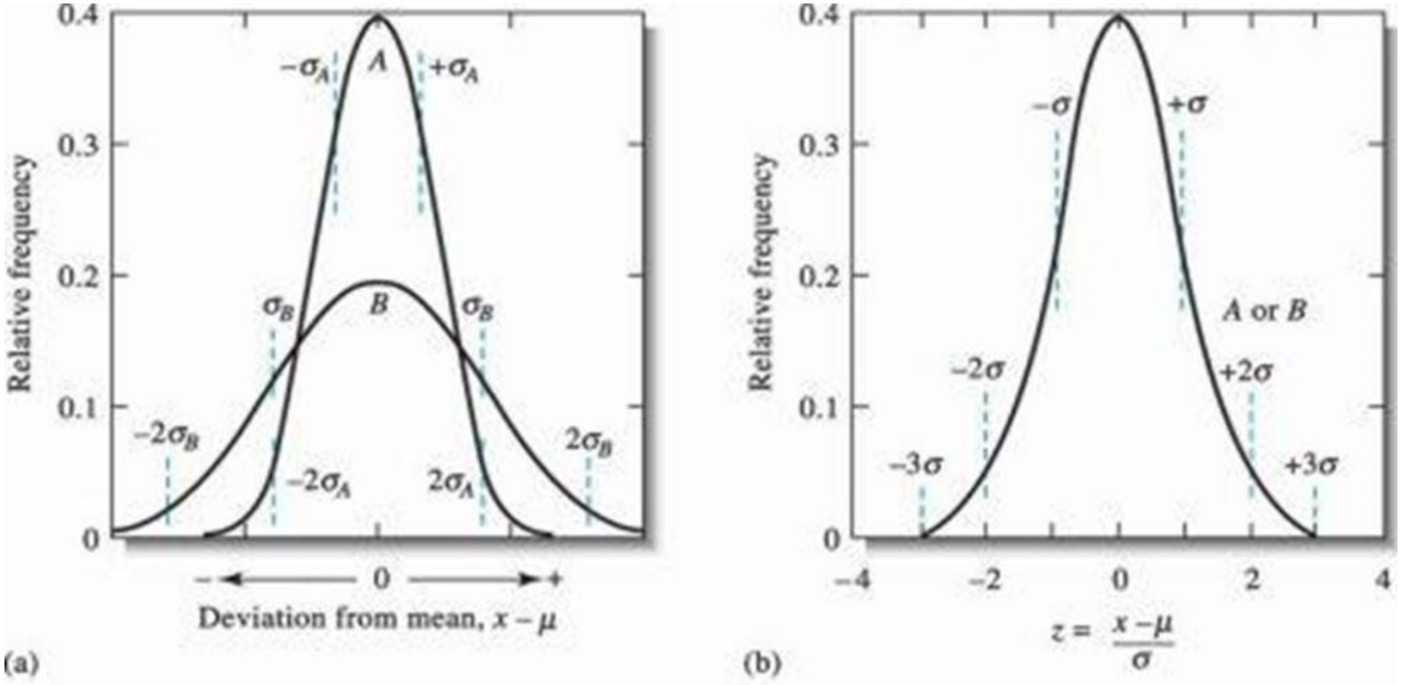
(a) $s^2 = (0.0038)^2 = 1.4 \times 10^{-5}$

b) 5.3×10^{-3}



(c) $\mathrm{CV} = \frac{0.0038}{0.754} \times 100\% = 0.50\%$

(d) $w = 0.760 - 0.751 = 0.009$ ppm Pb

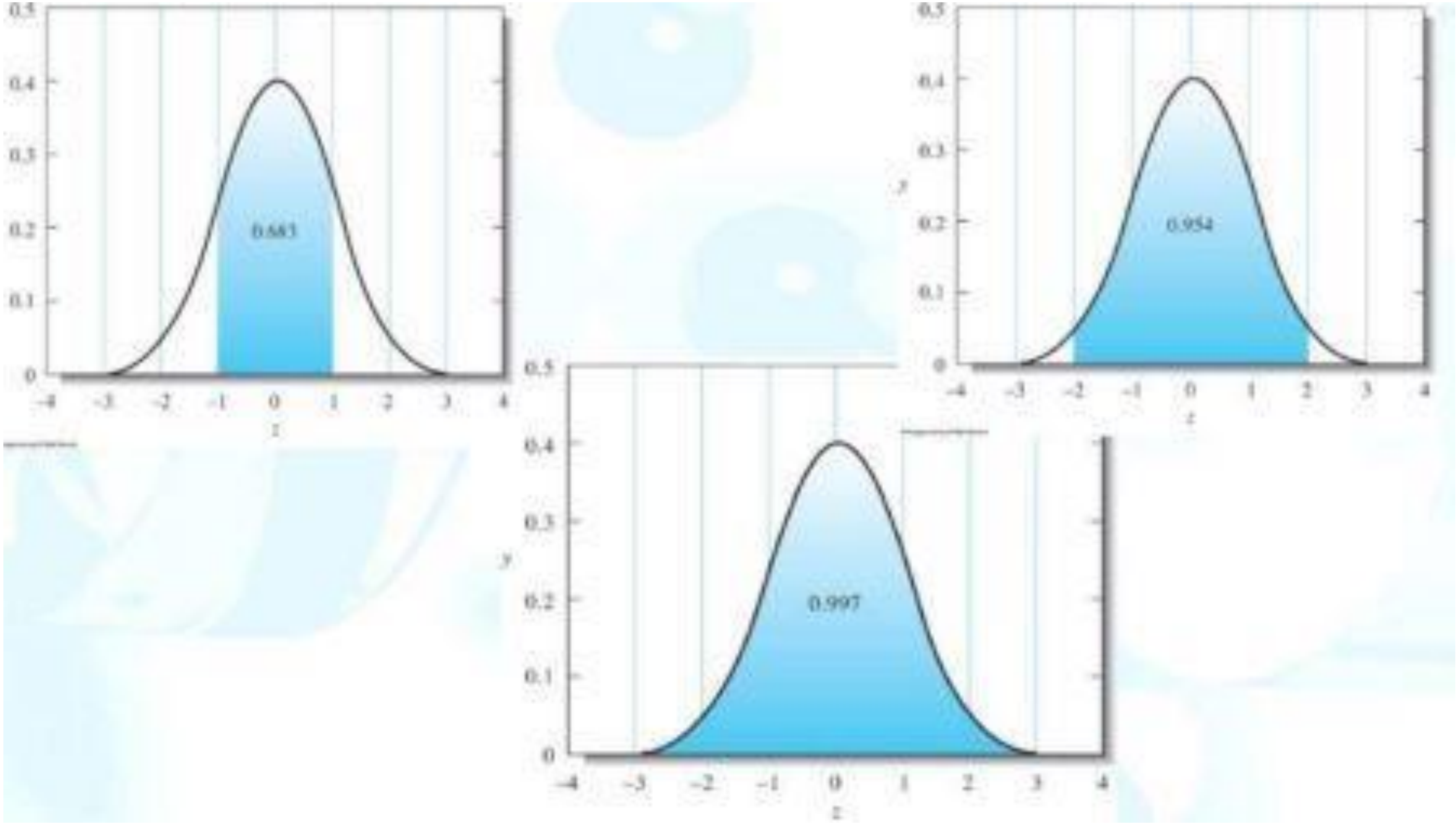


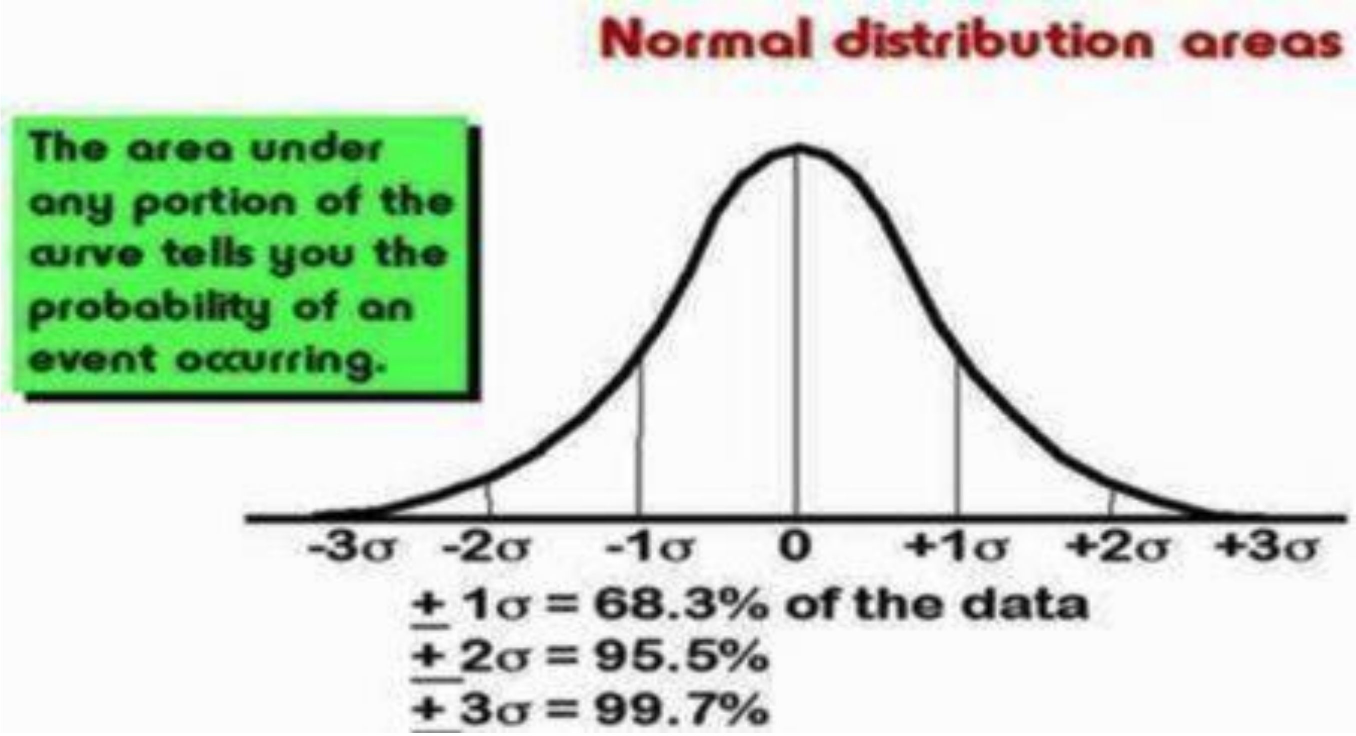
- The breadth of these curves is a measure of the precision of the two sets of data
- **The precision of the data set leading to curve A is twice as good as that of the data set represented by curve B**

- A Gaussian curve described all populations of data regardless of standard deviation; Both sets of data follow the normal errorcurve.
- Several general properties:
  - The mean occurs at the central point of maximum frequency.
  - There is a symmetrical distribution of positive and negative deviations about the maximum.
  - There is an exponential decrease in frequency as the magnitude of the deviations increases. Thus, small uncertainties are observed much more often than very large ones.

Areas under a Gaussian Curve

Regardless of its width, **68.3%** of the area beneath a Gaussian curve for a population lies within one standard deviation **(±1σ)** of the mean m. Approximately **95.4%** **of all data points are within ±2σ** of the mean and **99.7%** **within ±3σ**.





Area under a Gaussian Curve

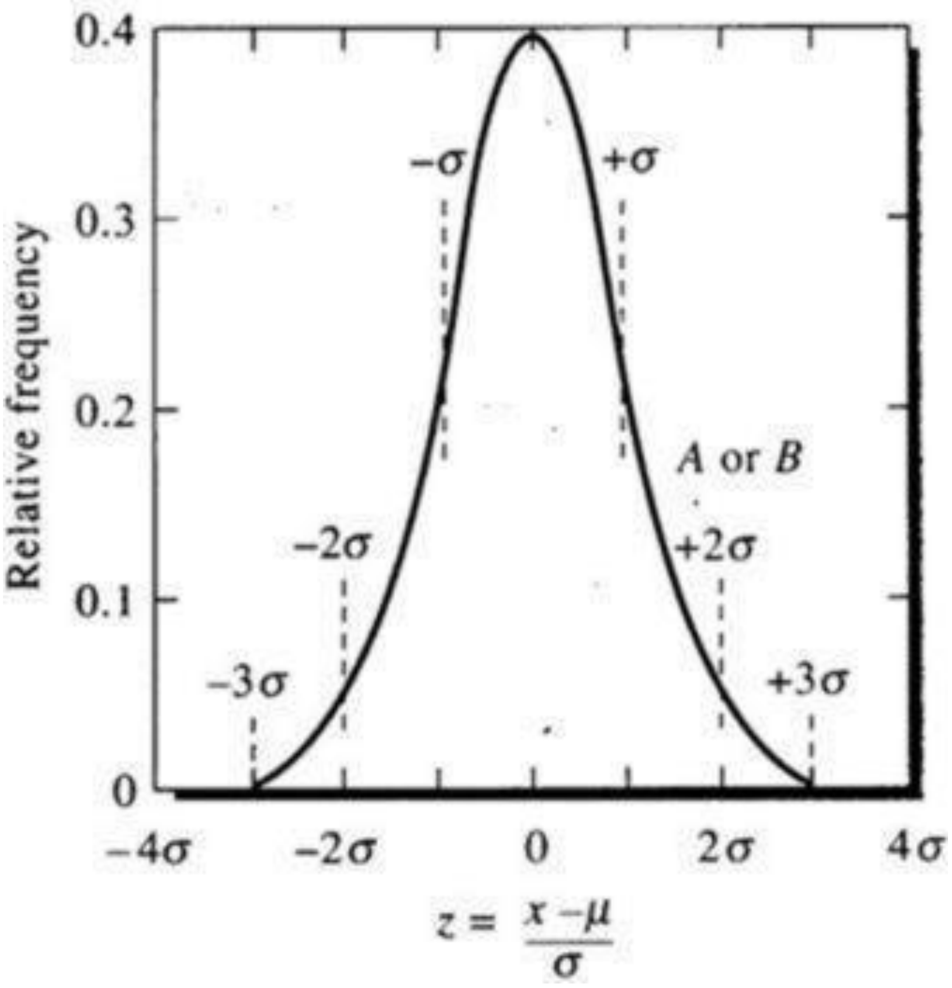
- 68.3% of the data lie within ±σ of the mean (μ), i.e. 68.3% of the area under the curve lies between ±σ of μ.
- Similarly, 95.5% of the area lies between ±2σ, and 99.7% between ±3σ.
- There are 68.3 chances in 100 that for a single datum the
- **random error** in the measurement will not exceed ±σ.
- The chances are 95.5 in 100 that the error will not exceed ±2σ.

- The Z-distribution is a normal distribution with mean **zero and standard deviation 1**
- A **z-value or z score represents the number of standard deviations** that a particular **value** lies above or below the mean. For example, **z** = 1 on the **Z-distribution represents** a **value** that **is** 1 **standard deviation** above the mean (i.e 68.3% of the data lie within ±1σ of the mean (μ)

Standardized normal variable, $z = \dfrac{(x-\mu)}{\sigma}$

Or $z\sigma = x - u$

Confidence level %	**z**
50	0.67
68%	**1.0**
80	1.29
90	1.64
95	1.96
96	2.00
99	2.58
99.7	3.00
99.9	3.29



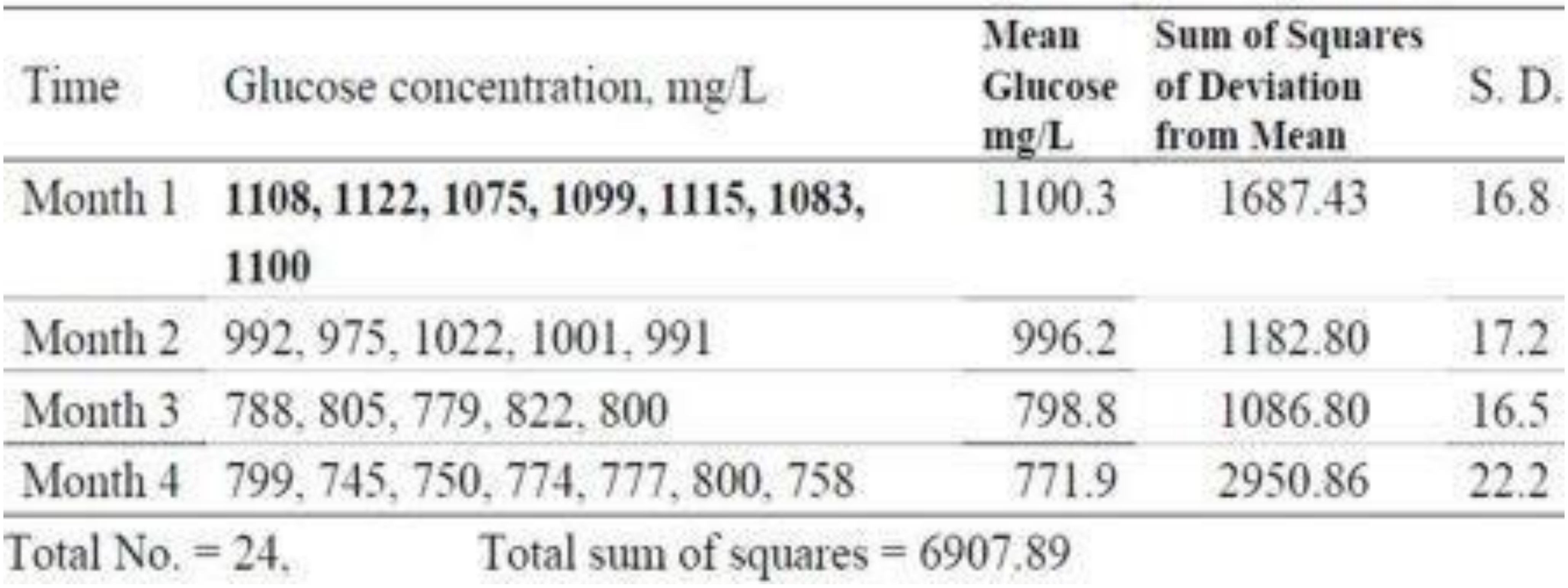
Pooled Data

- To achieve a value of s which is a good approximation to σ, i.e. $N \geq 20$, it is sometimes necessary to *pool* data from a number of sets of measurements (all taken in the same way).
- Suppose that there are ***t* small sets of data**, comprising N_1, N_2,….N_t measurements. The equation for the resultant sample standard deviation is:

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1}(x_i - \bar{x}_1)^2 + \sum_{i=1}^{N_2}(x_i - \bar{x}_2)^2 + \sum_{i=1}^{N_3}(x_i - \bar{x}_3)^2 + \ldots.}{N_1 + N_2 + N_3 + \ldots\ldots - t}}$$

(*Note:* one degree of freedom is lost for each set of data)

Ex. 6-2: Glucose levels are routinely monitored in patients suffering from diabetes. The glucose concentrations in a patient with mildly elevated glucose levels were determined in different months. The patient was placed on a low-sugar diet to reduce the glucose levels. The following results were obtained during a study to determine the effectiveness of the diet. Calculate a pooled estimate of the standard deviation for the method.



Time	Glucose concentration, mg/L	Mean Glucose mg/L	Sum of Squares of Deviation from Mean	S. D.
Month 1	**1108, 1122, 1075, 1099, 1115, 1083, 1100**	1100.3	1687.43	16.8
Month 2	992, 975, 1022, 1001, 991	996.2	1182.80	17.2
Month 3	788, 805, 779, 822, 800	798.8	1086.80	16.5
Month 4	799, 745, 750, 774, 777, 800, 758	771.9	2950.86	22.2

Total No. = 24, Total sum of squares = 6907.89

Solution

For the first month, the sum of the squares in the next to last column was calculated as follows:

$$\begin{aligned}\text{Sum of squares} &= (1108 - 1100.3)^2 + (1122 - 1100.3)^2 \\ &\quad + (1075 - 1100.3)^2 + (1099 - 1100.3)^2 + (1115 - 1100.3)^2 \\ &\quad + (1083 - 1100.3)^2 + (1100 - 1100.3)^2 = 1687.43\end{aligned}$$

The other sums of squares were obtained similarly. The pooled standard deviation is then

$$s_{\text{pooled}} = \sqrt{\frac{6907.89}{24 - 4}} = 18.58 \approx 19 \text{ mg/L}$$

6C Standard deviation of calculated results

- We must estimate the standard deviation of a result that has been calculated from **two or more experimental data points**, each of which has a known sample standard deviation.

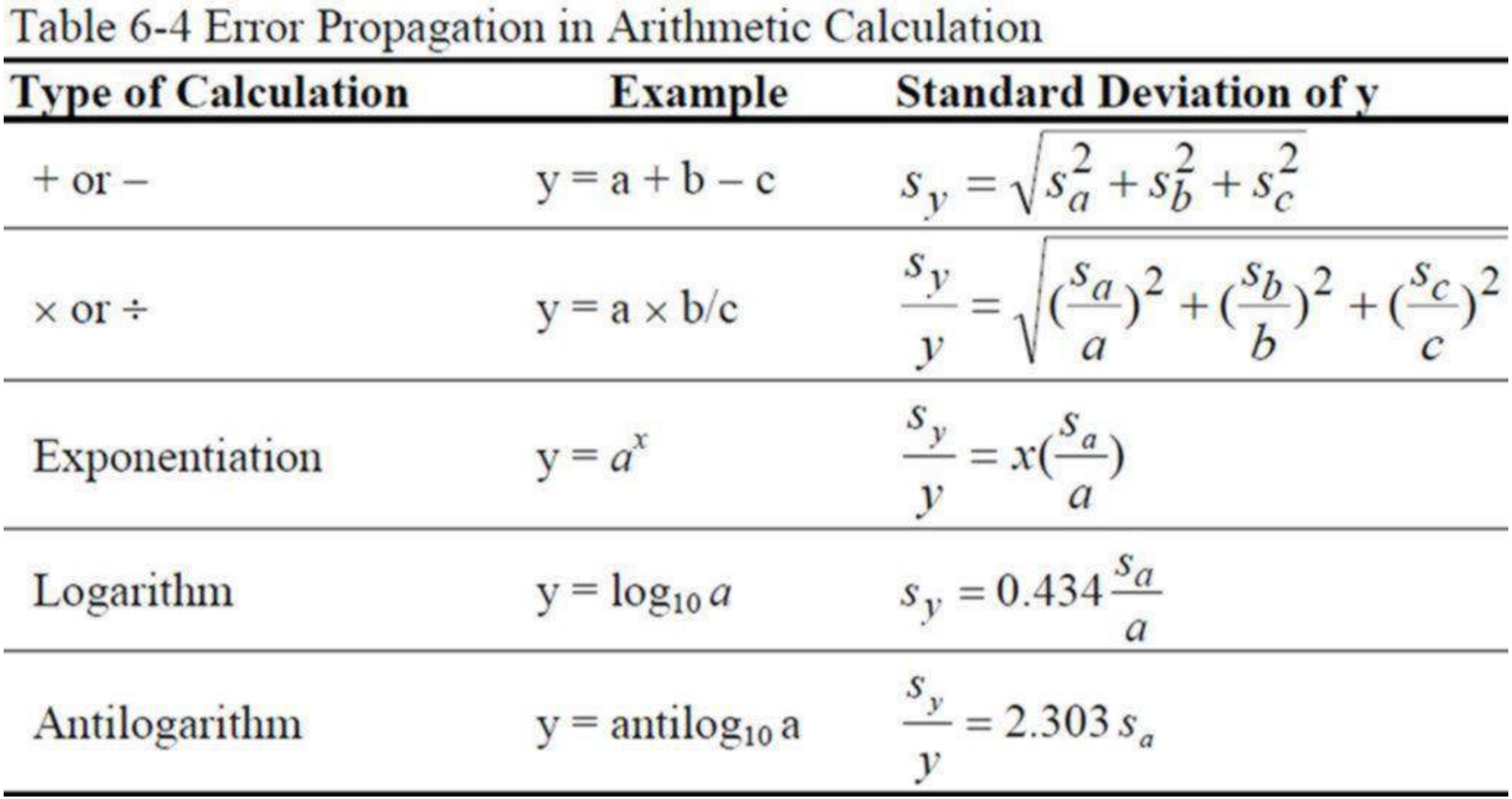


Table 6-4 Error Propagation in Arithmetic Calculation

Type of Calculation	**Example**	**Standard Deviation of y**
+ or −	$y = a + b - c$	$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$
× or ÷	$y = a \times b/c$	$\frac{s_y}{y} = \sqrt{(\frac{s_a}{a})^2 + (\frac{s_b}{b})^2 + (\frac{s_c}{c})^2}$
Exponentiation	$y = a^x$	$\frac{s_y}{y} = x(\frac{s_a}{a})$
Logarithm	$y = \log_{10} a$	$s_y = 0.434 \frac{s_a}{a}$
Antilogarithm	$y = \text{antilog}_{10}\, a$	$\frac{s_y}{y} = 2.303\, s_a$

Ex: Standard Deviation of a Sum or Differences

***y = *a* (± S$_a$) + b (± S$_b$) - c (± S$_c$)**

$$s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$$

Example

$$\begin{array}{rl} +0.50 & (\pm 0.02) \\ +4.10 & (\pm 0.03) \\ -1.97 & (\pm 0.05) \\ \hline 2.63 & \pm\ ?? \end{array}$$

$$s_y = \sqrt{(\pm 0.02)^2 + (\pm 0.03)^2 + (\pm 0.05)^2} = \pm 0.06$$

the sum should be reported as 2.63 (± 0.06)

Ex: Standard Deviation of a Product or quotient

$$*y = (a \times b)/c \; ; \quad \frac{4.10(\pm 0.02) \times 0.0050(\pm 0.0001)}{1.97(\pm 0.04)} = 0.010406 \; (\pm ?)$$

$$\frac{s_y}{y} = \sqrt{(\frac{s_a}{a})^2 + (\frac{s_b}{b})^2 + (\frac{s_c}{c})^2} = \sqrt{(\frac{\pm 0.02}{4.10})^2 + (\frac{\pm 0.0001}{0.005})^2 + (\frac{\pm 0.04}{1.97})^2}$$

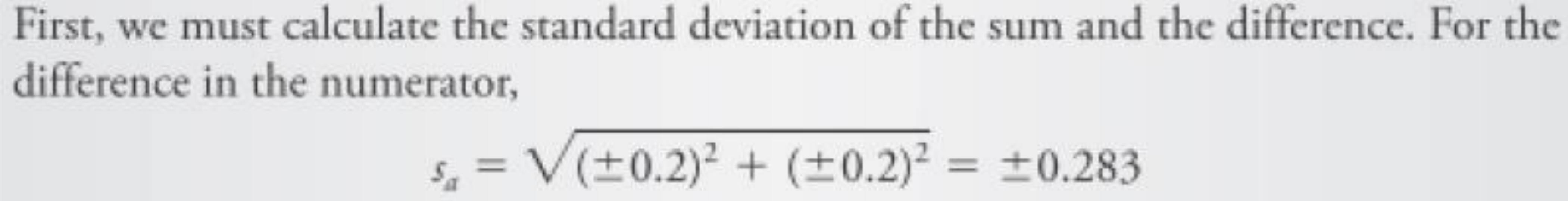
$$= \sqrt{(0.0049)^2 + (0.0200)^2 + (0.0203)^2} = \pm 0.0289$$

$$s_y = y \times (\pm 0.0289) = 0.0104 \times (\pm 0.0289) = \pm 0.000301$$

The answer is 0.0104 (± 0.0003)

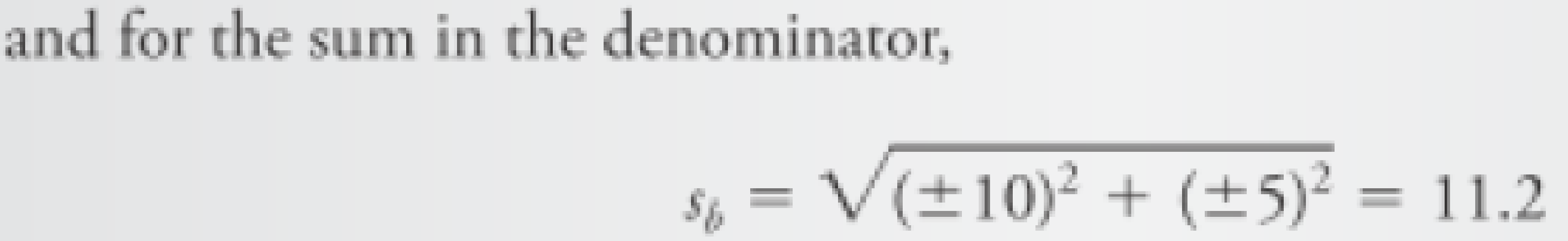
Ex 6-4. Calculate the standard deviation of the result of

$$\frac{[14.3(\pm0.2)-11.6(\pm0.2)]\times0.050(\pm0.001)}{[820(\pm10)+1030(\pm5)]\times42.3(\pm0.4)}=1.725(\pm?)\times10^{-6}$$



First, we must calculate the standard deviation of the sum and the difference. For the difference in the numerator,

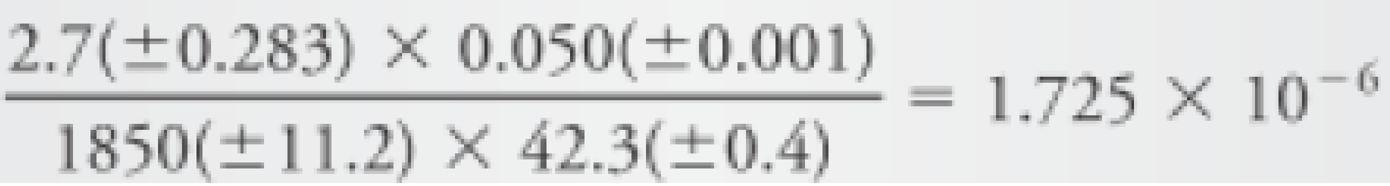
$$s_a=\sqrt{(\pm0.2)^2+(\pm0.2)^2}=\pm0.283$$



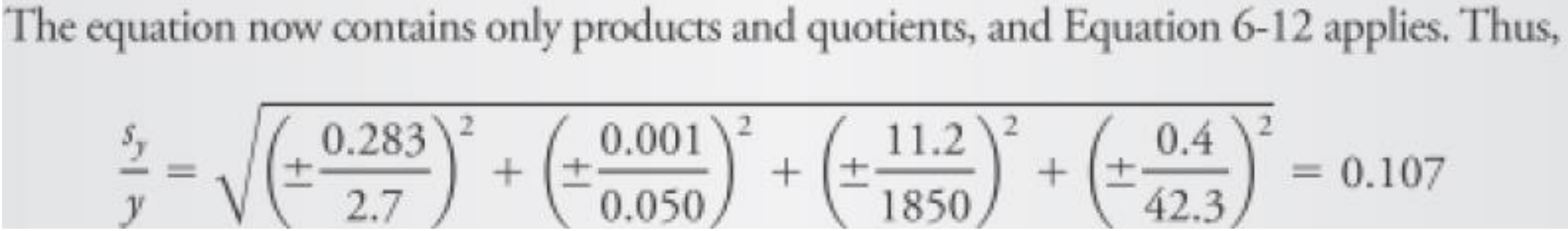
and for the sum in the denominator,

$$s_b=\sqrt{(\pm10)^2+(\pm5)^2}=11.2$$

Rewrite after the first two steps:



$$\frac{2.7(\pm0.283)\times0.050(\pm0.001)}{1850(\pm11.2)\times42.3(\pm0.4)}=1.725\times10^{-6}$$



The equation now contains only products and quotients, and Equation 6-12 applies. Thus,

$$\frac{s_y}{y}=\sqrt{\left(\pm\frac{0.283}{2.7}\right)^2+\left(\pm\frac{0.001}{0.050}\right)^2+\left(\pm\frac{11.2}{1850}\right)^2+\left(\pm\frac{0.4}{42.3}\right)^2}=0.107$$

$$s_y=y\times0.107=1.725\times10^{-6}\times(\pm0.107)=\pm0.185\times10^{-6}$$

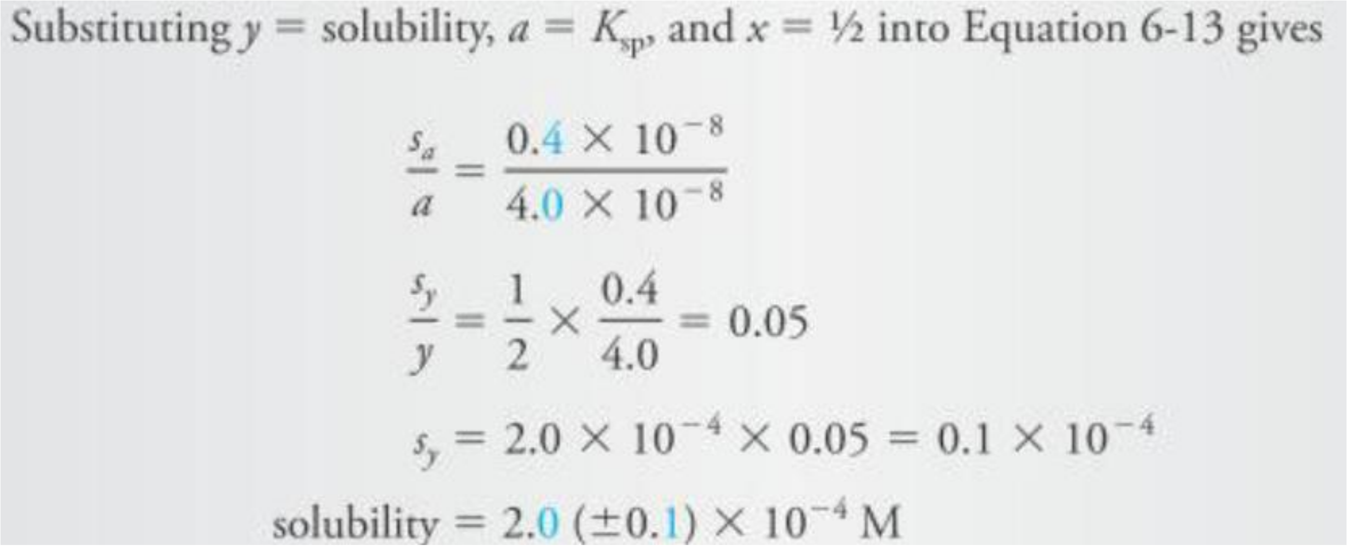
round the answer to $1.7(\pm0.2)\times10^{-6}$.

Ex: Standard Deviations in Exponential Calculations

$$y = a^x \qquad \boxed{\frac{S_y}{y} = x\left(\frac{S_a}{a}\right)}$$

Ex6-5: The solubility product Ksp for the silver salt AgX is 4.0 (± 0.4) × 10^{-8}. The molar solubility of AgX in water is; **Solubility = $(K_{sp})^{1/2}$ =$(4.0 \times 10^{-8})^{1/2}$ = 2.0×10^{-4} M**

<u>What is the uncertainty in the calculated solubility of AgX in water?</u>



Substituting y = solubility, $a = K_{sp}$, and x = ½ into Equation 6-13 gives

$$\frac{s_a}{a} = \frac{0.4 \times 10^{-8}}{4.0 \times 10^{-8}}$$

$$\frac{s_y}{y} = \frac{1}{2} \times \frac{0.4}{4.0} = 0.05$$

$$s_y = 2.0 \times 10^{-4} \times 0.05 = 0.1 \times 10^{-4}$$

solubility = 2.0 (±0.1) × 10^{-4} M

Ex: The standard deviation in measuring the diameter d of a sphere is ± 0.02 cm. What is the standard deviation in the calculated volume V of the sphere if d = 2.15 cm?

$$\mathrm{V} = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi\left(\frac{2.15}{2}\right)^3 = 5.20\ \mathrm{cm}^3$$

$$\frac{S_V}{V} = 3 \times \frac{S_d}{d} = 3 \times \frac{0.02}{2.15} = 0.0279,\ \mathrm{S_V} = 5.20 \times 0.0279 = 0.145,\ \boxed{\mathrm{V} = 5.2\ (\pm 0.1)\ \mathrm{cm}^3}$$

Standard Deviations of Logarithms and Antilogarithms

Logarithm $y = \log_{10} a$ $s_y = 0.434 \frac{s_a}{a}$

Antilogarithm $y = \text{antilog}_{10}\, a$ $\frac{s_y}{y} = 2.303\, s_a$

Ex. 6-7 Calculate the absolute standard deviations of the results of the following calculations.

(a) $y = \log[2.00(\pm 0.02) \times 10^{-4}] = -3.6990 \pm ?$ $\boxed{= -3.699\ (\pm 0.004)}$

$$s_y = 0.434 \frac{0.02 \times 10^{-4}}{2.00 \times 10^{-4}} = 0.004$$

(b) $y = \text{antilog}[1.200(\pm 0.003)] = 15.849 \pm ?$ $\boxed{= 15.8 \pm 0.1}$

$$\frac{s_y}{y} = 2.303 \times 0.003 = 0.0069, \quad S_y = 0.0069 \times 15.849 = 0.11$$

(c) $y = \text{antilog}[45.4(\pm 0.3)] = 2.5119 \times 10^{45} \pm ?$ $\boxed{= 3\ (\pm 2) \times 10^{45}}$

$$\frac{s_y}{y} = 2.303 \times 0.3 = 0.69, \quad S_y = 0.69 \times 2.5119 \times 10^{45} = 1.7 \times 10^{45}$$

6D Reporting computed data

- A numerical result is worthless to users of the data unless they know something about its quality.

– It is always essential to indicate your best estimate of the reliability of your data.

– A common indicator of data quality is the "significant figure convention".

- **SIGNIFICANT FIGURES:** The significant figures in a number are "all of the certain digitals *plus the first uncertain digit*". USED MAINLY IN MEASURMENTS

Exact Numbers

- Values with no uncertainties

- There are no uncertainties when counting objects or people
(24 students, 4 chairs, 10 pencils)

- There are no uncertainties in simple fractions
(1/4, 1/7, 4/7, 4/5)

Inexact Numbers

- Associated with uncertainties

- **Measurement** has uncertainties (errors) associated with it

- It is impossible to make exact measurements

RULES FOR SIGNIFICANT FIGURES

1. Nonzero integers are always significant

2. Leading zeros are not significant

0.0045 (2 sig. figs.)   0.00007895 (4 sig. figs.)

The zeros simply indicate the position of the decimal point

3. Captive zeros (between nonzero digits) are always significant

1.0025 (5 sig figs.)   ; 12000587 (8 sig figs)

4. Trailing zeros (at the right end of a number) are significant only if the number contains a decimal point

2.3400 (5 sig figs)   23400 (3 sig figs)

Sums andDifferences: The result contains the same number of **decimal places** as the measurement with the **<u>least number of decimal places</u>**

- 3.<u>4</u> + 0.020 + 7.31 = 10.730 (round to 10.7)
- the second and third decimal places in the answer cannot be significant because 3.4 is uncertain in the first decimal place. Hence, the result should be rounded to 10.7.

- When adding and subtracting numbers in scientific notation, express the numbers to the same power of 10:

$$2.432 \times 10^6 = 2.\underline{432} \times \mathbf{10^6}$$
$$+\ 6.512 \times 10^4 = +\ 0.06512 \times \mathbf{10^6}$$
$$-\ 1.277 \times 10^5 = -\ 0.1277 \times \mathbf{10^6}$$
$$2.37441 \times \mathbf{10^6}$$

(round to 2.374×10^6)

Multiplication and Division

- The result contains the same number of significant figures as the measurement with the least number of significant figures

$2.0456 \times \underline{4.02} = 8.223312 = 8.22$

$3.20014 \div \underline{1.2} = 2.6667833 = 2.7$

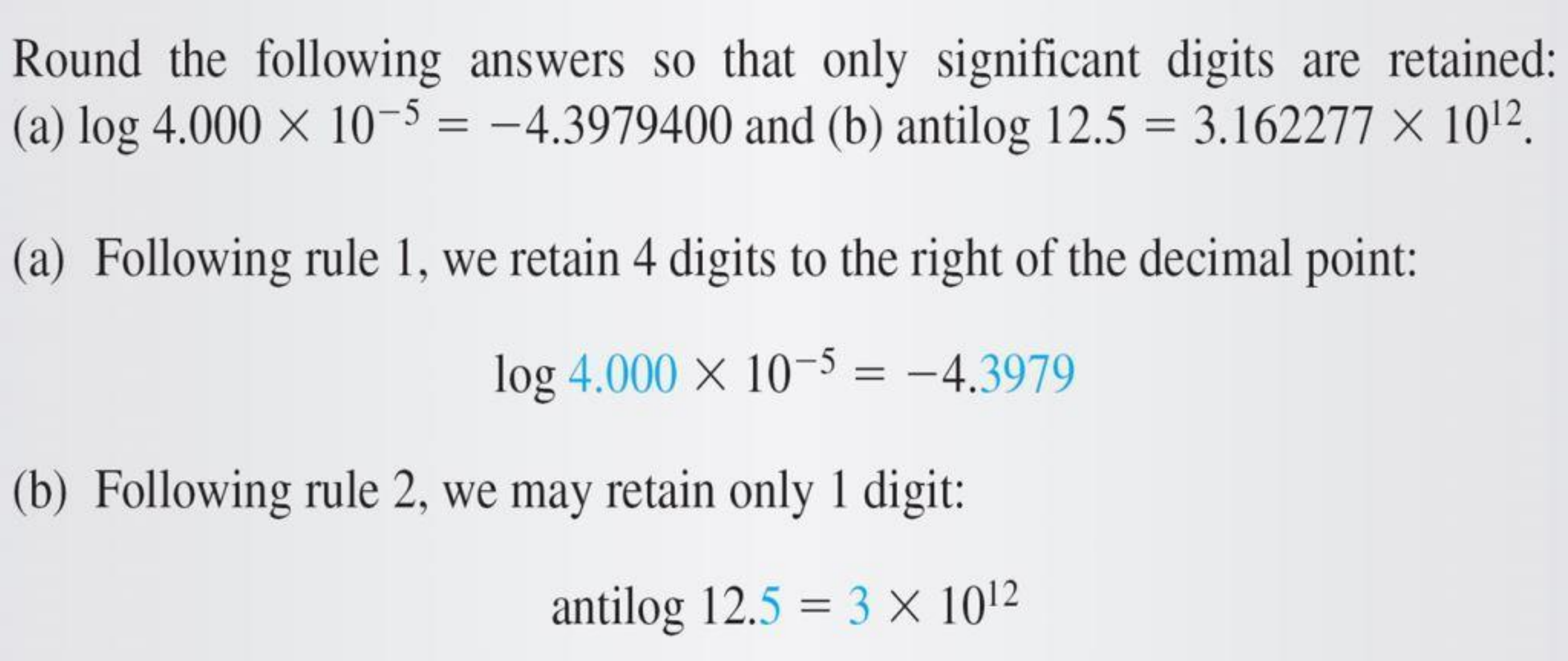
*Products and quotients

$$\frac{24 \times 4.52}{100.0} = 1.08 = 1.1 \qquad \frac{24 \times 4.02}{100.0} = 0.965 = 0.96$$

Logarithms and Antilogarithms

1. In a log. of a no., keep as many digits **to the right of the decimal point** as there are **significant figures in the original no**.

2. In an antilog. of a no., keep as many digits as there are digits to the right of the decimal point in the original no.



Round the following answers so that only significant digits are retained: (a) $\log 4.000 \times 10^{-5} = -4.3979400$ and (b) antilog $12.5 = 3.162277 \times 10^{12}$.

(a) Following rule 1, we retain 4 digits to the right of the decimal point:

$$\log 4.000 \times 10^{-5} = -4.3979$$

(b) Following rule 2, we may retain only 1 digit:

$$\text{antilog } 12.5 = 3 \times 10^{12}$$

$$\log \underline{9.57} \times 10^4 = 4.\underline{981}$$

Rounding off Numbers

1. In a series of calculations, carry the extra digits through to the final result before rounding off to the required significant figures

2. If the first digit to be removed is less than 5, the preceding digit remains the same (2.53 rounds to 2.5 and 1.24 rounds to 1.2)

3. If the first digit to be removed is greater than 5, the preceding digit increases by 1 (2.56 rounds to 2.6 and 1.27 rounds to 1.3)

4. If the digit to be removed is exactly 5,

-The preceding number is increased by 1 if that results in an even number (2.55 rounds to 2.6 and 1.35000 rounds to 1.4)

- The preceding number remains the same if that results in an odd number 2.45 rounds to 2.4 and 1.25000 rounds to 1.2)

- ❖ It is especially important to postpone rounding until the calculation is completed.
- ❖ At least one extra digit beyond the significant digits should be carried through all of the computations in order to avoid a *rounding error.*
- ❖ This extra digit is sometimes called a “guard” digit.

Ex. 6-9 A 3.4842-g sample of a solid mixture containing benzoic acid, C6H5COOH (122.123 g/mol), was dissolved and titrated with base to a phenolphthalein end point. The acid consumed 41.36 mL of 0.2328 M NaOH. Calculate the percent benzoic acid (HBz) in the sample.

$$\%\text{HBr} = \frac{41.36\ \text{mL} \times 0.2328\ \text{mmol/mL} \times 1 \times 122.123\ \text{mg/mmol}}{3.4842\ \text{g} \times 1000\ \text{mg/g}} \times 100\%$$

$$= 33.749\ \%$$

(1) buret : ± 0.02 mL → the S.D. of the volume will be

Initial and final readings

$$[(\pm 0.02)^2 + (\pm 0.02)^2]^{1/2} = \pm 0.028\ \text{mL}$$

$*y = a\ (\pm S_a) + b\ (\pm S_b) - c\ (\pm S_c)$ $\qquad s_y = \sqrt{s_a^2 + s_b^2 + s_c^2}$

(2) analytical balance : uncertainty = ± 0.0001 g

One reading

(3) the A.U. in the molarity of the reagent soln = ± 0.0001

One reading

(4) the R.U. in the molar mass of HBz is several orders of magnitude smaller than that of the three experimental data and is of no consequence.

(5) 100 % and 1000 mmol are exact numbers **And there is no uncertainty**

➢ Use the Standard Deviation of a Product or quotient

$$\frac{s_y}{y} = \sqrt{(\frac{s_a}{a})^2 + (\frac{s_b}{b})^2 + (\frac{s_c}{c})^2}$$

y= 33.749
Sa= 0.028, a= 41.36
Sb= 0.0001, a= 3.4842
Sa= 0.0001, a= 0.2328

Then

Sy= 0.027

The uncertainty in the result is 0.03% HBz, so the result should be reported as 33.75% (±0.03)%

Modified by Dr. Mohammed Rasheed

Chapter 7

Statistical Data Treatment and Evaluation

The sampling distribution of the mean

- In the absence of systematic errors, the mean of a sample of measurements provides us with an **estimate of the true value u**
- Even in the absence of systematic errors, the individual measurements vary due to random errors and so it is most **unlikely that the mean of the sample will be *exactly* equal to the true value.**
- For this reason it is more useful to give a **range** of values which is likely to include the true value.

- The width of this range or interval depends on two factors.
    1. The precision of the individual measurements, which in turn depends on the **standard deviation** of the population.
    2. The **number of measurements** in the sample. The more measurements, the more reliable the estimate of ,u, the true value, will be.

Confidence limits of the mean for large samples

- The range which may be assumed to include the true value is known as **a confidence interval** and the extreme values of the range are called the **confidence limits.**
- The term `confidence' implies that we can assert with a given degree of confidence, i.e. a **certain probability**, that the confidence interval does include the true value.
- The size of the confidence interval will obviously depend on how certain we want to be that it includes the true value: **the greater the certainty, the greater the interval required.**

Confidence limits of the mean for large samples

- How can we relate the observed mean value $\overline{x}$ to the true mean u?
  - **The latter can never be known exactly.**
- The range of uncertainty depends how closely s corresponds to σ.
- We can calculate the limits (above and below) around $\overline{x}$
  - That must lie, with a given degree of probability.

CONFIDENCE LIMITS

interval around the mean that probably contains μ.

CONFIDENCE INTERVAL

the magnitude of the confidence limits

CONFIDENCE LEVEL

fixes the level of probability that the mean *is* within the confidence limits

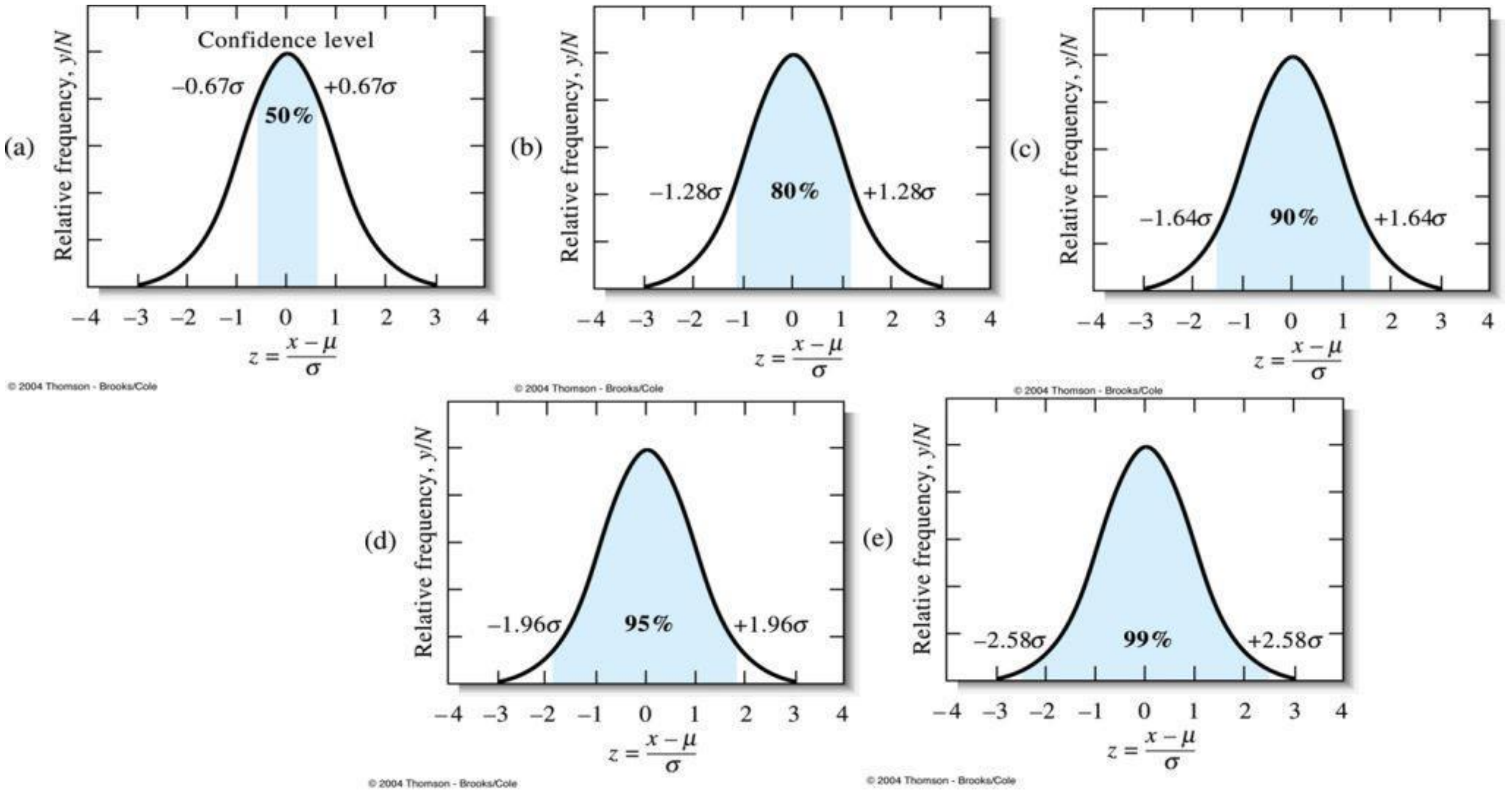
Finding the confidence interval when σ is known or s is a good estimate of σ

- In each of a series of five normal error curves, **the relative frequency is plotted as a function of the quantity z**. The shaded areas in each plot lie between the values of -z and +z that are indicated to the left and right of the curves.
- The numbers within the shaded areas are the percentage of the total area under the curve that is included within these values of z.

(a) 50% of the area under any Gaussian curve is located between -0.67 σ *and +0.67* σ*;*
(b) 80% of the total area lies between -1.28 σ *and +1.28* σ *and*
(c) 90% of the total area lies between -1.64 σ *and +1.64* σ*.*
(d)) 95% of the total area lies between -1.96 σ *and +1.96* σ*.*
(e)) 99% of the total area lies between -2.58 σ *and +2.58* σ*.*

- The confidence level (CL) is the probability that the true mean lies within a certain interval and is often expressed as a percentage.

Figure 7-1c the **confidence level** is 90% and the **confidence interval** is from -1.64 σ to +1.64 σ



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Areas under a Gaussian curve for various values of ±z.

What this means, for example, is that 80 times out of 100 the *true mean* will lie between $\pm 1.29\sigma$ of any measurement we make.

Thus, at a *confidence level* of 80%, the *confidence limits* are $\pm 1.29\sigma$.

For a single measurement: CL for $\mu = x \pm z\sigma$ (values of z on next overhead

For the sample mean of N measurements ($\bar{x}$), the equivalent expression is:

$$\text{CL for } \mu = \bar{x} \pm {}^{z\sigma}\!\big/_{\sqrt{N}}$$

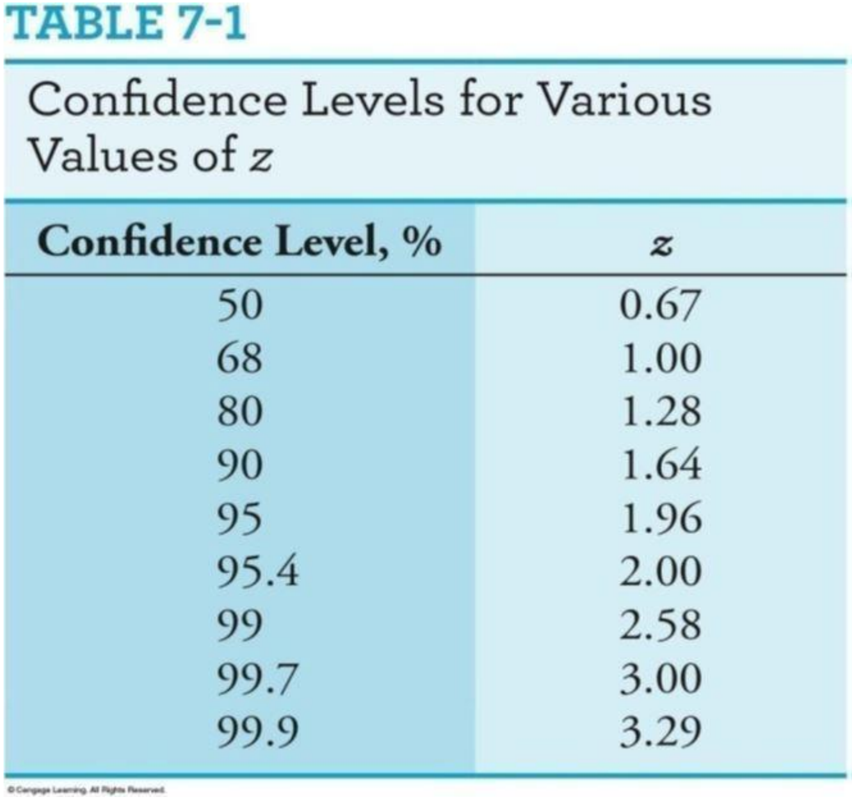
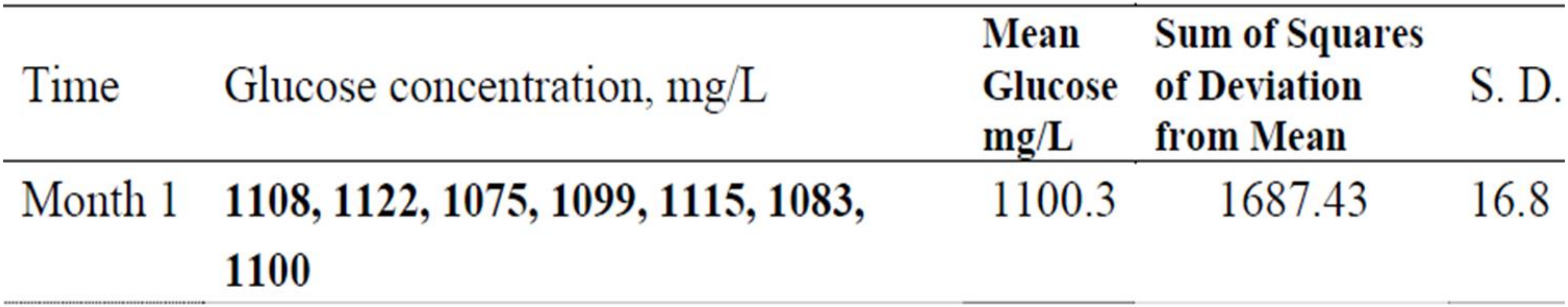


TABLE 7-1

Confidence Levels for Various Values of *z*

Confidence Level, %	***z***
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29

Values of *z* for determining Confidence Limits



Time	Glucose concentration, mg/L	**Mean Glucose mg/L**	**Sum of Squares of Deviation from Mean**	S. D.
Month 1	**1108, 1122, 1075, 1099, 1115, 1083, 1100**	1100.3	1687.43	16.8

Ex. 7-1

1) **Assume that in each part s = 19 is a good estimate of σ.**

Calculate the 80% and 95% confidence limits for

a) **the first entry** (1108 mg/L glucose)

From Table 7-1, ***z*=1.28 and 1.96 for the 80% and 95% confidence level (N=1)**

80% CI = 1108 ± 1.28 × 19 = 1108 ± 24.3 mg/L (1083.7 - 1132.3)

95% CI = 1108 ± 1.96 × 19 = 1108 ± 37.2 mg/L (1070.8 - 1145.2)

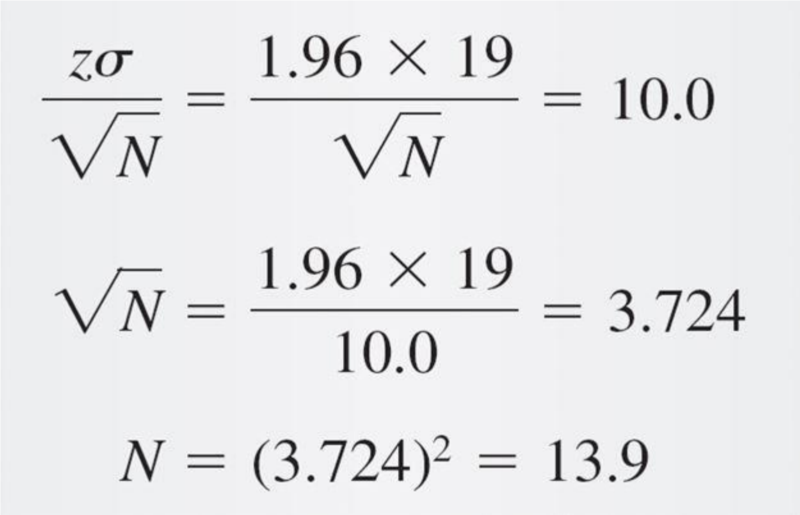
b) the mean value (1100.3 mg/L) for **month1** in the example.

$$80\%\ \text{CL} = 1100.3 \pm \frac{1.28 \times 19}{\sqrt{7}} = 1100.3 \pm 9.2\ \text{mg/L}$$

(1091.1 - 1109.5)

$$95\%\ \text{CL} = 1100.3 \pm \frac{1.96 \times 19}{\sqrt{7}} = 1100.3 \pm 14.1\ \text{mg/L}$$

Ex 17-1 c): How many replicate measurements in month 1 are needed to decrease the 95 % confidence interval to 1100.3 ± 10.0 mg/L glucose?



$$\frac{z\sigma}{\sqrt{N}} = \frac{1.96 \times 19}{\sqrt{N}} = 10.0$$

$$\sqrt{N} = \frac{1.96 \times 19}{10.0} = 3.724$$

$$N = (3.724)^2 = 13.9$$

i.e: 14 measurements are needed to provide a slightly better than 95% chance that the population mean will lie within ± 14 mg/L of the experimental mean

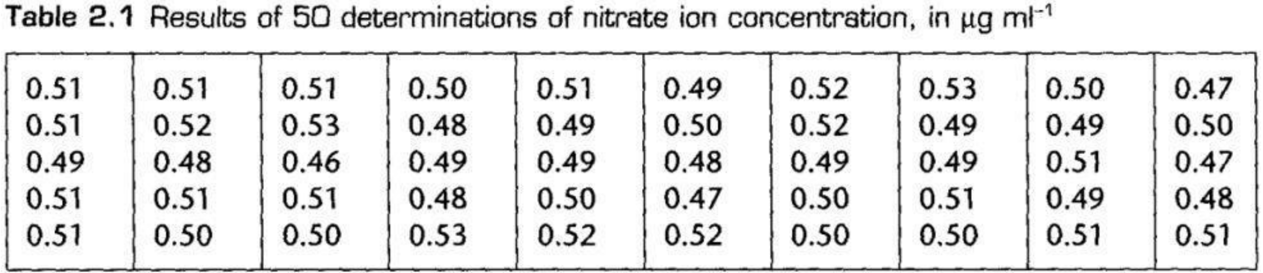
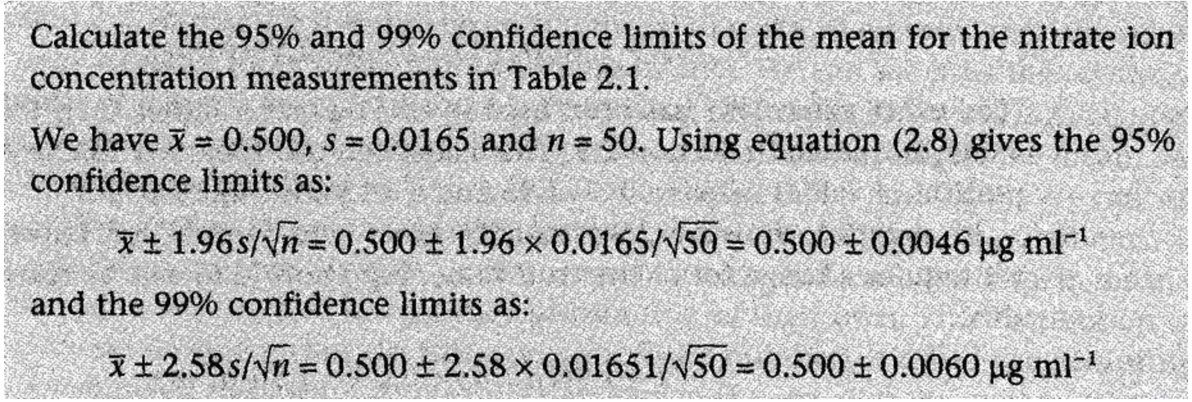


Table 2.1 Results of 50 determinations of nitrate ion concentration, in $\mu g\ ml^{-1}$

0.51	0.51	0.51	0.50	0.51	0.49	0.52	0.53	0.50	0.47
0.51	0.52	0.53	0.48	0.49	0.50	0.52	0.49	0.49	0.50
0.49	0.48	0.46	0.49	0.49	0.48	0.49	0.49	0.51	0.47
0.51	0.51	0.51	0.48	0.50	0.47	0.50	0.51	0.49	0.48
0.51	0.50	0.50	0.53	0.52	0.52	0.50	0.50	0.51	0.51



Calculate the 95% and 99% confidence limits of the mean for the nitrate ion concentration measurements in Table 2.1.

We have $\bar{x} = 0.500$, $s = 0.0165$ and $n = 50$. Using equation (2.8) gives the 95% confidence limits as:

$$\bar{x} \pm 1.96s/\sqrt{n} = 0.500 \pm 1.96 \times 0.0165/\sqrt{50} = 0.500 \pm 0.0046\ \mu g\ ml^{-1}$$

and the 99% confidence limits as:

$$\bar{x} \pm 2.58s/\sqrt{n} = 0.500 \pm 2.58 \times 0.01651/\sqrt{50} = 0.500 \pm 0.0060\ \mu g\ ml^{-1}$$

Finding the confidence interval when **σ** *is unknown*

- If we have no information on **σ**, and only have a value for **s** – the confidence interval is larger, i.e. there is a greater uncertainty.

- Instead of z, it is necessary to use the parameter t, defined as follows:

$$\boxed{t = (x - \mu)/s}$$

i.e. just like z, but using s instead of σ.

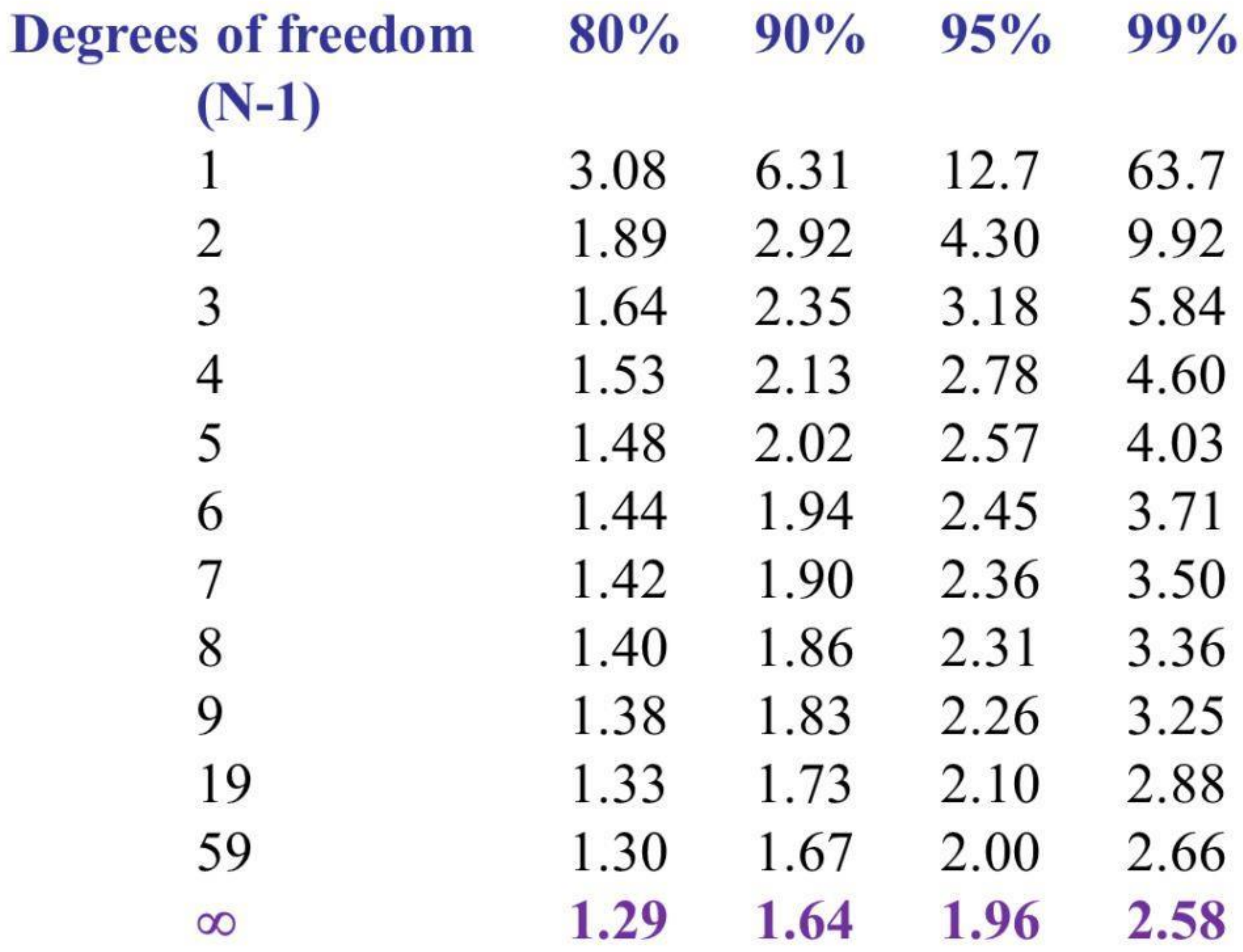
By analogy we have:

$$\text{CL for } \mu = \bar{x} \pm {}^{ts}\!/\!_{\sqrt{N}}$$

(where $\bar{x}$ = sample mean for N measurements)

The calculated values of t are given on the next overhead

Values of t *for various levels of probability*



Degrees of freedom (N-1)	80%	90%	95%	99%
1	3.08	6.31	12.7	63.7
2	1.89	2.92	4.30	9.92
3	1.64	2.35	3.18	5.84
4	1.53	2.13	2.78	4.60
5	1.48	2.02	2.57	4.03
6	1.44	1.94	2.45	3.71
7	1.42	1.90	2.36	3.50
8	1.40	1.86	2.31	3.36
9	1.38	1.83	2.26	3.25
19	1.33	1.73	2.10	2.88
59	1.30	1.67	2.00	2.66
∞	**1.29**	**1.64**	**1.96**	**2.58**

***Note*:** (1) As (N-1) → ∞, so t → z

(2) For all values of (N-1) < ∞, t > z, I.e. greater uncertainty

Example: Analysis of an insecticide gave the following values for % of the chemical lindane: 7.47, 6.98, 7.27. Calculate the CL for the mean value at the 90% confidence level.

x_i%	x_i^2
7.47	55.8009
6.98	48.7204
7.27	52.8529

$\Sigma x_i = 21.72$

$\Sigma x_i^2 = 157.3742$

$$s = \sqrt{\frac{\sum x_i^2 - \frac{(\sum x_i)^2}{N}}{N-1}} = \sqrt{\frac{157.3742 - {(21.72)^2}/{3}}{2}}$$

$$= 0.246 = 0.25\%$$

$$\bar{x} = \frac{\sum x_i}{N} = \frac{21.72}{3} = 7.24$$

$$90\%\ \text{CL} = \bar{x} \pm {ts}/{\sqrt{N}} = 7.24 \pm \frac{(2.92)(0.25)}{\sqrt{3}}$$

$$= 7.24 \pm 0.42\%$$

- **If repeated analyses showed that s → σ = 0.28%:**

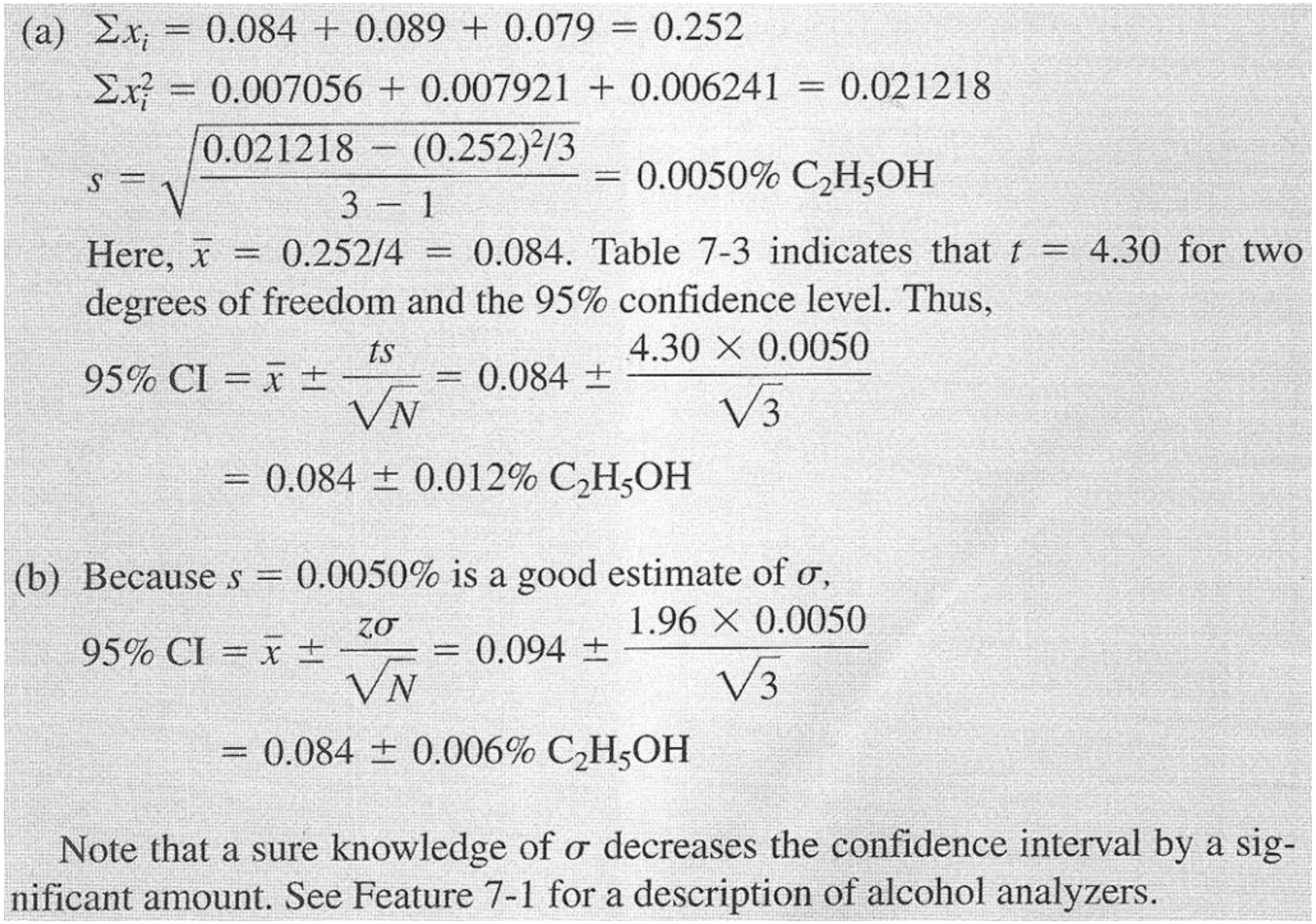
$$90\%\ \text{CL} = \bar{x} \pm {z\sigma}/{\sqrt{N}} = 7.24 \pm \frac{(1.64)(0.28)}{\sqrt{3}}$$

$$= 7.24 \pm 0.27\%$$

Ex7-3: A chemist obtained the following data for the alcohol content of a sample of blood: % C_2H_5OH: **0.084, 0.089 and 0.079**. Calculate the 95% confidence interval for the mean assuming

a) the three results obtained are the only indication of the precision of the method and

b) from previous experience on hundreds of samples, we know that the standard deviation of the method s = 0.005% C_2H_5OH and is a good estimate of σ.



(a) $\Sigma x_i = 0.084 + 0.089 + 0.079 = 0.252$

$$\Sigma x_i^2 = 0.007056 + 0.007921 + 0.006241 = 0.021218$$

$$s = \sqrt{\frac{0.021218 - (0.252)^2/3}{3 - 1}} = 0.0050\%\ C_2H_5OH$$

Here, $\bar{x} = 0.252/4 = 0.084$. Table 7-3 indicates that $t = 4.30$ for two degrees of freedom and the 95% confidence level. Thus,

$$95\%\ \text{CI} = \bar{x} \pm \frac{ts}{\sqrt{N}} = 0.084 \pm \frac{4.30 \times 0.0050}{\sqrt{3}}$$

$$= 0.084 \pm 0.012\%\ C_2H_5OH$$

(b) Because $s = 0.0050\%$ is a good estimate of σ,

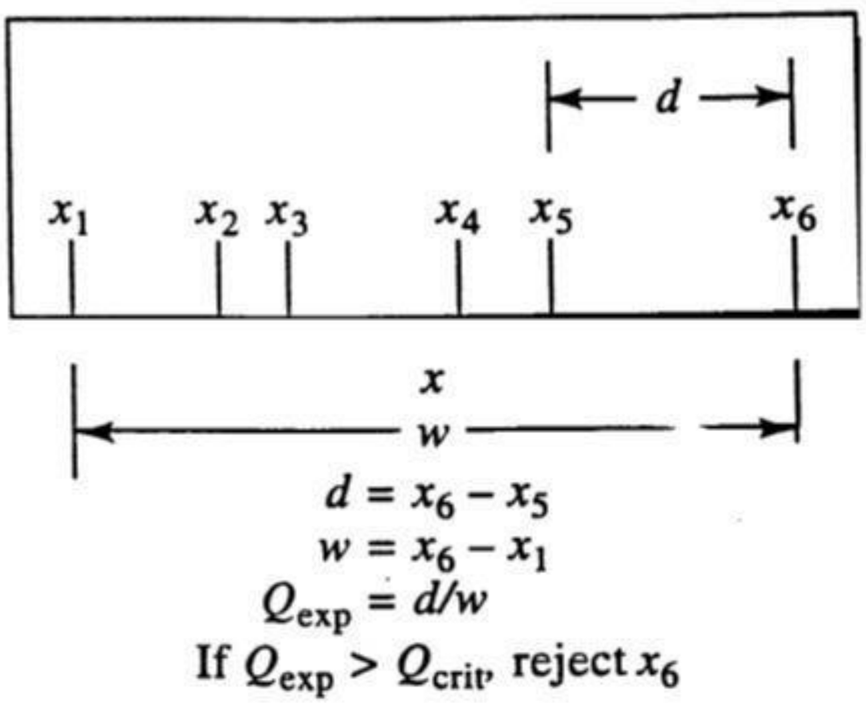
$$95\%\ \text{CI} = \bar{x} \pm \frac{z\sigma}{\sqrt{N}} = 0.094 \pm \frac{1.96 \times 0.0050}{\sqrt{3}}$$

$$= 0.084 \pm 0.006\%\ C_2H_5OH$$

Note that a sure knowledge of σ decreases the confidence interval by a significant amount. See Feature 7-1 for a description of alcohol analyzers.

Detection of Gross Errors

- ✓ A set of results may contain an outlying result out of line with the others.
- ✓ **Should it be retained or rejected?**
- ✓ There is no universal criterion for deciding this. One rule that can give guidance is the ***Q test***.



$d = x_6 - x_5$

$w = x_6 - x_1$

$Q_{exp} = d/w$

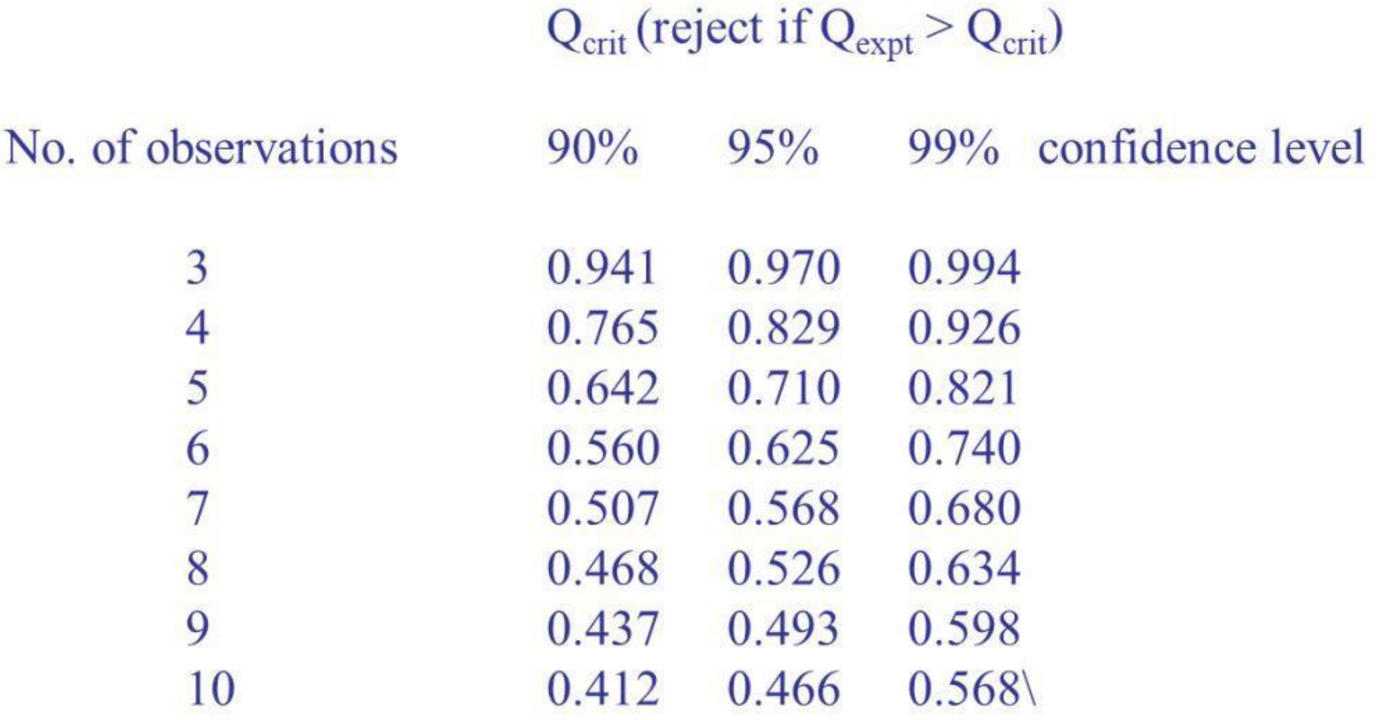
If $Q_{exp} > Q_{crit}$, reject x_6

The parameter Q_{exp} is defined as follows:

$$Q_{exp} = \left| x_q - x_n \right| / w$$

where x_q = questionable resul
x_n = nearest neighbour
w = spread of entire se

Q_{exp} is then compared to a set of values Q_{crit}:



Q_{crit} (reject if $Q_{expt} > Q_{crit}$)

No. of observations	90%	95%	99% confidence level
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568\

- Rejection of outlier recommended if $Q_{exp} > Q_{crit}$ for the desired confidence level.

- The higher the confidence level, the less likely is rejection to be recommended.

For 95%, 5 times in 100 it will be wrong to reject this suspect value

- Rejection of outliers can have a marked effect on mean and standard deviation, esp. when there are only a few data points. *Always try to obtain more data*.
- If outliers are to be retained, it is often better to report the *median* value rather than the *mean*.

Example: a) The following values were obtained for the concentration of nitrite ions in a sample of river water: 0.403, 0.410, 0.401, 0.380 mg/l. Should the last reading be rejected at 95% level?

$$Q_{\exp} = |0.380 - 0.401|/(0.410 - 0.380) = 0.7$$

- But Q_{crit} = 0.829 (at 95% level) for 4 values; Therefore, $Q_{exp} < Q_{crit}$, and we cannot reject the suspect value.

b) Suppose If 3 further measurements taken, giving total values of: 0.403, 0.410, 0.401, 0.380, 0.400, 0.413, 0.411 mg/l. Should 0.380 still be retained?

$$Q_{\exp} = |0.380 - 0.400|/(0.413 - 0.380) = 0.606$$

- But Q_{crit} = 0.568 (at 95% level) for 7 values; therefore, $Q_{exp} > Q_{crit}$, and rejection of 0.380 is recommended.

Note that 5 times in 100 it will be wrong to reject this suspect value!

Also note that if 0.380 is retained, s = 0.011 mg/l, but if it is rejected, s = 0.0056 mg/l, i.e. precision appears to be twice as good, just by rejecting one value.

Q7-6: The analysis of a calcite sample yielded CaO percentages of 55.95, 56.00, 56.04, 56.08 and 56.23. The last value appears anomalous; should it be retained or rejected at 90% confidence Level?

Ans: The difference between 56.23 and 56.08 is 0.15%. The spread (56.23 – 55.95) is 0.28%. Thus,

$$Q = \frac{0.15}{0.28} = 0.54$$

- For five measurements, Q_{crit} at the 95% confidence level is 0.71.
- Because 0.54 < 0.71, we must retain the outlier at the 95% confidence level.

✓ Recommendations for Treating Outliers

- Reexamine carefully all data relating to the outlying result to see if a gross error could have affected its value.
- If possible, estimate the precision that can be reasonably expected from the procedure to be sure that the outlying result actually is questionable.
- Repeat the analysis if sufficient sample and time are available.
- If more data cannot be secured, apply the *Q* test to the existing set to see if the doubtful result should be retained or rejected on statistical grounds.
- If the *Q* test indicates retention, consider **reporting the median** of the set rather than the mean.

Modified by

Dr. Mohamed Rasheed

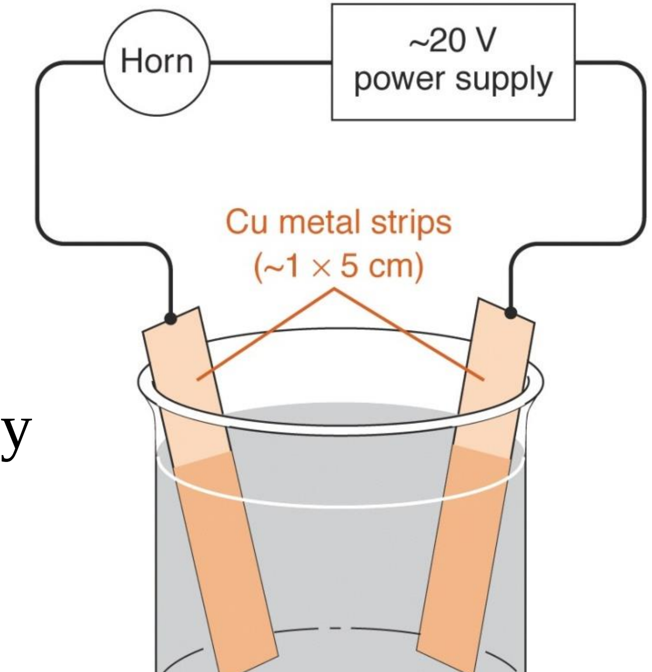
Chapter 9

Aqueous Solutions and Chemical Equilibria

9A-1 Classification of electrolytes

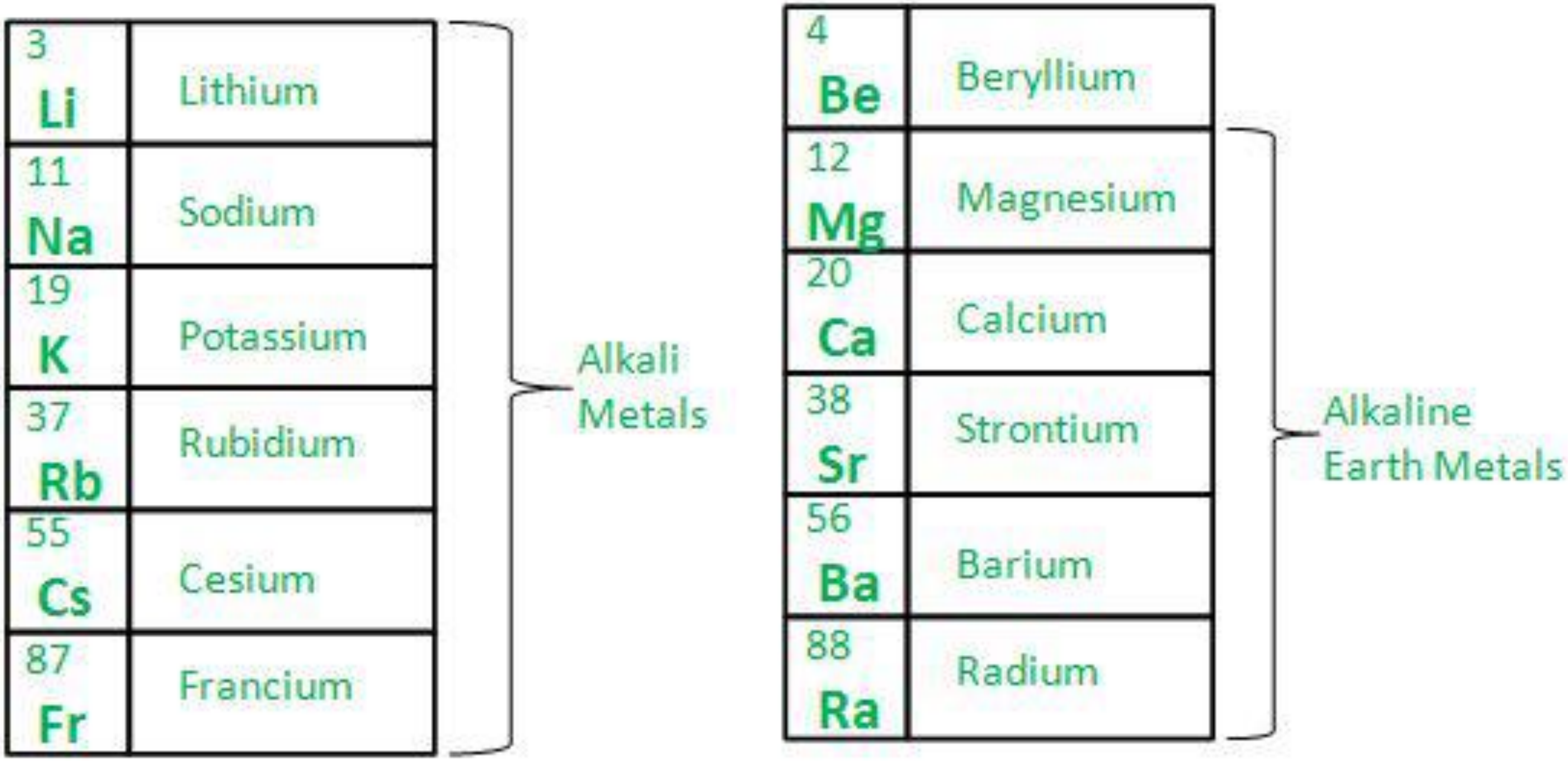
Electrolytes: Form ions when dissolved in water or other solvents and produce solutions that conduct electricity.

- **Strong Electrolytes:** Ionize essentially completely. Strong conductor of electricity.
- **Weak Electrolytes:** Ionize only partially. Poorer conductor than strong electrolyte.
- **Nonelectrolytes:** Are substances that dissolve in water but do not produce any ions and do not conduct an electric current.



Apparatus for demonstrating conductivity of electrolyte solutions.

Strong	Weak
1. Inorganic acids such as HNO_3, $HClO_4$, H_2SO_4, HCl, HI, HBr, $HClO_3$, $HBrO_3$	1. Many inorganic acids, including H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3 HF
2. Alkali and **some** alkaline-earth hydroxides	2. Most organic acids
3. Some salts (ex. NaCl, CH_3COONa) **(see solubility rules)**	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd



3 **Li**	Lithium
11 **Na**	Sodium
19 **K**	Potassium
37 **Rb**	Rubidium
55 **Cs**	Cesium
87 **Fr**	Francium

Alkali Metals

4 **Be**	Beryllium
12 **Mg**	Magnesium
20 **Ca**	Calcium
38 **Sr**	Strontium
56 **Ba**	Barium
88 **Ra**	Radium

Alkaline Earth Metals

Solubility Rules

Solubility Rules for Common Ionic Compounds In water at 250C

Soluble Compounds	Exceptions
Compounds containing alkali metal ions (Nli$^+$, Na$^+$, K$^+$ and NH_4^+)	
Acetate ($C_2H_3O_2^-$), and NO_3^-	
Cl^-, Br^-, I^-	Halides of Ag^+, Hg_2^{2+}, Pb^{2+}
SO_4^{2-}	Sulfates of **Ag**$^+$, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Pb^{2+}
Insoluble Compounds	**Exceptions**
CO_3^{2-}, PO_4^{3-}, CrO_4^{2-}, S^{2-}	Compounds containing alkali metal ions and NH_4^+
OH^-	Compounds containing alkali metal ions and Ca^{2+} , Sr^{2+} , Ba^{2+}

Memorize!

9A-2 Theory of acid and base

1) Arrhenius' definition

Acid = a substance that increases the concentration of H_3O^+

$$HA + H_2O = A^- + H_3O^+$$

Base = a substance that yields OH^- ion in aqueous solution

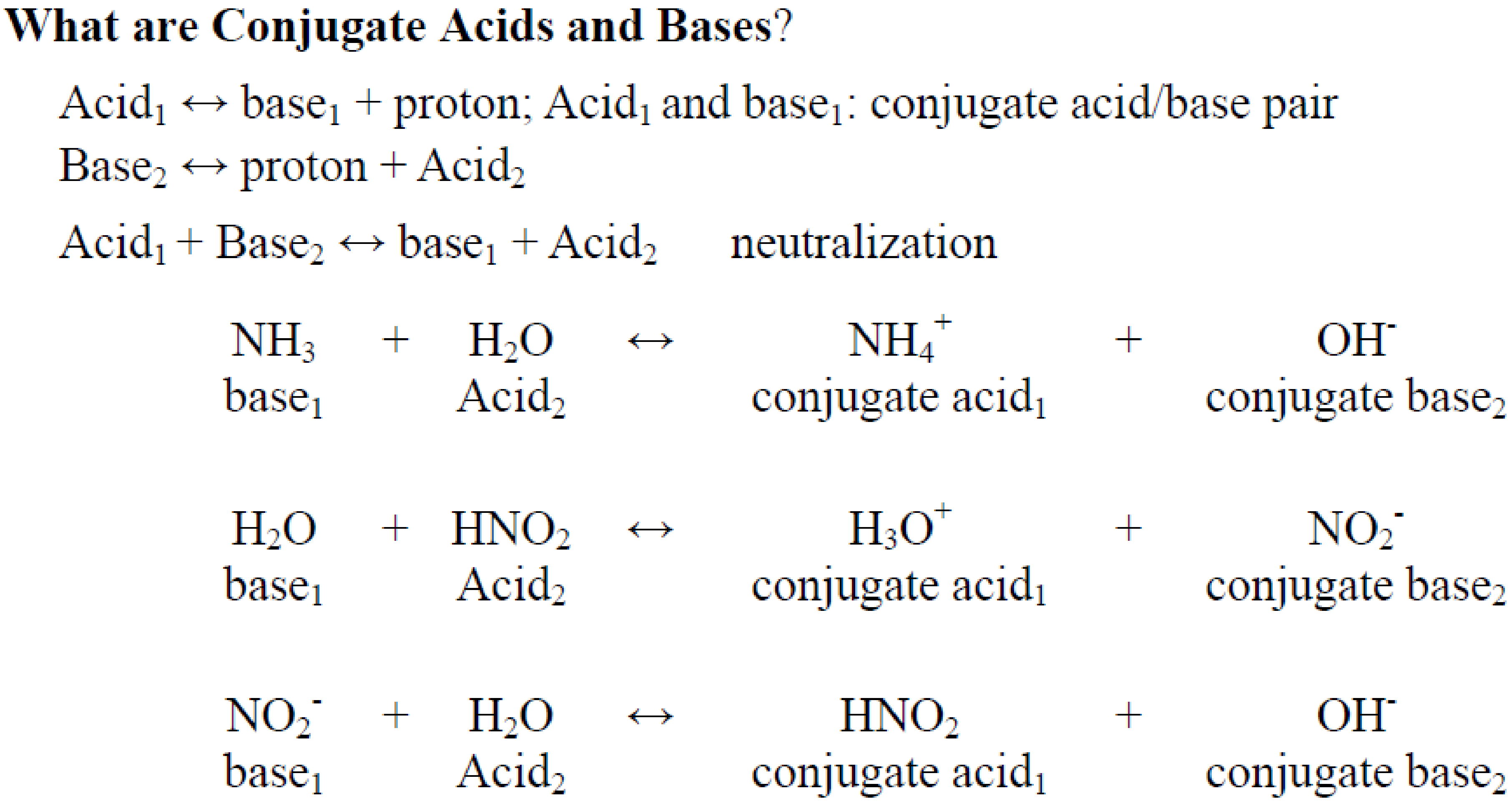
$$B + H_2O = BH^+ + OH^-$$

2) *Proton concept* (*Brönsted-Lowry definition*)

Acid = **proton donor** $A = B + H_3O^+$

Base = **proton acceptor** $B + H_3O^+ = BH^+ + OH^-$

- **A conjugate acid is the species formed when a base accepts a proton.**
- **A conjugate base is the species formed when acid donates proton.**
- When two processes are combined, the result is an acid/base or neutralization reaction.



What are Conjugate Acids and Bases?

$\text{Acid}_1 \leftrightarrow \text{base}_1 + \text{proton}$; Acid_1 and base_1: conjugate acid/base pair

$\text{Base}_2 \leftrightarrow \text{proton} + \text{Acid}_2$

$\text{Acid}_1 + \text{Base}_2 \leftrightarrow \text{base}_1 + \text{Acid}_2$ neutralization

$$\underset{\text{base}_1}{NH_3} + \underset{\text{Acid}_2}{H_2O} \leftrightarrow \underset{\text{conjugate acid}_1}{NH_4^+} + \underset{\text{conjugate base}_2}{OH^-}$$

$$\underset{\text{base}_1}{H_2O} + \underset{\text{Acid}_2}{HNO_2} \leftrightarrow \underset{\text{conjugate acid}_1}{H_3O^+} + \underset{\text{conjugate base}_2}{NO_2^-}$$

$$\underset{\text{base}_1}{NO_2^-} + \underset{\text{Acid}_2}{H_2O} \leftrightarrow \underset{\text{conjugate acid}_1}{HNO_2} + \underset{\text{conjugate base}_2}{OH^-}$$

9A-3 Amphiprotic Species

- Species that posses both **acidic and basic** properties are amphiprotic. Amphiprotic solvent (that can act either as an acid or as a base): Water, methanol, ethanol, and anhydrous acetic acid.

- **Amphiprotic Solvents:** A solvent that can act either as an acid or as a base depending on the solute. **Water** is the classic example.

NH_3	+	CH_3OH	↔	NH_4^+	+	CH_3O^-
base$_1$		Acid$_2$		conjugate acid$_1$		conjugate base$_2$
CH_3OH	+	HNO_2	↔	$CH_3OH_2^+$	+	NO_2^-
base$_1$		Acid$_2$		conjugate acid$_1$		conjugate base$_2$
$H_2PO_4^-$	+	H_3O^+	↔	H_3PO_4	+	H_2O
base$_1$		Acid$_2$		acid$_1$		base$_2$
$H_2PO_4^-$	+	OH^-	↔	HPO_4^{2-}	+	H_2O
acid$_1$		base$_2$		base$_1$		Acid$_2$

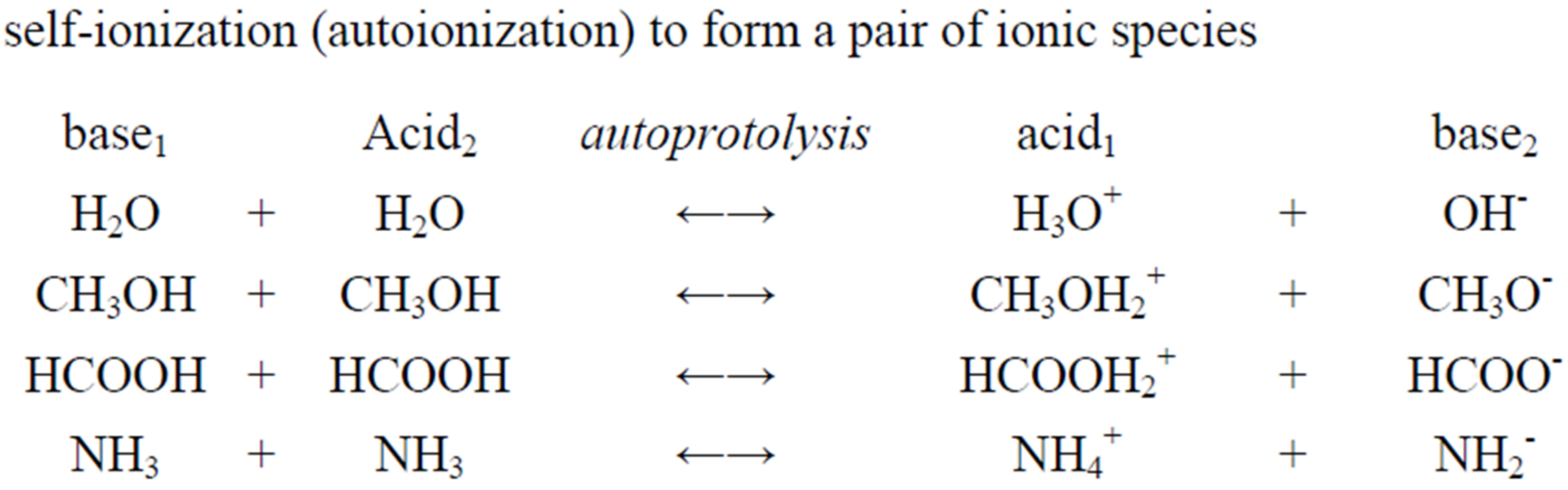
- Is Amphoteric and Amphiprotic the same?

Amphoteric substances are compounds that can act as both acids and bases depending on the medium. ... The main difference between amphiprotic and amphoteric is that **amphiprotic refers to the ability to donate or accept** protons whereas amphoteric refers to the ability to act as an acid or a base.

- **Zwitterions:** a species that bears both a positive and a negative charge.

$$\underset{\text{glycine}}{NH_2CH_2COOH} \leftrightarrow \underset{\text{zwitterion}}{NH_3^+CH_2COO^-}$$

- **Autoprotolysis:** Amphiprotic solvents undergo self ionization to form a pair of ionic species.



self-ionization (autoionization) to form a pair of ionic species

$base_1$		$Acid_2$	*autoprotolysis*	$acid_1$		$base_2$
H_2O	+	H_2O	$\longleftrightarrow$	H_3O^+	+	OH^-
CH_3OH	+	CH_3OH	$\longleftrightarrow$	$CH_3OH_2^+$	+	CH_3O^-
$HCOOH$	+	$HCOOH$	$\longleftrightarrow$	$HCOOH_2^+$	+	$HCOO^-$
NH_3	+	NH_3	$\longleftrightarrow$	NH_4^+	+	NH_2^-

9A-5 Strengths of acids and bases

- Acids and bases are commonly classified as **strong or weak**, depending on whether they react “**completely**” or only “**partly**” to produce H^+ or OH^-.

- ✓ **Strong acids and bases:** A strong acid or base is completely dissociated in aqueous solution (Strong Electrolyte).

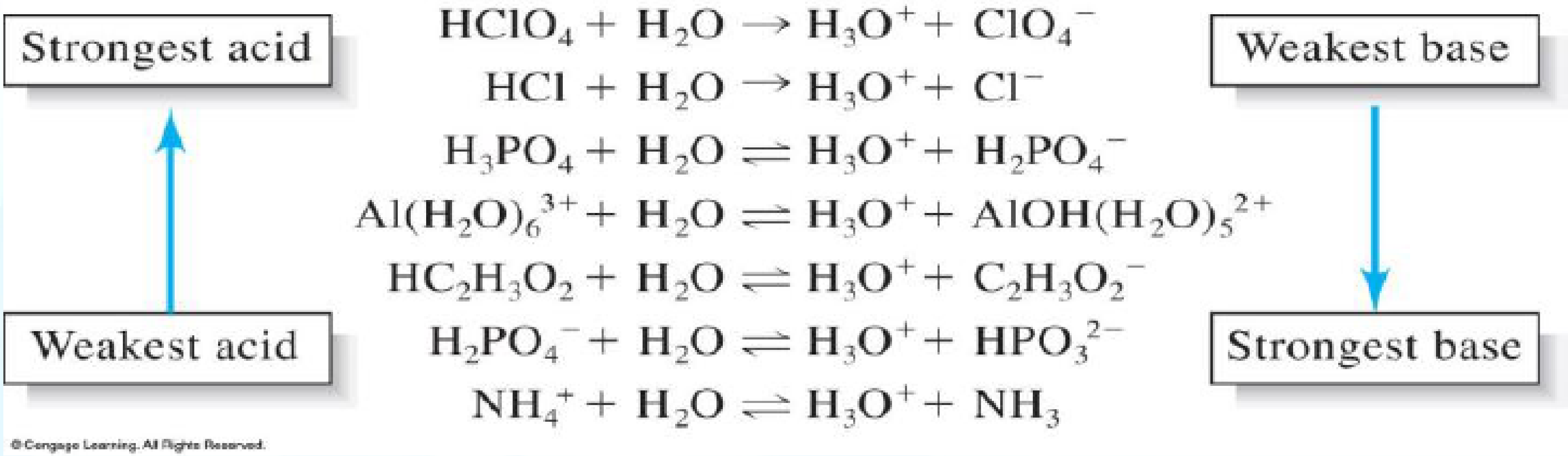
- ✓ **Weak acid or base:** Reacts incompletely with water to give solution that contain significant amounts of both the parent acid and its conjugate base.

Common strong acids and bases

HCl	Hydrochloric acid	LiOH	Lithium hydroxide
HBr	Hydrogen bromide	NaOH	Sodium hydroxide
HI	Hydrogen iodide	KOH	Potassium hydroxide
H_2SO_4	Sulfuric acid	RbOH	Rubidium hydroxide
HNO_3	Nitric acid	CsOH	Cesium hydroxide
$HClO_4$	Perchloric acid	$Ca(OH)_2$	Calcium hydroxide
$HBrO_4$	Perbromic acid	$Ba(OH)_2$	Barium hydroxide
$HClO_3$	Chloric acid	$Sr(OH)_2$	Strontium hydroxide
$HBrO_3$	Bromic acid		

9A-5 Strengths of Acids and Bases

Figure 9-2 Dissociation reactions and relative strengths of some common acids and their conjugate bases. **Relative Strength**



$$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$$

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

$$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$$

$$Al(H_2O)_6^{3+} + H_2O \rightleftharpoons H_3O^+ + AlOH(H_2O)_5^{2+}$$

$$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_3^{2-}$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

- The first two are *strong acids* because reaction with the solvent is sufficiently complete that no undissociated solute molecules are left in aqueous solution.
- The remainder are *weak acids*, which react incompletely with water to give solutions containing significant quantities of both the parent acid and its conjugate base.
- Note that acids can be cationic, anionic, or electrically neutral. The same holds for bases.

➢ The weakest acid forms the strongest conjugate base. The tendency of a solvent to accept or donate protons determine the strength of a solute acid or base dissolved in it. For example, perchloric and hydrochloric acids are strong acids in water

$$H_2O + HClO_4 \longrightarrow H_3O^+ + ClO_4^-$$

❖ If anhydrous acetic acid, a **weaker proton acceptor** than water, is substituted *as the solvent, neither of these acids undergoes complete dissociation.* Instead, equilibria such as the following are established:

$$\begin{array}{ccccccc} CH_3COOH & + & HClO_4 & \rightleftharpoons & CH_3COOH_2^+ & + & ClO_4 \\ \text{base}_1 & & \text{acid}_2 & & \text{acid}_1 & & \text{base}_2 \end{array}$$

❖ Perchloric acid is, however, about 5000 times stronger than hydrochloric acid in this solvent. Acetic acid thus acts as a **differentiating solvent toward the two acids by** revealing the inherent differences in their acidities.

✓ In a **differentiating solvent**, such as acetic acid, various acids dissociate to different degrees and have different strengths.

❖ Water, on the other hand, is a **leveling solvent** for perchloric, hydrochloric, and nitric acids because all three are **completely ionized in this solvent and show no differences in strength.**

9B Chemical equilibrium

- Many reactions never result in complete conversion of reactants to products. They proceed to a state of chemical equilibrium in which the ratio of concentrations of reactants and products is constant.
- Equilibrium-constant expressions are algebraic equations that describe the concentration relationships among reactants and products at equilibrium.

The Equilibrium State

- The final position of a chemical equilibrium is independent of the route to the equilibrium state.

✓ This relationship can be altered by applying stressors such as changes in temperature, in pressure, or in total concentration of a reactant or a product

✓ The **mass-action effect** is a shift in the position of an equilibrium caused by adding one of the reactants or products to a system.

- Equilibrium is a **dynamic process**; at equilibrium, the amounts of reactants and products are constant because the rates of the forward and reverse processes are exactly the same.

Equilibrium-Constant Expressions

- w moles of W react with x moles of X to form y moles of Y and z moles of Z. $wW + xX \leftrightarrow yY + zZ$

- The equilibrium-constant expression becomes

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

The square-bracketed terms are: [ ]

1. molar concentrations if they represent dissolved solutes.
2. partial pressures in atmospheres if they are gas-phase reactants or products. $[Z]_z$ is replaced with pz (partial pressure of Z in atmosphere).

- **No term for Z is included in the equation if this species is a pure solid , a pure liquid, or the solvent of a dilute solution.**

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

Equilibrium-Constant Expressions

- The constant K in is a temperature-dependent numerical quantity called the equilibrium constant.
- The concentrations of the products, as the equation is written, are always placed in the **numerator** and the concentrations of the reactants are always in the **denominator.**
- The exact equilibrium-constant expression takes the form:

$$K = \frac{a_Y^y a_Z^z}{a_W^w a_X^x}$$

- **where a_Y, a_Z, a_W, and a_X are the activities of species Y, Z, W, and X; therefore K is a unitless term**

The form of K and the equilibrium equation

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$\tfrac{1}{2}\ N_2O_4\ (g) \rightleftharpoons NO_2\ (g)$$

$$K' = \frac{[NO_2]}{[N_2O_4]^{1/2}} = 0.068$$

$$K' = K^{1/2}$$

TABLE 9-2

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	$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ $CH_3COO^- + H_2O \rightleftharpoons OH^- + CH_3COOH$	$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$ $K_b = \frac{[OH^-][CH_3COOH]}{[CH_3COO^-]}$
Formation of a complex ion	Formation constant, β_n	$Ni^{2+} + 4CN^- \rightleftharpoons Ni(CN)_4^{2-}$	$\beta_4 = \frac{[Ni(CN)_4^{2-}]}{[Ni^{2+}][CN^-]^4}$
Oxidation/reduction equilibrium	K_{redox}	$MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftharpoons Mn^{2+} + 5Fe^{3+} + 4H_2O$	$K_{redox} = \frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	K_d	$I_2(aq) \rightleftharpoons I_2(org)$	$K_d = \frac{[I_2]_{org}}{[I_2]_{aq}}$

9B-4 Applying the Ion-Product Constant for Water

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

$$2H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)} + OH^-_{(aq)}$$

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

❖ The concentration of water in dilute aqueous solutions is enormous, however, when compared with the concentration of hydronium and hydroxide ions. As a result, $[H_2O]^2$ can be considered as constant and we write

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

the ion-product constant for water

Negative logarithm of the equation gives;

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

By definition of p function, we have:

$$pK_w = pH + pOH$$

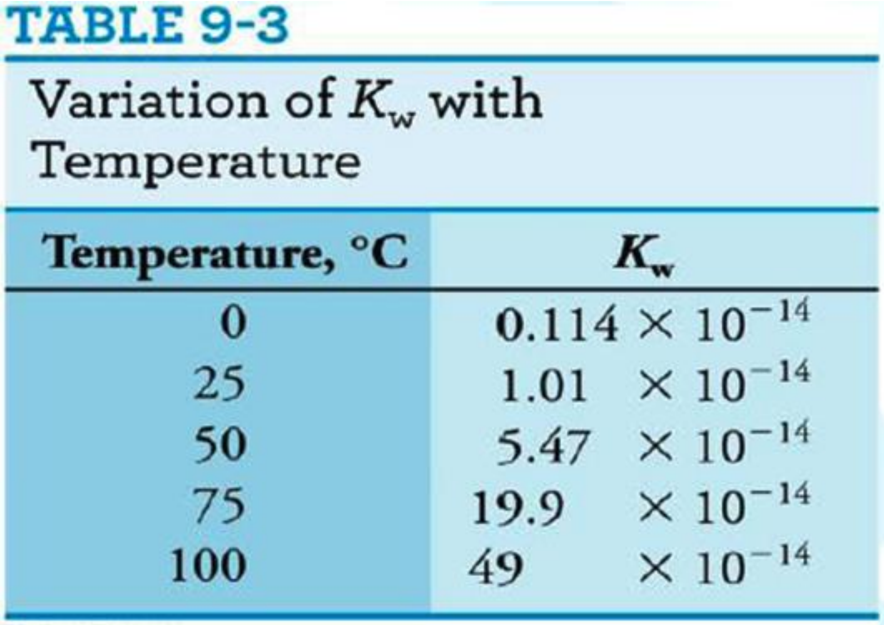


TABLE 9-3

Variation of K_w with Temperature

Temperature, °C	K_w
0	0.114×10^{-14}
25	1.01×10^{-14}
50	5.47×10^{-14}
75	19.9×10^{-14}
100	49×10^{-14}

Ex 9-1 Calculate the $[H_3O^+]$ and $[OH^-]$ of pure water at 25°C and 100°C.

Ans; 1×10^{-7}

Variation of K_w with Temperature

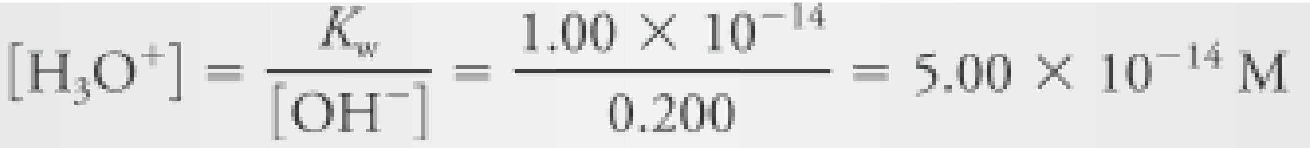
Temperature	K_w	pKw
0	0.114×10^{-14}	
25	1.01×10^{-14}	(14)
50	5.44×10^{-14}	
100	49×10^{-14}	

Example 9-2: Calculate the hydroxide ion, hydronium ion, pH and pOH for 0.200 M NaOH

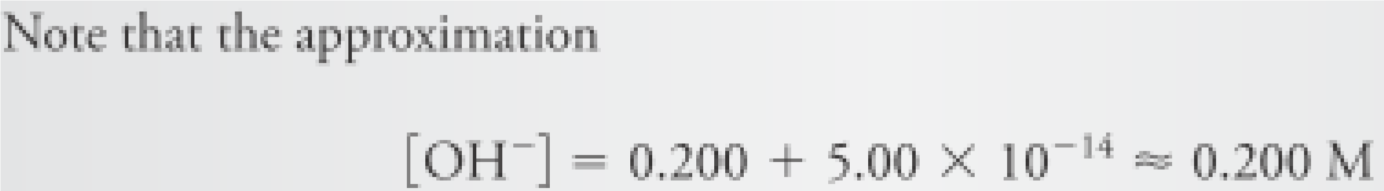
- Hydroxide ion has two sources; from NaOH and from water

$= 0.200 + [H^+] \approx 0.200$; pOH = 0.699

- **pH = 14 – pOH = 13.301;**
- **Hydronium ion;**



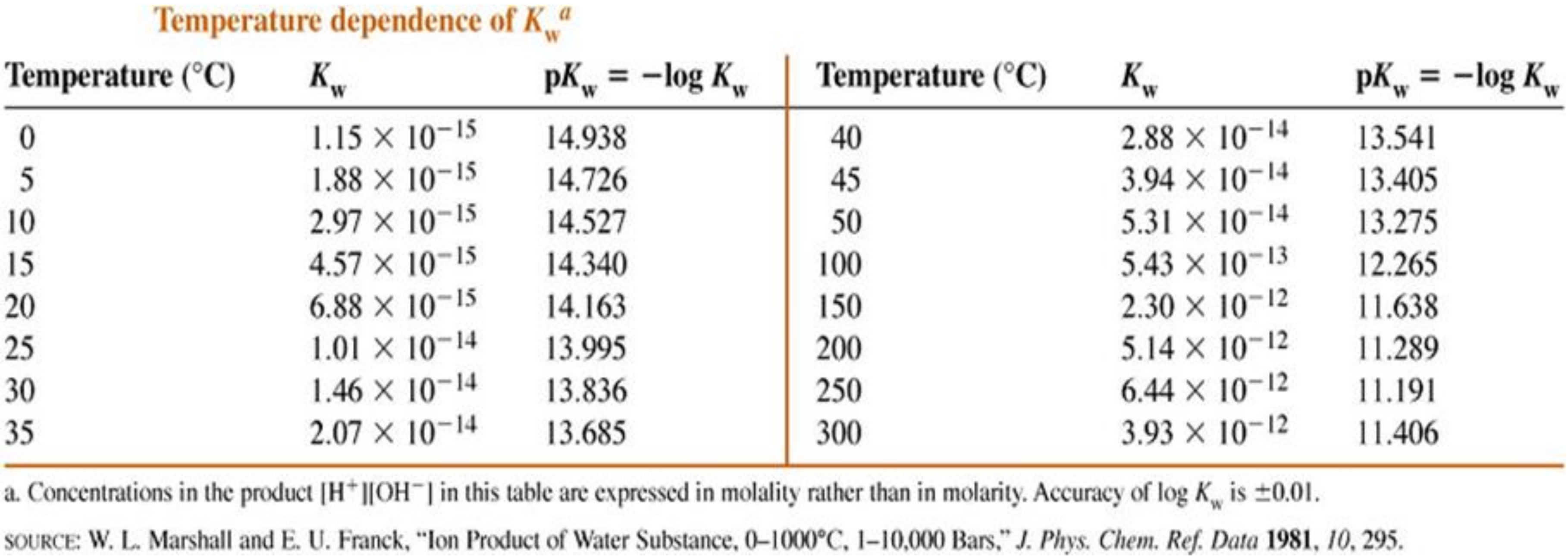
$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.200} = 5.00 \times 10^{-14}\ M$$



Note that the approximation

$$[OH^-] = 0.200 + 5.00 \times 10^{-14} \approx 0.200\ M$$

Temperature dependence of pH

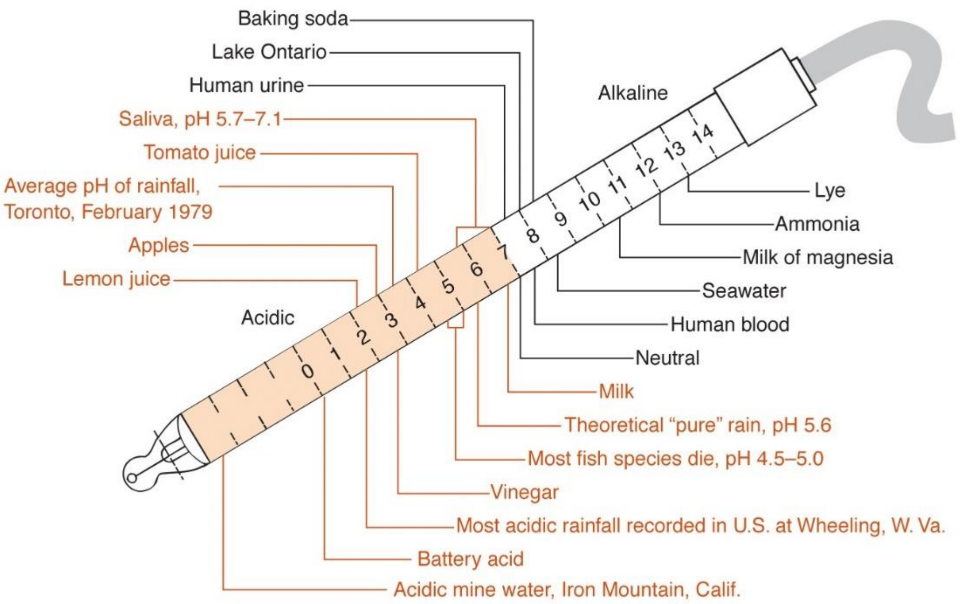


Temperature dependence of K_w [a]

Temperature (°C)	K_w	$pK_w = -\log K_w$	Temperature (°C)	K_w	$pK_w = -\log K_w$
0	1.15×10^{-15}	14.938	40	2.88×10^{-14}	13.541
5	1.88×10^{-15}	14.726	45	3.94×10^{-14}	13.405
10	2.97×10^{-15}	14.527	50	5.31×10^{-14}	13.275
15	4.57×10^{-15}	14.340	100	5.43×10^{-13}	12.265
20	6.88×10^{-15}	14.163	150	2.30×10^{-12}	11.638
25	1.01×10^{-14}	13.995	200	5.14×10^{-12}	11.289
30	1.46×10^{-14}	13.836	250	6.44×10^{-12}	11.191
35	2.07×10^{-14}	13.685	300	3.93×10^{-12}	11.406

a. Concentrations in the product $[H^+][OH^-]$ in this table are expressed in molality rather than in molarity. Accuracy of $\log K_w$ is ±0.01.

SOURCE: W. L. Marshall and E. U. Franck, "Ion Product of Water Substance, 0–1000°C, 1–10,000 Bars," *J. Phys. Chem. Ref. Data* **1981**, *10*, 295.



Using Solubility-Product Constants

- When an excess of barium iodate is equilibrated with water, the dissociation process is described as

$$Ba(IO_3)_2(s) \leftrightarrow Ba^{2+}(aq) + 2IO_3^-(aq)$$

$$K = \frac{[Ba^{2+}]\cdot[IO_3^-]^2}{[Ba(IO_3)_2(s)]}$$

- Some solid $Ba(IO_3)_2$ is in contact with the saturated solution. The concentration of a compound in its solid state is, however, constant. In other words, the number of moles of $Ba(IO_3)_2$ divided by the *volume of the solid* $Ba(IO_3)_2$ *is constant* no matter how much excess solid is present. Therefore, the previous equation can be rewritten in the form

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

- **Solubility-Product Constants**

- The equation shows that the position of this equilibrium is independent of the amount of $Ba(IO_3)_2$ as long as some solid is present.

Ex 9.3 What Mass In Grams Can Be Dissolved Of Barium Iodate ($Ba(IO_3)_2$ (487 g/mol) in 500 Ml Of Distilled Deionized Water?

Ksp= 1.57×10^{-9}

$$Ba(IO_3)_2(s) \leftrightarrow Ba^{2+}(aq) + 2IO_3^-(aq)$$

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9}$$

Ans; 7.32×10^{-4} M;
3.66×10^{-4} /500ml;
Then mass/500ml = 0.178 g

The Effect of a Common Ion on the Solubility of a Precipitate

- The **common-ion effect** is a mass-action effect predicted from Le Châtelier's principle and is demonstrated by the following examples.

Ex 9-4: Calculate the molar solubility of $Ba(IO_3)_2$ in a 0.00200 M $Ba(NO_3)_2$; **Ksp= 1.57 x 10^{-9}**

$$Ba(IO_3)_2(s) \leftrightarrow Ba^{2+}(aq) + 2IO_3^-(aq)$$

$$K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9}$$

Ans; 4.4 x 10^{-4} M; comparing this solubility with the solubility of water in Ex 9-3 (7.32 x 10^{-4} M); the presence of common ion decreased the solubility by a factor of 5.

- The solubility of an ionic precipitate decreases when a soluble compound containing one of the ions of the precipitate is added to the solution. This behavior is called the **common-ion effect**.

The Effect of a Common Ion on the Solubility of a Precipitate

Calculate the solubility of $Ba(IO_3)_2$ in a solution prepared by mixing 200 mL of 0.0100 M $Ba(NO_3)_2$ with 100 mL of 0.100 M $NaIO_3$

- Check whether either reactant is present in excess at equilibrium

$$\mathbf{Ba}(NO_3)_{2(aq)} + 2Na\mathbf{IO_3}_{(aq)} \rightarrow 2NaNO_{3(aq)} + \mathbf{Ba(IO_3)_{2\,(s)}}$$

- Mole Ba= 2.00×10^{-3}; Mole IO_3= 10×10^{-3}

- If the formation of **$Ba(IO_3)_{2\,(s)}$** is complete then excess **IO_3^-** is

= $10 \times 10^{-3} - 2(2.00 \times 10^{-3}) = 6.00 \times 10^{-3}$ **mole**

$[IO_3^-]$ After mixing = 6.00×10^{-3} **mole/0.3L = 0.02M**

$$Ba(IO_3)_2(s) \leftrightarrow Ba^{2+}(aq) + 2IO_3^-(aq) \qquad K_{sp} = [Ba^{2+}][IO_3^-]^2 = 1.57 \times 10^{-9}$$

Ans; 3.93×10^{-6} M;

- A 0.02 M excess of Ba^{+2} (Ex9-4) decreases the solubility of $Ba(IO_3)_2$ by a factor of about 5; **this same excess of IO_3^- lowers the solubility by a factor of about 200**.

Q: Calculate solubility of $Ca_3(PO_4)_2$ (310 g/mole) in

a) pure water 1.08×10^{-23}? **Ans**: 3,1 x 10^{-3} g/L

b) In 0.1 $CaCl_2$; $K_{sp} = 1.08\times10^{-23}$

What is the solubility of $PbCl_2$ in grams per 100.0 mL at 25 ° C? $\boldsymbol{K_{sp} = 1.7 \times 10^{-5}}$, $PbCl_2$ MM = 278.11 g/mol

A. 0.56 g

B. 0.72 g

C. 0.45 g

D. 0.39 g

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = 1.7 \times 10^{-5} = [Pb^{2+}][Cl^-]^2 = x(2x)^2$$

$$x = 1.62 \times 10^{-2}\ M$$

$$\frac{1.62 \times 10^{-2}\ \text{mol } PbCl_2}{1\ \text{L}} \times \frac{278.11\ \text{g } PbCl_2}{\text{mol } PbCl_2} \times \frac{0.1\ \text{L}}{100\ \text{mL}} = 0.45\ \text{g } PbCl_2/100\ \text{mL}$$

What is the solubility (M) of $Ba(IO_3)_2$ at 25 ° C?

$K_{sp} = 1.5 \times 10^{-9}$

A.1.4 × 10^{-3} M

B.9.1 × 10^{-4} M

C.7.2 × 10^{-4} M

D.3.9 × 10^{-5} M

Example: What is the molar solubility of calcium oxalate in 0.15 *M* calcium chloride? Compare this molar solubility with that found for CaC_2O_4 in pure water (4.8×10^{-5} *M*). The solubility product constant for calcium oxalate is 2.3×10^{-9}.

Conc. (M)	***Ca^{2+}(aq)***	***$C_2O_4^{\,2-}$(aq)***
Initial	**0.15**	0
Change	$+\,x$	$+\,x$
Equilibrium	$0.15 + x$	x

$$\left[Ca^{2+}\right]\left[C_2O_4^{2-}\right] = K_{sp} \qquad \left(0.15+x\right)x = 2.3\times10^{-9}$$

$$x = \frac{2.3\times10^{-9}}{0.15+x}$$

Assumption

$$x \approx \frac{2.3\times10^{-9}}{0.15} = 1.5\times10^{-8}$$

- ❖ Therefore, the molar solubility of calcium oxalate is 0.15 M $CaCl_2$ is **1.5×10^{-8} *M***.

- ❖ In pure water, the molar solubility is **4.8×10^{-5} *M***, which is over **3000 times greater**.

The molar solubility of PbF_2 in 0.10 M $Pb(NO_3)_2$ solution is 2.85×10^{-4} M. What is K_{sp} for PbF_2?

A. 1.2×10^{-6} B. 3.1×10^{-7} C. 9.6×10^{-13} **D. 3.2×10^{-8}**

$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$

$[Pb^{2+}] = 0.10$ M $[F^-] = 2(2.85 \times 10^{-4})$ M

$K_{sp} = [Pb^{2+}][F^-]^2 = (0.1)(5.7 \times 10^{-4})^2$

$K_{sp} = 3.2 \times 10^{-8}$

What is the molar solubility of PbI_2 in pure water? $K_{sp} = 9.8 \times 10^{-9}$

A. 2.1×10^{-3} B. 1.7×10^{-3} C. 4.9×10^{-5} **D. 1.3×10^{-3}**

What is the molar solubility of PbI_2 in 0.20 M $Pb(NO_3)$ solution? $K_{sp} = 9.8 \times 10^{-9}$

A. 4.9×10^{-8} B. 3.7×10^{-3} **C. 1.1×10^{-4}** D. 2.2×10^{-4}

$PbI_2(s\ ) \rightleftharpoons Pb^{2+} + 2I^-$ $[Pb^{2+}] = 0.20$ M

$K_{sp} = 9.8 \times 10^{-9} = [Pb^{2+}][2x]^2 = (0.20)\ [2x]^2$

Exercise 17.5 a. Calculate the molar solubility of barium fluoride, BaF_2, in water at 25°C. The solubility product constant for BaF_2 at this temperature is 1.0×10^{-6}.

b. What is the molar solubility of barium fluoride in 0.15 *M* NaF at 25°C? Compare the solubility in this case with that of BaF_2 in pure water.

Ans: ***a. 6.3×10^{-3} M***

b. 4.4×10^{-5} M

Note: The solubility of calcium sulfate ($CaSO_{4,}$; Mwt= 163.2g/mole) is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate

The solubility product for $CaSO_4$ is

$$K_{sp} = [Ca^{2+}][SO_4^{2-}] = s^2$$

$[Ca^{2+}] = 4.9 \times 10^{-3}$ M and $[SO_4^{2-}] = 4.9 \times 10^{-3}$ M

$$\frac{0.67 \text{ g } CaSO_4}{1 \text{ L soln}} \times \frac{1 \text{ mol } CaSO_4}{136.2 \text{ g } CaSO_4} = 4.9 \times 10^{-3} \text{ mol/L} = s$$

Now we can calculate K_{sp}:

$$K_{sp} = [Ca^{2+}]][SO_4^{2-}]$$

$$= (4.9 \times 10^{-3})(4.9 \times 10^{-3})$$

$$= \mathbf{2.4 \times 10^{-5}}$$

Note: Calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$, in g/L. Ksp $Cu(OH)_2$= 2.2×10^{-20}

$$2.2 \times 10^{-20} = 4s^3$$

$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

$$s = 1.8 \times 10^{-7} \; M$$

9B-6 Using Acid/Base Dissociation Constants

When a weak acid or a weak base is dissolved in water, partial dissociation occurs.

$$HNO_2 + H_2O \leftrightarrow H_3O^+ + NO_2^-$$

K_a is the acid dissociation constant for nitrous acid.

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

$$NH_3 + H_2O \leftrightarrow NH_4 + OH^-$$

In an analogous way, the

base dissociation constant (K_b) for ammonia is:

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

$[H_2O]$ does not appear in the denominator because the concentration of water is very large relative to the concentration of the weak acid or base that the dissociation does not alter $[H_2O]$ appreciably.

9B-6 Applying Acid and base Dissociation Constants

Dissociation constants for conjugated acid/base pairs

$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^-$ $K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$	$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+$ $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$	$K_a K_b = K_w$

Ex 9-6: What is Kb for the equilibrium CN^- + H2O $\Leftrightarrow$ HCN + OH^-
If Ka for HCN= 6.2×10^{-10}

$$\text{HCN: } K_a = 6.2 \times 10^{-10}; \quad K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.61 \times 10^{-5}$$

$[H_3O^+]$ in a weak acid solution

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

From:

$C_{HA} = [H_3O^+] + [HA]$

$[HA] = C_{HA} - [H_3O^+]$

$$K_a = \frac{[H_3O^+]^2}{C_{HA} - [H_3O^+]}$$

$$[H_3O^+]^2 + Ka[H_3O^+] - KaC_{HA} = 0$$

$$[H_3O^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_aC_{HA}}}{2}$$

Assumption if $[H_3O^+] << C_{HA}$ then: $K_a = \dfrac{[H_3O^+]^2}{C_{HA}}$

$$[H_3O^+] = \sqrt{K_aC_{HA}}$$

Assumption depends on C_{HA}/K_a ; if $C_{HA}/K_a > 100$ then assumption is valid

Table 9-4 shows that the error introduced by the assumption that $[H_3O^+] << c_{HA}$ increases as the molar concentration of acid becomes smaller and its dissociation constant becomes larger. Note that the error introduced by the assumption is about 0.5% when the ratio c_{HA}/K_a is 10^4. The error increases to about 1.6% when the ratio is 10^3, to about 5% when it is 10^2, and to about 17% when it is 10.

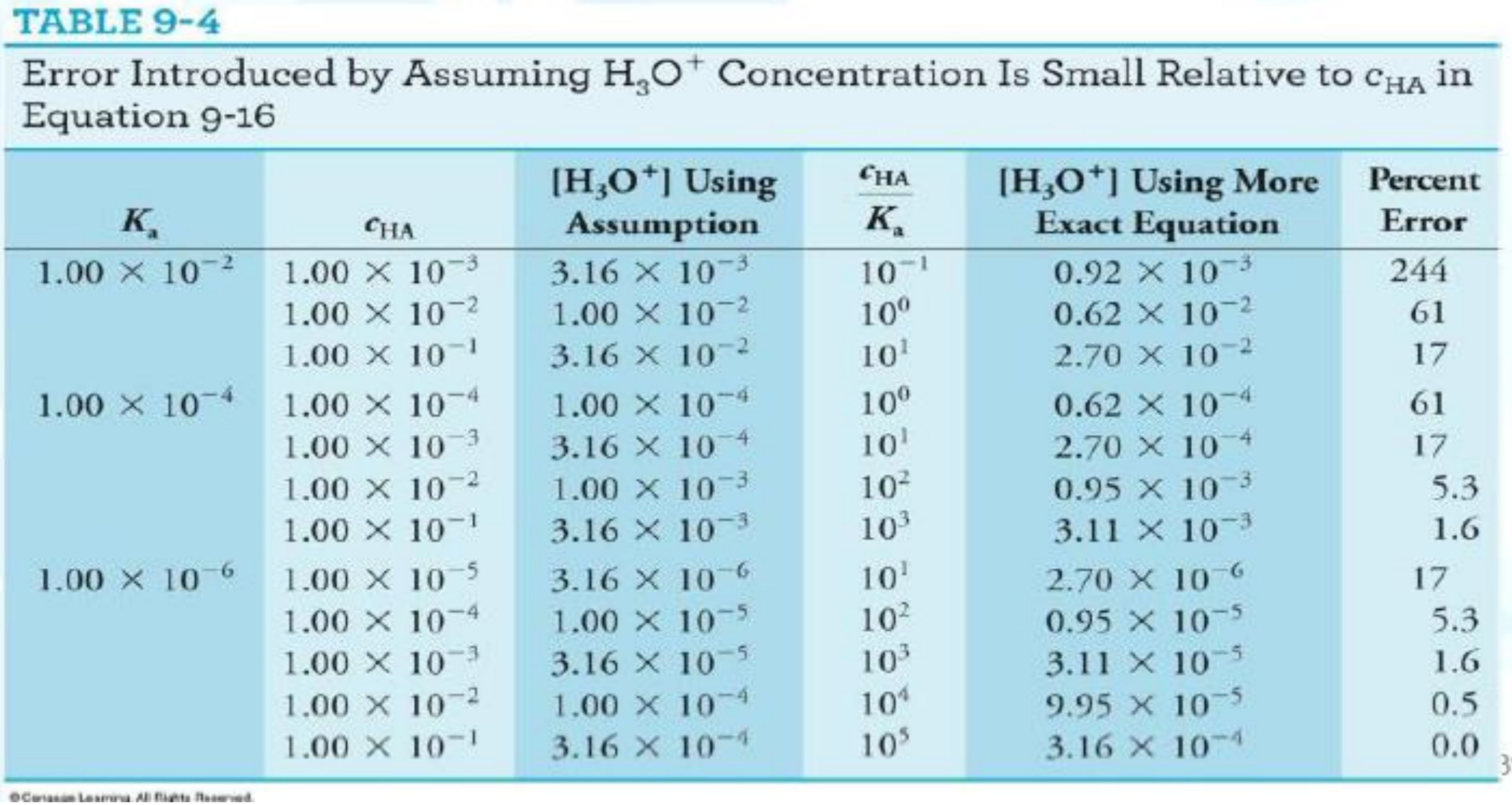


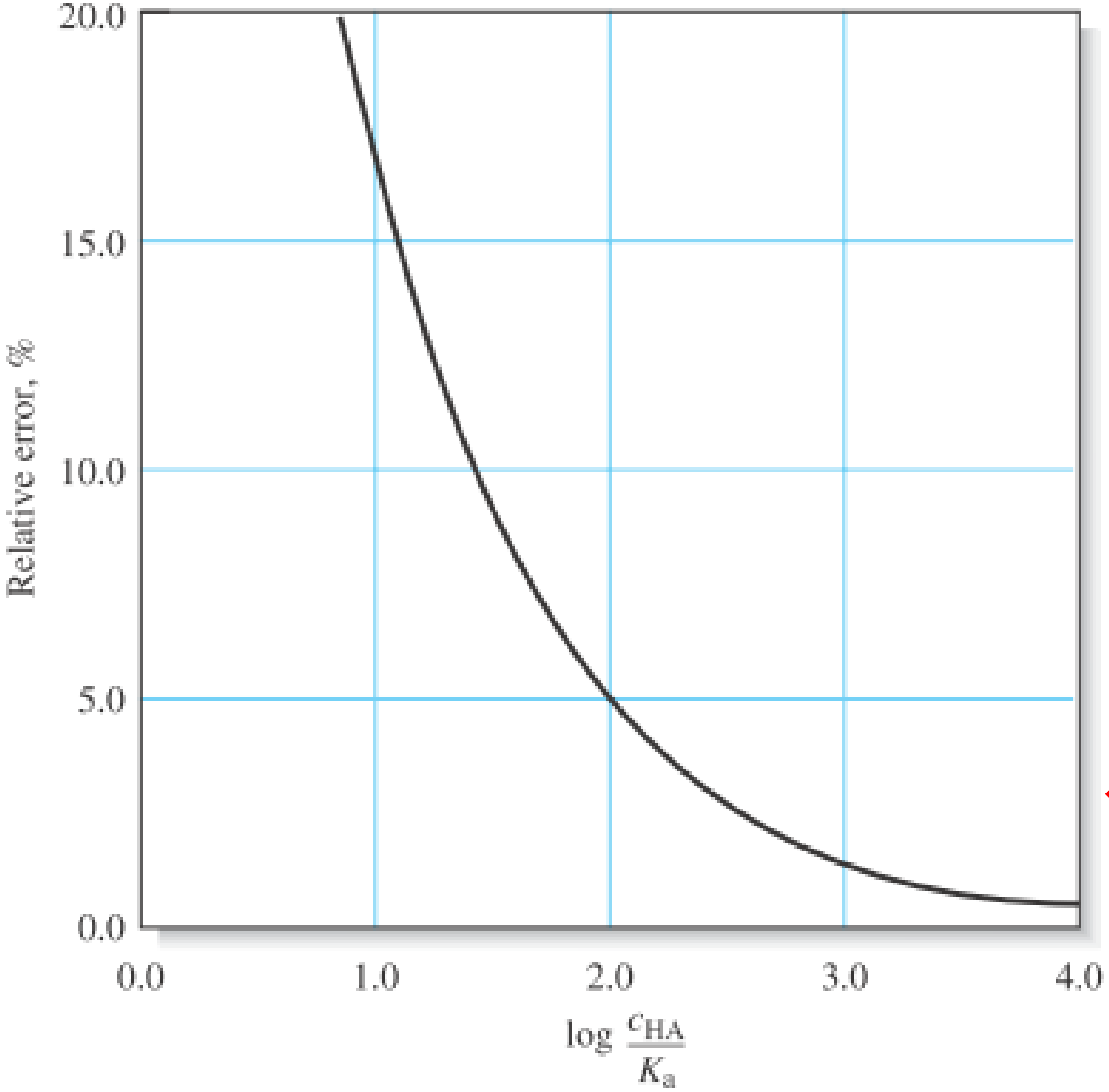
TABLE 9-4

Error Introduced by Assuming H_3O^+ Concentration Is Small Relative to c_{HA} in Equation 9-16

K_a	c_{HA}	$[H_3O^+]$ Using Assumption	$\frac{c_{HA}}{K_a}$	$[H_3O^+]$ Using More Exact Equation	Percent Error
1.00×10^{-2}	1.00×10^{-3}	3.16×10^{-3}	10^{-1}	0.92×10^{-3}	244
	1.00×10^{-2}	1.00×10^{-2}	10^{0}	0.62×10^{-2}	61
	1.00×10^{-1}	3.16×10^{-2}	10^{1}	2.70×10^{-2}	17
1.00×10^{-4}	1.00×10^{-4}	1.00×10^{-4}	10^{0}	0.62×10^{-4}	61
	1.00×10^{-3}	3.16×10^{-4}	10^{1}	2.70×10^{-4}	17
	1.00×10^{-2}	1.00×10^{-3}	10^{2}	0.95×10^{-3}	5.3
	1.00×10^{-1}	3.16×10^{-3}	10^{3}	3.11×10^{-3}	1.6
1.00×10^{-6}	1.00×10^{-5}	3.16×10^{-6}	10^{1}	2.70×10^{-6}	17
	1.00×10^{-4}	1.00×10^{-5}	10^{2}	0.95×10^{-5}	5.3
	1.00×10^{-3}	3.16×10^{-5}	10^{3}	3.11×10^{-5}	1.6
	1.00×10^{-2}	1.00×10^{-4}	10^{4}	9.95×10^{-5}	0.5
	1.00×10^{-1}	3.16×10^{-4}	10^{5}	3.16×10^{-4}	0.0

- **Assumption depends on C_{HA}/K_a; as this ratio is larger the error is smaller**

Figure 9-3 Relative error resulting from the assumption that **$[H_3O^+] << C_{HA}$**



❖ Remember that
when **C_{HA}** /Ka = 100
then log **C_{HA}** /Ka = 2.0

What is the $[H_3O^+]$ **in a 0.120 M** nitrous acid **solution?** (Ka=7.1×10^{-4})

- Assumption: C_{HA} /Ka = 0.12/ 7.1 x 10^{-4} = 169.0 >100; error is accepted

$$[H_3O^+] = \sqrt{K_a C_{HA}}$$

Answer: 9.2 x 10^{-3}

Calculate the pH of a 2.0 x 10^{-4} M solution of aniline hydrochoride, $C_6H_5NH_3^+$.

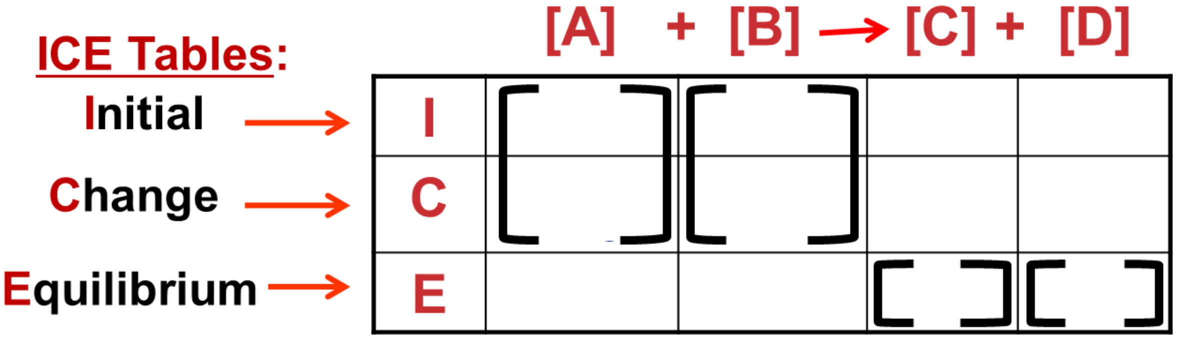
$$C_6H_5NH_3^+ + H_2O \Leftrightarrow C_6H_5NH_2 + H_3O^+ \qquad K_a = 2.51\times10^{-5}$$

Assumption: C_{HA} /Ka = 2.0 x 10^{-4}/ 2.51 x 10^{-5} = 8

- very low (from figure 9-3; error about 20%) we have to go to the **quadratic equation and discriminator**

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$C_6H_5NH_3^+ + H_2O \Leftrightarrow C_6H_5NH_2 + H_3O^+$$



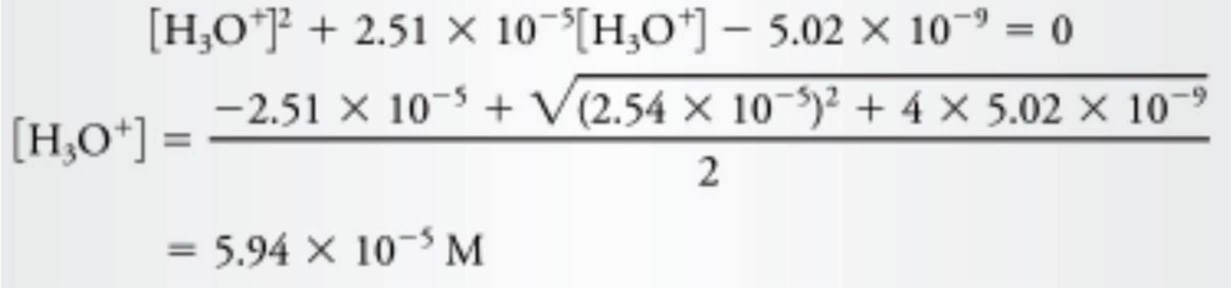
$$[A] + [B] \rightarrow [C] + [D]$$

ICE Tables:

Initial → I

Change → C

Equilibrium → E



$$[H_3O^+]^2 + 2.51 \times 10^{-5}[H_3O^+] - 5.02 \times 10^{-9} = 0$$

$$[H_3O^+] = \frac{-2.51 \times 10^{-5} + \sqrt{(2.54 \times 10^{-5})^2 + 4 \times 5.02 \times 10^{-9}}}{2}$$

$$= 5.94 \times 10^{-5}\ M$$

Answer:

$[H_3O^+] = 5.94 \times 10^{-5}$

$[H_3O^+]$ in a weak acid solution

$$NH_3 + H_2O \Leftrightarrow NH_4^+ + OH^- \; ; \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \; ; \quad Kw = [H_3O^+][OH^-]$$

$$\boxed{[OH^-] = \sqrt{K_b C_B}}$$

Calculate The OH^- Concentration and pH pf a 0.075 M NH_3 Solution. K_a $NH4^+$= 5.70 x 10^{-10}

Answer: kb= 1.75 x10^{-5}; Assumption is valid; $[OH^-]$ =4.65 x 10^{-6} ; $[H_3O^+]$ =2.15 x 10^{-9}

Ex 9-10: Calculate the hydroxide ion concentration in 0.0100M Sodium Hypochlorite solution NaOCl? K_a $HOCl^-$ = 3 x 10^{-8};

$$OCl^- + H_2O \rightleftharpoons HOCl + OH^-$$

Answer: kb= 3.33 x10^{-7}; Assumption is valid

$[OH^-]$ =5.8 x 10^{-5} ; $[H_3O^+]$ =1.73 x 10^{-10}

9C Buffer solutions

- A buffer solution resists changes in pH when it is diluted or when acids or bases are added to it.
- Buffer solutions are prepared from a conjugate acid/base pair, such as acetic acid/sodium acetate or ammonium chloride/ammonia.
- Buffers are used in chemical applications whenever it is important to maintain the pH of a solution at a constant and predetermined level.

9C-1 Calculating the pH of Buffer Solutions

A solution containing a weak acid, HA, and its conjugate base, A^-, may be acidic, neutral, or basic, depending on the positions of two competitive equilibria:

$$HA + H_2O \leftrightarrow H_3O^+ + A^- \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$A^- + H_2O \leftrightarrow OH^- + HA \qquad K_b = \frac{[OH^-][HA]}{[A^-]} = \frac{K_w}{K_a}$$

If the first equilibrium lies farther to the right than the second, the solution is acidic. If the second equilibrium is more favorable, the solution is basic.

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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

$$K_b = \frac{K_w}{K_a} = \frac{[OH^-][HA]}{[A^-]}$$

$$[HA] = C_{HA} - [H_3O^+] + [OH^-],\ [HA] \approx C_{HA}$$

$$[A^-] = C_{NaA} + [H_3O^+] - [OH^-],\ [A^-] \approx C_{NaA}$$

When Assumption is valid then; $$[H_3O^+] = K_a \frac{C_{HA}}{C_{NaA}}$$

And; $$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

Henderson-Hasselbalch equation

What is the pH of a solution that is 0.400 M in formic acid (HCOOH) and 1.00 M in sodium formate? Ka = 1.80×10^{-4}

Answer: pH = 4.14

Ex. 9-12 **Calculate the pH of a solution that is 0.200 M in NH_3 and 0.300 M in NH_4Cl.**

$$NH_4^+ + H_2O \Leftrightarrow NH_3 + H_3O^+ \qquad K_a = 5.70 \times 10^{-10}$$

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

Answer: pH = 9.07

Blood plasma has a pH of 7.40. If we assume that the buffer system is HCO_3^-/H_2CO_3 what ratios of base and acid must it have. **Ka = 4.2 x 10^{-7}**

A. 1.02

B. **10.05**

C. 6.38

D. Not enough information

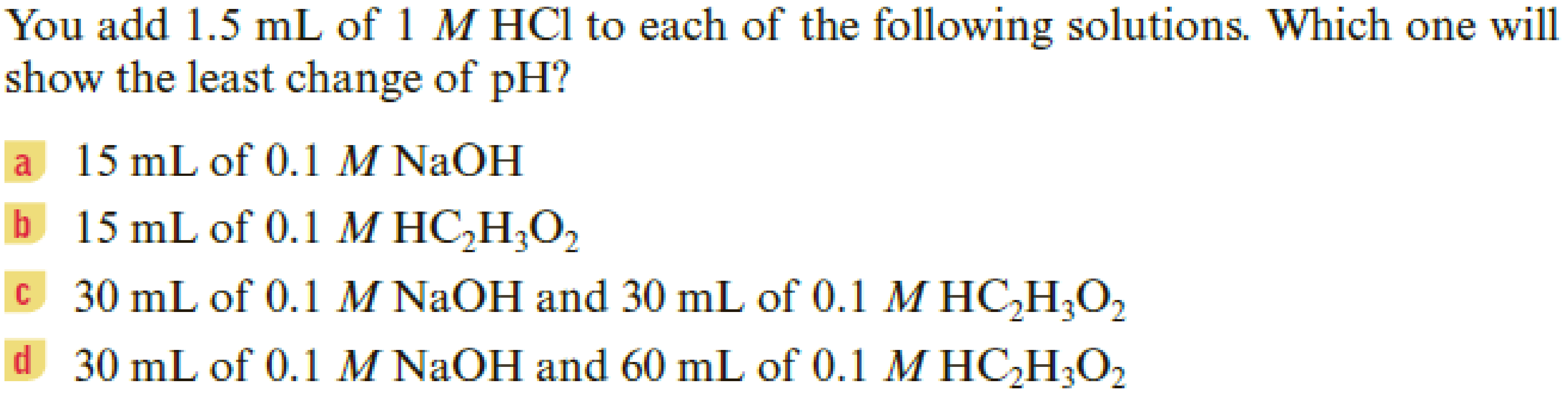
$K_a = 4.2 \text{ x } 10^{-7}$

$pK_a = -\log(4.2 \text{ x } 10^{-7}) = 6.38$

$$pH = 6.38 + \log\frac{\left[HCO_3^-\right]}{\left[H_2CO_3\right]}$$

$$7.40 = 6.38 + \log\frac{\left[HCO_3^-\right]}{\left[H_2CO_3\right]}$$

$$\log\frac{\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = 1.02 \qquad \frac{\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = 10^{1.02} = 1.05x10^{1}$$



You add 1.5 mL of 1 *M* HCl to each of the following solutions. Which one will show the least change of pH?

a 15 mL of 0.1 *M* NaOH

b 15 mL of 0.1 *M* $HC_2H_3O_2$

c 30 mL of 0.1 *M* NaOH and 30 mL of 0.1 *M* $HC_2H_3O_2$

d 30 mL of 0.1 *M* NaOH and 60 mL of 0.1 *M* $HC_2H_3O_2$

The amount of any substance in a solution is proportional to the volume times molarity. Let's look at each solution

a. The 1.5 mL of 1 M HCl just neutralizes 15 mL of 0.1 M NaOH, giving a solution of NaCl. Thus, the pH of the original solution changes from very basic to neutral (pH = 7) after the addition of HCl.

b. The solution of acetic acid changes from weakly acidic to strongly acidic with the addition of HCl.

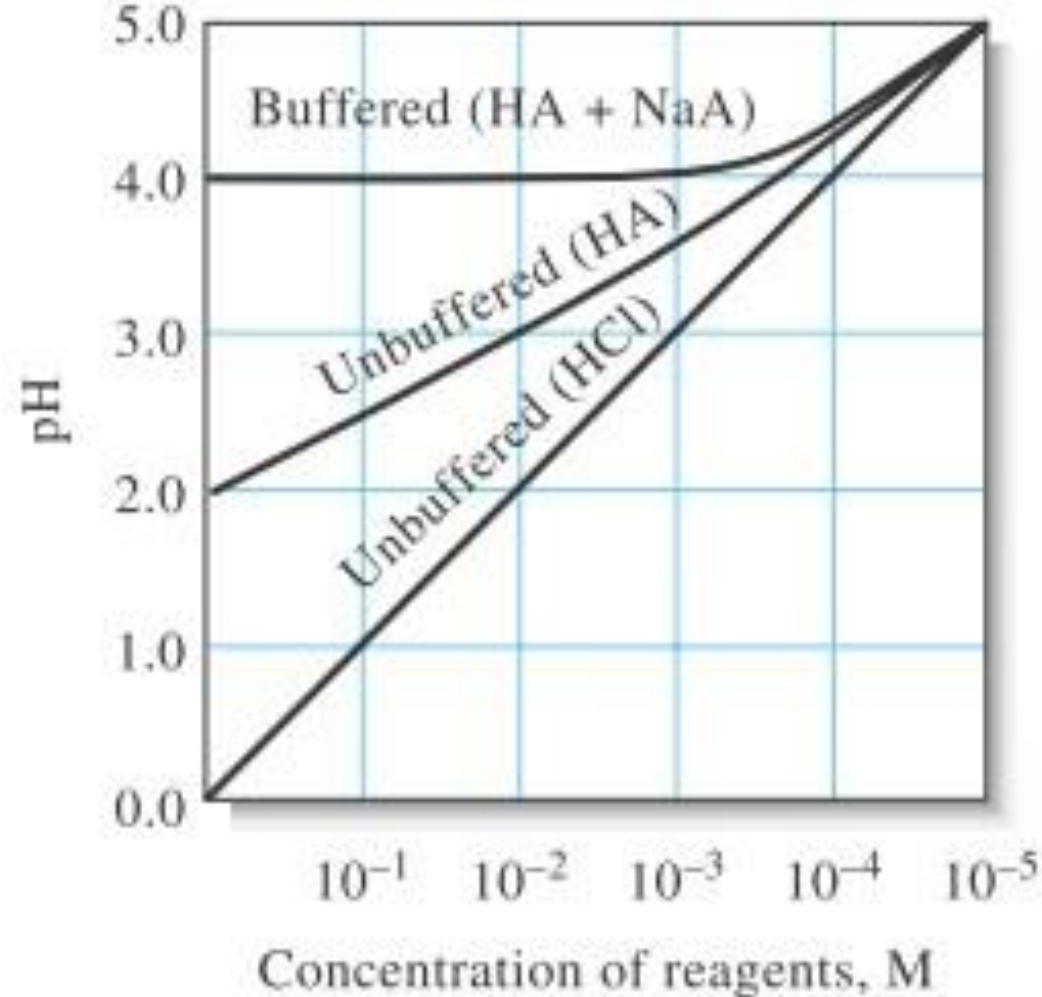
c. Equal amounts of NaOH and $HC_2H_3O_2$ in the original solution exactly neutralize each other to produce the salt $NaC_2H_3O_2$, which is slightly basic. The addition of the strong acid HCl gives an acidic solution.

d. The 30 mL of NaOH reacts with 30 mL of $HC_2H_3O_2$ to give the salt $NaC_2H_3O_2$, leaving an equal amount of the corresponding acid, $HC_2H_3O_2$. The result is a buffer solution. The addition of HCl to the buffer does not change the pH appreciably. (This is true as long as the amount of added acid does not overwhelm the capacity of the buffer. In this case, it does not. The amount of acid and base conjugates in the buffer is twice the amount of added acid.)

Only d does not change appreciably in pH.

Properties of Buffer Solutions

Figure 9-4 The effects of dilution on the pH of a strong acid, weak acid (unbuffered solution) and a weak acidic buffer



- ❖ The pH of a strong acid and weak acid in unbuffered solutions increase with dilution while
- ❖ in the buffer the pH remains constant unless the concentrations are very low

- ➢ The pH of the buffered solution remains constant until the concentrations of the species it contains are decreased to the point where approximation is not valid (the concentration of the buffer is not large enough relative to Ka value < 100)

❖ The Effect of Added Acids and Bases

Buffers do not maintain pH at an absolutely constant value, but changes in pH are relatively small when small amounts of acid or base are added.

In addition of strong acid or base to the buffer; we have two cases

1) When strong acid is added to the buffer **then**

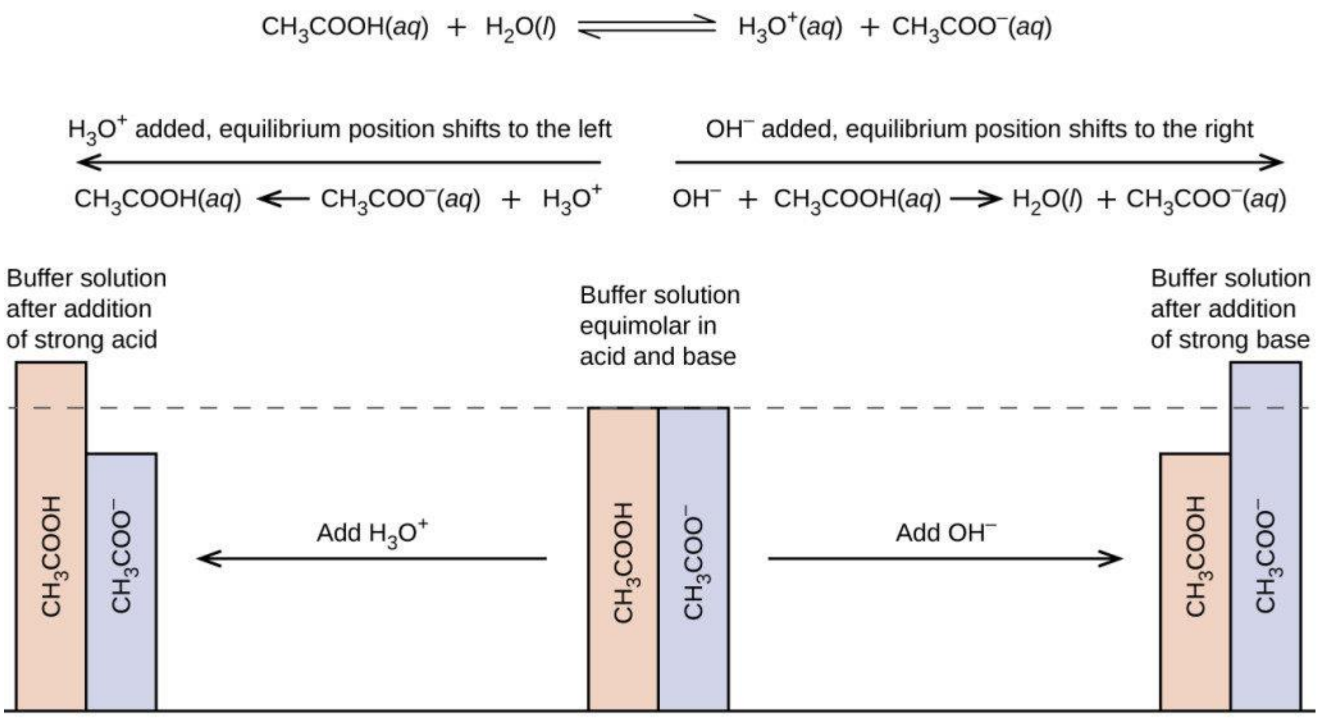
conc. of weak base after the addition = conc. weak base before – conc. the added acid

conc. of weak acid after the addition = conc. weak acid before + conc. the added acid

2) When strong base is added to the buffer **then**

conc. of weak base after the addition = conc. weak base before + conc. the added base

conc. of weak acid after the addition = conc. weak acid before - conc. the added base



Adding an Acid or a Base to a Buffer

Example: Calculate the pH of 75 mL of the buffer solution prepared from 0.10 *M* a cetic acid, $HC_2H_3O_2$, and 0.20 *M* sodium acetate, $NaC_2H_3O_2$ **to which 9.5 mL of 0.1 0 *M* hydrochloric acid is added**. Compare the pH change with what would occur if this amount of acid were added to pure water. **Ka is 1.7 x 10^{-5}**

Before addition of HCL

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\text{base}]}{[\text{acid}]}$$

Then pH = 4.77 + log 0.2/0.1 = 5.07

When H_3O^+ (from HCl) is added to the buffer, it reacts with the acetate ion (weak base).

$$H_3O^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(l)$$

Since acetic acid is a weak acid, it can be assumed as a first approximation that the reaction goes to completion,

- calculate the new Molarity of the strong acid and the buffer after mixing (dilution)

  $M_1V_1 = M_2V_{2;}$ Then $M_2 = M_1V_1/V_2$

Molarity of added acid (HCl) = 0.1 x 9.5ml/ (75+9.5ml) = 0.011 M

M of acetic acid = 0.1 x 75ml/ (75+9.5ml) = 0.09 M

M of acetate = 0.2 x 75ml/ (75+9.5ml) = 0.18 M

After the reaction you have:

$$H_3O^+(aq) + C_2H_3O_2^-(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(l)$$

Start	0.011	0.18	0.09
Change	-0.011	-0.011	+0.011
final	0.0	0.169	0.101e

$$pH = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Then pH = 4.77 + log 0.16/0.10 = 4.96

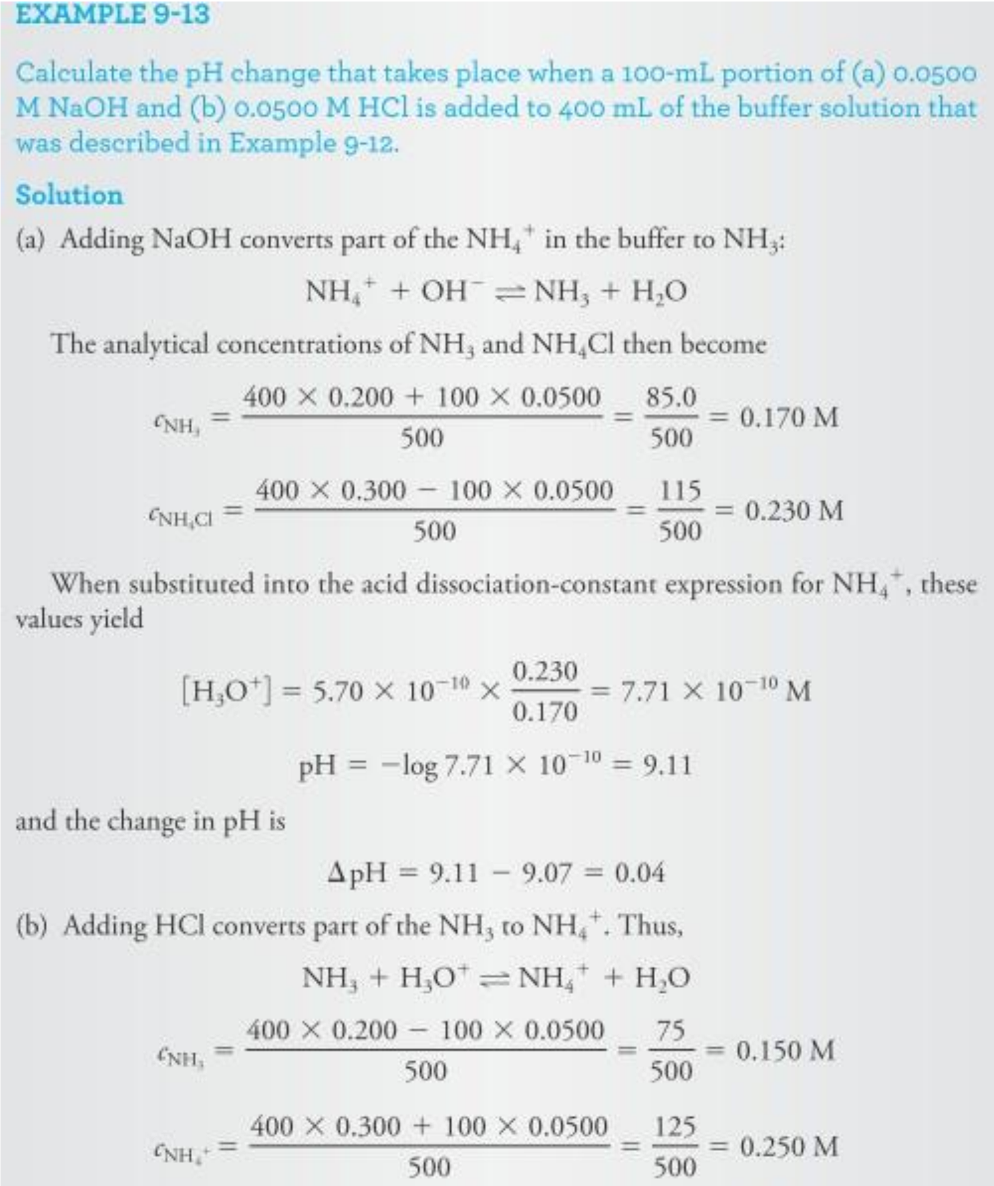
$$\text{pH change} = 5.07 - 4.96 = 0.11 \text{ unit}$$

- **Adding HCl to pure water instead of adding to the buffer**
- If 9.5. mL of 0.10 M HCl were added to 75. mL of pure water, the hydronium-ion concentration would change to

- **Molarity of added acid (HCl) After mixing with pure water:**
  = 0.1 x 9.5ml/ (75+9.5ml) = 0.011 M

$$pH = -\log\left[H_3O^+\right] = -\log(0.011) = 1.96$$

pH change = 7.00 – 1.96 = 5.04



EXAMPLE 9-13

Calculate the pH change that takes place when a 100-mL portion of (a) 0.0500 M NaOH and (b) 0.0500 M HCl is added to 400 mL of the buffer solution that was described in Example 9-12.

Solution

(a) Adding NaOH converts part of the NH_4^+ in the buffer to NH_3:

$$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

The analytical concentrations of NH_3 and NH_4Cl then become

$$c_{NH_3} = \frac{400 \times 0.200 + 100 \times 0.0500}{500} = \frac{85.0}{500} = 0.170\text{ M}$$

$$c_{NH_4Cl} = \frac{400 \times 0.300 - 100 \times 0.0500}{500} = \frac{115}{500} = 0.230\text{ M}$$

When substituted into the acid dissociation-constant expression for NH_4^+, these values yield

$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.230}{0.170} = 7.71 \times 10^{-10}\text{ M}$$

$$\text{pH} = -\log 7.71 \times 10^{-10} = 9.11$$

and the change in pH is

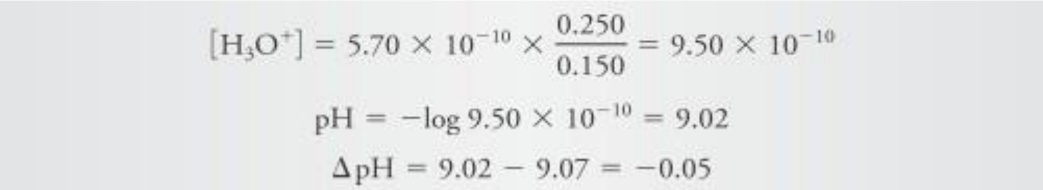
$$\Delta\text{pH} = 9.11 - 9.07 = 0.04$$

(b) Adding HCl converts part of the NH_3 to NH_4^+. Thus,

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

$$c_{NH_3} = \frac{400 \times 0.200 - 100 \times 0.0500}{500} = \frac{75}{500} = 0.150\text{ M}$$

$$c_{NH_4^+} = \frac{400 \times 0.300 + 100 \times 0.0500}{500} = \frac{125}{500} = 0.250\text{ M}$$



$$[H_3O^+] = 5.70 \times 10^{-10} \times \frac{0.250}{0.150} = 9.50 \times 10^{-10}$$

$$\text{pH} = -\log 9.50 \times 10^{-10} = 9.02$$

$$\Delta\text{pH} = 9.02 - 9.07 = -0.05$$

Example: What is the pH change after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer solution?

Ka= 5.6×10^{-10}

- ❖ Using $\mathbf{M_1V_1 = M_2V_{2;}}$ **Then** $\mathbf{M_2 = M_1V_1/V_2}$
- ➢ M of NaOH after mixing = 0.05 x (20ml/100ml) = 0.01 M
- ➢ M of NH_3 = 0.3 x (80/100) = 0.24 M
- ➢ M of NH_4Cl = 0.29 M

	NH_4^+ (*aq*)	+ OH^- (*aq*)	$\longrightarrow$	H_2O (*l*)	+ NH_3 (*aq*)
start (M)	0.29	0.01			0.24
end (M)	0.28	0.0			0.25

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

pH = 9.2

Note: If the volume of the added acid is not mentioned we neglect it and consider the final volume as initial volume. See next Example

Note: A student has available 1.00 L of the buffered solution: 0.55 *M* acetic acid (CH_3COOH, $K_a = 1.8 \times 10^{-5}$) and 0.45 *M* sodium acetate ($NaCH_3COO$). What is the pH of this buffer after **0.060 mol of OH^- are generated (ADDED to the buffer) by the reaction**?

Step 1. Calculate pH of buffer befor the addition of **OH^-**

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad \mathbf{pH = 4.66}$$

- After the addition , we neglect the volume of the added OH^- ***because it is generated during the reaction***

- The new Molarity of NaOH = 0.06mole/1L **= 0.06M**

Step 2: Calculate of HA and A⁻ from reaction

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(aq)$$

	$[CH_3COOH]$ **mol**	$OH^-(aq)$ **mol**	$CH_3COO^-(aq)$ **mol**
Start	0.55 M	0.060	0.45
Change	–0.060	–0.060	+0.060
Final	= 0.49	0.00	= 0.51

$$pH = pK_a + \log\frac{[A^-]}{[HA]} \qquad \mathbf{pH = 4.76} \qquad \mathbf{\Delta pH = 4.76 - 4.66 = 0.10\ unit}$$

A) Calculate the pH of a buffer solution that is 0.040 *M* $NH_4Cl(aq)$ and 0.030 *M* $NH_3(aq)$. B) Can **<u>1.00 L</u>** of this buffer system deal with the addition of **0.010 mol of H^+**? What is the final pH in this case? **Kb (NH_3)= 1.8 x 10^{-5}**

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$ Buffer equation before H^+ add.

A) $$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = 9.25 + \log\frac{0.030\ M}{0.040\ M} \qquad pH = 9.25 + \log(0.75) = 9.13$$

B) After the addition of 0.010 mol of H^+ ; i.e 0.01mol/1L = 0.01 M

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

Moles	**$[NH_3$**	**$[NH_4^+]$**	
Before	**0.030 M**	**0.040 M**	
Rxn	*–0.010 (from H+)*	*+0.010*	
End	***0.030 – 0.010 = 0.020***	***0.040 + 0.010 = 0.050***	

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} \qquad \boldsymbol{pH = 8.86}$$

$$\boldsymbol{\Delta\ pH = 8.86 - 9.13 = -0.27\ pH\ units}$$

- While If we added this 0.010 mol of H^+ to 1.00 L of pure water, the pH would be… pH = –log(0.010) = 2.00 and
- Δ pH = 2.00 – 7.00 = –5.00 pH units

The Composition of Buffer Solutions as a Function of pH: Alpha Values

- **The composition of buffer solutions can be visualized by plotting the relative equilibrium concentrations of the two components of a conjugate acid/base as a function of the pH of the solution**.
- These relative concentrations are called alpha values.
- If cT is the sum of the analytical concentrations of acetic acid and sodium acetate in a typical buffer solution, we can write:

$$c_T = c_{HOAc} + c_{NaOAc}$$

α_0 the fraction of the total concentration of acid that is undissociated is

$$\alpha_0 = \frac{[HOAc]}{c_T}$$

α_1, the fraction dissociated is

$$\alpha_1 = \frac{[OAc^-]}{c_T}$$

Alpha values are unitless ratios whose sum must equal unity. These values depend only on $[H_3O^+]$ and K_a.

$$\alpha_0 + \alpha_1 = 1$$

$$[OAc^-] = \frac{K_a[HOAc]}{[H_3O^+]}$$

$$c_T = [HOAc] + [OAc^-]$$

$$c_T = [HOAc] + \frac{K_a[HOAc]}{[H_3O^+]} = [HOAc]\left(\frac{[H_3O^+] + K}{[H_3O^+]}\right)$$

The re-arranged equation becomes $$\frac{[HOAc]}{c_T} = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

$[HOAc]/c_T = \alpha_0$ Thus,

$$\alpha_0 = \frac{[HOAc]}{c_T} = \frac{[H_3O^+]}{[H_3O^+] + K_a} \qquad \alpha_1 = \frac{[OAc^-]}{c_T} = \frac{K_a}{[H_3O^+] + K_a}$$

Alpha values depend only on $[H_3O^+]$ and K_a and are independent on c_T.

Calculate the degree of the undissociation of acetate at pH 3.0?

Ka = 1.74×10^{-5}

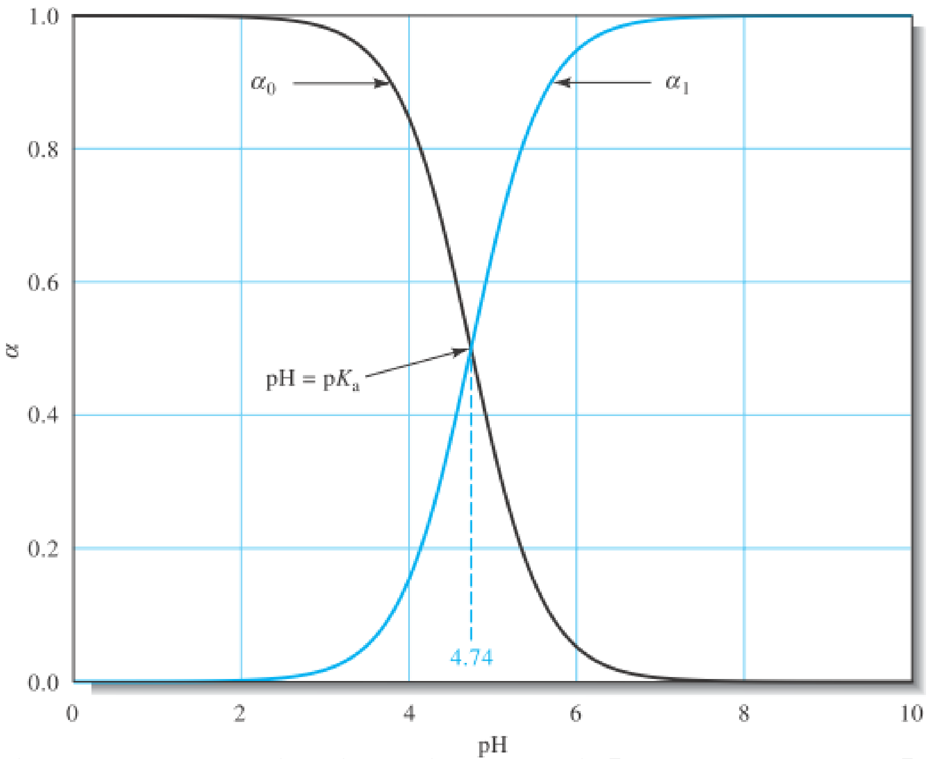
$\alpha 1 = K_a/([H^+] + K_a) = 1.74 \times 10^{-5}/(10^{-3} + 1.74 \times 10^{-5}) = 0.0171$

$\alpha_0 = 1 - 0.0171 = 0.929$

* When using this formula we will get the same answer

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

$$\alpha_0 + \alpha_1 = 1$$



Ka = 1.74×10^{-5}

$$\alpha_1 = \frac{[OAc^-]}{c_T} = \frac{K_a}{[H_3O^+] + K_a}$$

$$\alpha_0 = \frac{[HOAc]}{c_T} = \frac{[H_3O^+]}{[H_3O^+] + K_a}$$

Fig. 9-5. Variation in α with pH. Note that most of the transition between α_0 and α_1 occurs within ±1 pH unit of the crossover point of the two curves. The crossover point where $\alpha_0 = \alpha_1 = 0.5$ occurs when pH = $\mathrm{p}K_{\mathrm{HOAc}}$ = 4.74

Buffer capacity β:

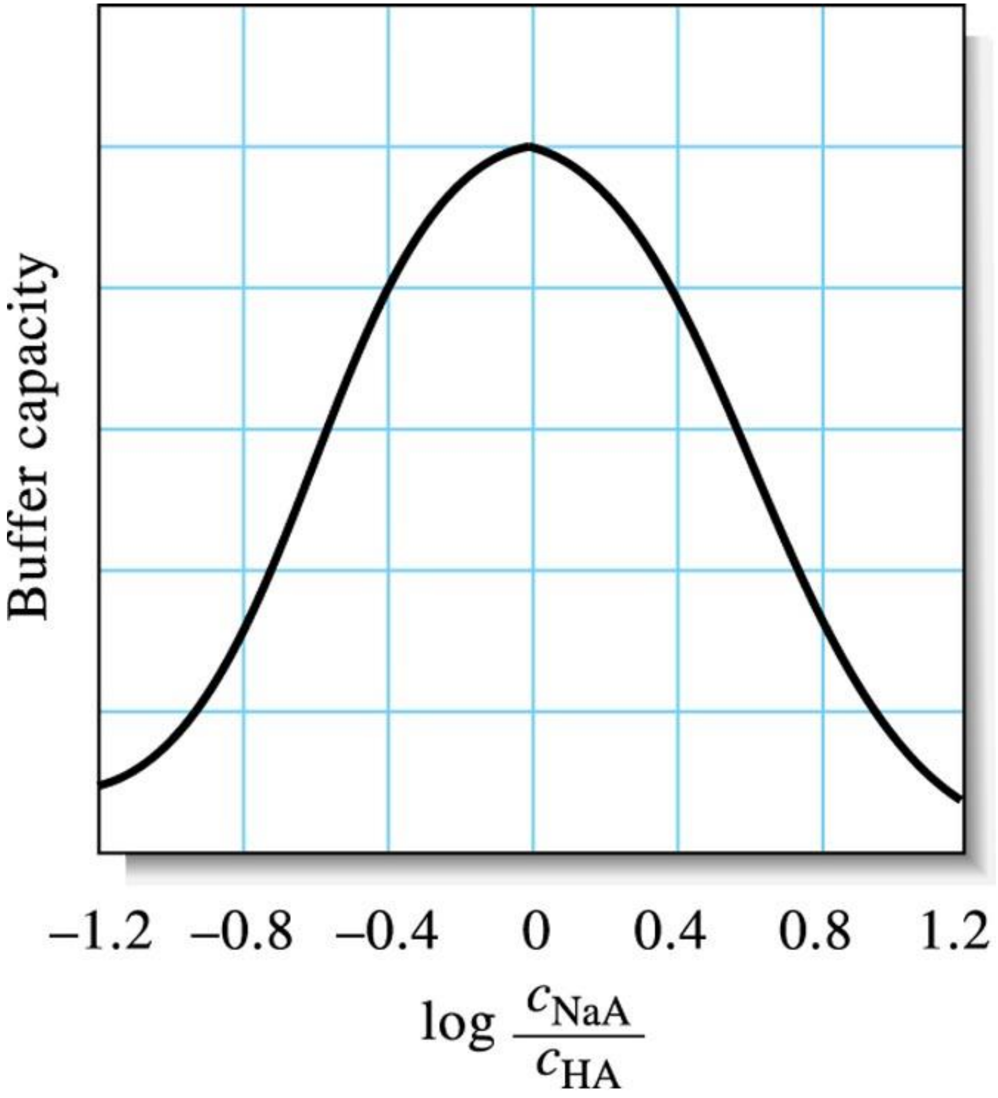
- The relative ability of a buffer solution to resist pH change upon addition of an acid or a base.

- Or the number of moles of strong acid or strong base that causes 1.00 L of the buffer to undergo a 1.00-unit change in pH.

- **A buffer is most effective in resisting changes in pH when pH= pK_a (i.e., when [HA] = [A^-]).**

Choose a buffer for an experiment whose pK_a is as close as possible to the desired pH.

- **The useful pH range of a buffer is usually considered to be $pK_a \pm$ 1 pH unit.**



Buffer capacity as a function of the logarithm of the ratio C_{NaA}/C_{HA}. The maximum buffer capacity occurs when the concentration of acid and conjugated base are equal.

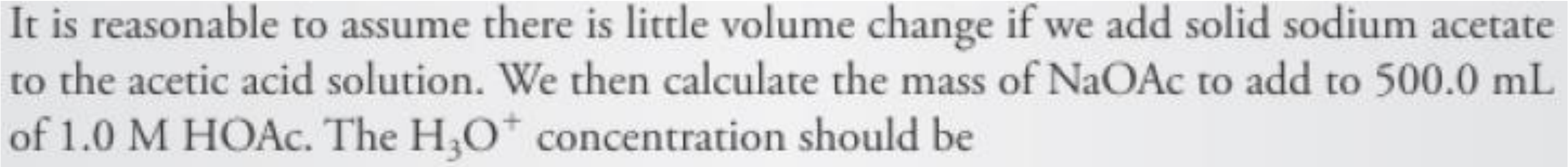
At $C_{NaA}/C_{HA} = 1$; Log $C_{NaA}/C_{HA} = 0$

- Buffer capacity is maximum when **α = 0.5**

Preparation of Buffers

- In principle, a buffer solution of any desired pH can be prepared by combining calculated quantities of a suitable conjugate acid/base pair.
- In practice, however, the pH values of buffers prepared from theoretically generated recipes differ from the predicted values because of uncertainties in the numerical values of many dissociation constants and from the simplifications used in calculations.
- Because of these uncertainties, we prepare buffers by making up a solution of approximately the desired pH (see Example 9-14) and then adjusting it by adding strong acid or strong base until the required pH is indicated by a pH meter.
- Alternatively, empirically derived recipes for preparing buffer solutions of known pH are available in chemical handbooks and reference works.
- Buffers are of tremendous importance in biological and biochemical studies in which a low but constant concentration of hydronium ions (10^{-6} to 10^{-10} M) must be maintained throughout experiments. Chemical and biological supply houses offer a variety of such buffers.

Q9-14: Describe how you might prepare approximately 500.0 mL of a pH 4.5 buffer solution from 1.0 M acetic acid (HOAc) and sodium acetate (NaOAc; 82.035g/mol). $K_a = 1.74 \times 10^{-5}$


It is reasonable to assume there is little volume change if we add solid sodium acetate to the acetic acid solution. We then calculate the mass of NaOAc to add to 500.0 mL of 1.0 M HOAc. The H_3O^+ concentration should be

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

$4.5 = 4.76 + \log$ **[**OAC^-**]** / **[**HOAC**]**

- Then: OAC/HOAC = 0.55
- If HOAC is 1.0 M then we have to prepare 0.55 M OAC^-
- However, if we want to prepare 500 ml then we need

0.55 mole/L x 0.5 l = 0.275 mole

0.275 mole x 82.035 g/mol = 22.56 g

- Then we have to dissolve 22.56 g of NaOAc in 500ml of HOAC (1.0 M) solution

Example: A solution buffered at pH 3.90 is needed for a reaction. **Would formic acid and its salt, sodium formate, make a good choice for this buffer**? If so, **what ratio** of moles of the conjugate base anion ($HCOO^-$) to the acid (HCOOH) is needed?

- **K_a= 1.8 x 10^{-4}** then **pK_a of formic acid is 3.74**.
- This is within pH = $pK_a \pm 1$ range
  - 2.90 to 4.90; So we can use this buffer system

$$pH - pK_a = \log\frac{[A^-]}{[HA]} \qquad \log\frac{[HCOO^-]}{[HCOOH]} = 3.90 - 3.74 = 0.16$$

$$\frac{[HCOO^-]}{[HCOOH]} = 10^{0.16} = 1.4 \qquad \mathbf{1.4 \times [HCOOH] = [HCOO^-]}$$

Modified by Dr. Mohammed Rasheed

Chapter 10

Effect of Electrolytes on Chemical Equilibria

Chemical Equilibrium Electrolyte Effects

- **Electrolytes:**
- ✓ Substances producing ions in solutions
- ✓ Can electrolytes affect chemical equilibria?
- ✓ (A) "Common Ion Effect" ➔ Yes
  - ❖ **Decreases** solubility of BaF_2 with NaF
  - ❖ F^- is the "common ion"
- ✓ (B) No common ion: "**inert electrolyte effect**" or "diverse ion effect"
  - ❖ Add Na_2SO_4 to saturated solution of AgCl
  - ❖ **Increases** solubility of AgCl **Why???**

Chemical Equilibrium Electrolyte Effects

- The position of most solution equilibria depends on the electrolyte concentration of the medium, even when the added electrolyte contains no ion in common with those involved in the equilibrium.

$$H_3AsO_4 + 3I^- + 2H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$$

- If an electrolyte, such as barium nitrate, potassium sulfat, or sodium perchlorate, is added to this solution, the color of the triiodide ion (I_3^-) becomes less intense.
- This decrease in color intensity indicates that the concentration of I_3^- has decreased and that **the equilibrium has been shifted to the left by the added electrolyte**.

Concentration-based equilibrium constant:

- At **low electrolyte concentration (ex. NaCl), concentration-based equilibrium** constant becomes independent of the electrolyte concentration and is equal to **thermodynamic equilibrium constant.**

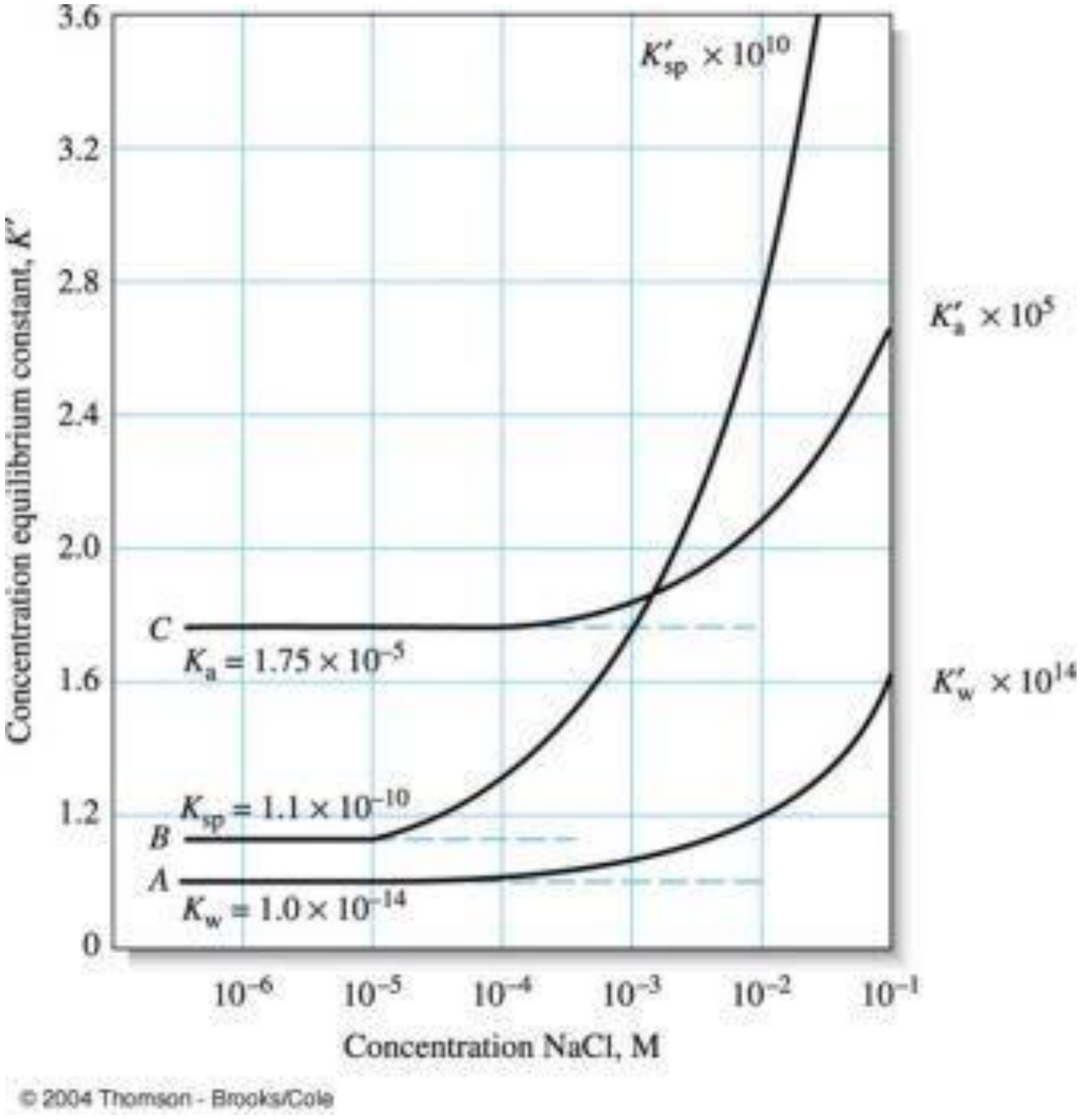
- **Concentration-based equilibrium constant : K_w', K_{sp}', K_a'**

- **Thermodynamic equilibrium constant : K_w, K_{sp}, K_a (The usual aquarium constant that we presented before)**

❖ **If [NaCl] = 10^{-4} M : $K_w' = K_w = 10^{-14}$**

❖ **If [NaCl] = 10^{-1} M : $K_w' = 10^{14}$**

- Effect of electrolyte concentration on concentration-based equilibrium constants.



How Do Ionic Charges Affect Equilibria?

- The magnitude of the electrolyte effect is highly dependent on the **charges of the participants in an equilibrium**. When only neutral species are involved, the position of equilibrium is essentially independent of electrolyte concentration.

- With ionic participants, the magnitude of the electrolyte effect increases with charge.

- **In a 0.02 M solution of potassium nitrate,**

✓ **the solubility of barium sulfate is larger than it is in pure water by a factor of 2.**

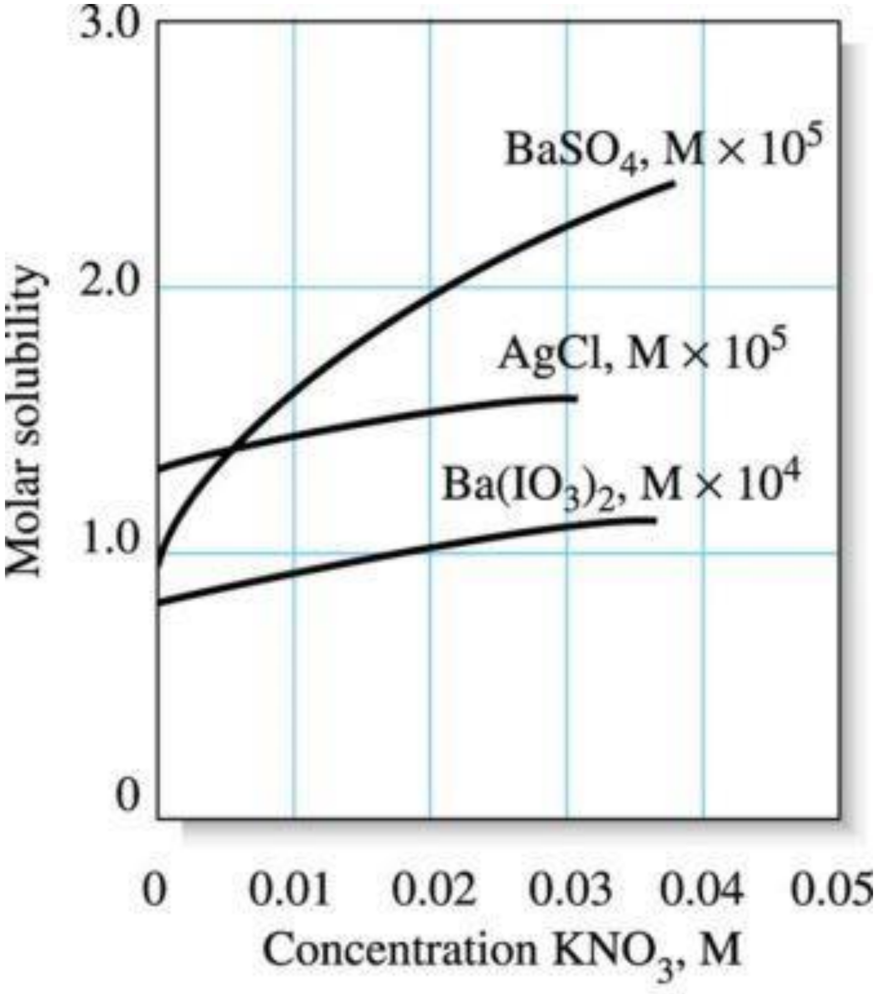
✓ **The solubility of barium iodate by a factor of only 1.25**

✓ **and that of silver chloride by 1.2**

Next Figure

Effect of electrolyte concentration on the solubility of some salts.

- The solubility increases by increasing the concentration of KNO_3



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What Is the Effect of Ionic Strength on Equilibria?

- The effect of added electrolyte on equilibria is independent of the chemical nature of the electrolyte but depends on a property of the solution called the **ionic strength**. This quantity is defined as:

ionic strength = μ 1/2([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + …)

- Where [A], [B], [C], … represent the molar species conc. ions of ions A, B, C, … and Z_A, Z_B, Z_C, … are **their ionic charges**.

- For solutions with **ionic strengths of 0.1 M or less**, the electrolyte effect is independent of the kind of ions and dependent only on the ionic strength.
- This independence with respect to electrolyte species disappears at high ionic strengths.

Ex. 0.1M Na_2SO_4 + 0.1M KCl

$$\mu = (1/2)\{(0.1\times2)(+1)^2+(0.1)(-2)^2+(0.1)(+1)^2+(0.1)(-1)^2\}$$

$$= 0.4M$$

Calculate the ionic strength of the following:

- 0.040M $FeSO_4$

μ = ……………………………………………………………= 0.16

- 0.20M $(NH_4)_2CrO_4$

μ = ……………………………………………………= 0.60

- 0.10M $FeCl_3$ and 0.20M $FeCl_2$

μ = ……………………………………………………………….= 1.2

- 0.060M $La(NO_3)_3$ and 0.030M $Fe(NO_3)_2$

μ = …………………………………………………………= 0.45

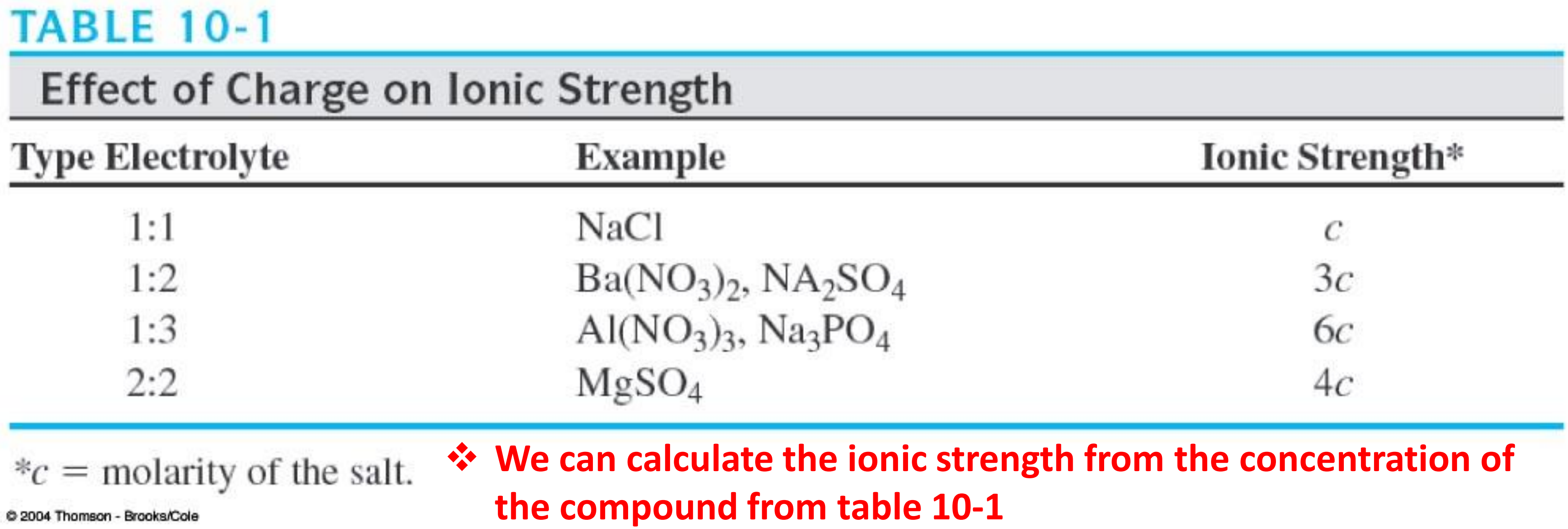


TABLE 10-1

Effect of Charge on Ionic Strength

Type Electrolyte	Example	Ionic Strength*
1:1	NaCl	*c*
1:2	$Ba(NO_3)_2$, NA_2SO_4	3*c*
1:3	$Al(NO_3)_3$, Na_3PO_4	6*c*
2:2	$MgSO_4$	4*c*

*c = molarity of the salt.

❖ **We can calculate the ionic strength from the concentration of the compound from table 10-1**

- 0.040M FeSO4

  μ = ½ [0.04(2)2 + 0.04(2)2] = 0.16 **or 2:2** **4c = 4*0.04 = 0.16**

- 0.20M (NH4)2CrO4

  μ = ½[2(0.2)(1)2 + 0.2(-2)2] = 0.60 **or 1:2** **3c = 3*0.2 = 0.60**

- 0.10M FeCl3 and 0.20M FeCl2

  μ = ½ [0.10(3)2 + 0.3(-1)2 + 0.2(2)2 + 0.4(-1)2 = 1.2

  or (1:3) 6c = 6*0.10 = 0.6 + (1:2) 3*0.2=0.6 then 0.6+0.6=1.2

EXAMPLE 10-1

Calculate the ionic strength of (a) a 0.1 M solution of KNO_3 and (b) a 0.1 M solution of Na_2SO_4.

Solution

(a) For the KNO_3 solution, $[K^+]$ and $[NO_3^-]$ are 0.1 M and

$$\mu = \frac{1}{2}(0.1\ M \times 1^2 + 0.1\ M \times 1^2) = 0.1\ M$$

(b) For the Na_2SO_4 solution, $[Na^+] = 0.2$ M and $[SO_4^{2-}]$ 0.1 M. Therefore,

$$\mu = \frac{1}{2}(0.2\ M \times 1^2 + 0.1\ M \times 2^2) = 0.3\ M$$

EXAMPLE 10-2

What is the ionic strength of a solution that is 0.05 M in KNO_3 and 0.1 M in Na_2SO_4?

Solution

$$\mu = \frac{1}{2}(0.05\ M \times 1^2 + 0.05\ M \times 1^2 + 0.2\ M \times 1^2 + 0.1\ M \times 2^2) = 0.35\ M$$

The effect of ionic strength on solubility of salts

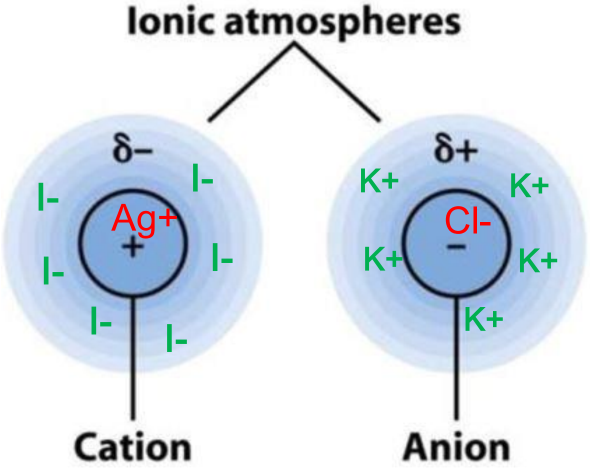
- The electrolyte effect results from the electrostatic attractive and repulsive forces that exist between the ions of an electrolyte and the ions involved in an equilibrium.
- These forces cause each ion from the dissociated reactant to be surrounded by a cover of solution that contains a slight excess of electrolyte ions of opposite charge.
- When a barium sulfate precipitate is equilibrated with a sodium chloride solution,
- **each dissolved barium ion is surrounded by an ionic atmosphere carries a small net negative charge.**
- each sulfate ion is surrounded by an ionic atmosphere that tends to be slightly positive.

- **These charged layers make the barium ions somewhat less positive and the sulfate ions somewhat less negative than they would be in the absence of electrolyte.**
- **The consequence of this effect is a decrease in overall attraction between barium and sulfate ions <u>and an increase in solubility</u>, which becomes greater as the number of electrolyte ions in the solution becomes larger.**

The effect of ionic strength on solubility of salts

- Increase ionic strength decrease the attraction between the positive and negative ion which increase solubility by preventing these two ions to move toward each other and precipitate

- Suppose a solubility of AgCl in KI solution



Ex. Mercurous iodate in distilled water

$$Hg_2(IO_3)_2 = Hg_2^{2+} + 2IO_3^{-} \qquad \boldsymbol{K_{sp} = 1.3 \times 10^{-18}}$$

$$K_{sp} = [Hg_2^{2+}][IO_3^{-}]^2 = x(2x)^2 = 1.3 \times 10^{-18}$$

$$\boldsymbol{x = [Hg_2^{2+}] = 6.9 \times 10^{-7}\,M}$$

- Adding 0.050M KNO_3 to saturated solution of mercurous iodate;

$$\boldsymbol{[Hg_2^{2+}] = 1.0 \times 10^{-6}\,M}$$

⇒ Ion dissociation (solubility) is increased by increasing the ionic strength

ACTIVITY COEFFICIENT

Activity and activity coefficient

- **Activity** : a thermodynamic quantity which measures the effective concentration or intensity of a particular substance in a given chemical system.
- **For dilute, ideal solutions the activity is directly proportional to the concentration**; for ideal gases, activity is proportional to the partial pressure of the gas.

$$aA + bB \leftrightarrow cC + dD$$

The equilibrium constant (K) is given by

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

❖ **K does not account for the effect of ionic strength**

ACTIVITY COEFFICIENT

- Activities (A) are used in place of concentrations to account for ionic strength $a_X = \gamma_x[X]$;

  where γ is dimensionless quantity the activity coefficient

- Activity coefficient depends on ionic strength; Activity coefficient decreases with increasing ionic strength
- **Activity coefficient is 1 when there is no effect of ionic strength**

❖ K_{sp}' is the concentration equilibrium constant is generally expressed as follows $C_cD_d \leftrightarrow cC + dD$

$$K_{sp} = a_C^c . \ a_D^d$$

$$K_{sp} = [C]^c \gamma_C^c . \gamma_D^d [D]^d$$

❖ **To solve the equil. Problem we have to calculate the new K`**

$$K_{sp}` = [C]^c [D]^d = K_{sp} / \gamma_C^c . \gamma_D^d$$

Properties of Activity Coefficients

- The activity coefficient of a species is a measure of the effectiveness with which that species influences an equilibrium in which it is a participant.

- In very dilute solution, **where the ionic strength μ is minimal**, then the activity coefficient becomes unity (1); **under such circumstances**,

a) the activity and the molar concentration are identical.

b) thermodynamic and concentration equilibrium constants are also identical.

- For a given ionic strength, the activity coefficient of an ion **decreases** more dramatically from unity as the **charge on the species increases**.

- As the ionic strength μ increases, however, an ion loses some of its effectiveness and its activity coefficient decreases.

Properties of Activity Coefficients

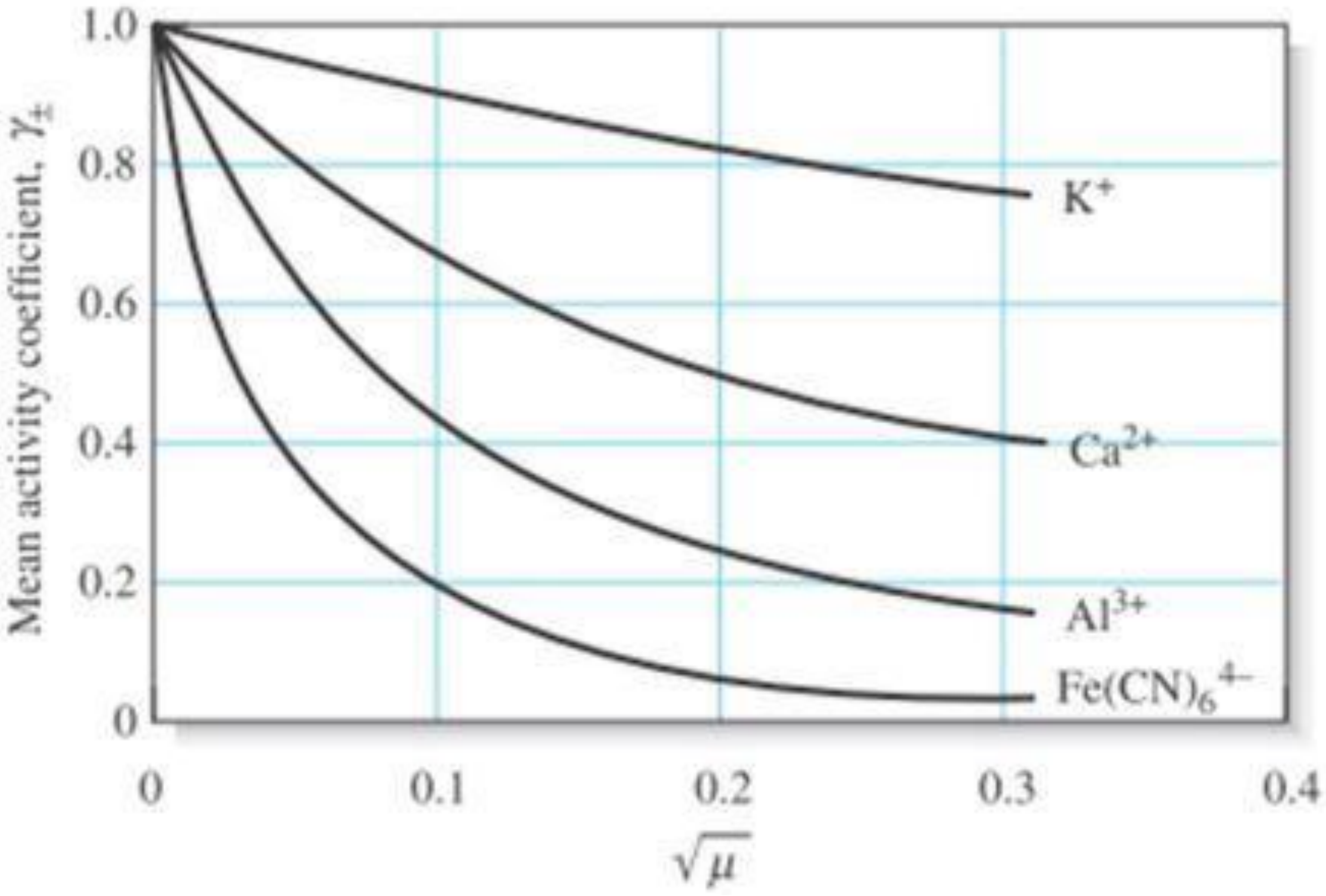
- **As the solution approaches infinite dilution then $\mu \rightarrow 0$; $\gamma_x \rightarrow 1$; and thus $a_x \rightarrow [X]$ and $K`_{sp} \rightarrow K_{sp}$**

- The activity coefficient of an uncharged molecule is approximately unity, regardless of ionic strength.

- In solutions that are **not too concentrated**, the activity coefficient for a given species is independent of the nature of the electrolyte and **dependent only on the ionic strength**.

- However, at any given ionic strength, the activity coefficients of ions of the same charge are approximately equal. The small variations among ions of the same charge can be correlated with the effective diameter of the hydrated ions (see **Debye-Hückel Equation later)** .

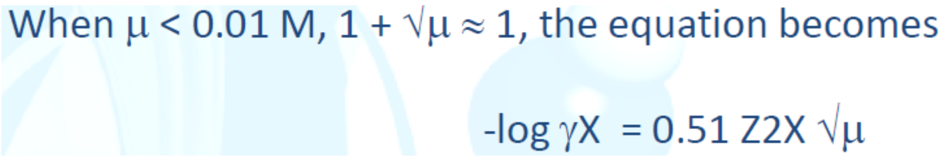
- **As the solution approaches infinite dilution then $\mu \rightarrow 0$; $\gamma_x \rightarrow 1$; and thus $a_x \rightarrow [X]$ and $K`_{sp} \rightarrow K_{sp}$**



ACTIVITY COEFFICIENT

- **Debye-Hückel Equation:** P. Debye and E. Huckel derive a theoretical expression that permits the calculation of activity coefficients of ion from their charge and their average size. This equation takes the form
- Relates activity coefficients to ionic strength (at 25 °C)

$$-\log \gamma_x = \frac{0.51 Z_x^2 \sqrt{\mu}}{1 + 3.3 \alpha_x \sqrt{\mu}}$$



When $\mu < 0.01$ M, $1 + \sqrt{\mu} \approx 1$, the equation becomes

$$-\log \gamma X = 0.51\ Z2X\ \sqrt{\mu}$$

where, γ_x : activity coefficient of the species X

Z_x : charge on the species X

μ : ionic strength of the solution

α_x : effective diameter of the hydrated ion X in nanometer (10^{-9} m)

- ✓ The constants 0.51 and 3.3 are applicable to aqueous solution at 25°C;
- ✓ The magnitude of α_x appears to be approximately 0.3 nm for most singly charged ions; then, the denominator of the Debye-Huckel equation simplifies to approximately $1 + \sqrt{\mu}$.
- ✓ For ions with higher charge, α_x may be as large as 1.0 nm.

Tab 10-1 Activity Coefficients for Ions at 25℃

Ion		**Activity Coefficient at Indicated Ionic Strength**				
	α_x, nm	**0.001**	**0.005**	**0.01**	**0.05**	**0.1**
H_3O^+	0.9	0.967	0.934	0.913	0.85	0.83
Li^+, $C_6H_5COO^-$	0.6	0.966	0.930	0.907	0.83	0.80
Na^+, IO_3^-, HSO_3^-, HCO_3^-, $H_2PO_4^-$, $H_2AsO_4^-$, OAc^-	0.4-0.45	0.965	0.927	0.902	0.82	0.77
OH^-, F^-, SCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-	0.35	0.965	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-, $HCOO^-$	0.3	0.965	0.925	0.899	0.81	0.75
Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+	0.25	0.965	0.925	0.897	0.80	0.75
Mg^{2+}, Be^{2+}	0.8	0.872	0.756	0.690	0.52	0.44
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $Phthalate^{2-}$	0.6	0.870	0.748	0.676	0.48	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}	0.5	0.869	0.743	0.668	0.46	0.38
Pb^{2+}, CO_3, SO_3^{2-}, $C_2O_4^{2-}$	0.45	0.868	0.741	0.665	0.45	0.36
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, CrO_4^{2-}, HPO_4^{2-}	0.40	0.867	0.738	0.661	0.44	0.35
Al^{3+}, Fe^{3+}, Cr^{3+}, La^{3+}, Ce^{3+}	0.9	0.737	0.540	0.443	0.24	0.18
PO_4^{3-}, $Fe(CN)_6^{3-}$	0.4	0.726	0.505	0.394	0.16	0.095
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1.1	0.587	0.348	0.252	0.10	0.063
$Fe(CN)_6^{4-}$	0.5	0.569	0.305	0.200	0.047	0.020

Ex.10-3 Use Eq. 10-5 to calculate the activity coefficient for Hg^{2+} in a solution that has an ionic strength of 0.085. Use 0.5 nm for the effective diameter of the ion. Compare the calculated value with γHg^{2+} obtained by interpolation of data from Table 10-1.

(a)

$$-\log \gamma_{Hg^{2+}} = \frac{(0.51)(2)^2\sqrt{0.085}}{1 + (3.3)(0.5)\sqrt{0.085}} \approx 0.4016$$

$$\gamma_{Hg^{2+}} = 10^{-0.4016} = 0.397 \approx 0.40$$

b) From table 10-1

μ	$\gamma_{Hg^{2+}}$
0.1M	0.38
0.05M	0.46

0.085 M

~ 0.40

Thus, when $\Delta\mu = (0.10\text{ M} - 0.05\text{ M}) = 0.05\text{ M}$, $\Delta\gamma_{Hg^{2+}} = 0.46 - 0.38 = 0.08$. At an ionic strength of 0.085 M,

$$\Delta\mu = (0.100\text{ M} - 0.085\text{ M}) = 0.015\text{ M}$$

$$\Delta\gamma_{Hg^{2+}} = \frac{0.015}{0.05} \times 0.08 = 0.024$$

$$\Delta\gamma_{H_g^{2+}} = 0.38 + 0.024 = 0.404 \approx 0.40$$

Calculate the activity coefficients for K^+ and SO_4^{2-} in a 0.020 M solution of K_2SO_4.

$$\mu = \frac{1}{2}\left([A]Z_A^2 + [B]Z_B^2 + [C]Z_C^2 + ...\right)$$

$$\mu = \frac{1}{2}\left([K]1^2 + [SO_4](-2)^2\right)$$

$$\mu = \frac{1}{2}\left([2 \times 0.020]1^2 + [0.020](-2)^2\right) = 0.060$$

$$-\log \gamma_{\mathsf{K+}} = \frac{0.51\ 1^2\ \sqrt{0}.060}{1 + 3.3\ 0.3\ \sqrt{0}.060} = 0.1005 \qquad \gamma_{\mathsf{K+}} = 10^{-0.101} = 0.79$$

$$-\log \gamma_{\mathsf{SO_4}} = \frac{0.51\ (-2)^2\ \sqrt{0}.060}{1 + 3.3\ 0.4\ \sqrt{0}.060} = 0.463 \qquad \gamma_{\mathsf{SO_4}} = 10^{-0.463} = 0.344$$

Solubility for LiF in pure water and at two different ionic strength

1) Solubility of LiF in distilled water;

$Ksp \approx [Li^+][F^-] = x^2 = 1.7 \times 10^{-3}$; **$x = [Li^+] = [F^-] = 0.041$ M**

2) Solubility in salt with $\mu = 0.05 \Rightarrow$

- From table 10.1 $\gamma_{Li+} = 0.83$, $\gamma_{F^-} = 0.81$
- **$Ksp` = Ksp/\gamma_{Li+}\,\gamma_{F^-}$;**

$Ksp` = Ksp/$ $(0.83)*(0.81) =$ **2.53×10^{-3} (the new Ksp that used for equil. calculation)**

$Ksp` = (x))(x) = 2.53 \times 10^{-3}$; then **$x = [Li^+] = 0.050$ M**

3) Solubility in salt with $\mu = 0.1 \Rightarrow$

- From table 10.1 $\gamma_{Li+} = 0.80$, $\gamma_{F^-} = 0.76$; **$x = [Li^+] = 0.053$M;**

$\therefore\ \mu\uparrow \Rightarrow$ solubility $\uparrow$

Q10-2; What is the solubility of CaF_2 in 0.0125M $MgSO_4$ solution? What is the relative error of neglecting the presence of $MgSO_4$?

- For 0.0125M $MgSO_4$ $\Rightarrow$

1) $\mu = (1/2)[(0.0125)(+2)^2 + (0.0125)(-2)^2] = 0.05$;

❖ From table 10.1: $\gamma_{Ca2+} = 0.485$, $\gamma_{F^-} = 0.81$

$CaF_2\,(s) \leftrightarrow Ca^{2+} + 2\,F^-$ Ksp = **3.9×10^{-11}**

Equil. x $2x$

$K_{sp} = \mathbf{a}_{Ca^{2+}}\,(\mathbf{a}_{F^-})^2 = [Ca^{+2}]\,\gamma_{ca2+}\,[F^-]^2\,\gamma_{F^-}^2$

2) $K_{sp}` = K_{sp} / \gamma_{Ca2+}\,(\gamma_{F^-})^2 = 1.226 \times 10^{-10}$** **(the new Ksp` that used for equil. calculation)

$K_{sp}` = [Ca^{2+}]\,[F^-]^2$ $= (x)(2x)^2 =$ **1.226×10^{-10}; $x = 3.1 \times 10^{-4}$ M**

3) For solubility in pure water Ksp= $4x^3$ **$x = 2.14 \times 10^{-4}$ M**

4) Relative error = (Solubility in pure water – true solubility/true solubility) x 100%

Relative error = $(2.14 \times 10^{-4} - 3.1 \times 10^{-4}) / 3.1 \times 10^{-4} \times 100 = -30.97\%$

Q10-3: Find the relative error introduced by neglecting activities in calculating the solubility of $Ba(IO_3)_2$ in a 0.033 M solution of $Mg(IO_3)_2$. The thermodynamic solubility product for $Ba(IO_3)_2$ is 1.57×10^{-9}.

$BaIO_3\ (s) \leftrightarrow Ba^{2+} + 2\ IO_3^{-}$ ksp= 1.57×10^{-8}

1) $\mu = 0.1M$; From table 10.1: $\gamma_{Ba2+} = 0.38$, $\gamma_{IO3-} = 0.77$

2) $\boldsymbol{K_{sp}^{-}}$ **=** $\boldsymbol{K_{sp}}$**/** $\gamma_{Ba2+} (\gamma_{IO3-})^2 = 6.97 \times 10^{-7}$ **(the new Ksp that used for calculation)**

$BaIO_3\ (s) \leftrightarrow Ba^{2+} + 2\ IO_3^{-}$

Equil. solid x 0.066

6.97×10^{-7} **= (x) (0.066)²** **then x = 1.6 x 10⁻⁶**

3) Neglecting the activities; Common ion;

$BaIO_3\ (s) \leftrightarrow Ba^{2+} + 2\ IO_3^{-}$

Equil. solid x 0.066 ksp= $1.57 \times 10^{-8} = x\ (0.006)^2$

then x = 3.6 x 10⁻⁷

4) Relative error = (($3.60 \times 10^{-7} - 1.6 \times 10^{-6}) / 1.6 \times 10^{-6}) \times 100\% = -77\%$

Q10-4: Use the activities to calculate the $[H_3O^+]$ in a 0.120M HNO_2 solution that is also 0.05 M NaCl. What is the relative error introduced by neglecting activity corrections? $Ka_{HNO2} = 7.1 \times 10^{-4}$.

$$HNO_{2(aq)} + H_2O_{(l)} \leftrightarrow H_3O^+ + NO_2^-$$

$$\mu = \frac{1}{2}(0.0500 \times 1^2 + 0.0500 \times 1^2) = 0.0500\,\text{M}$$

$$\mu = 0.050 \rightarrow \quad \gamma_{H_3O^+} = 0.85; \quad \gamma_{NO_2^-} = 0.81; \quad \gamma_{HNO_2} = 1.0$$

Ka^{-} = $Ka.\gamma HNO_2 / \gamma NO_2^- . \gamma H_3O^+$ = 1.03×10^{-3}

$$[H_3O^+] = \sqrt{K_a^{-}\; C_{HA}}$$

$$[H_3O^+] = \sqrt{0.120 \times 1.03 \times 10^{-3}} = 1.11 \times 10^{-2}\,\text{M}$$

$$\text{If assuming all } \gamma = 1\text{:} \quad [H_3O^+] = \sqrt{0.120 \times 7.1 \times 10^{-4}} = 9.2 \times 10^{-3}$$

$$\text{relative error} = \frac{9.2 \times 10^{-3} - 1.11 \times 10^{-2}}{1.11 \times 10^{-2}} \times 100\% = -17\%$$

Omitting Activity Coefficients in Equilibrium Calculations

- Activity coefficients are usually neglected and molar concentrations are used in applications of the equilibrium law. This approximation simplifies the calculations and greatly decreases the amount of data needed. For most purposes, the error introduced by the assumption of unity for the activity coefficient is not large enough to lead to false conclusions.

- Significant discrepancies occur when the ionic strength is large (0.01 M or larger) or when the participating ions have multiple charges.

- With dilute solutions ($\mu < 0.01$ M) of nonelectrolytes or of singly charged ions, mass-law calculations using concentrations are often reasonably accurate.

Calculate the pH of a solution that is 0.05000 M NH_4Cl and 0.0300 M NH_3 (Kb for $NH_3 = 1.8 \times 10^{-5}$)

Answer:

- **Neglecting activity coefficient 9.033**
- **Taking activity coefficient into account 9.22**

Ex) Calculate the % relative error in solubility using concentration instead of activities for the $Fe(OH)_3$ ($Ksp= 2 *10^{-39}$) in 0.0500 M KNO_3?

$$Fe(OH)_3(s) \underset{\leftarrow}{\overset{\rightarrow}{}} Fe^{3+} + 3OH^-$$

$$(1) \quad \gamma_{Fe^{3+}} = 0.24 \quad \gamma_{OH^-} = 0.81 \quad K_{sp} = a_{Fe^{3+}} a_{OH^-}{}^3 = \gamma_{Fe^{3+}} [Fe^{3+}] \times (\gamma_{OH^-}[OH^-])^3$$

$$[\mathrm{Fe}^{3+}][\mathrm{OH}^-]^3 = \frac{2 \times 10^{-39}}{\gamma_{\mathrm{Fe}^{3+}} \gamma_{\mathrm{OH}^-}{}^3} = \frac{2 \times 10^{-39}}{(0.24)(0.81)^3} = 2 \times 10^{-38}$$

$$\mathrm{Solubility} = \mathrm{S} = [\mathrm{Fe}^{3+}] = \frac{1}{3}[\mathrm{OH}^-]$$

$$\mathrm{S}(3\mathrm{S})^3 = 2 \times 10^{-38}$$

$$\mathrm{S} = \left(\frac{2 \times 10^{-38}}{27}\right)^{\frac{1}{4}} = 1.55 \times 10^{-10}\,\mathrm{M}$$

$$(2) \quad \mathrm{S} = \left(\frac{2 \times 10^{-39}}{27}\right)^{\frac{1}{4}} = 9.3 \times 10^{-11}\,\mathrm{M}$$

$$\text{relative error} = \frac{9.3 \times 10^{-11} - 1.55 \times 10^{-10}}{1.55 \times 10^{-10}} \times 100\% = \underline{\underline{-40\%}}$$

Modified by:

Dr. Mohammed Rasheed

Chapter 11

Solving Equilibrium Problems for Complex Systems

- Aqueous solutions often contain species that interact with one a nother and water to yield two or more simultaneous equilibria.
- Ex., for a sparingly soluble salt in water, there are three equilibra.

❖ The solubility of $BaSO_4$ is not only depend on the first equilibrium but also on the second and third ones

1- $BaSO_4(s) \leftrightarrow Ba^{2+} + SO_4^{2-}$

2- $SO_4^{2-} + H_3O^+ \leftrightarrow HSO_4^- + H_2O$

3- $2H_2O \leftrightarrow H_3O^+ + OH^-$

How can we predict these equations?

- The addition of hydronium ions to this system causes the second equilibrium to be shifted to the right by the common-ion effect.
- The resulting decrease in sulfate concentration causes the first equilibrium to shift to the right.

❖ *The introduction of a new equilibrium system into a solution does not change the equilibrium constants for any existing equilibria.*

11 A Solving multiple-equilibrium problems using A systematic method

- To solve a multiple-equilibrium problem, **we must write as many independent equations as there are chemical species in the system.**
- We use three types of algebraic equations to solve multiple-equilibrium problems:
  (1) equilibrium-constant expressions,
  (2) mass-balance equations, and
  (3) a single charge-balance equation.

Mass-Balance Equations

- Mass-balance equations relate the equilibrium concentrations of various species in a solution to one another and to the analytical concentrations of the various solutes.
- **These equations are a direct result of the conservation of mass and moles.**

- **Writing mass balance equations may be as straightforward as the case of a weak acid:**

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

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

- ✓ The only source of the two A^- containing species, HA and A^-, is the original solute, HA, whose **analytical concentration is cHA**:

$$c_{HA} = [HA] + [A^-]$$

- ✓ Hydronium ions in the solution come from two sources: the dissociation of HA and the dissociation of water.

$$[H_3O^+] = [H_3O^+]_{HA} + [H_3O^+]_{H2O}$$

- ✓ The concentration of hydronium from the dissociation of the acid $[H_3O^+]$HA is equal to $[A^-]$, and the hydronium concentration from water $[H_3O^+]H_2O$ is equal to $[OH^-]$.

$$\text{Thus, } [H_3O^+] = [A^-] + [OH^-]$$

- ❖ **This is referred to as the *proton balance* equation because it account s for all sources of protons**

Mass balance ; material balance

- The sum of the amounts of all species containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution. **The mass balance is a statement of the conservation of matter.** It really refers to conservation of atoms.

Ex. 1) 0.050 mol of acetic acid in water ⇒ 1L solution

$$CH_3COOH = CH_3COO^- + H^+$$

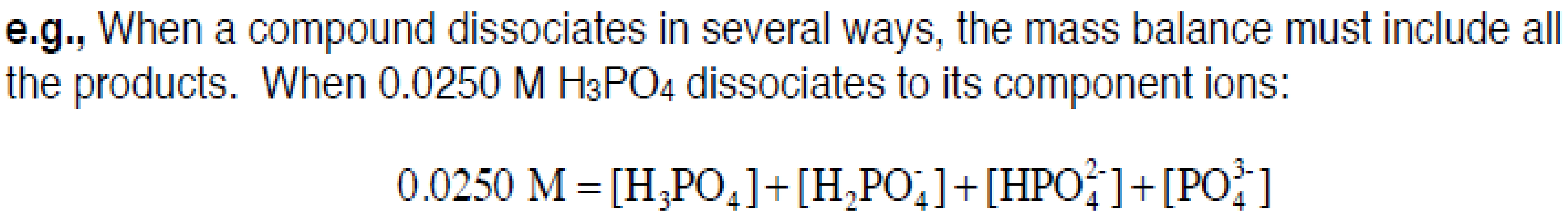
mass balance : $0.050M = [CH_3COOH] + [CH_3COO^-]$

2) Aqueous solution of $La(IO_3)_3$

	$La(IO_3)_3$ =	La^{3+} +	$3\ IO_3^-$
initial	solid	0	0
final	solid	x	$3x$

mass balance : $[IO_3^-] = 3\,[La^{3+}]$

- Concentration of IO_3 3 times the concentration of La^{+3}



e.g., When a compound dissociates in several ways, the mass balance must include all the products. When 0.0250 M H_3PO_4 dissociates to its component ions:

$$0.0250\ M = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

Charge balance

- The charge balance is the sum of the positive charges in an electrolyte solution equals the sum of the negative charges in solution.

- **Solution must have zero total charge**

- *To obtain the charge concentration of an ion, multiply the molar concentration of the ion by its charge.*

no. mol/L positive charge = no. mol/L negative charge

$$\Sigma[\text{positive charges}] = \Sigma[\text{negative charges}]$$

The general form of the charge balance for any solution:

$$n_1[C_1] + n_2[C_2] + \cdots = m_1[A_1] + m_2[A_2] + \cdots$$

where n_i = charge of the ith cation

$[C_i]$ = concentration of the ith **cation**

m_i = charge of the ith **anion**

$[A_i]$ = concentration of the ith **anion**

The concentration of charge contributed to a solution by an ion equals to the molar concentration of that ion multiplied by its charge.

For Na^+

mol positive charge/L = (mol Na^+/L) x (1 mol positive charge/mol Na^+)

$= 1 \times [Na^+]$

For Mg^{2+}

mol positive charge/L = (mol Mg^{2+}/L) x (2 mol positive charge/mol Mg^{2+})

$= 2 \times [Mg^{2+}]$

For PO_4^{3-}

mol negative charge/L = (mol PO_4^{3-}/L) x(3 mol negative charge/mol PO_4^{3-})

$= 3 \times [PO_4^{3-}]$

- Now consider how we would write a **charge-balance equation** for a **0.100 M solution of sodium chloride**.

- ✓ Positive charges are supplied by the Na^+ and the H_3O^+ (from the dissociation of water). Negative charges are supplied by the Cl^- and the OH^-. The molarities of positive and negative charges are

mol positive charge/L = $[Na^+] + [H_3O^+] = 0.100 + 1 X 10^{-7}$
mol negative charge/L = $[Cl-] + [OH^-] = 0.100 + 1 X 10^{-7}$

We write the charge-balance equation by equating the concentrations of positive and negative charges. That is,

$$\mathbf{[Na^+] + [H_3O^+] = [Cl^-] + [OH^-] = 0.100}$$

- Now consider how we would write a charge-balance equation for a 0.100 M solution of Magnesium chloride.

- ✓ Positive charges are supplied by the Mg^{+2} and the H_3O^+ (from the dissociation of water). Negative charges are supplied by the Cl^- and the OH^-. The molarities of positive and negative charges are

mol positive charge/L = $2[Mg^{+2}] + [H_3O^+] = (2 \times 0.100) + 1 \text{ X } 10^{-7}$
mol negative charge/L = $[Cl\text{-}] + [OH^-] = (2 \times 0.100) + 1 \text{ X } 10^{-7}$

- 1mole Magnesium contribute 2 moles of positive charge to the solution **(2 x 0.100)**
- The molar Chloride ion concentration is twice that of magnisium cholride concentration or **(2 x 0.100)**

$$\mathbf{2[Mg^{+2}] + [H_3O^+] = [Cl\text{-}] + [OH^-] = 0.200\ M}$$

Ex. 1. Charge balance of a solution containing

H^+, OH^-, K^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}

$$[H^+] + [K^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Ex. 2. Charge balance of a solution containing

H_2O, H^+, OH^-, ClO_4^-, $Fe(CN)_6^{3-}$, CN^-, Fe^{3+}, Mg^{2+}, CH_3OH, HCN, NH_3, NH_4^+

$$[H^+] + 3[Fe^{3+}] + 2[Mg^{2+}] + [NH_4^+] = [OH^-] + [ClO_4^-] + 3[Fe(CN)_6^{3-}] + [CN^-]$$

- **Neutral species (H_2O, CH_3OH, HCN, and NH_3) do not appear in the charge balance.**

Ex.3 Neglecting the dissociation of water, write a charge-balance equation for a solution that contains NaCl, $Ba(ClO_4)_2$, and $Al_2(SO_4)_3$.

$$[Na^+] + 2[Ba^{2+}] + 3[Al^{3+}] = [Cl^-] + [ClO_4^-] + 2[SO_4^{2-}]$$

Calculate the solubility of $Mg(OH)_2$ in water? $Ksp = 7.1 \times 10^{-12}$.

$$Mg(OH)_2 = Mg^{2+} + 2OH^{-}$$

final	solid	x	$2x$

$7.1 \times 10^{-12} = x\,(2x)^2$

$X = 1.2 \times 10^{-4}$ (larger than 1×10^{-7}; OH^- from water)

What is the solubility of $Fe(OH)_3$?

Ksp= 2×10^{-39}

$$Fe(OH)_3 \;=\; Fe^{3+} + 3OH^-$$

Common Ion

$$x \qquad\qquad 10^{-7}$$ (From H_2O dissociation)

- **OH^- from H_2O is much larger that OH^- from solubility of Fe $(OH)_3$**

Ksp= $2 \times 10^{-39} = x\,(10^{-7})^3$

$X = 2 \times 10^{-18}$ M

Modified by

Dr. Mohammed Rasheed

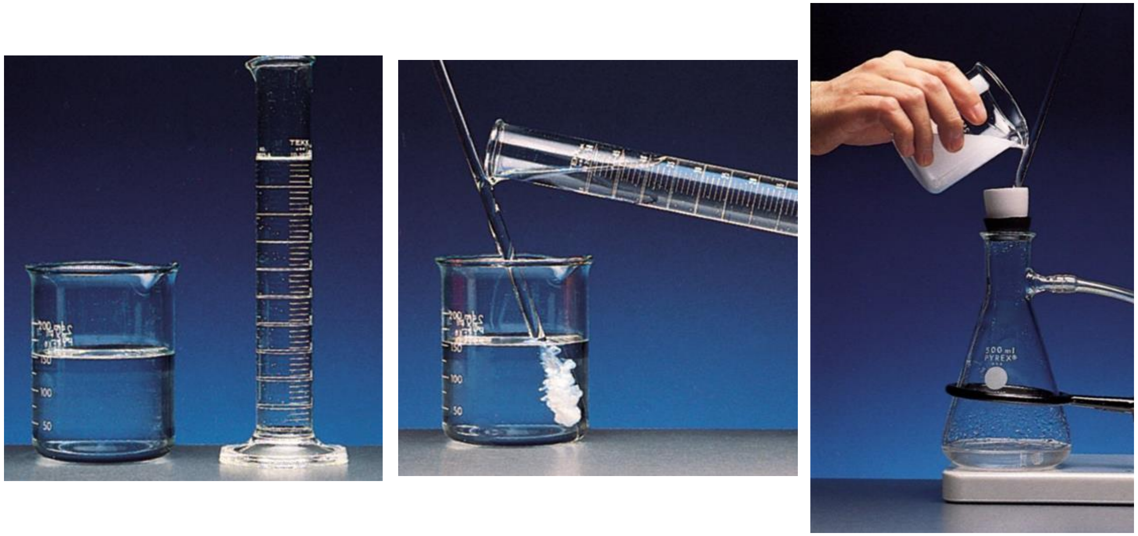
Chapter 12

Gravimetric Methods of Analysis

Gravimetric Analysis

❖ **Gravimetric analysis is an analytical technique based on the measurement of mass**

1. Dissolve unknown substance in water
2. React unknown with known substance to form a precipitate
3. Filter and dry precipitate
4. Weigh precipitate
5. Use chemical formula and mass of precipitate to determine amount of unknown ion



➢ **Advantages of Gravimetric analysis**

1. Accuracy

2. Single fundamental chemical precipitation reaction

ex: Cl- + Ag+ → AgCl(s)

3. Require no accuracy known standard solution

Gravimetry

Gravimetric methods are quantitative methods that are based on determining the mass of pure compound to which the analyte is chemically related.

1- Precipitation gravimetry: the analyte is separated from a solution of the sample as **a precipitate** and is converted to a compound of known composition that can be weighed.

Example: $\mathbf{Ba^{2+} + SO4^{2-} \rightarrow BaSO4\ (s)}$

ex: For Calcium in natural water

$$2NH_3 + H_2C_2O_4 \rightarrow 2NH_4^+ + C_2O_4^{2-}$$

$$Ca^{2+}(aq) + C_2O_4^{2-}\ (aq) \rightarrow CaC_2O_4\ (s)$$

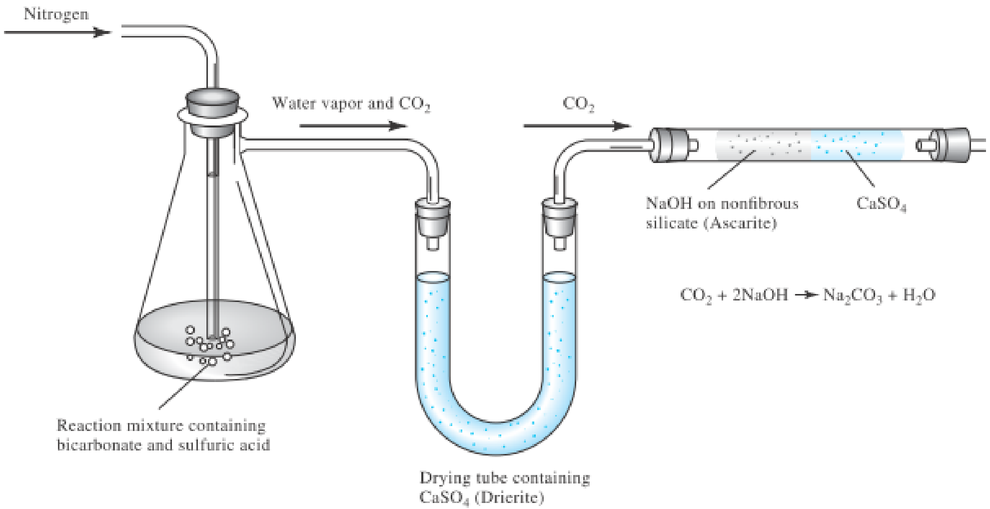
$$CaC_2O_4 \xrightarrow{\Delta} CaO(s) + CO(g) + CO_2(g)$$

- **Measure the mass of CaO to determine Ca^{2+}**

2- Volatilization gravimetry: the analyte is separated from other constituents of a sample by conversion to a **gas of known chemical composition**. The weight of this gas then serves as a measure of the analyte concentration.

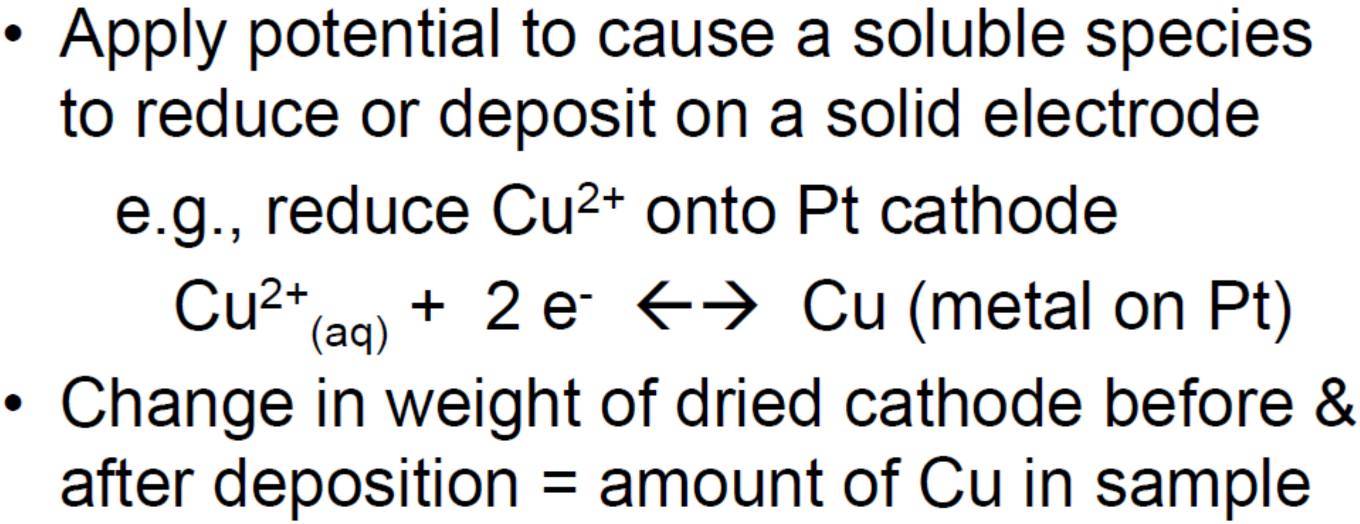
ex: For $NaHCO_3$ in antacid tablets

$$NaHCO_3(aq) + H_2SO_4\ (aq) \rightarrow \underset{\substack{\downarrow \\ \text{absorption tube}}}{CO_2\ (g)} + H_2O\ (l) + NaHSO_4(aq)$$



Example: Determining the water content of a compound can be determined by vaporizing the water using heat.

3- Electrogravimetry: the analyte is separated by deposition on an electrode by electrical current. The mass of this product then provides a measure of the analyte concentration.



- Apply potential to cause a soluble species to reduce or deposit on a solid electrode

  e.g., reduce Cu^{2+} onto Pt cathode

  $Cu^{2+}_{(aq)} + 2\ e^- \leftarrow\rightarrow$ Cu (metal on Pt)

- Change in weight of dried cathode before & after deposition = amount of Cu in sample

12A-1 Properties of Precipitates and Precipitating Reagents

- A gravimetric **precipitating agent** should react **specifically** or at least **selectively** with the **analyte** and give **precipitates** that is:

1. Enough **particle size** for retaining on filter paper
2. High **purity** (free of contaminants)
3. **Low solubility** that no significant loss of the analyte occurs during filtration and washing
4. Unreactive with air **(stable)**
5. **Known stoichimetric composition** after it is dried or, if necessary, ignited.

Precipitating Reagents:

- **Specific reagents: react only with a single chemical species.**
- **Selective reagents: react with a limited number of species.**

- **Example;** $AgNO_3 \rightarrow Cl^-, Br^-, I^- \ \& \ SCN^-$

12A-2 Particle Size and Filterability of Precipitates

➢ *Characteristics of Ion, colloid and particle*

➢ The particle size of solids formed by precipitation varies enormously.

1. At one extreme are **colloidal suspensions**, whose tiny particles are invisible to the naked eye **(10^{-7} to 10^{-4} cm in diameter**). Colloidal particles show no tendency to settle from solution and are difficult to filter. **ex: $Fe(OH)_3$ (Gelatinous).**
2. At the other extreme are particles with dimensions on the order of tenths of a millimeter or greater. The temporary dispersion of such particles in the liquid phase is called a crystalline suspension. The particles of a **crystalline suspension** tend to settle spontaneously and are easily filtered. **ex: $BaSO_4$**

Name	Diameter	Characteristics
Ion	~10^{-8} cm (A°)	Dissolved
Colloid	10^{-7}~10^{-4} cm (nm-μm)	Suspended
Crystalline	>10^{-4}cm (μm)	**Settled from solution (filterable)**

❖ **Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities.**

What Factors Determine Particle Size?

- Precipitate formation has been studied for many years, but the mechanism of the process is still not fully understood. What is certain, however, is that the particle size of a precipitate is influenced by:

1. **Precipitate solubility,**
2. **Temperature,**
3. **Reactant concentrations,**
4. **The rate at which reactants are mixed.**

- The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called **relative supersaturation**, where

$$RSS = \frac{Q - S}{S}$$

Q: the concentration of the solute at **any instant**

S: the concentration solute **at equilibrium**

- **Experimentally, the particle size of a precipitate is inversely related with the Relative supersaturation;**

✓ **if Q-S/S is large then the precipitate will be colloidal**

✓ **If Q-S/S is small then the precipitate will be crystalline**

- **Relative supersaturation (RSS)**

How particles are formed (Mechanism)?

1. Supersaturated solution formed

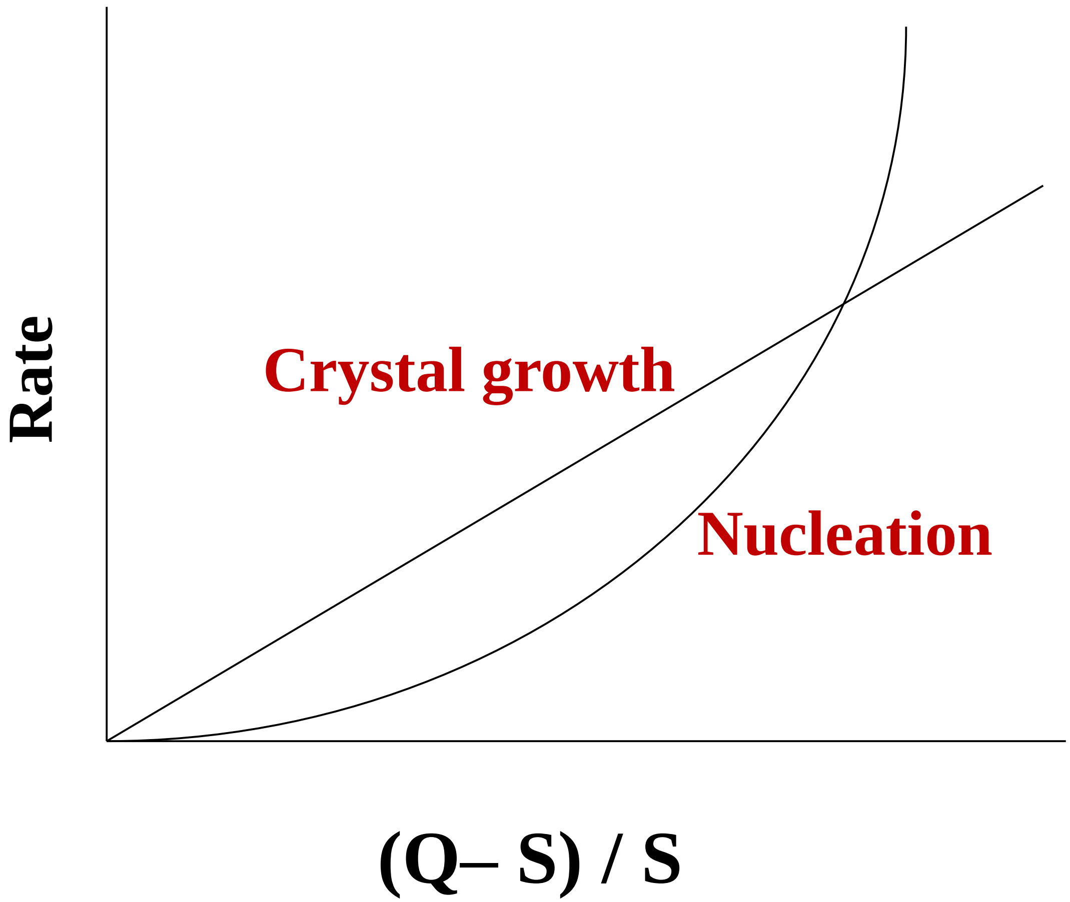
2. Nucleation: formation of a solid particle with a minimum number of atoms or molecules.

2. Particle growth: enlargement of existing particle (**Nuclei**) with new atoms or molecules

- Precipitates form by **nucleation and particle growth**
- More nucleation yields large number of small particles
- More growth yields small number of large particles

RSS	Process	Result
Large	Nucleation dominate	Smaller particles (colloidal)
Small	**Particle growth dominate**	**Larger Particle (Crystalline)**

- **nucleation rate, increases exponentially with increasing supersaturation while rate of growth increases linearly**



- Techniques to decrease supersaturation (promote particle growth)

❖RS↓, Q↓, S↑ → particle size ↑

1. Dilute sample soln and dilute reagents (Q↓)

2. **Slow addition** of precipitating agent with **good stirring** (Q↓)

3. Keeping the volume of solution large so that the concentration of analyte and precipitant are low (Q↓)

4. Heating to increase S↑

5. pH control (If the solubility of the precipitate depends on pH) (S↑)

ex: precipitation of calcium oxalate

$$Ca^{2+} + C_2O_4^{2-} \leftrightarrows CaC_2O_4\,(s)$$

$$H_2C_2O_4 \leftrightarrows 2\,H^+ + C_2O_4^{2-}$$

- **If H^+ present the ppt and H^+ will react to form $H_2C_2O_4$.**

a. After dissolving a sample that contains Ca^{2+}, the solution is made acidic with HCl. Because the solution is acidic, a precipitate of CaC_2O_4 does not form

b. adding aqueous ammonia → pH↑ →. After several minutes, a precipitate of CaC_2O_4 begins to form, with precipitation reaching completion in about 30 min.

- **Precipitates with very low solubilities, such as many sulfides and hydrous oxides, generally form a colloids.**

12A-3 Colloidal Precipitates

- ➢ Individual colloidal particles are so small that they are not retained by ordinary filters and particle motion prevents settling. Therefore, **Coagulation of colloids is needed**.
- **Coagulation** of colloids: converting a colloid suspension into a filterable solid. (*When liquid starts to thicken and become solid, it coagulates)*

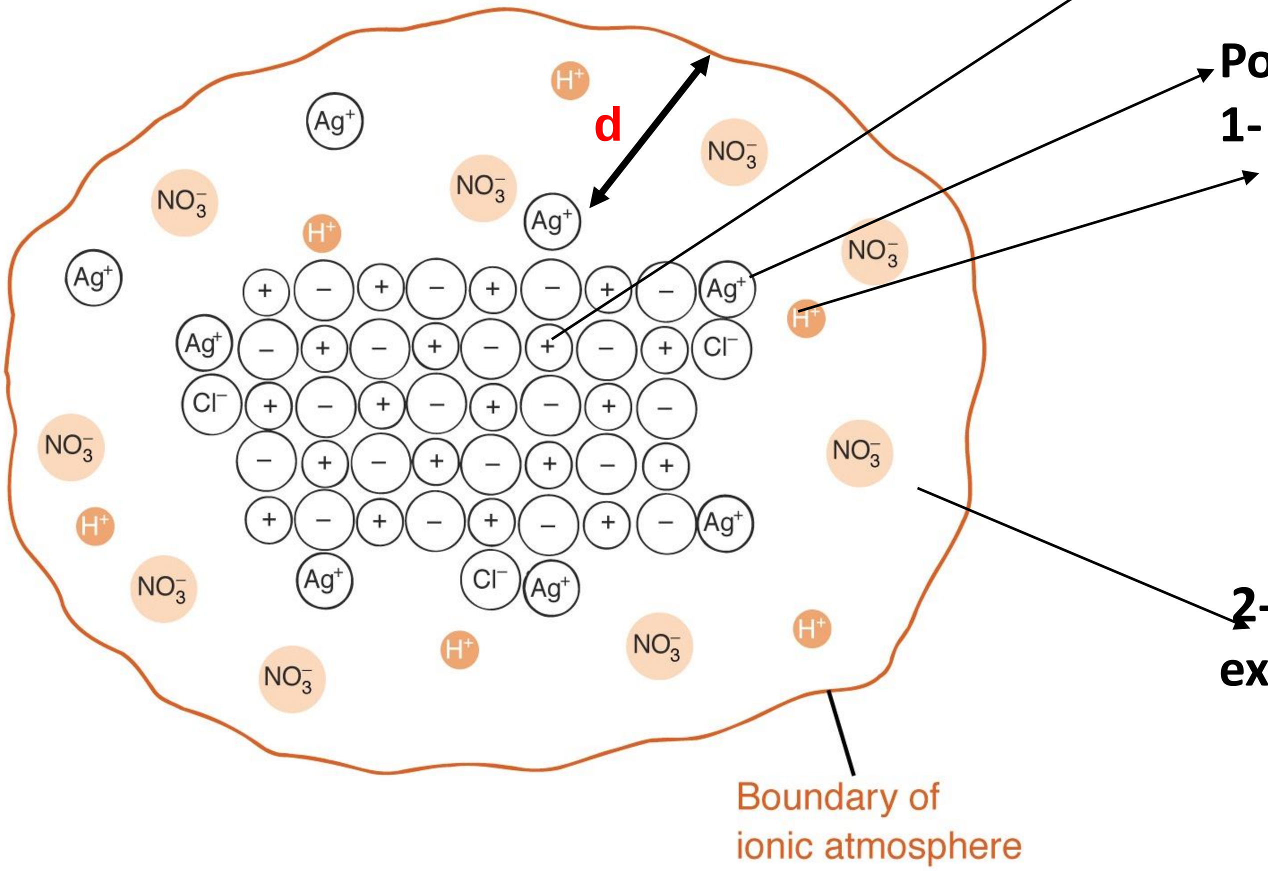
➢ Coagulation of Colloids

- ✓ Coagulation can be accelerated by **heating, stirring, and adding an electrolyte** (like HNO_3) to the medium.
- ✓ **Colloidal suspensions are stable** because all the particles present are either **positively or negatively charged**
- ✓ **Adsorption**: a process in which a substance (gas, liquid or solid) is held on the surface of a solid. In contrast, **absorption**, involves retention of a substance within the pores of a solid.
- ✓ The effective charge on a colloidal particle formed in a gravimetric analysis is determined by the charge of the lattice ion that is **in excess** when the precipitation is complete

Coagulation of colloids:

$Ag^+ + Cl^-$ (Analyte)= AgCl **Excess $AgNO_3$** (Precipitating agent)

Figure 12.1 A colloidal silver chloride (AgCl) suspended in a solution of **excess $AgNO_3$**



Silver chloride colloidal lattice

Positively charged (H^+ & Ag^+

1- Primary adsorption layer

2- Counter ion layer with excess anion (mainly NO_3^-)

- These layers (adsorption and counter ion) constitute an electric double layer that impacts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering.

- **Primary adsorbed layer**

Primary adsorbed ion:

1. lattice ions which **are in excess**
2. held by chemical bound
3. fixed on precipitate surface

AgCl in excess Ag^+ → AgCl (s) : **Ag^+**

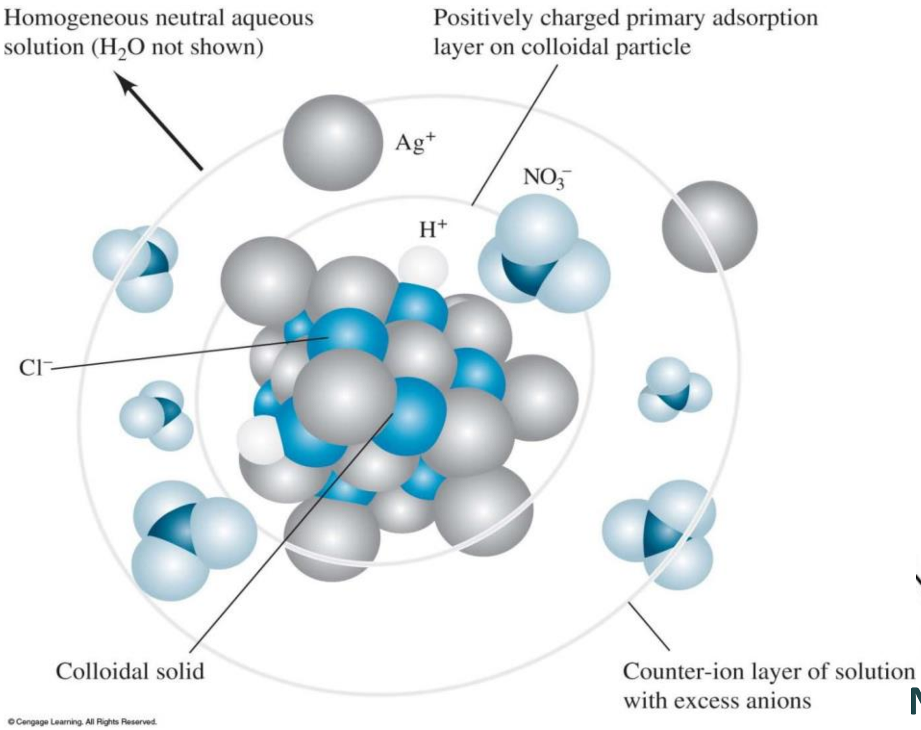
- **Counter-ion layer**

Counter-ions

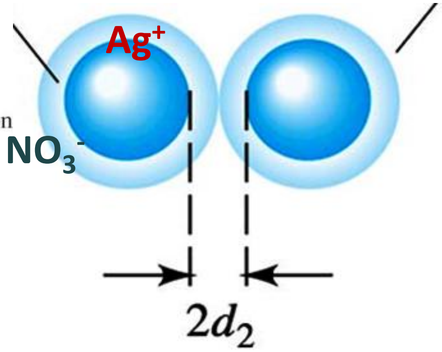
1. **opposite charge** of primary adsorbed ion
2. held by electrostatic attraction
3. loosely held in soln surrounding the ppt

AgCl in excess $AgNO_3$ → AgCl:Ag^+ · · · **NO_3^-**

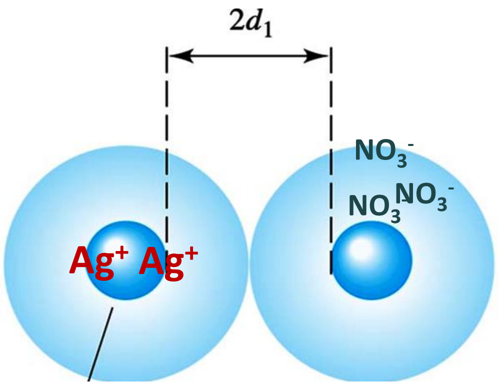
- **As colloidal particles approach one another, the Electrical double layer exerts an electrostatic repulsive force that prevents particles from adhering**



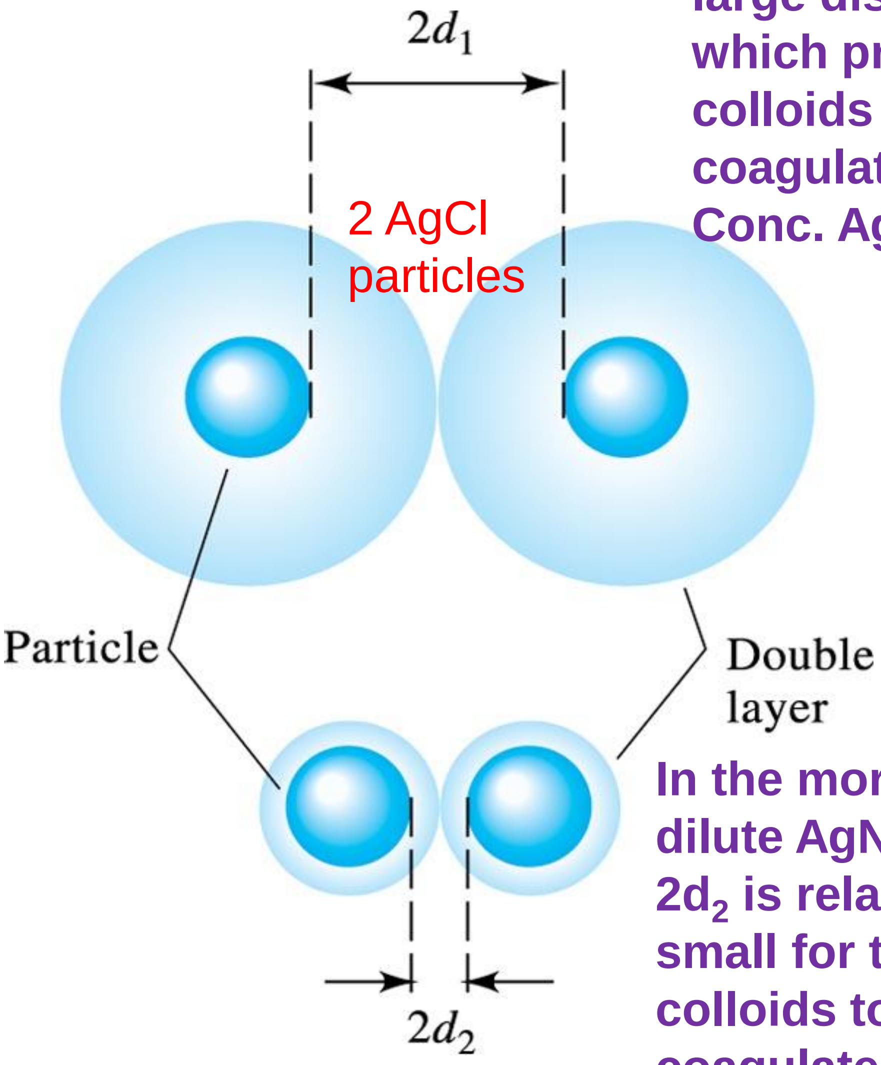
1- Suppose that we have excess of Ag^+ ions as first adsorption layer. If the number of the counter-ions (e.g NO_3^-) in the layer is approximately equal the number of adsorbed ions on the surface of the particles then **d is minimum**.



NO_3^- ions in the first counter ion layer are almost equal to Ag^+ ion



NO_3^- ions in the first counter ion layer are much less equal to Ag^+ ions, so we need more than one layer to equalize the positive Ag ion of the first adsorbed layer



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2 d_1 is very large distance which prevent colloids to coagulate. Conc. $AgNO_3$

In the more dilute $AgNO_3$, $2d_2$ is relatively small for the colloids to coagulate

- The upper portion of Figure 12-3 depicts two silver chloride particles and their counter- ion layers as they approach each other in the concentrated silver nitrate just considered. Note that the effective charge on the particles prevents them from approaching one another more closely than about 2*d1—a distance that is too great for* coagulation to occur.
- As shown in the lower part of Figure 12-3, in the more dilute silver nitrate solution, the two particles can approach within 2*d2 of one another.* Ultimately, as the concentration of silver nitrate is further decreased, the distance between particles becomes small enough for the forces of agglomeration to take effect And a coagulated precipitate to appear.

- **Diluted $AgNO_3$ (*Precipitating Reagents*) is desirable to have small d**

Figure 12-3 The electrical double layer of a colloid consists of a layer of charge adsorbed on the surface of the particle (the primary adsorption layer) and a layer of opposite charge (the counter-ion layer) in the solution surrounding the particle. Increasing the electrolyte concentration has the effect of decreasing the volume of the counter-ion layer, thereby increasing the chances for coagulation.

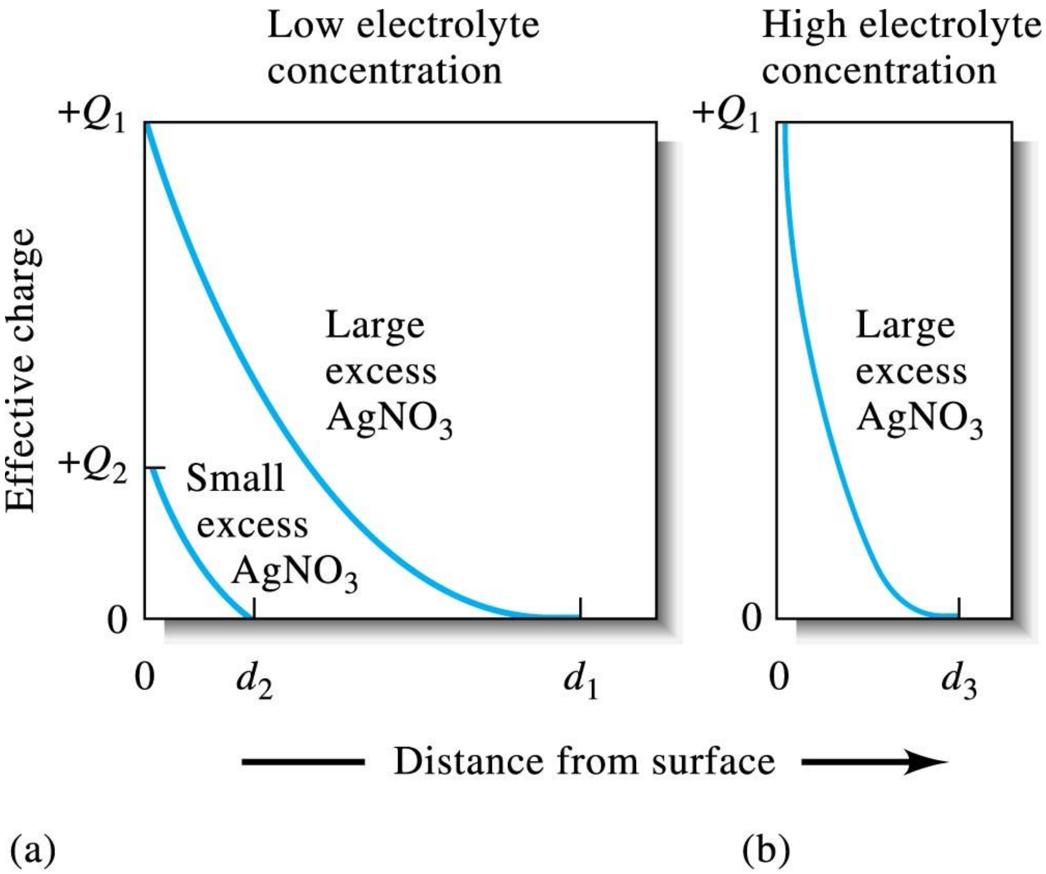

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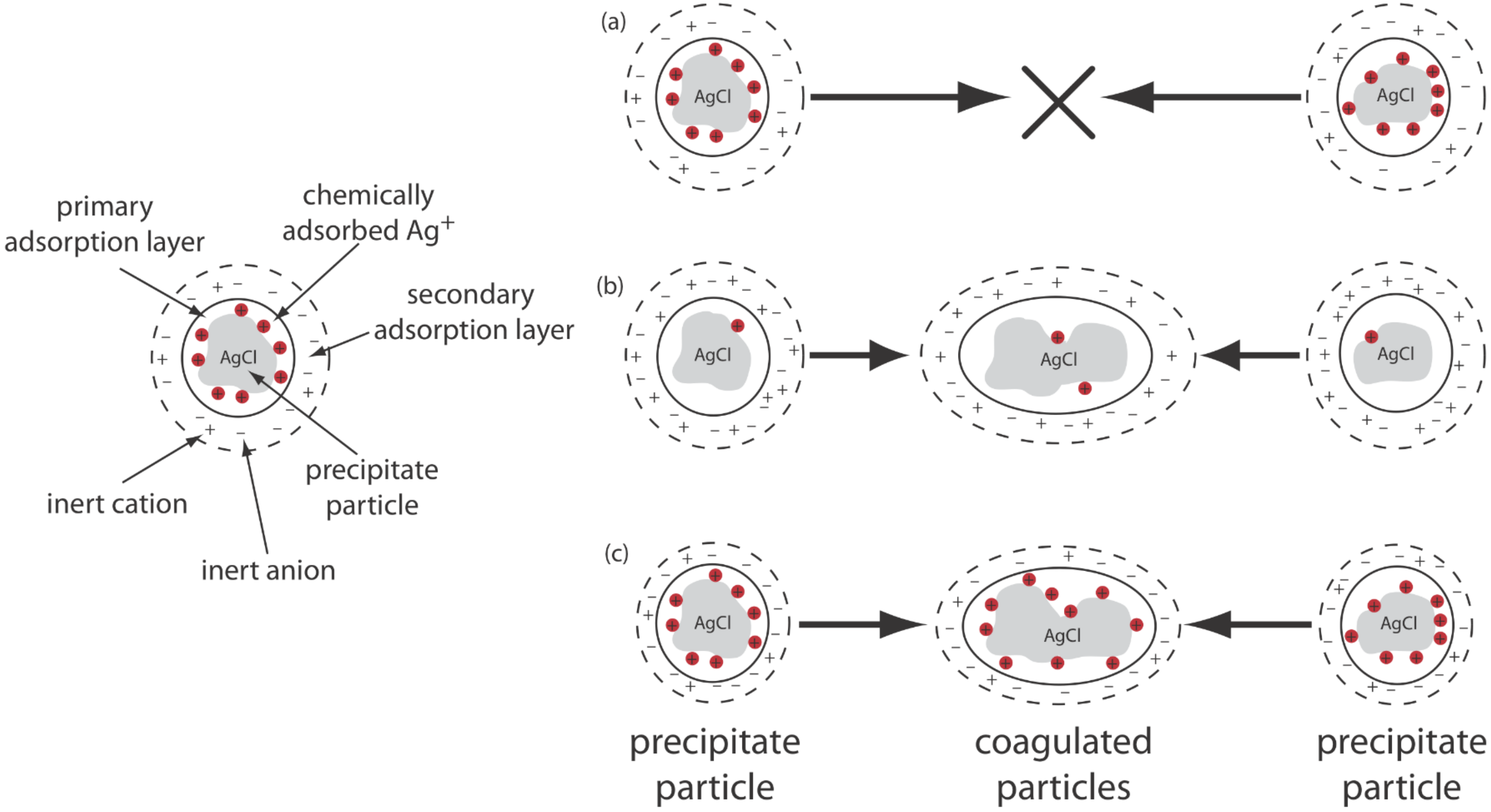
Figure 12-2 Effect of $AgNO_3$ and **electrolyte** concentration on the thickness of double layer surrounding a colloidal AgCl particle in a solution containing excess $AgNO_3$.

- Effective charge Q is the measure of the repulsion between the colloids

- The effective charge can be thought as a measure of the repulsive force that the particle exerts on like particles in the solution.

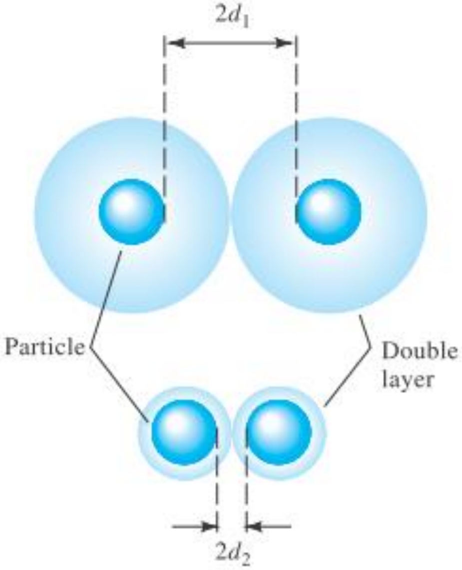
Q is dropped rapidly when **high inert electrolyte such as HNO_3 is present even if there is large excess of** $AgNO_3$. Note that the effective charge falls off rapidly as the distance from the surface increases, and it approaches zero at the points *d1 or d2.* because the number of the counter-ions in the layer is approximately equal the number of adsorbed ions on the surface of the particles.



Two methods for coagulating a precipitate of AgCl. (a) Coagulation does not occur due to the electrostatic repulsion between the positively charged particles. (b) Decreasing the charge within the primary adsorption layer, by adding additional NaCl, decreases the electrostatic repulsion and allows the particles to coagulate. (c) Adding additional inert ions decreases the thickness of the secondary adsorption layer. Because the particles can approach each other more closely, they are able to coagulate.

Coagulation of a colloidal suspension

1. **heating**
   - a. **Decrease** the number of the adsorbed ions and the thickness d1 of the double layer
   - b. gain enough kinetic energy to overcome the barrier to close approach posed by the double layer.
2. **Stirring**
3. **adding an electrolyte**: conc. of counter ions increase → shrinkage of the counter-ion layer → particle can then approach one another more closely and agglomerate.



Peptization of Colloids

Peptization : a process by which a coagulated colloid returns to its dispersed state.

washing coagulated colloid
→ removal of the inert electrolyte
→ volume of the counter-ion layer increase and the repulsive forces are then reestablished and the particles detach themselves from the coagulated mass.

- Peptization is prevented by **washing ppt with a solution of a volatile electrolyte when the ppt is dried or ignited.**

ex: AgCl, washed with a diluted HNO_3 which is volatilized during drying

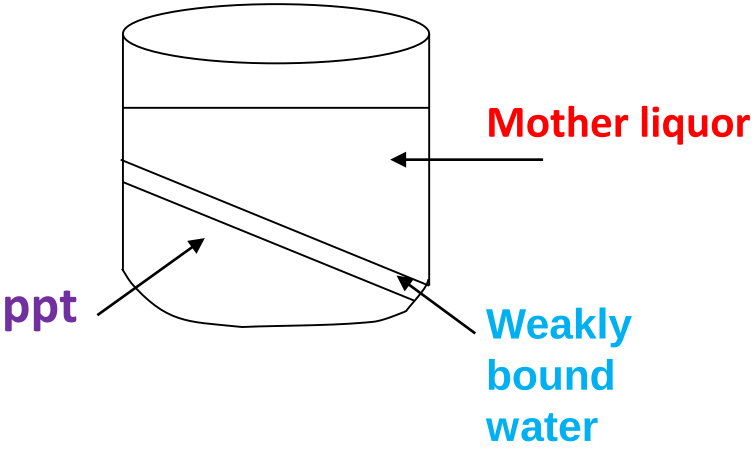
Washing with volatile solution:

ex: in Ag^+ analysis, primary adsorbed ion: Cl^-
Washing with an acidic soln → counter-ion layer: H^+
→ HCl volatilized when ppt is dried

Treatment of Colloidal Precipitates

- **Digestion** : a process in which a ppt is heated for an hour or more in the solution from which it was formed (the mother liquor).

❖ Through digestion; weakly bound water appears to be lost from the precipitate. The result is a denser mass that is easier to filter.



This would increase purity and filterability

1. colloidal suspension → coagulated to curdy ppt
2. small crystalline particles → reprecipitated on the large crystalline particles (**Double precipitation**)
3. **impurities tend to dissolve** → pure crystalline particles

☐ Digestion (without stirring) improves the purity and filterability of crystalline solids. This process start recrystallization by building bridges between adjacent particles.

12 A-4 Crystalline Precipitates

- Crystalline precipitates are generally more easily filtered and purified than coagulated colloids

- **Improving Particle Size and Filterability**

☐ The particle size and filterability of crystalline solids can be improved by minimizing Q and/or maximizing S

1. Dilute sample soln and dilute reagents (Q↓)
2. **Slow addition** of precipitating agent with **good stirring** (Q↓)
3. In hot solution (S↑)
4. Keeping the volume of solution large so that the concentration of analyte and precipitant are low (S↑)
4. pH control, acidity solution (S↑)

12A-5 Coprecipitation

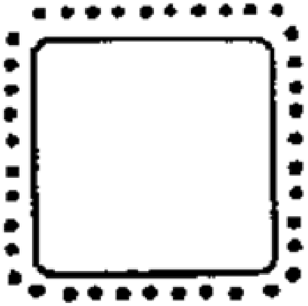
- Coprecipitation is a phenomenon in which otherwise soluble compounds are removed from solution during precipitate formation.
- Any contamination of a precipitate by a second substances whose Ksp is more than the target ppt does not constitute coprecipitation

Four types of coprecipitation:

1. **surface adsorption**
2. **mixed-crystal formation**
3. **occlusion**
4. **mechanical entrapment**

Sources of precipitates (contaminations):

1- Surface Adsorption



ex: in chloride analysis

primary adsorbed ion : Ag+

counter-ion layer : NO_3 or other anions

→ $AgNO_3$ (normally soluble) is coprecipitated with the AgCl.

*Methods for Minimizing Adsorbed Impurities on Colloids

a. Digestion:

particle size↑→ specific surface area↓→ adsorption↓

b. Washing with volatile electrolyte soln

ex: in Ag+ analysis, primary adsorbed ion : Cl washing with an acidic soln

→ counter-ion layer : H+

→ HCl volatilized when ppt is dried

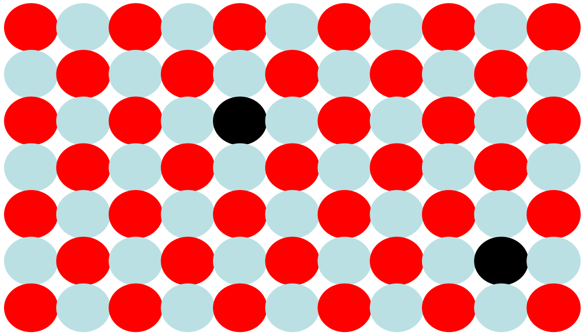
c. Reprecipitation, double precipitation; In this process, the filtered solid is re-dissolved and re-precipitated. This may add to the time required for the analysis but is often necessary.

Sources of precipitates (contaminations):

2- Mixed-Crystal Contamination

Type of coprecipitation in which a contaminant ion **replaces an ion** in the lattice of a crystal. This occurs usually for both crystalline precipitation and colloidal precipitation. Solved by using selective precipitating agent

- **a contaminant ion replaces an ion in the lattice of a crystal; the two ions should** have the same charge and almost the same size

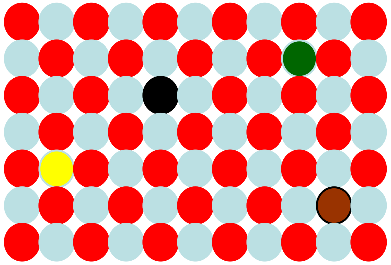


Ex: $BaCl_2$ + soln containing sulfate, lead & acetate → $BaSO_4$ + **Contaminants ($PbSO_4$ and lead acetate)**

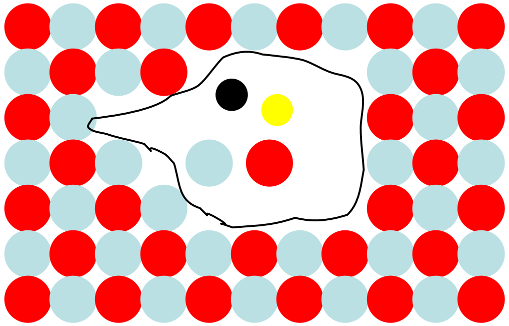
Can be solved by 1- Separating the interfering ion before the final precipitation 2- Using of different precipitating agents.

Sources of precipitates (contaminations):

3- Occlusion ; Compound is trapped or occluded within a pocket formed during rapid crystal growth. This occurs usually for crystalline precipitation. The occluded material usually greatest in the part of a crystal that form first.



4- Mechanical Entrapment; Several crystals grow together & in so doing trap a portion of the solution in a tiny pocket.



Both **Occlusion and Mechanical Entrapment** Solved by
1- minimize the rate of precipitate formation 2- digestion 3- reprecipitation

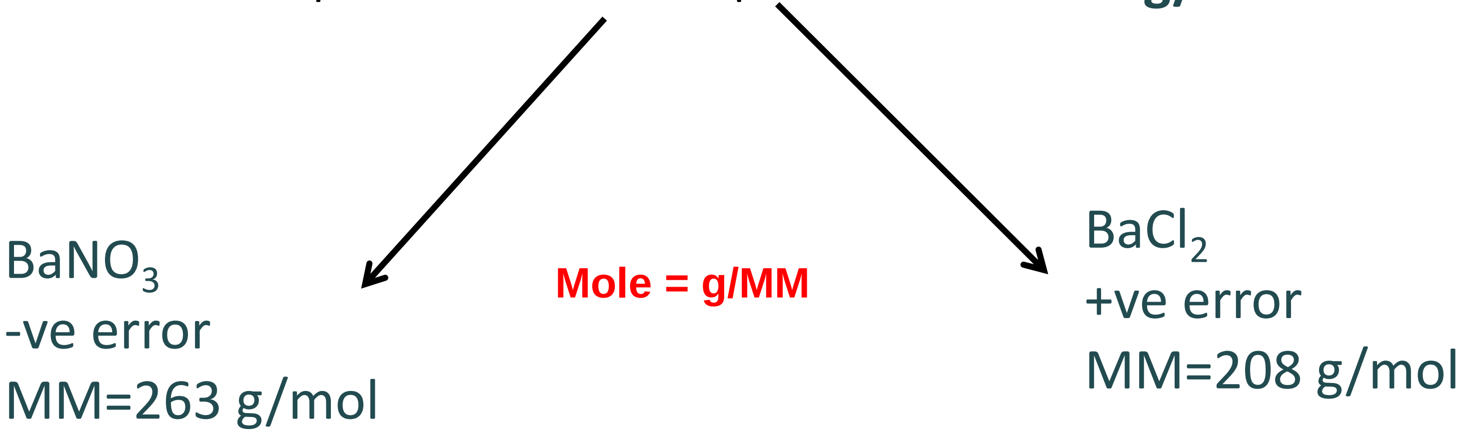
Coprecipitation error:

1) a positive error will always result from a contamination with species **that does not involve the analyte**.

2) positive or negative error always result if the coprecipitation **involves the analyte itself.**

Example: ppt $BaSO_4$ (s) (Ba^{2+} is the anlayte)

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4(s)$ **MM=233 g/mol**



$BaNO_3$
-ve error
MM=263 g/mol

Mole = g/MM

$BaCl_2$
+ve error
MM=208 g/mol

12A-6 Precipitation from Homogeneous Solution

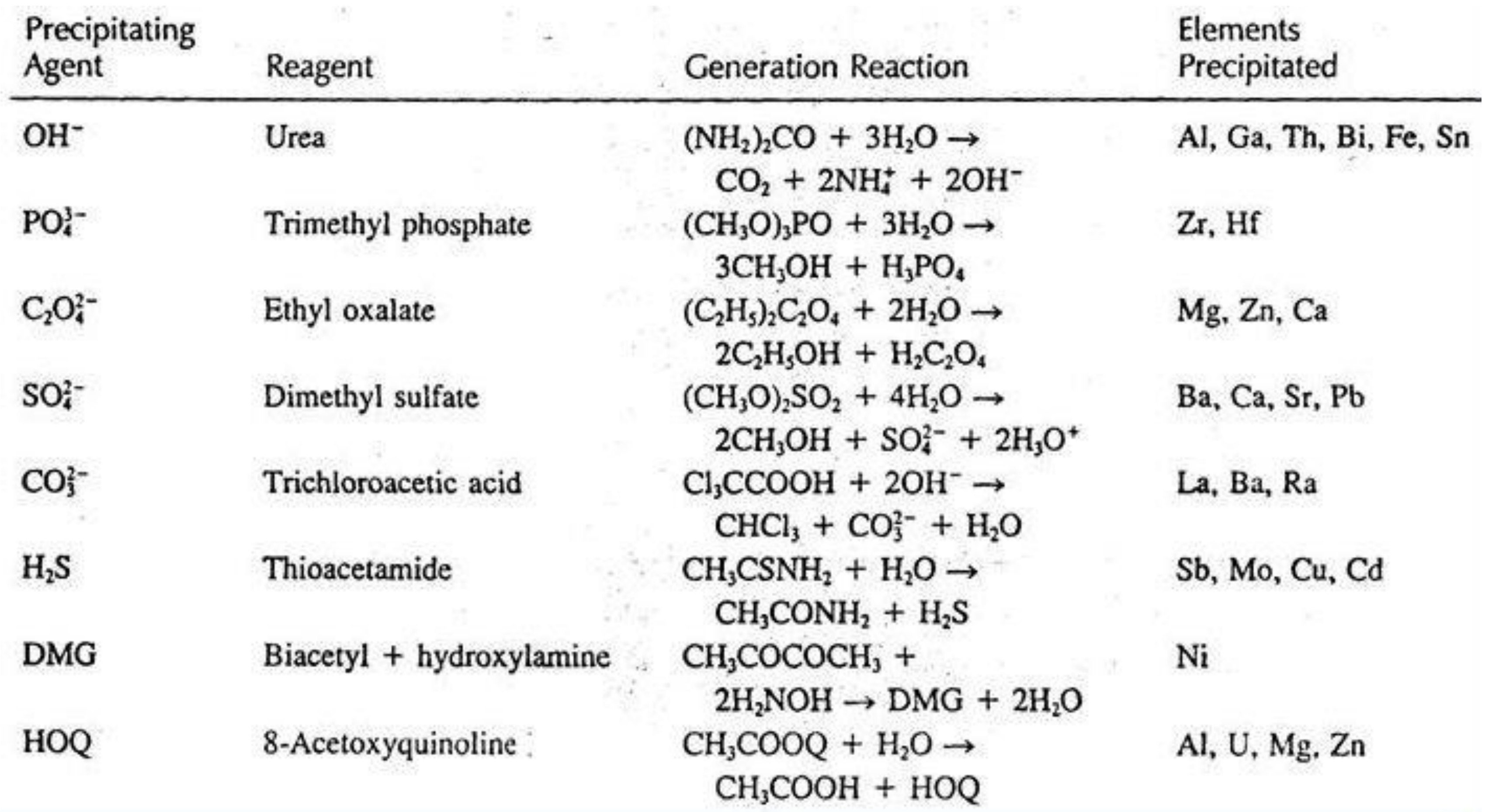
- Is a technique in which a **precipitating reagent is generated in a solution of the analyte by a slow chemical reaction**.

Ex: Urea → OH^- used for the precipitation of of Fe & Al

$(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + \mathbf{2OH^-}$

- **Solid formed by homogeneous precipitation are generally purer and more easily filtered than precipitate generated by direct addition of a reagent to the analyte solution.**

12A-6 Precipitation from Homogeneous Solution (Table 12-1)



Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ	8-Acetoxyquinoline	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

Filtration

1.Sintered-glass filtering crucible: 110 °C～250 °C

crystalline or granular type ppt

pore: **coarse, medium, fine**

2. Gooch crucible with an asbestos mat: 800 °C～1000 °C

3. Filter paper

ashless filter paper : residue **< 0.1 mg**.

Washing the Precipitate

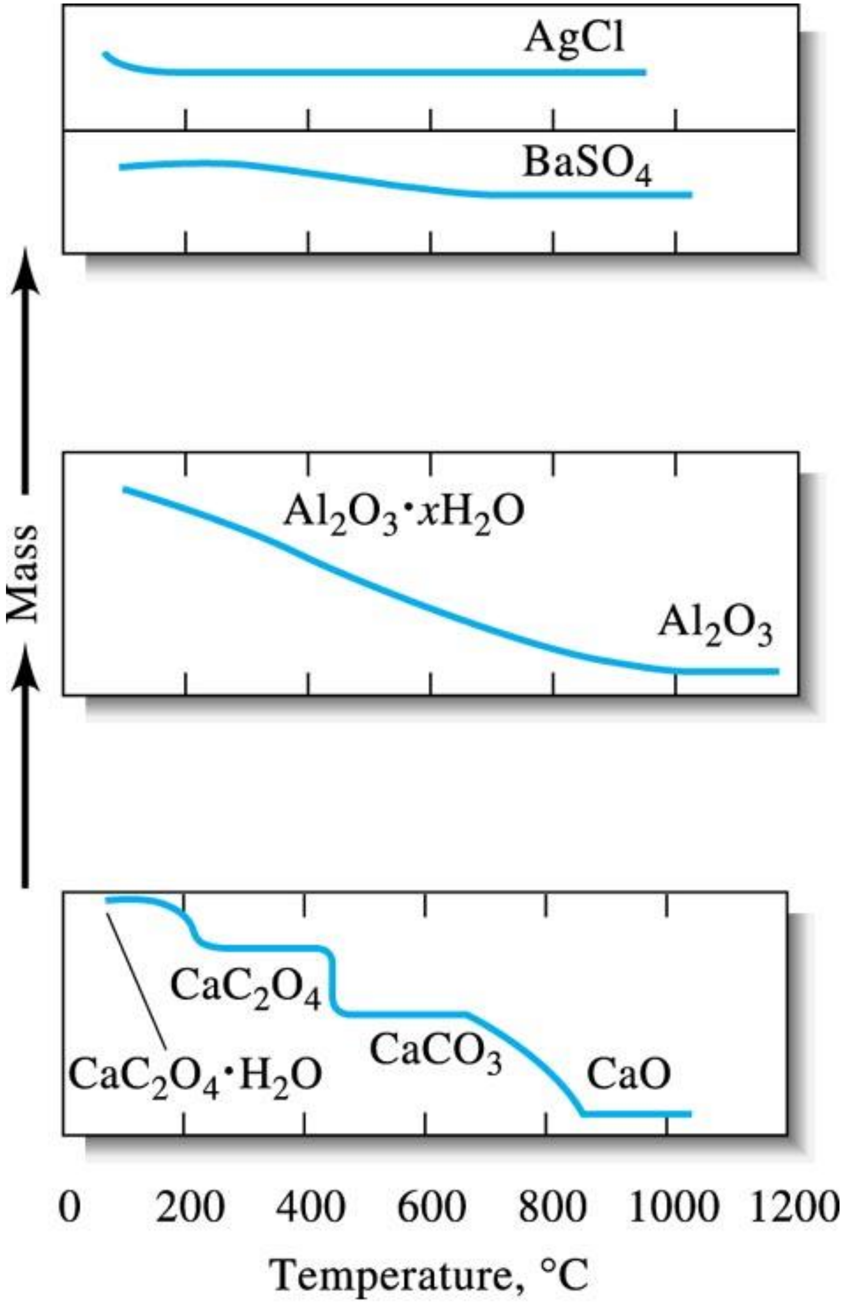
washing solution prop.

1. Wash out all impurity but leave it unchanged in composition.
2. Not introduce insoluble product into ppt
3. completely volatile at drying temp of ppt

- pure water → peptization
- electrolyte solution

12 A—7: Drying and Ignition of Precipitates

- After filtration, a gravimetric precipitate is heated until its mass is constant (**weighing form**). This remove the solvent and any volatile species carried down with the precipitate.



Effect of temperature on precipitate mass

Q12-1 **The calcium** in a 200.0ml sample of natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty mass of 26,6002g**. The mass of crucible plus CaO (56,077g/mol) was 26,7134g.** Calculate the concentration of Ca (40,078g/mol) in water in units of grams per 100ml of water?

1- The mass of CaO = 0.1123

2- mole Ca = mole CaO; then **mole of CaO = 2.0186 x 10^{-3}**

3- mass Ca = 0.081 g in the total soln

4- then we have 0.0404 g/100ml

12-2 An iron ore was analyzed by dissolving a **1.1324 gram sample** in concentrated HCl. The resulting solution was diluted with water and the iron III (Fe^{+3}) was precipitated as hydrous oxide ($Fe_2O_3 \cdot xH_2O$) by the addition of ammonia. After the filtration and washing, the residue was ignited at a high temperature to give **0.5394 gram of pure ferric oxide (Fe_2O_3; MM = 159.69).** Calculate

a) the percentage of iron in the original sample (MM= 55.847 g/mol),

b) and the percentage of Fe_3O_4 in the original sample (MM= 231.54 g/mol).

The mole of **Fe_2O_3 = 3.3778×10^{-3}.**

a) 1- Mole Fe in the resulting oxide = 6.7556×10^{-3}.

2- mass Fe = 0.3773; % = 33.32%

b) 1- mole Fe_3O_4 = 2.2519×10^{-3}.

2- mass Fe_3O_4 = 0.52140 g.

% Fe_3O_4 = 46.04 %

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + \frac{1}{2}O_2$$

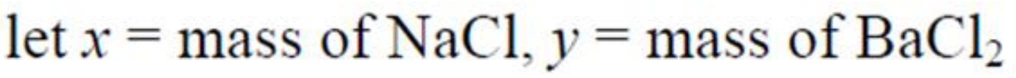
Ex: **A 0.703 g sample** of a commercial detergent was ignited at a red heat to destroy the organic matter. The residue was then taken up in hot HCl which converted the P to H_3PO_4. The phosphate was precipitated as $MgNH_4PO_4.6H_2O$ by addition of Mg^{2+} followed by aqueous NH_3. After being filtered and washed, the precipitate was converted to **$Mg_2P_2O_7$ by ignition at 1000ºC. This residue weighed 0.432 g.** Calculate the percent P in the sample. (Mwt $Mg_2P_2O_7$ = 222.6 g/mol, atomic weights for P = 30.97 g/mol.

2 mol P = 1 mol $Mg_2P_2O_7$

mass P = 0.120g P

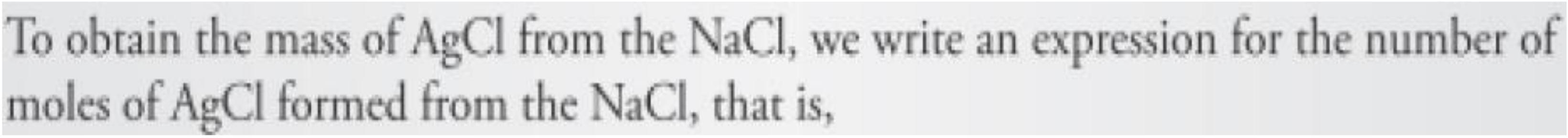
% P = 0.120 g/ 0.703 g × 100 = 17.1 %

Example: 0.2356 g sample containing **only** NaCl (MM= 58.44 g/mol) and $BaCl_2$ (MM= 208.23 g/mol) yielded **0.4637g of dried AgCl** (MM= 143.32 g/mole) ppt. Calculate the percent of each compound in the sample?


let x = mass of NaCl, y = mass of $BaCl_2$ → $x + y = 0.2356$ g 1

- **0.4637g the total mass of AgCl produced from both $BaCl_2$ and NaCl**

NaCl → AgCl
$BaCl_2$ → 2 AgCl

1- 24

To obtain the mass of AgCl from the NaCl, we write an expression for the number of moles of AgCl formed from the NaCl, that is,

- **Mole AgCl = mole NaCl + 2 mole $BaCl_2$**

0.4637g/143.32g/mole= x/58.44g/mole + 2 (y/208.23g/mole)

$x + y = 0.2356$ g ………. (1)

0.4637g/143.32g/mole= x/58.44g/mole + 2 (y/208.23g/mole)25 …………… (2)

3- Then substitute 1: the mass of AgCl =

3.23×10^{-3}g = x/58.44 g + ((0.2356 –x)/(208.23))g

x = 0.1296 g ; y = 0.106 g

% NaCl = 55.01%, % $BaCl_2$ = 44.99%

Example; A mixture of mercurous chloride (MW 472.09) and mercurous bromide (MW 560.99) weighs 2.00 g. The mixture is quantitatively reduced to mercury metal (At wt 200.59) which weighs 1.50 g. Calculate the % mercurous chloride and mercurous bromide in the original mixture.

- Again, important to set up correct equation:

$$1.50 = \frac{2*200.59*x}{472.09} + \frac{2*200.59(2-x)}{560.99}$$

- Rearranging and solving:

$$0.8498 + 0.7151(2-x) = 1.50$$

$$x = 0.5182g$$

Example: How many mL of 1% potassium chloride would be needed to precipitate all of the silver in a 0.5 g ore sample that contains 1.5 parts per thousand silver? Allow for a 50% excess of the chloride solution.

Consider a 1.0000 g sample containing 75% potassium sulfate (MW 174.25) and 25% MSO4. The sample is dissolved and the sulfate is precipated as BaSO4 (MW 233.39). If the BaSO4 ppt weighs 1.4900, what is the atomic weight of M2+ in MSO4?

$$1.4900 = \frac{0.75 * 233.39}{174.25} + \frac{0.25 * 233.39}{x + 96.06}$$

- Rearranging and solving:

$$0.4855 = \frac{58.3475}{x + 96.06}; x = 24.12(Mg^{2+})$$

7. A certain barium halide exists as the hydrated salt BaX2.2H2O, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 cm3) and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.

2. Which of the following processes is true regarding the digestion of a solution containing a precipitate?

(a) Digestion tends to increase particle size of the precipitate.
(b) Digestion is used to slow down the coagulation of a colloidal precipitate because of the increased energy added to the solution.
(c) A long digestion is not recommended because the higher temperatures enable impurities to become trapped in the crystal lattice of the precipitate

3. In the gravimetric analysis of iron, hydroxide may be added to a solution containing Fe^{3+} to precipitate a gelatinous mess which is ignited to form Fe_2O_3. If 0.2864 grams of Fe_2O_3 were formed from the ignition of the precipitated mess, how many grams of $FeCO_3$ were contained in the original sample analyzed?

(a) 0.4155 g $FeCO_3$
(b) The answer cannot be computed because the sample did not contain any Fe^{2+}.
(c) 0.2078 g $FeCO_3$

4 A sample of ore containing manganese weighed 1.2354 grams. This sample was heated in a solution of nitric acid, which dissolved the manganese ion producing manganese(III) nitrate ($Mn(NO_3)_3$). The acidity of the solution was adjusted, and Hydrogen sulfide gas was bubbled into the solution producing 0.2876 grams of manganese(III) sulfide (Mn_2S_3). What is the percentage of manganese in the original sample?

(a) 12.37% Mn
(b) 6.19% Mn
(c) 3.09% Mn

6 In Gravimetric Determination of Nickel, heating gently during the coagulation stage would aid what process?

a. Precipitation -- more Nickel diglyme would come out of solution.
b. Digestion -- particle size and purity increases due to recrystallization.
c. Evaporation -- the solution becomes more concentrated so more precipitation occurs and filtering is easier.
d. Calculation -- the waiting gives you time to work example problems and ask questions.

Applications to Gravimetric Analysis

1- By using inorganic precipitating agent

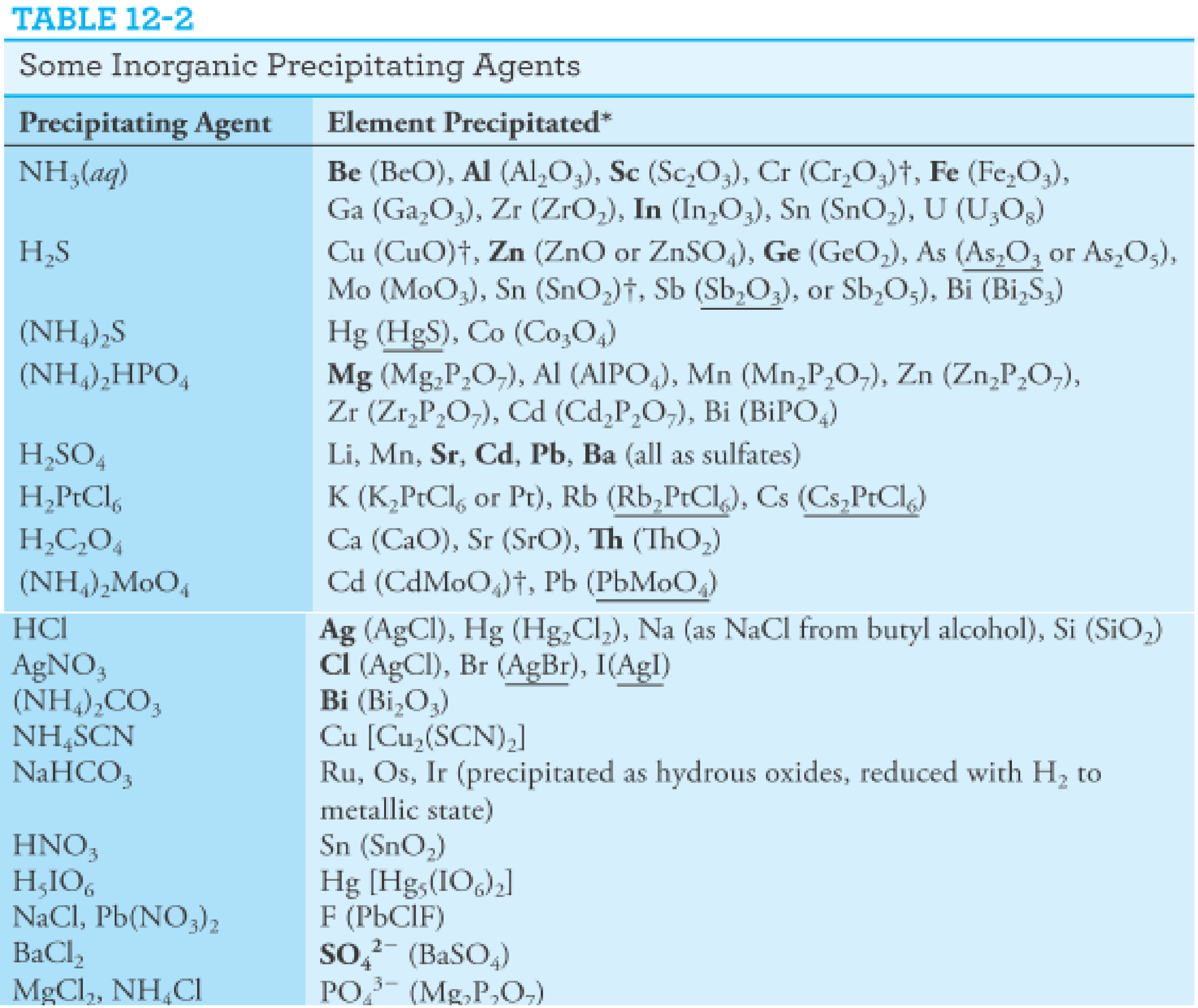


TABLE 12-2

Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), Cr (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO or $ZnSO_4$), **Ge** (GeO_2), As (As_2O_3 or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb (Sb_2O_3), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg (HgS), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr**, **Cd**, **Pb**, **Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6 or Pt), Rb (Rb_2PtCl_6), Cs (Cs_2PtCl_6)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($PbMoO_4$)
HCl	**Ag** (AgCl), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** (AgCl), Br (AgBr), I(AgI)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides, reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
NaCl, $Pb(NO_3)_2$	F (PbClF)
$BaCl_2$	**SO_4^{2-}** ($BaSO_4$)
$MgCl_2$, NH_4Cl	PO_4^{3-} ($Mg_2P_2O_7$)

2- Reducing agents

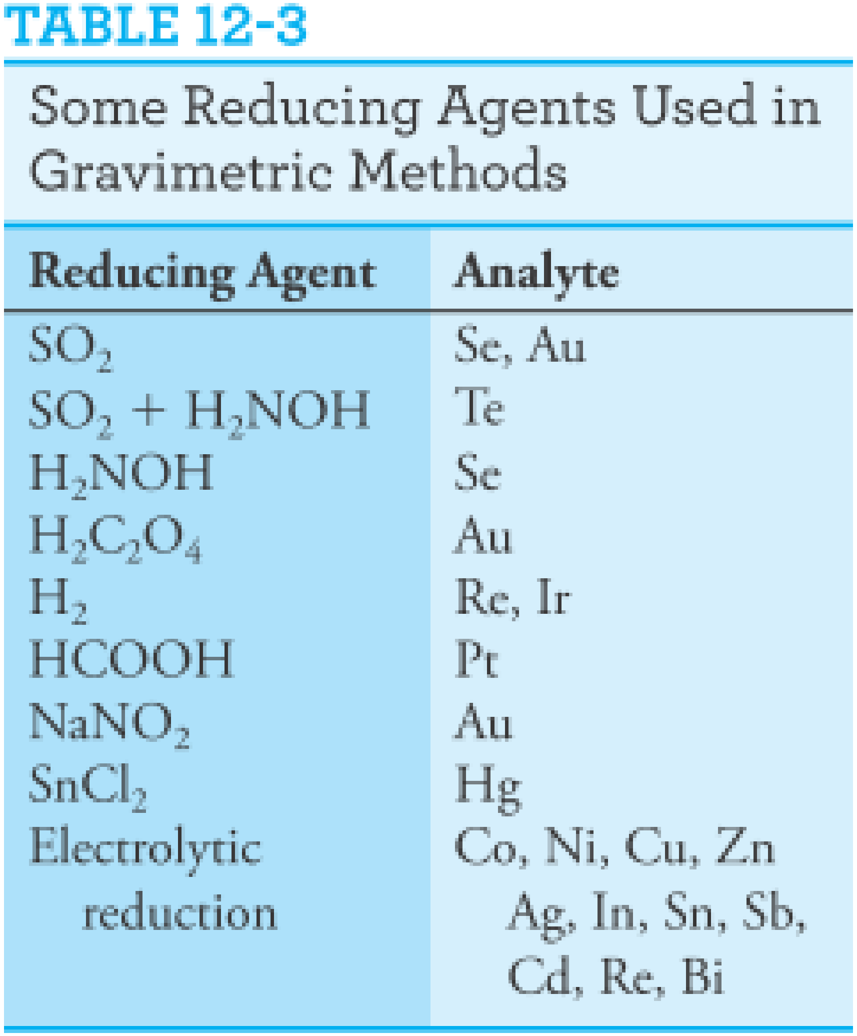
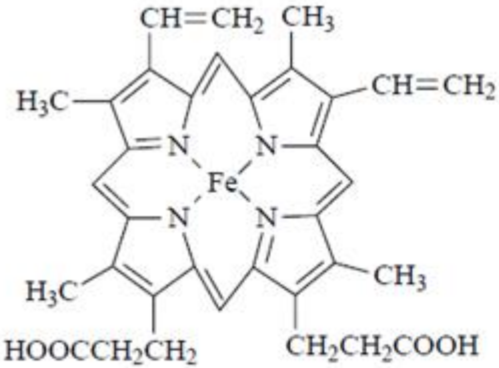


TABLE 12-3

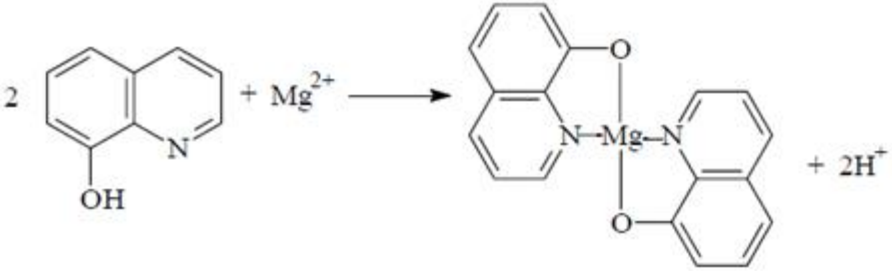
Some Reducing Agents Used in Gravimetric Methods

Reducing Agent	Analyte
SO_2	Se, Au
$SO_2 + H_2NOH$	Te
H_2NOH	Se
$H_2C_2O_4$	Au
H_2	Re, Ir
HCOOH	Pt
$NaNO_2$	Au
$SnCl_2$	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

12C-3 Organic precipitating agents



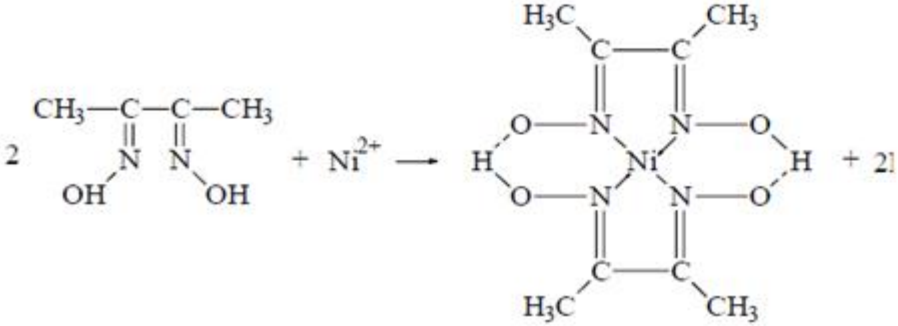
(a). Hydroxyquinoline(oxine):
24 cations



8-Hydroxyquinoline Mg 8-hydroxyquinolate

(b) Dimethylglyoxime:

specific for Ni^{2+}



(c) Sodium tetraphenylboron, $(C_6H_5)B^-Na$: for K^+ & NH_4^+

12C-4 Organic Functional Group Analysis

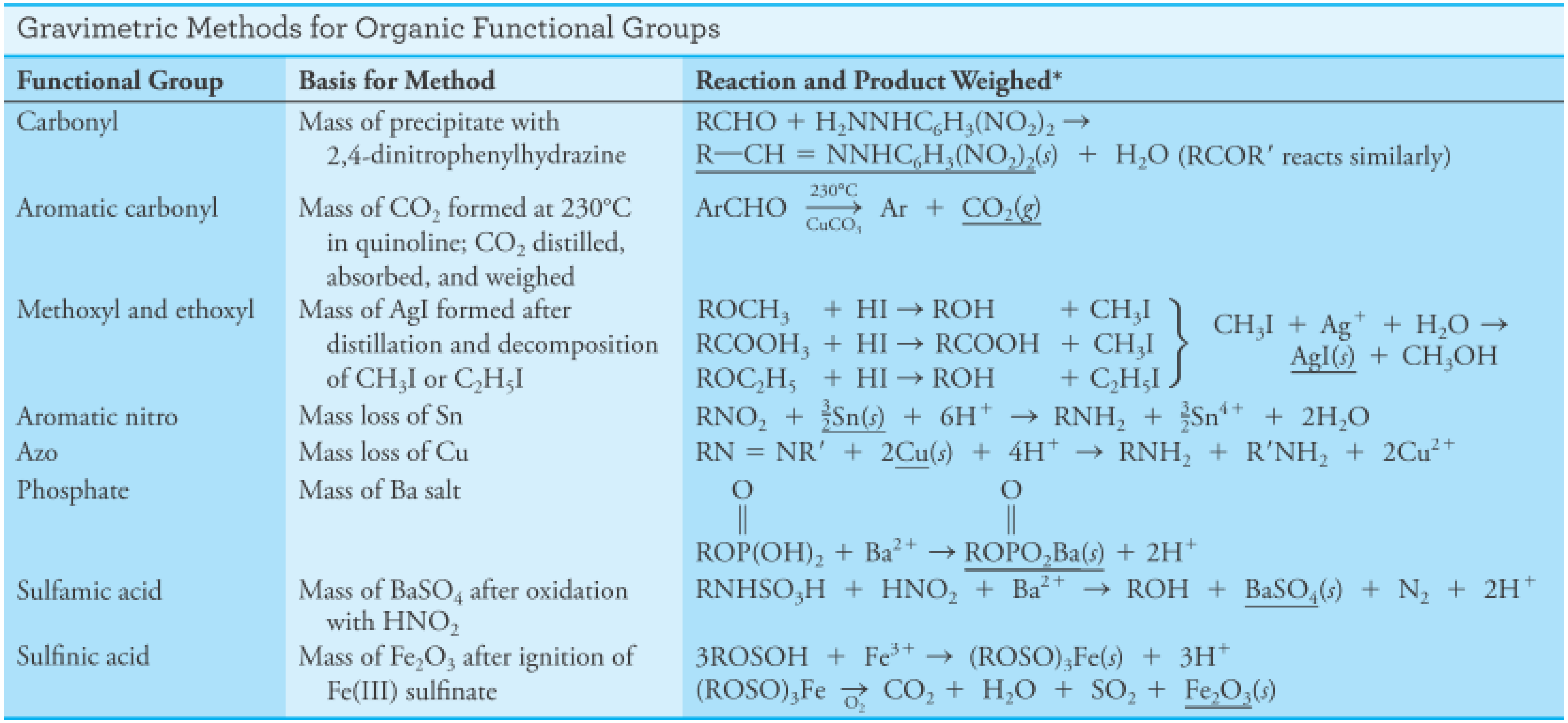


TABLE 12-4

Gravimetric Methods for Organic Functional Groups

Functional Group	Basis for Method	Reaction and Product Weighed*
Carbonyl	Mass of precipitate with 2,4-dinitrophenylhydrazine	$RCHO + H_2NNHC_6H_3(NO_2)_2 \rightarrow$ $\underline{R{-}CH = NNHC_6H_3(NO_2)_2}(s) + H_2O$ ($RCOR'$ reacts similarly)
Aromatic carbonyl	Mass of CO_2 formed at 230°C in quinoline; CO_2 distilled, absorbed, and weighed	$ArCHO \xrightarrow[CuCO_3]{230°C} Ar + \underline{CO_2(g)}$
Methoxyl and ethoxyl	Mass of AgI formed after distillation and decomposition of CH_3I or C_2H_5I	$\left.\begin{array}{l} ROCH_3 + HI \rightarrow ROH + CH_3I \\ RCOOH_3 + HI \rightarrow RCOOH + CH_3I \\ ROC_2H_5 + HI \rightarrow ROH + C_2H_5I \end{array}\right\}$ $CH_3I + Ag^+ + H_2O \rightarrow \underline{AgI(s)} + CH_3OH$
Aromatic nitro	Mass loss of Sn	$RNO_2 + \underline{\tfrac{3}{2}Sn(s)} + 6H^+ \rightarrow RNH_2 + \tfrac{3}{2}Sn^{4+} + 2H_2O$
Azo	Mass loss of Cu	$RN = NR' + 2\underline{Cu}(s) + 4H^+ \rightarrow RNH_2 + R'NH_2 + 2Cu^{2+}$
Phosphate	Mass of Ba salt	$RO\overset{\overset{O}{\Vert}}{P}(OH)_2 + Ba^{2+} \rightarrow \underline{RO\overset{\overset{O}{\Vert}}{P}O_2Ba(s)} + 2H^+$
Sulfamic acid	Mass of $BaSO_4$ after oxidation with HNO_2	$RNHSO_3H + HNO_2 + Ba^{2+} \rightarrow ROH + \underline{BaSO_4}(s) + N_2 + 2H^+$
Sulfinic acid	Mass of Fe_2O_3 after ignition of Fe(III) sulfinate	$3ROSOH + Fe^{3+} \rightarrow (ROSO)_3Fe(s) + 3H^+$ $(ROSO)_3Fe \xrightarrow[O_2]{} CO_2 + H_2O + SO_2 + \underline{Fe_2O_3}(s)$

*The substance weighed is underlined.

Modified by

Dr. Mohammed Rasheed

Chapter 13

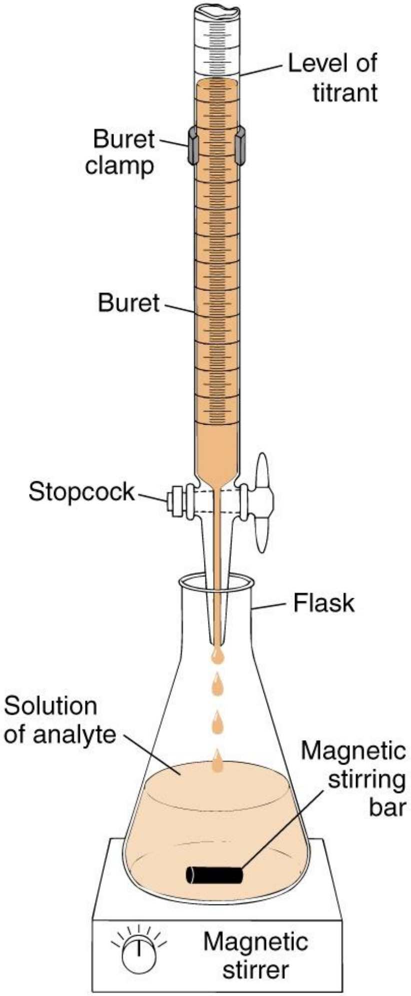
Volumetric Titrimetry

Principles of volumetric analysis

- **Volumetry** : the volume of standard reagent needed to react with analyte is measured
- **Titrimetry** : increments of the titrant are added to the analyte until their **reaction is complete**.

- Titrant *vs* Analyte
- x mole = y mole

- ✓ Depending on molar ratio between the anlyte and titrant in the balanced equations

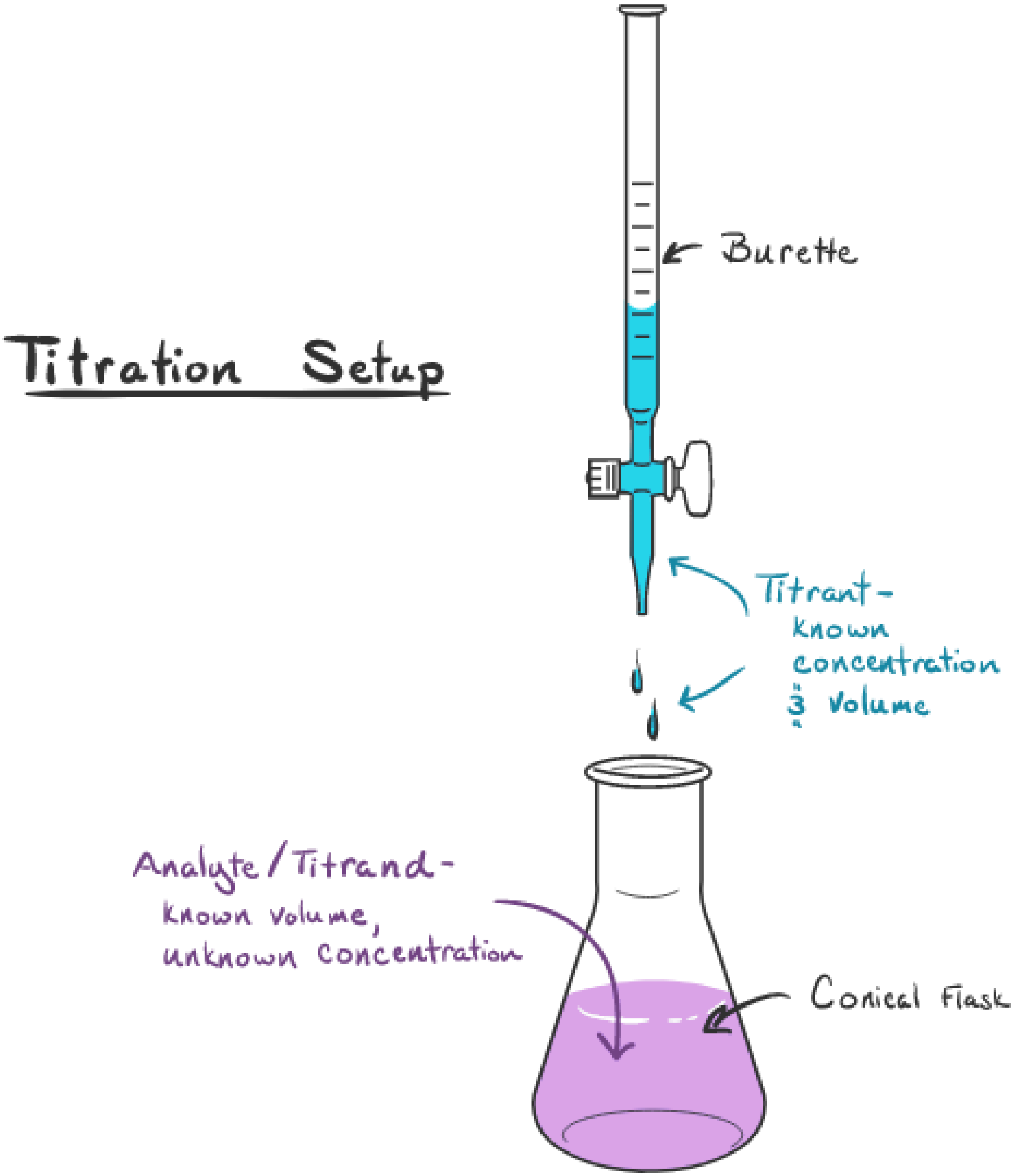


- **Titration:**

A procedure for determining the amount of **unknown** substance (the analyte) by **quantitative reaction** with a measured volume of a solution of precisely known concentration (the titrant).

- **Titrant:**

The substance that quantitatively reacts with the **analyte** in a titration. The titrant is **usually a standard solution** added carefully to the analyte **until the reaction is complete**. The amount of analyte is calculated from the volume of titrant required for complete reaction.



Standard Solutions (Titrant)

- Standard solutions play a key role in titrimetric methods.

Desirable Properties of Standard Solutions:

- accurate known conc.: 4 significant figures
- Sufficiently stable when preparing
- stoichiometric reaction: whole-number ratio
- React rapidly with analyte (should be very fast reaction).
- React completely with analyte: 99.9 %
- Endure a selective reaction with analyte

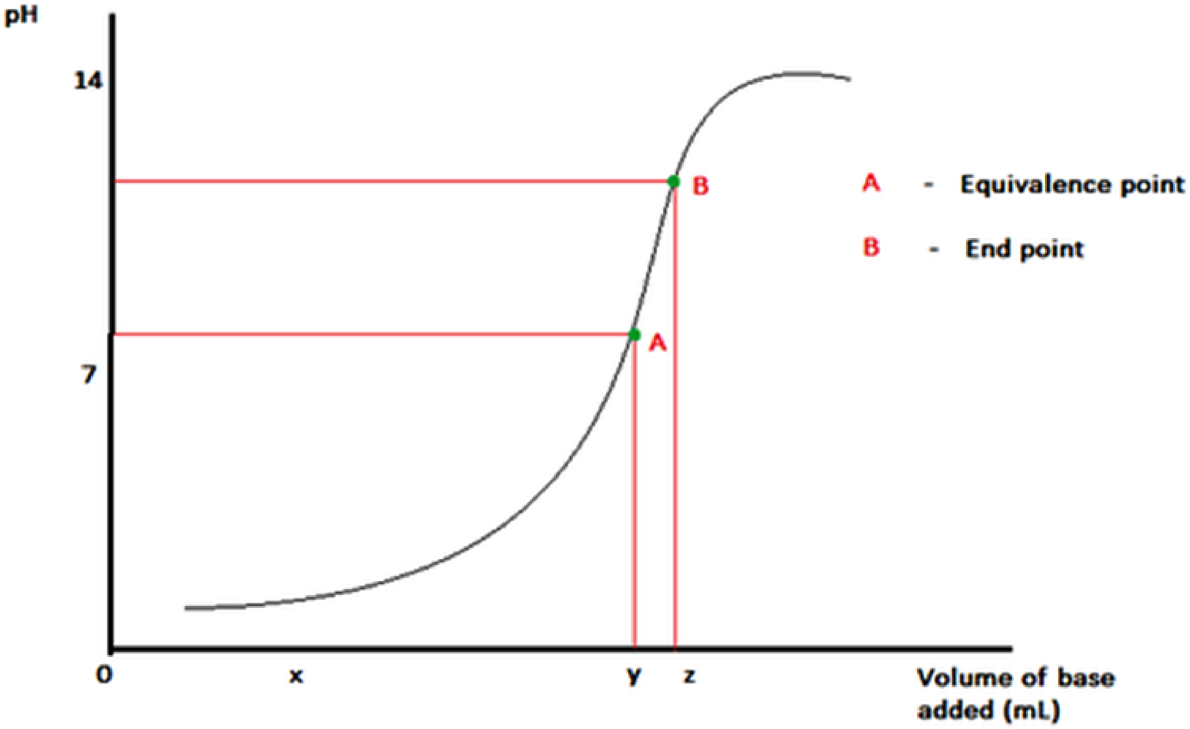
➢ Equivalence point:

Point in a titration at which equivalent amounts of titrant is the exact amount necessary for **stoichiometric reaction** with the analyte.

➢ End point:

- The point in a titration when a **physical change occurs** that is associated with the condition of chemical equivalence.
- It represents the experimental estimate of the equivalence point in a titration
- V_{ep} = actual volume at end point,

V_{eq} = theoretical volume of equivalence point



➢ titration error : $e_T = V_{ep} - V_{eq}$

➢ Indicator :

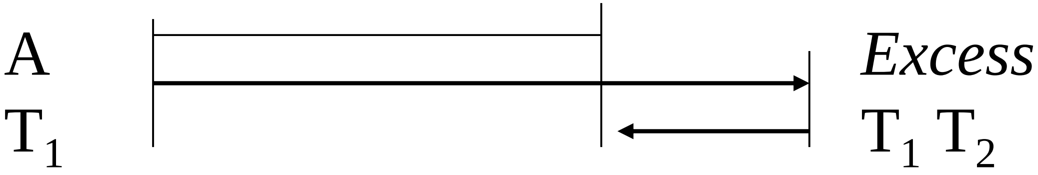
A substance that undergoes an sharp, easily observable physical change when conditions in its solutions change, for example, acid-base indicator and redox indicator. OR large changes in the relative conc. of analyte or titrant occur in the equivalence-point region.

a. appearance or disappearance of a color.
b. change in color
c. appearance or disappearance of turbidity.

Instruments for detect end point: volt meters, ohmmeters, colorimeter, temperature recorders, refractometers.

- **Direct titration** : titrant is added to the analyte until the reaction is complete.
- **Back titration or residual-titration** : Adding a *known excess* of reagent to the analyte, then, a second reagent is used to titrate the *excess* of the first reagent.

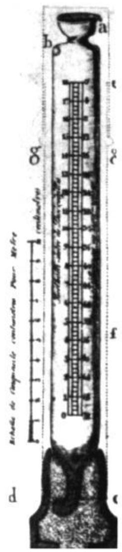
- **This is used when the rate of reaction between the analyte and reagent is slow or when the reagent lacks stability.**



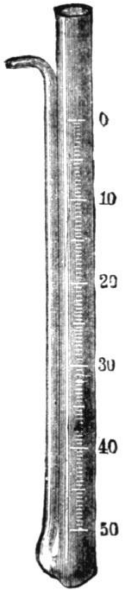
Ex. $PO_4^{3-} + 3Ag^+ \rightarrow Ag_3PO_4\,(s)$

$Ag^+ + SCN^- \rightarrow AgSCN\,(s)$

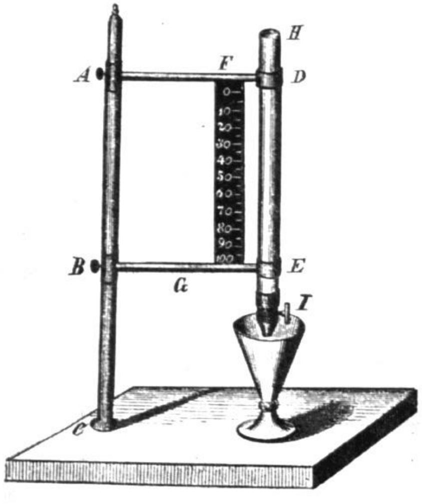
Evolution of the buret



Descroizilles (1806)
Pour out liquid

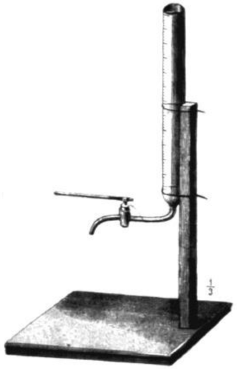


Gay-Lussac (1824)
Blow out liquid



Henry (1846)
Copper stopcock

Mohr (1855)
Compression clip



Mohr (1855)
Glass stopcock

Buret,

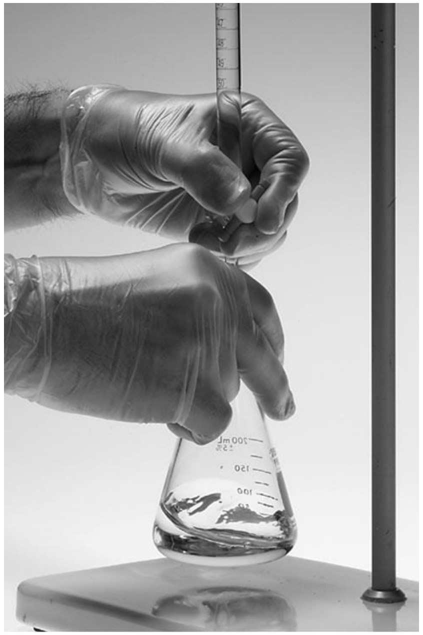
buret stand,

clamp,

white porcelain base,

wide-mouth Erlenmeyer flask

- Normally, the buret is filled titrant solution to within 1 or 2 mL of the zero position at the top. The initial volume of the buret is read to the nearest 0.01 mL.



Standard solution:

A solution of **precisely known** concentration.

Primary standard :

An ultra-pure (99.9% purity) compound that serves as the reference material for a titrimetric method of analysis.

Secondary standard :

A compound whose purity has been established by chemical analysis and that serves as the reference material for a titrimetric method of analysis

Standardization :

- **a process in which the concentration of a solution is determined by using the solution to titrate a known amount of another reagent.**

➢ Primary standard:

A *primary standard* is a highly purified compound that serves as a reference material in all volumetric and mass titrimetric properties. The accuracy depends on the properties of a compound and the important properties are:

1. High purity

2. Atmospheric stability

3. Absence of hydrate water

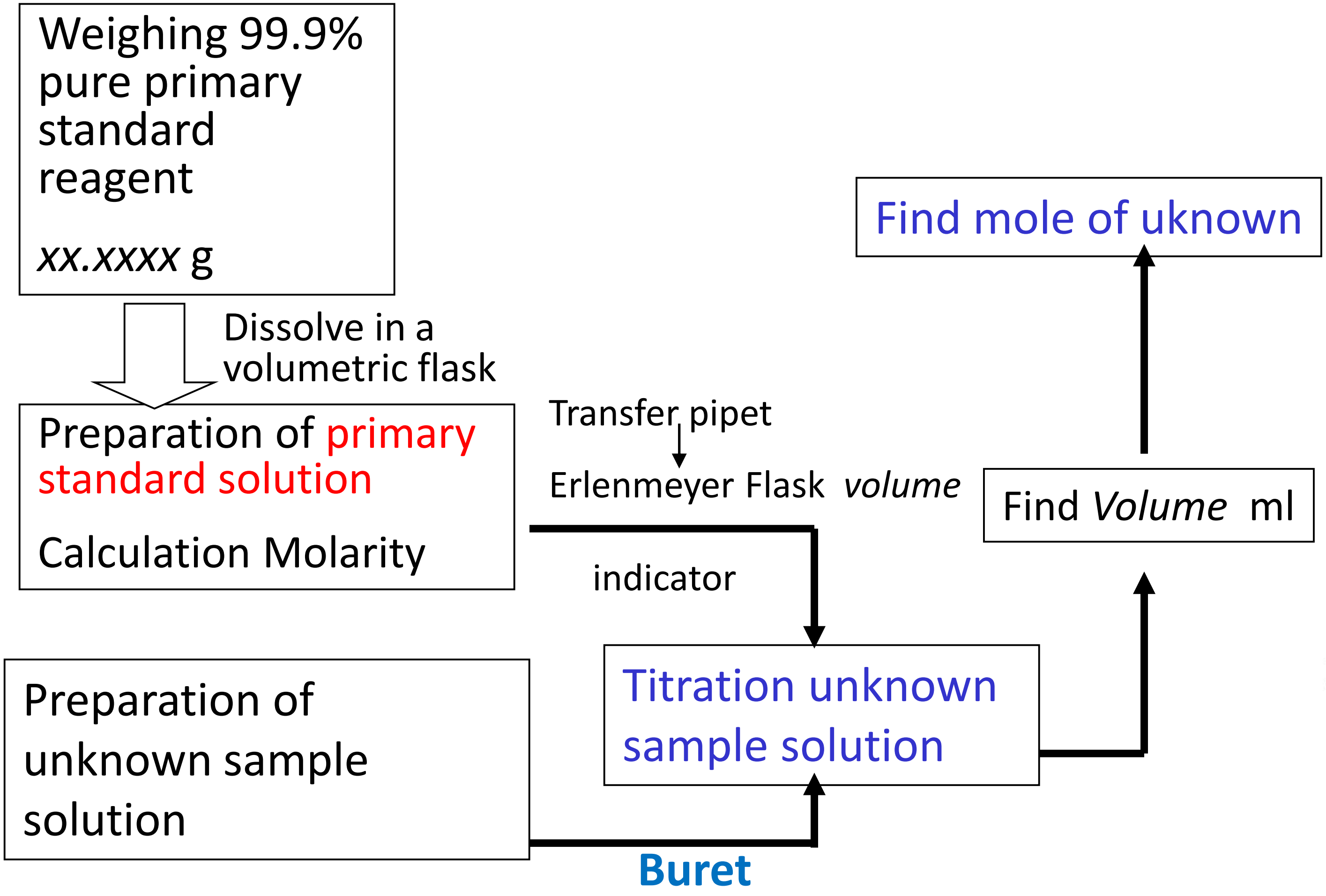
4. Readily available at a modest cost

5. Reasonable solubility in the titration medium

6. Reasonably large molar mass

- **Compounds that meet or even approach these criteria are few, and only a few primary standards are available.**

➢ Steps in a titrimetry



Weighing 99.9% pure primary standard reagent

xx.xxxx g

Dissolve in a volumetric flask

Preparation of primary standard solution

Calculation Molarity

Transfer pipet

Erlenmeyer Flask *volume*

indicator

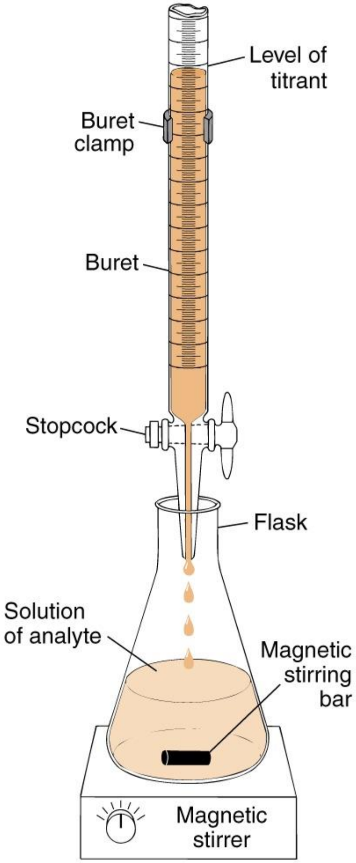
Preparation of unknown sample solution

Buret

Titration unknown sample solution

Find *Volume* ml

Find mole of uknown



- **Remember mole is calculated by two ways**

1- Mass(g)/MM(g/mol) 2- M(mol/L) x V(L)

Ex1: Describe the preparation of 2.000 L of 0.0500 M $AgNO_3$ (169.87 g/mol) from the primary standard-grade solid

Ans: dissolve 16.9 g in 2.00 L soln

Ex2: Describe how we 500ml of 0.01 M Na^+ solution can be prepared from primary Na_2CO_3 standard solution (105.99 g/mol)

Ans: 2.5 x10-3 mole Na_2CO_3**; mass** $Na_2CO_3 = 0.256$ g
Diisove 0.256 g in water and diliuted to 500 ml.

Ex2: Describe how you prepare 50.0 ml portion of standard solutions that are 0.00500 M, 0.00200 M and 0.00100 M from the stock solution in example 2

Ans: M1V1 = M2V2; 25.0ml; 10.0 ml, 5.00 ml

Ex. 13-4. Describe how you would prepare 2.0 L of approximate 0.25 M $HClO_4$ (100.46 g/mol) from the conc. reagent, which has a specific gravity of 1.67 g/mL and contains 71 % (w/w) $HClO_4$.

C_{HClO_4} = 1.67 g/mL× 0.71 = 1.19 g of the acid/ml

1.19g/(100.46 g/mol) = 0.012 mole; 0.012/ml then the conc is 11.8 mole/L

(Or conc. In M = (Sp.grav x % (m/m) / molar mass) x 10

Now M1V1=M2V2

11.8 x V1 = 0.25 x 2 ; V1= 0.042 L; i.e diluted about 42 mL of 71 % $HClO_4$ to 2.0 L.

Ex. 13-5. A 50.00-mL of an HCl solution required 29.71 mL of 0.01963 M $Ba(OH)_2$ to reach an end point with bromocresol green indicator. Calculate the molarity of the HCl.

$$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + 2H_2O$$

- **From eqn 1mole $Ba(OH)_2$ react with 2 mole HCl**
- **From titration: 5.83×10^{-4} $Ba(OH)_2$ will react with x mole HCL**
- **Mole HCL = 1.166×10^{-3} mole; MHCL = 1.166×10^{-3}/0.05L**

Ans: 0.0233 M HCL

Ex 13.6: 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

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

- **From eqn 5 mole $Na_2C_2O_4$ react with 2 mole MnO_4^-**
- **From the titration**

0.2121 g $Na_2C_2O_4$ = 1.58×10^{-3} mole then

5 mole $Na_2C_2O_4 \rightarrow$ 2 mole MnO_4^-

1.58×10^{-3} mole $\rightarrow$ x mole

Mole of the unkown (MnO_4^-) = 6.33×10^{-4} mole

Molarity = 6.33×10^{-4} mole / 0.04331 L = 0.0146 M

Ex 13.7: 0.804 g sample of iron ore was dissolved in acid. The iron is then reduced to Fe^{+2} and titrated with 47.2 mL of 0.02242 of $KMnNO_4$. Calculate the results of this analysis in term of a) %Fe (55,846 g/mole)

b) % Fe_3O_4 (231.54 g/mole).

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

- From titration; Mole Fe^{2+} = 5.3×10^{-3} mole
- Mass Fe^{2+} = 0.2956 g; then % Fe^{2+} = 36.77%
- Mole Fe_3O_4 = 1/3 x mole Fe = 1.767×10^{-3} mole
- Mass Fe_3O_4 =0.41; % Fe_3O_4 = 50.8%

Ex 13.8: A 100.0-mL sample of brackish water was made ammoniacal, and the sulfide it contained was titrated with 16.47 mL of 0.02310 M $AgNO_3$. The analytical reaction is $2Ag^{+}+S^{2-}\rightarrow Ag_2S(s)$

Calculate the concentration of H_2S (34.08 g/mole) the water in ppm.

- From titration; Mole Ag^{+} = 3.8×10^{-4} mole
- Mole S^{2-} = 1.9×10^{-4} mole
- Mass H_2S = 6.5×10^{-3} g; mass in mg = 6.5 mg
- Ppm H_2S = 6.5mg/0.1L = 65 ppm

Ex 13.9: The phosphate in a 4.258 g sample of plant food was converted to PO_4^{3-} and precipitated as Ag_3PO_4 through the addition of 50.00 ml of 0.0820 M $AgNO_3$. The excess $AgNO_3$ was back titrated with 4.06 mL of0.0625 M KSCN. Express the result of analysis in terms of the percentage of % P_2O_5

$$
\begin{aligned}
P_2O_5 + 9H_2O &\rightarrow 2PO_4^{3-} + 6H_3O^+ \\
2PO_4^{3-} + 6Ag^+_{(\text{excess})} &\rightarrow 2Ag_3PO_4(s) \\
Ag^+ + SCN^- &\rightarrow AgSCN(s)
\end{aligned}
$$

- From eqn3 (titn) Mole SCN^- = 2.54×10^{-4} mole
- Reaction 2; total mole of $AgNO_3$ = 4.1×10^{-3} mole
- Mole Ag^+ reacted with PO_4^{3-} = 4.1×10^{-3} mole - 2.54×10^{-4} mole = 3.85×10^{-3} mole
- From molar ratio, Mole PO_4^{3-} = 3.85×10^{-3} mole x 2/6 = $1.28\ 10^{-3}$ mole
- Mole P_2O_5 = Mole $PO_4^{3-}/2$ = 6.42×10^{-4}
- Mass P_2O_5 = 6.42×10^{-4} x 141.9 g/mole =0.091 g
- P_2O_5 Mass% = 2.14%

Ex 11: The CO in a 20.3-L sample of gas was converted to CO_2 by passing the gas over iodine pentoxide heated to 150°C, and I_2 was distilled and collected to 8.25 mL of 0.01101 M $Na_2S_2O_3$, then back titration with 2.16 mL of 0.00947 M I_2 solution.

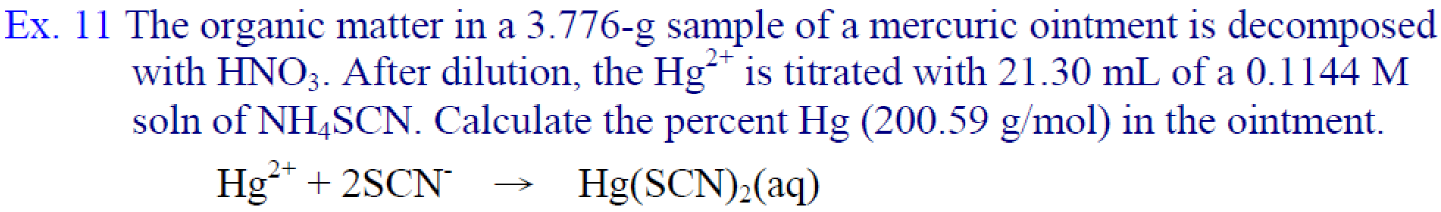
Calculate the mg of CO (28.01 g/mol) per liter of sample.

a. $I_2O_5(s) + 5CO\ (g) \rightarrow 5CO_2(g) + I_2\ (g)$ ……… **rxn**

b. $I_2(aq) + 2S_2O_3\ (aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}\ (aq)$ ……. **rxn**

b. $2S_2O_3\ (aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}\ (aq)$ ….. **Back Titration**

- **From eqn3** (titn); mole $S_2O_3^{2-}$ = 4.09×10^{-5} mole
- From eqn2 (rxn) **total** mole $S_2O_3^{2-}$ = 9.08×10^{-5} mole
- mole $S_2O_3^{2-}$ reacted with I_2 (which is resulted from 1) = 4.99×10^{-5} mole
- mole I_2 reacted in 2 (which is resulted from 1) = 2.50×10^{-5} mole
- From molar ratio (eqn 1), mole CO = 1.2×10^{-4} mole
- mg/L CO = 0.166 mg/L



Ex. 11 The organic matter in a 3.776-g sample of a mercuric ointment is decomposed with HNO_3. After dilution, the Hg^{2+} is titrated with 21.30 mL of a 0.1144 M soln of NH_4SCN. Calculate the percent Hg (200.59 g/mol) in the ointment.

$$Hg^{2+} + 2SCN^- \rightarrow Hg(SCN)_2(aq)$$

- From titration; Mole SCN^- = 2.4×10^{-3} mole
- Mole Hg^{2+} = 1.2×10^{-3} mole
- Mass Hg^{2+} = 0.244g
- **% Hg^{2+} = 6.47%**

Ex 12: A sample containing 0.4775 g of $(NH_4)_2C_2O_4$ and inert materials was dissolved in water and made strongly alkaline with KOH which converted NH_4^+ to NH_3. The liberated ammonia was distilled into exactly 50.0 mL of 0.05035 M H_2SO_4, The excess H_2SO_4 was back titrated with 11.3 mL of 0.1214 M NaOH. Calculate:

(i) percentage of N,

(ii) percentage of $(NH_4)_2C_2O_4$

[At. mass of nitrogen = 14.0078 g/mol ; MM of $(NH4)_2C_2O_4$=124.10 g/mol]

$(NH_4)_2C_2O_4 + 2KOH \rightarrow \mathbf{2}NH_3 + K_2C_2O_4 + H_2O$ ------- 1

$2NH_3 + H_2SO_4 \rightarrow \mathbf{(NH_4)_2SO_4}$ **--------- 2**

Back titration

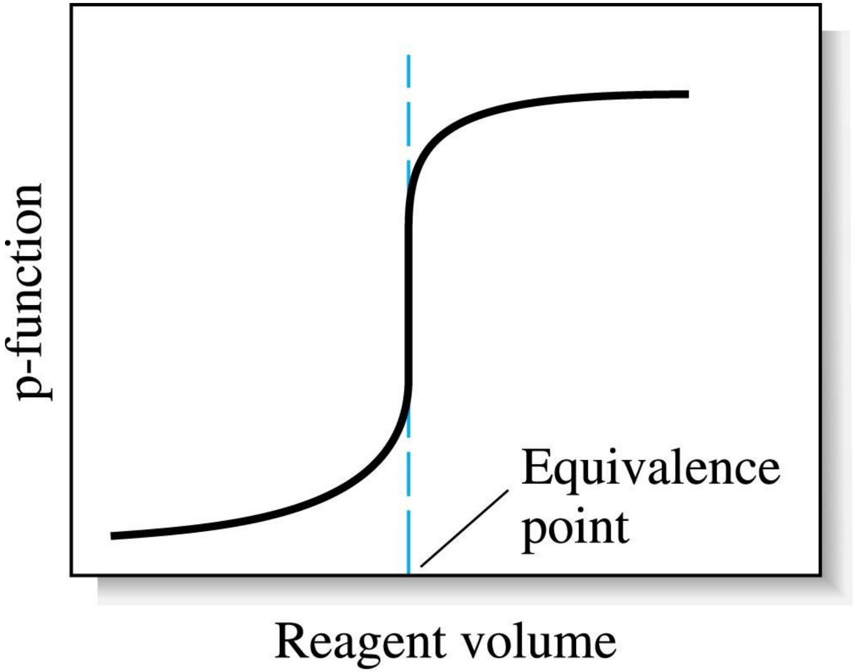
$H_2SO_4 + 2NaOH \rightarrow \mathbf{Na_2SO_4 + H_2O}$ **--------- 3**

- **From eqn3** (titn); mole $H_2SO_4 = 6.85 \times 10^{-4}$ mole
- From eqn2 (rxn) **total** mole $H_2SO_4 = 2.52\times10^{-3}$ mole
- mole H_2SO_4 reacted with NH_3 (which is resulted from 1) = 1.835×10^{-3} mole
- mole NH_3 reacted in 2 (which is resulted from 1) = 3.67×10^{-3} mole
- From molar ratio (eqn 1), mole $(NH_4)_2C_2O_4 = 1.835 \times10^{-3}$ mole;
- Mole N = 3.76×10^{-3} mole
- **% of N 11.0%; % $(NH_4)_2C_2O_4$ = 47.7%**

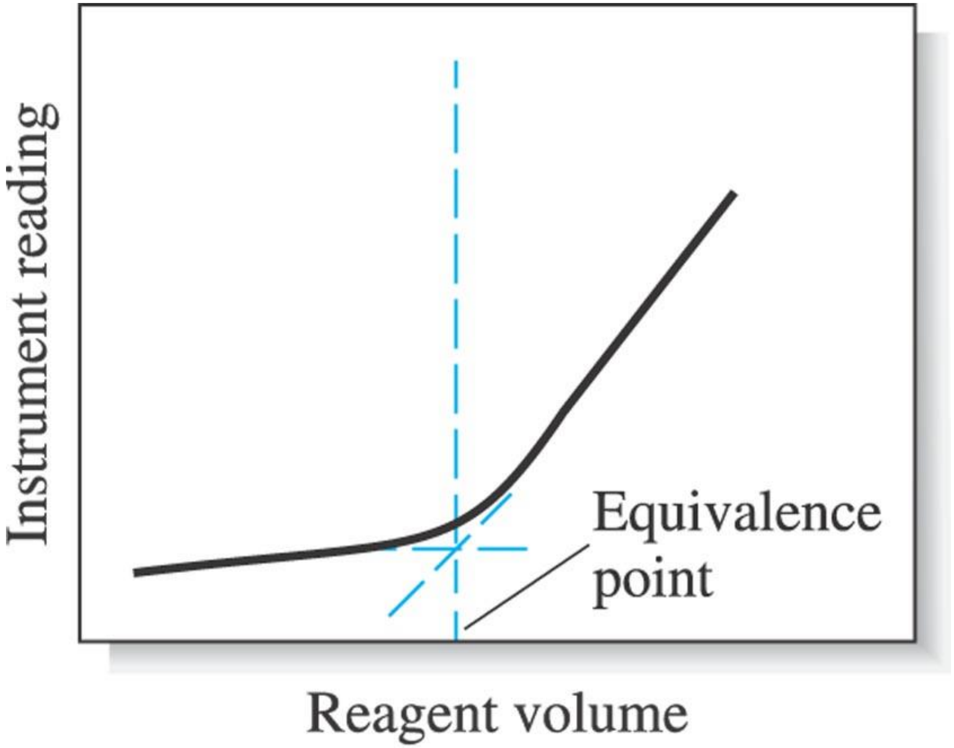
Titration Curves

- **Two types of titration curves routinely encountered in titrimetric methods; they are**

  sigmoidal curve and linear segment curve.



(a) Sigmoidal curve



(b) Linear-segment curve

Table 13-1 Concentration changes during a titration of 50.00 mL of 0.1000M $AgNO_3$ with 0.1000M KSCN

0.1000M KSCN, mL	$[Ag^+]$ mmol/L	mL of KSCN to cause a tenfold decrease in $[Ag^+]$	pAg	pSCN
0.00	1.000×10^{-1}		1.00	
40.91	1.000×10^{-2}	40.91	2.00	10.00
49.01	1.000×10^{-3}	8.10	3.00	9.00
49.90	1.000×10^{-4}	0.89	4.00	8.00
49.99	1.000×10^{-5}	0.09	5.00	7.00
50.00	1.000×10^{-6}	0.01	6.00	6.00
50.01	1.000×10^{-7}	0.01	7.00	5.00
50.10	1.000×10^{-8}	0.09	8.00	4.00
51.01	1.000×10^{-9}	0.91	9.00	3.00
61.11	1.000×10^{-10}	10.10	10.00	2.00

- Titration curves: plots of a conc.-related variable as a function of reagent volume.

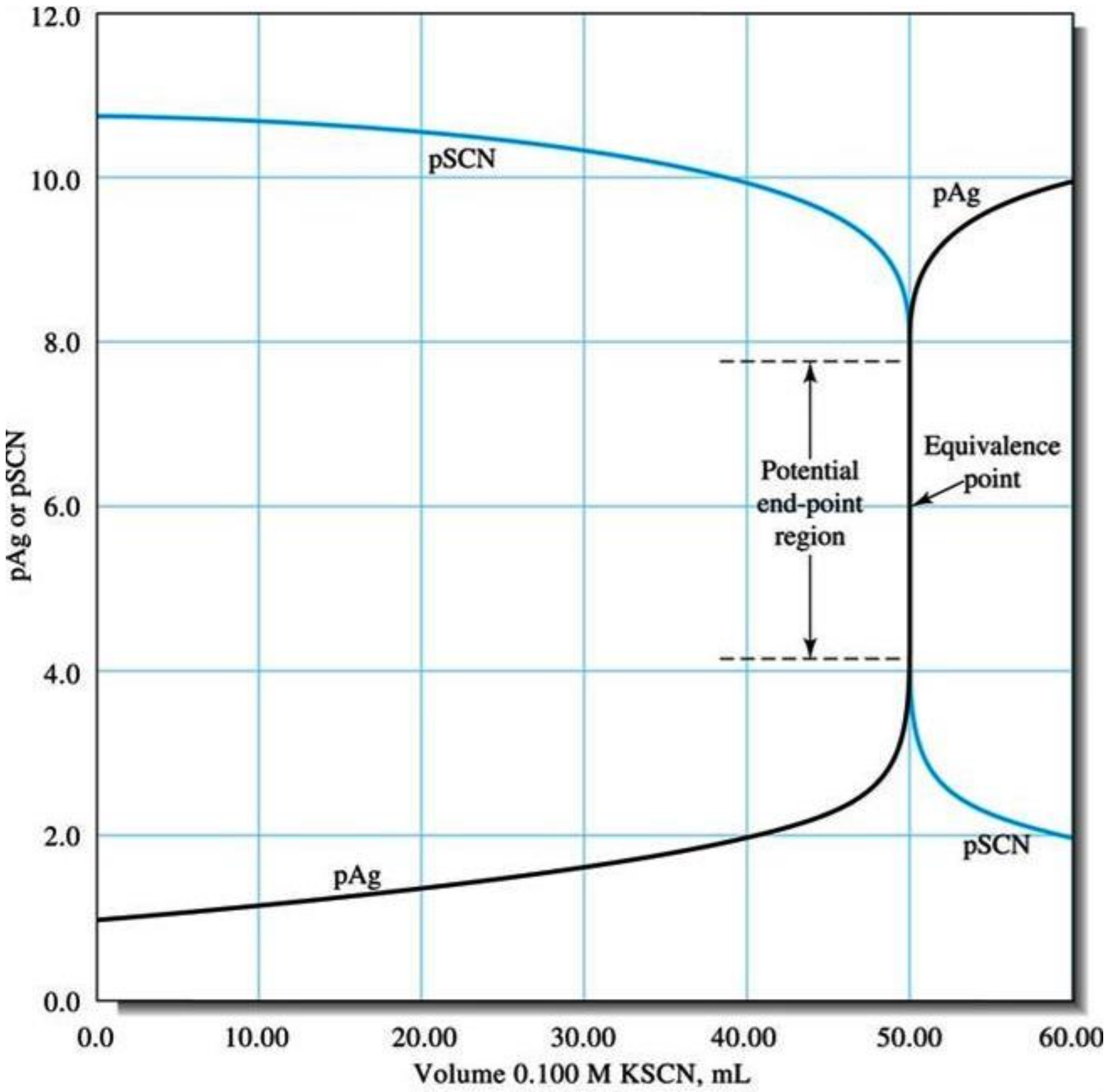


Fig. 13-3 Titration curve for the titration of 50.00 mL Of 0.1000 M $AgNO_3$ with 0.1000 M KSCN.

Precipitation Titrations

- A titration in which the reaction between the analyte and titrant involves a precipitation.

Silver nitrate titrations : Argentometric methods

for : halides, halide-like anion (SCN-, CN-, CNO-) several

End point:

1. A change in color due to the reagent, the analyte or an indicator.
2. A change in potential of an electrode that responds to the conc. of one of the reactants.

- **Titration curve: Guidance in precipitation titration calculation**

- Find V_e (volume of titrant at equivalence point)
- Find y-axis values:
  - **At beginning**
  - **Before V_e**
  - **At V_e**
  - **After V_e**

Example 13-13: For the titration of 50.0 mL of 0.0500 M Cl^- with 0.100 M Ag^+ (Ksp for AgCl= 1.8×10^{-10}). The reaction is:

$Ag^+_{(aq)} + Cl^-_{(aq)} \leftrightarrows AgCl_{(s)}$ K here is the inverse of K_{sp}

Find pAg and pCl of Ag^+ solution added

a) 0 mL b) 10.0 mL c) 25.0 mL d) 26.0 mL

❖ **Ag^+ is the titrant and Cl^- is the analyte**

a) **At 0ml addition** of Ag^+ we only have Cl^- with a concentration of 0.0500 M; Then PCl = -log Cl^- = -1.3; **PAg^+ is indeterminate**

b) **At 10 ml addition**

Mole Cl^- = 2.5 x 10^{-3}; mole Ag^+ added = 1 x 10^{-3}; after the titration reaction

Mole Cl^- = 1.5 x 10^{-3}; M $[Cl^-]$ = 1.5 x 10^{-3}/ (0.06L (**total volume after mixing**) = **0.025**

mole Ag^+ = 0; **however AgCl ppt** will be formed and partially soluble depending on Ksp ; $AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ **$K_{sp} = 1.8\times10^{-10}$ (common ion)**

$K_{sp} = 1.8\times10^{-10} = (X)$ 0.025 ; then x = $[Ag^+]$ = 7.2 x10^{-9};

P Ag^+ = 8.14; PCl- = 1.6

c) **At 25ml addition**; mole Cl^- = 2.5 x 10^{-3}; mole Ag^+ added = 2.5 x 10^{-3}; after the titration reaction; 0ml of both **(Equivalence point); but** AgCl ppt;

$K_{sp} = 1.8\times10^{-10} = X^2$; then x = $[Ag^+]$ = $[Cl^-]$ = 1.34 x10^{-5}; **PAg^+ = PCl^- = 4.87**

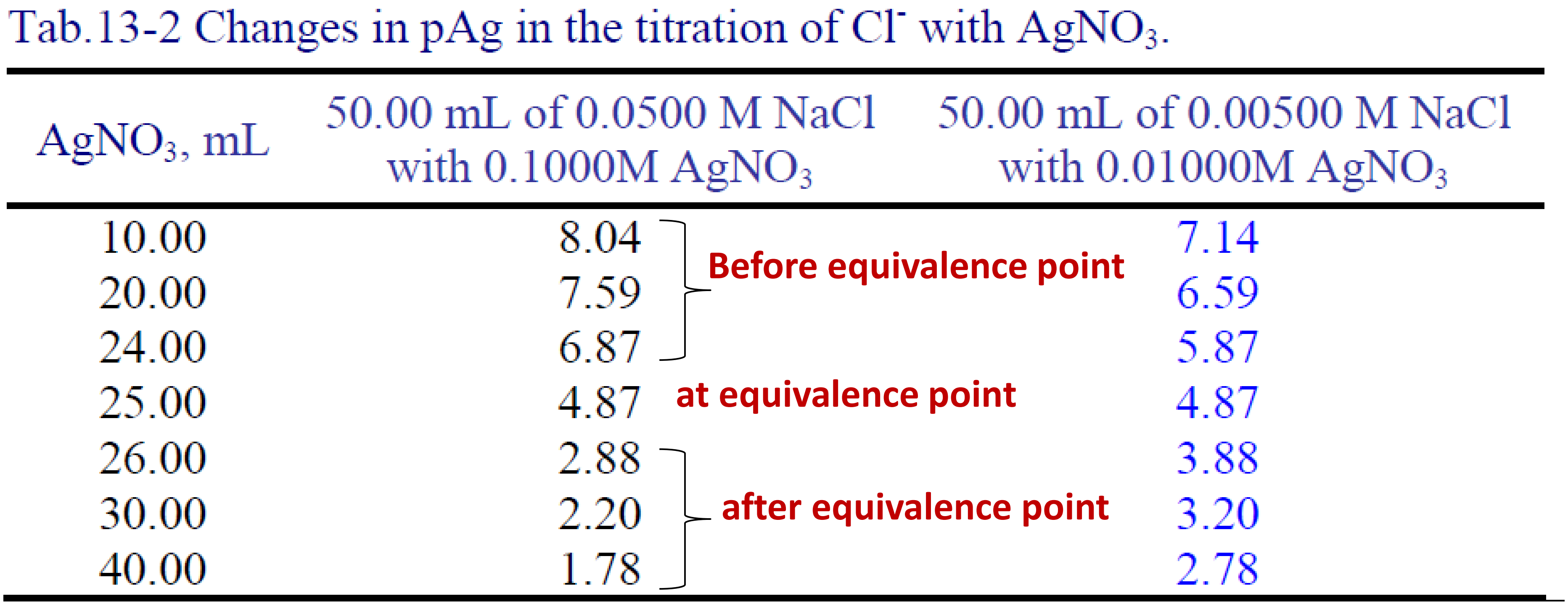
d) After 26 ml addition; mole Ag^+ added = 2.6×10^{-3} mole;

M $[Ag^+]$= 2.6×10^{-3} mole/76 $\times 10^{-3}$ L (Total Volume) =**1.3×10^{-3} M**

Ksp ; $AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ **$K_{sp} = 1.8 \times 10^{-10}$ (common ion)**

Then $[Cl^-]$= 1.3×10^{-7}

$PAg^+ = 2.88$; $PCl^- = 6.9$



Tab.13-2 Changes in pAg in the titration of Cl^- with $AgNO_3$.

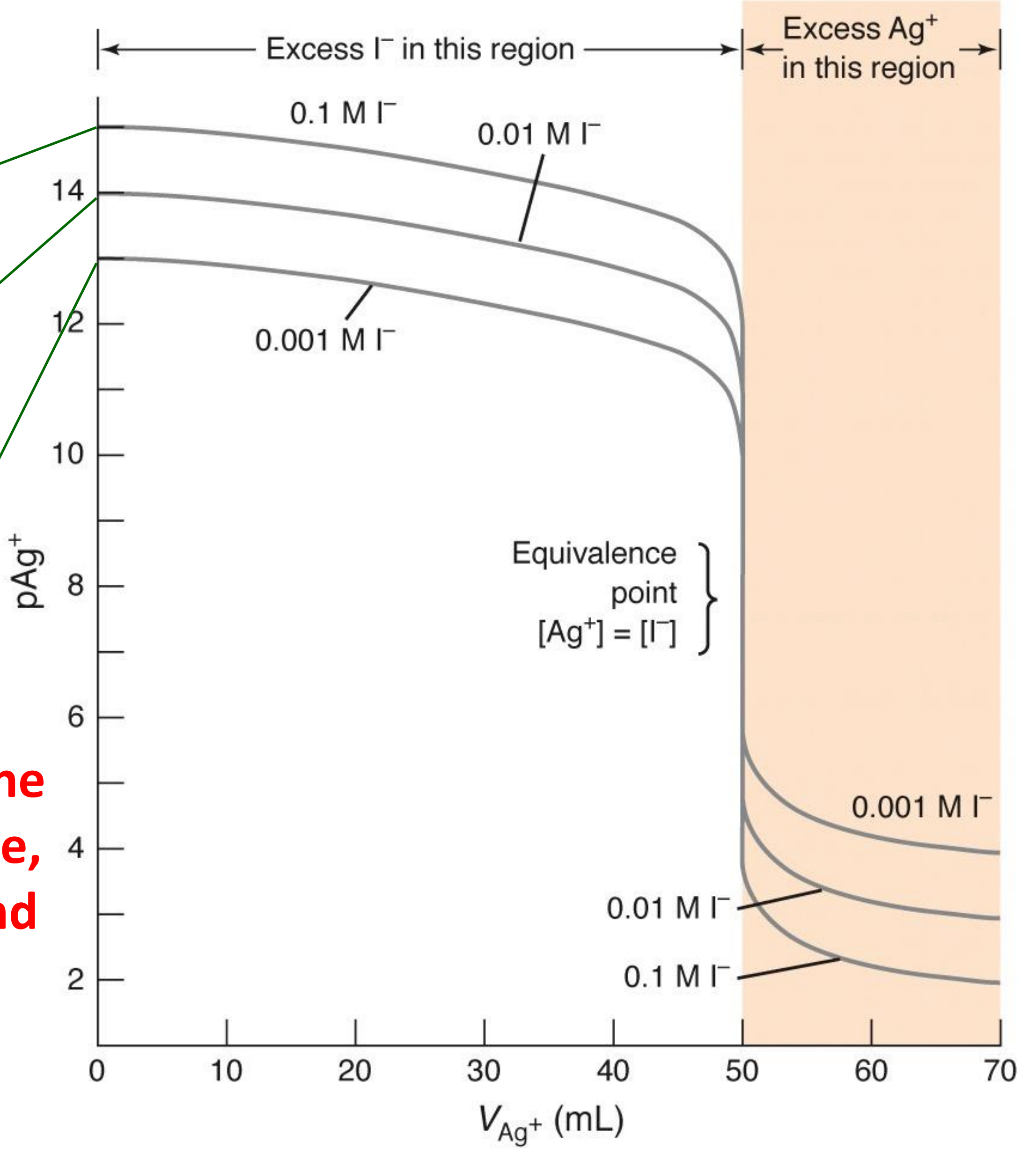
$AgNO_3$, mL	50.00 mL of 0.0500 M NaCl with 0.1000M $AgNO_3$		50.00 mL of 0.00500 M NaCl with 0.01000M $AgNO_3$
10.00	8.04	**Before equivalence point**	7.14
20.00	7.59		6.59
24.00	6.87		5.87
25.00	4.87	**at equivalence point**	4.87
26.00	2.88	**after equivalence point**	3.88
30.00	2.20		3.20
40.00	1.78		2.78

Dilution effect of the titration curves

25.00 mL 0.1000 M I^- titrated with 0.05000 M Ag^+

25.00 mL 0.01000 M I^- titrated with 0.005000 M Ag^+

25.00 mL 0.001000 M I^- titrated with 0.0005000 M Ag^+

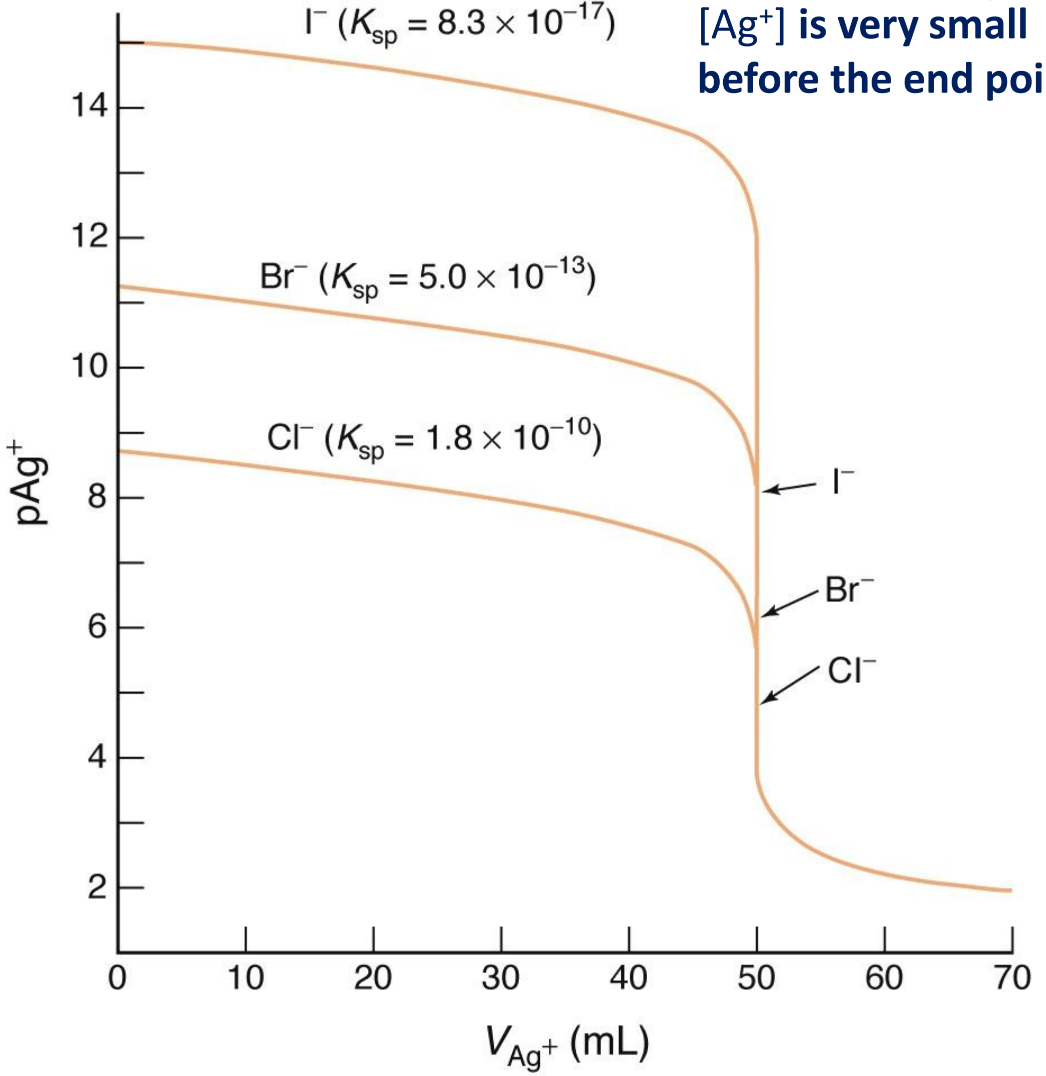


- **As the concentrations of the anlayte and titrant increase, it is easier to detect the end point.**

K_{sp} effect of the titration curves

25.00 mL 0.1000 M halide (X^-) titrated with 0.05000 M Ag^+

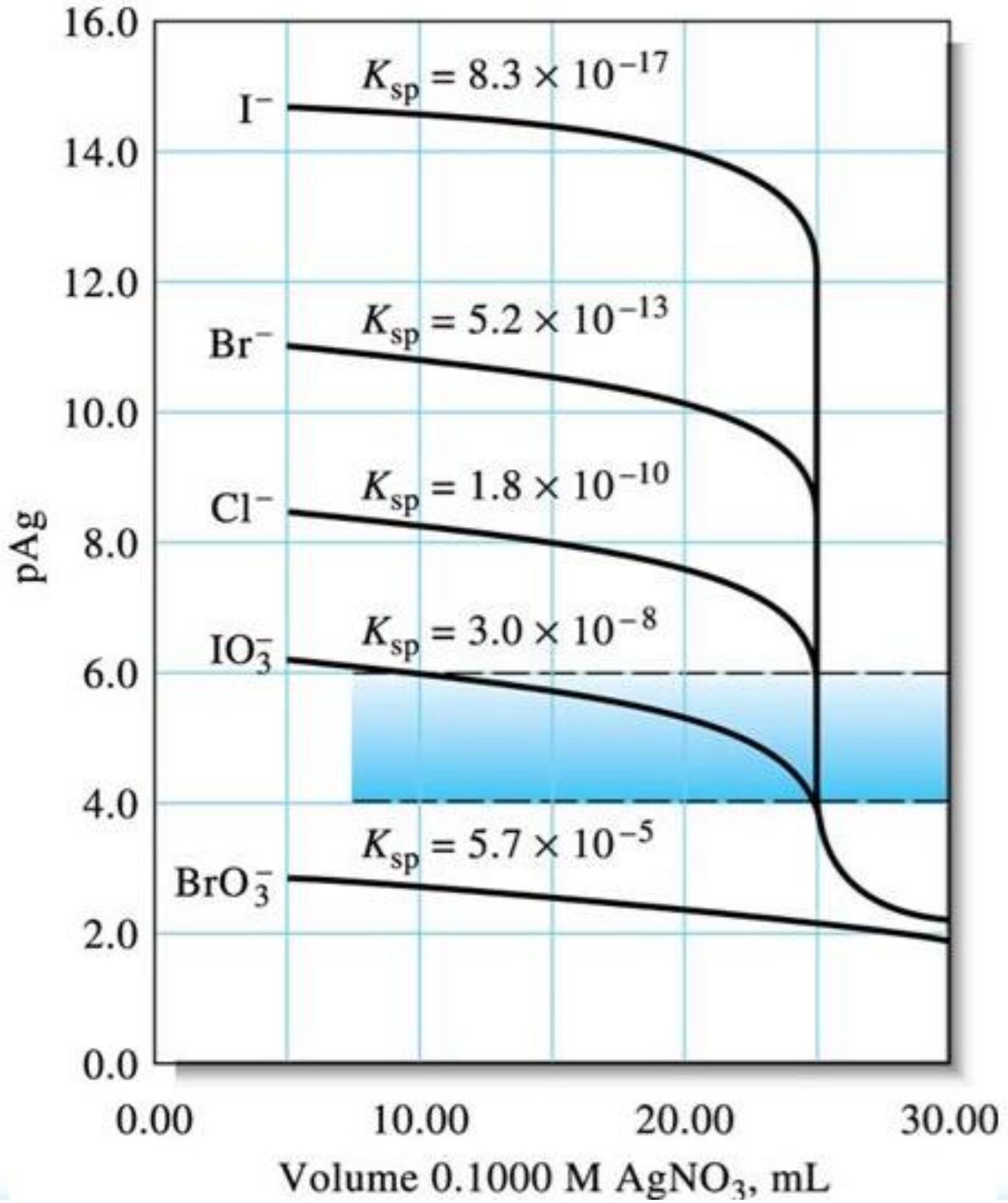
At very small K_{sp} [Ag^+] is very small before the end point



- ❖As Ksp smaller it is easier to detect the end point.
- ❖ The change in P_{Ag} at the eqivelence point is greater, and
- ❖ The reaction between the analyte and Ag+ becomes more complete (K=1/Ksp)

Effect of reaction completeness on precipitation titration curves. For each curve, 50.00m of a M solution of the anon was titrated with M AgNO3.

- **Note that smaller values of Ksp give much sharper breaks at the end point.**



Indicators for Argentometric Titrations

***$AgNO_3$ titrations**

Method	**Mohr (Direct)**	**Fajans (Direct)**	**Volhard (Residual)**
Titrant	**$AgNO_3$**	**$AgNO_3$**	**$AgNO_3$-KSCN**
Indicator	**Na_2CrO_4**	**Fluorescein**	**Fe^{3+}**
End point	**Ag_2CrO_4 (s) red ppt**	**$AgX{:}Ag^+ \cdot\cdot Fl^-(s)$ red ppt**	**$Fe(SCN)^{2+}$ red solution**
Titration pH	**6.5 ~ 10.3**	**≥ 7**	**Acidic**

1. Chromate Ion; The Mohr method

sample: Cl^-, Br^-, CN^-

$$AgNO_3 + X^- \Leftrightarrow \underset{\text{white}}{AgX(s)} + NO_3^-$$

$$AgNO_3 + CN^- \Leftrightarrow Ag(CN)_2^-(aq) + NO_3^-$$

End point: $$\mathbf{2AgNO_3 + \underset{\text{yellow}}{CrO_4^{2-}} \Leftrightarrow Ag_2CrO_4(s) + 2\,NO_3^-}$$

red ($Ksp = 1.1 \times 10^{-12}\ M^3$)

not for arsenate, I^-, SCN^-

Solubility: **$Ag_2CrO_4 > AgX$**

*Choice of indicator:

$$[Ag^+]_{ep} = (Ksp)^{½} = (1.82 \times 10^{-10}\ M^2)^{½} = 1.35 \times 10^{-5}\ M$$

Conc. of CrO_4^{2-} needed to form red ppt

$$2AgNO_3 + CrO_4^{2-} \Leftrightarrow Ag_2CrO_4(s) + 2\ NO_3^-$$

- ❖ **The chromate ion required to initiate the formation of silver chromate**

At equiv. point $K_{sp} = 1.8\times10^{-10} = X^2$; then $x = [Ag^+] = [Cl^-] = 1.34\ x10^{-5}$

$$\text{equivalence point}: [Ag^+] = [Cl^-] = 1.35 \times 10^{-5}\ M$$

$$[CrO_4^{2-}] = Ksp/[Ag^+]^2 = 1.2 \times 10^{-12}/(1.35 \times 10^{-5})^2 = 6.6 \times 10^{-3}\ M$$

- ❖ **pH should be between 6.5-10.3**

***pH : 6.5 ~ 10.3 (7~10)**

$$pH < 6.5 \qquad Ag_2CrO_4(s) \Leftrightarrow 2Ag^+ + CrO_4^{2-}$$

$$CrO_4^{2-} + H^+ \Leftrightarrow Cr_2O_7^{2-} + H_2O$$

$$pH > 10.3 \qquad Ag^+ + OH^- \Leftrightarrow AgOH(s)$$

2. Adsorption indicators: The Fajans method

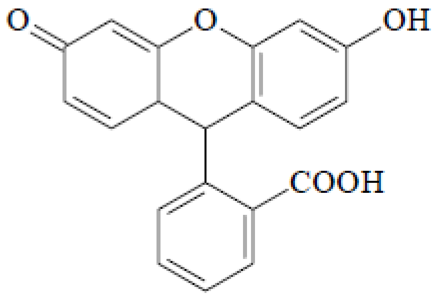
- The indicator is an organic compound that tends to adsorbed onto the surface of the solid in a precipitation
- Titration. Ideally, the adsorption occur near the equivalence point.

❖ Advantages: rapid, accurate and reliable

AgNO3 + X- ⇔ AgX(s) + NO3-

End point: Ag+ + AgX(s) + Fl- ⇔ AgX:Ag+ · · Fl-(s) **Yellow-green red**

Indicator: Fluorescein anion



fluorescein

* avoid ppt coagulation → ppt surface ↑

a. adding dextrin or polyethylene glycol

b. quick titration and avoid excessive stirring

c. halide ion conc. : 0.005 ~ 0.025 M

3. Iron(III) Ion; The Volhard method

(back titration): Iron(III) ion as indicator

sample: halide ion, C_2O_4, AsO_4, SCN^-

$nAgNO_3$ (excess) + $B^{n-} \Leftrightarrow$ AgnB(s) + nNO3-

KSCN + unreacted $AgNO_3 \Leftrightarrow$ AgSCN(s) + K^++ NO_3^-

End point: $$Fe^{3+} + SCN^- \Leftrightarrow \underset{\text{red}}{Fe(SCN)^{2+}}$$

$$K_f = \frac{[Fe(SCN)^{2+}]}{[Fe^{3+}][SCN^-]} = 1050$$

***pH : in acidic soln to prevent Fe(III) → $Fe(OH)_3(s)$**

***advantage: carbonate, oxalate & arsenate do not interfere.**

***For Cl^- ion in blood serum, urine.** (sample: HNO_3 digestion)

Ex. The As in a 9.13-g sample of pesticide was converted to AsO_4^{3-} and precipitated as Ag_3AsO_4 with 50.00 mL of 0.02015 M $AgNO_3$. The excess Ag^+ was then titrated with 4.75 mL of 0.04321 M KSCN. Calculate the % of As_2O_3 in the sample.

$$2AsO_3 + 6AgNO_3 \rightarrow 2Ag_3AsO_3 + 6NO_2 + 3O_2$$

Answer:
Total mole $AgNO_3$ = 1.0075×10^{-3}
Mole KSCN = 2.052×10^{-4} mole
Mole $AgNO_3$ consumed by AsO_4^{3-} = 0.8023 mole
$As_2O_3 = 2AsO_4^{3-} = 6\ AgNO_3$
Mole As_2O_3 = (mole $AgNO_3$)/6
% As_2O_3 = 0.299%

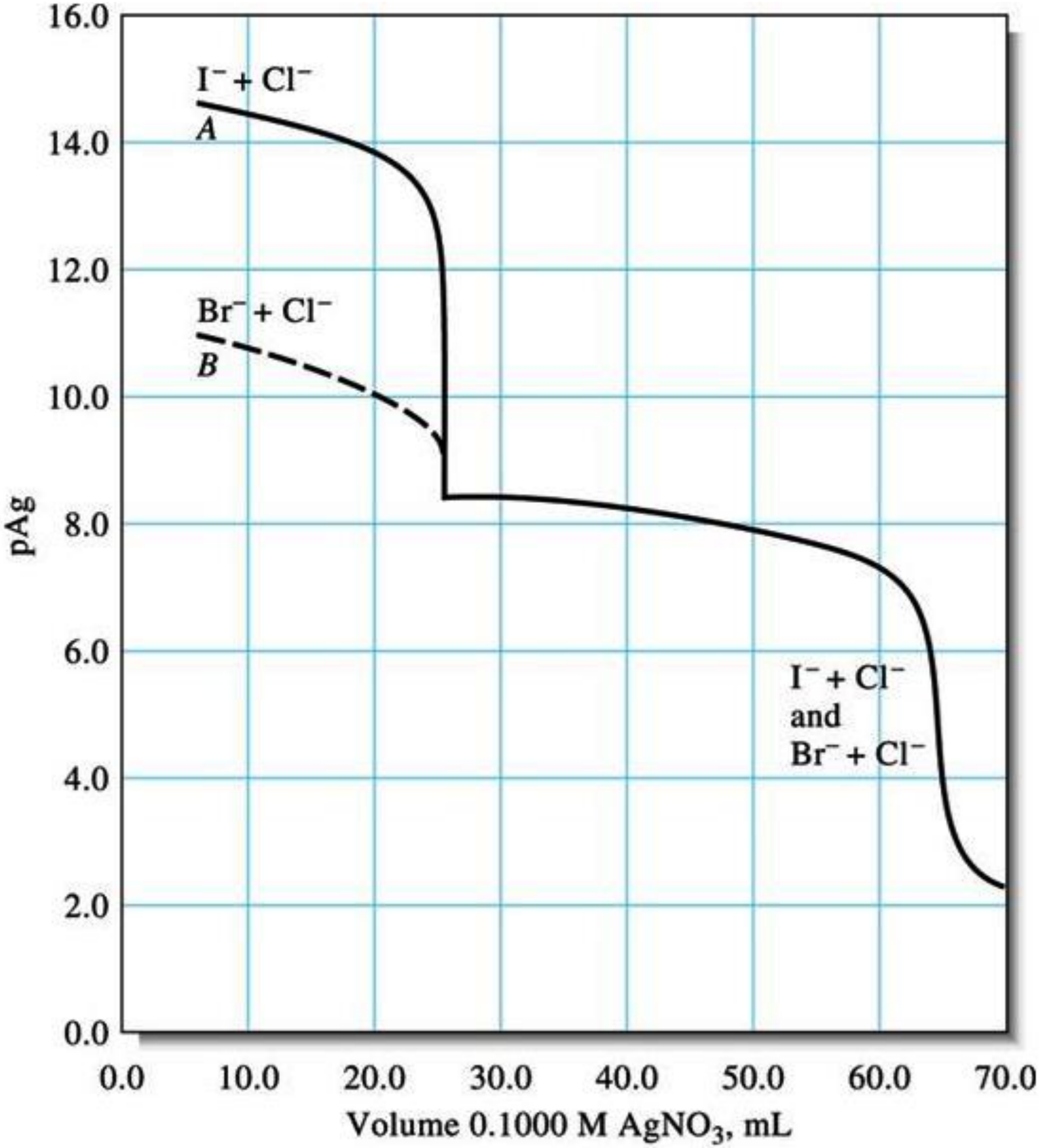
Titration curve of a mixture of anions

Fig. 13-6 Titration curves for 50.00 mL of a solution 0.0800 M in Cl^- and 0.0500 M in I^- or Br^-.

AgI: $K_{sp} = 8.3 \times 10^{-17}$

AgBr: $K_{sp} = 5.2 \times 10^{-13}$

AgCl: $K_{sp} = 1.8 \times 10^{-10}$



Example: A 25.00 mL solution containing Br^- and Cl^- was titrated with 0.03333 M $AgNO_3$. $K_{sp}(AgBr)=5\text{x}10^{-13}$, $K_{sp}(AgCl)=1.8\text{x}10^{-10}$.

(a) Which analyte is precipitated first?

(b) The first end point was observed at 15.55 mL. Find the concentration of the first that precipitated in the original solution (Br^- or Cl^-?).

(c) The second end point was observed at 42.23 mL. Find the concentration of the second that precipitated (Br^- or Cl^-?).

(a) $Ag^+_{(aq)} + Br^-_{(aq)} \leftrightarrows AgBr_{(s)}$ $\quad K = 1/K_{sp}(AgBr) = 2\text{x}10^{12}$

$Ag^+_{(aq)} + Cl^-_{(aq)} \leftrightarrows AgCl_{(s)}$ $\quad K = 1/K_{sp}(AgCl) = 5.6\text{x}10^{9}$

Ans: AgBr precipitated first

(b) The first end point is for Br^- (mole Br^-= mole Ag^+)

Mole Ag^+ = 5.1 x 10^{-4} mole = mole Br^-

Conc. Br^-= 5.1 x 10^{-4} /0.025 L (volume in original soln) = 0.0207 M

(c) The second end point is for Cl^- (After all Br^- reacted with the Ag^+ from the first end point); (mole Cl^-= mole Ag^+)

Volume to react with Cl- = 42.23-15.55ml = 26.68ml

Mole Ag^+ = 8.89 x 10^{-4} mole = mole Cl^-

Conc. Cl^-= 8.89 x 10^{-4} /0.025 L (volume in original soln) = 0.0355 M

Modified by Dr. Mohammed
Rasheed

Chapter 14

Principles of Neutralization Titration

Neutralization titrations are widely used to determine the amounts of acids and bases and to monitor the progress of reactions that produce or consume hydrogen ions.

14 A Solutions and indicators for acid/base titrations

Neutralization titrations depend on a chemical reaction of the analyte with a standard reagent. There are several different types of acid/base titrations.

1. The titration of a strong acid, such as hydrochloric or sulfuric acid, with a strong base, such as sodium hydroxide.
2. The titration of a weak acid, such as acetic or lactic acid, with a strong base.
3. The titration of a weak base, such as sodium cyanide or sodium salicylate, with a strong acid.

14A-1 Standard Solutions

- The standard reagents used in acid/base titrations are always strong acids or strong bases, such as HCl, $HClO_4$, H_2SO_4, NaOH, and KOH. They produce sharper end point.
- Weak acids and bases are never used as standard reagents because they react incompletely with analytes.
- Standard solutions of acids are prepared by diluting concentrated hydrochloric, perchloric, or sulfuric acid.
- Nitric acid is seldom used because its oxidizing properties offer the potential for undesirable side reactions.
- Hot concentrated perchloric and sulfuric acids are potent oxidizing agents and are very hazardous.
- Standard solutions of bases are ordinarily prepared from solid sodium, potassium, and occasionally barium hydroxides.
- Eye protection should always be used when handling dilute solutions of these reagents.

General goal and procedure of acid-base titration

1) Standardization

Acid or base standard solution unknown moles

Primary standard solution known mole

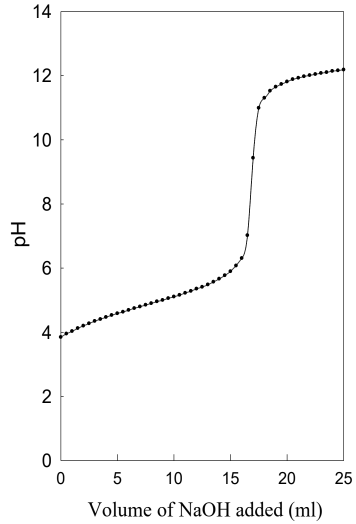
2) Determination

Acid or base standard solution known mole

Analyte Sample solution unknown mole

3) Titration curve

Plots of pH versus volume of titrant



4) Interpret titration curve, understand what is happening during titration

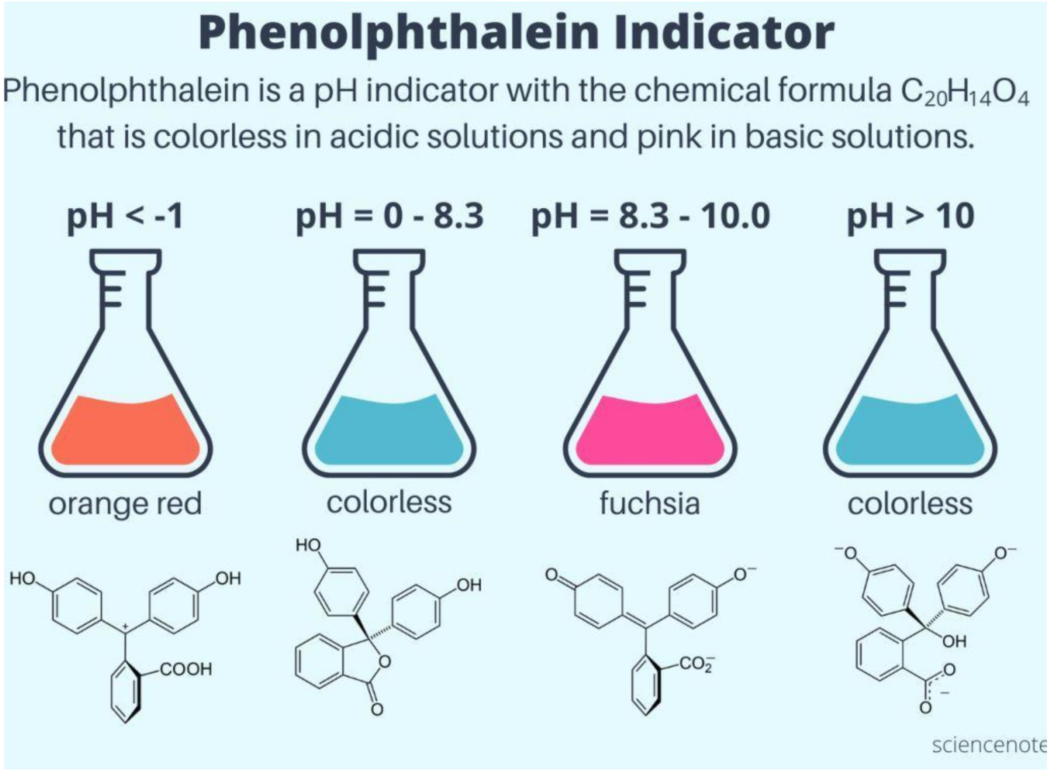
14A-2 Acid/Base Indicators

An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate base or its conjugate acid form. For example, the behavior of an acid-type indicator, HIn:

$$HIn + H_2O \Leftrightarrow In^- + H_3O^+$$

acid color base color

- At different pH both acid and base may be present) like the buffer)



Phenolphthalein Indicator

Phenolphthalein is a pH indicator with the chemical formula $C_{20}H_{14}O_4$ that is colorless in acidic solutions and pink in basic solutions.

$$HIn + H_2O \Leftrightarrow In^- + H_3O^+$$

acid color base color

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

$$In + H_2O \Leftrightarrow InH^+ + OH^-$$

base color acid color

$$[H_3O^+] = K_a \frac{[HIn]}{[In^-]}$$

❖ **Remember buffer equation**

$$\frac{[HIn]}{[In^-]} \geq \frac{10}{1} \rightarrow [HIn] \text{ acid color, } [H_3O^+] \geq 10Ka$$

→ about 90% or more of the indicator is in the acid form (HIn) → you see the acid color.

$$\frac{[HIn]}{[In^-]} \leq \frac{1}{10} \rightarrow [In^-] \text{ base color, } [H_3O^+] \leq 0.1Ka$$

→ about 90% or more is in the base form (In^-) → you see the base color.

$$pH(\text{acid color}) = -\log(10Ka) = pKa - 1$$

$$pH(\text{basic color}) = -\log(0.1Ka) = pKa + 1$$

indicator pH range = pKa ± 1

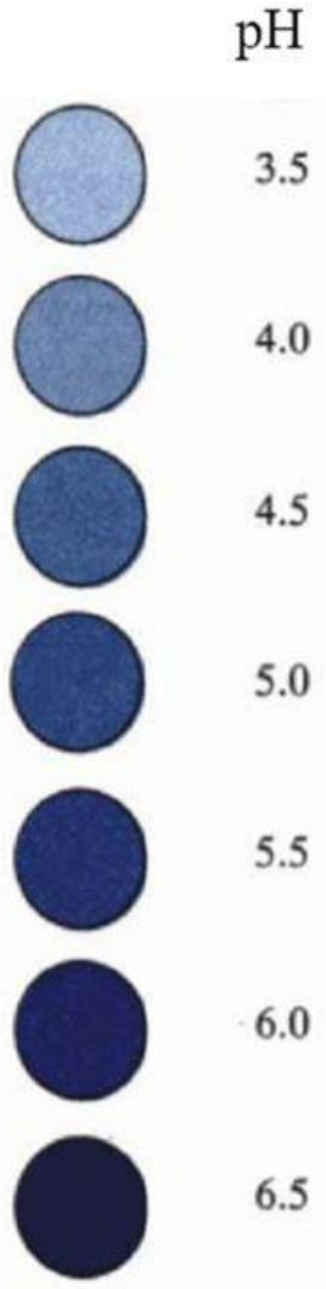


Fig. 14-2 Indicator color as a function of pH ($pK_a = 5.0$).

Table 14-1 Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pKa*	Color Change†	Indicator Type#
Thymol blue	1.2 - 2.8	1.65 @	R - Y	1
	8.0 - 9.6	8.90 @	Y - B	
Methyl yellow	2.9 - 4.0		R - Y	2
Methyl orange	3.0 - 4.4	3.46 @	R - O	2
Bromocresol green	3.8 - 5.4	4.66 @	Y - B	1
Methyl red	4.2 - 6.3	5.00 @	R - Y	2
Bromocresol purple	5.2 - 6.8	6.12 @	Y - P	1
Bromothymol blue	6.2 - 7.6	7.10 @	Y - B	1
Phenol red	6.8 - 8.4	7.81 @	Y - R	1
Cresol purple	7.6 - 9.2		Y - P	1
Phenolphthalein	8.3 - 10.0		C - R	1
Thymolphthalein	9.3 - 10.5		C - B	1
Alizarin yellow GG	10 -12		C - Y	2

* At ionic strength of 0.1

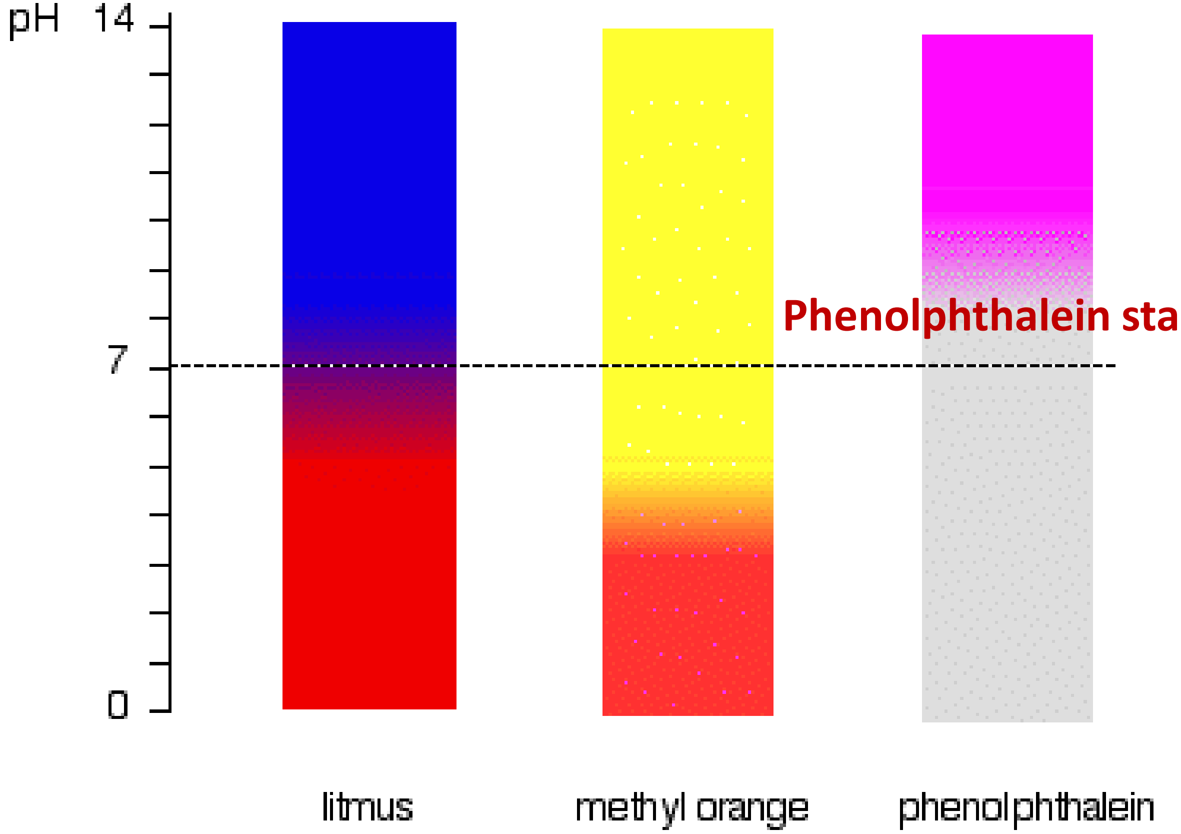
† B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

\# (1) Acid type: $HIn + H_2O \Leftrightarrow H_3O^+ + In^-$

\# (2) Base Type: $In + H_2O \Leftrightarrow InH^+ + OH^-$

@ For the reaction $HIn^+ + H_2O \Leftrightarrow H_3O^+ + In$

Phenolphthalein	8.3 - 10.0		C - R	
Methyl orange	3.0 - 4.4	3.46 @	R - O	2



Phenolphthalein start to change its color at pH= 8.3

Titration Errors with Acid/Base Indicators

There are two types of titration error in acid/base titrations:

- Determinate error that occurs when the pH at which the indicator changes color differs from the pH at the equivalence point. It can usually be minimized by choosing the indicator carefully or by making a blank correction.
- Indeterminate error that originates from the limited ability of the human eye to distinguish reproducibly the intermediate color of the indicator. The magnitude of this error depends on the change in pH per milliliter of reagent at the equivalence point, on the concentration of the indicator, and on the sensitivity of the eye to the two indicator colors.

On the average, the visual uncertainty with an acid/base indicator is in the range of ±0.5 to ±1 pH unit. This uncertainty can often be decreased to as little as ± 0.1 pH unit by matching the color of the solution being titrated to that of a reference standard containing a similar amount of indicator at the appropriate pH.

Variables That Influence the Behavior of Indicators

- The pH interval over which a given indicator exhibits a color change is influenced by temperature, the ionic strength of the medium, and the presence of organic solvents and colloidal particles.
- Some of these effects can cause the transition range to shift by one or more pH units.

14 B Titration of strong acids and bases

The hydronium ions in an aqueous solution of a strong acid have two sources: (1) the reaction of the acid with water, and (2) the dissociation of water itself. In all but the most dilute solutions, however, the contribution from the strong acid far exceeds that from the solvent. *So,* for a solution of HCl with a concentration greater than about 10^{-6} M, we can write:

$$[H_3O^+] = c_{HCL} + [OH^-] \approx c_{HCL}$$

where $[OH^-]$ represents the contribution of hydronium ions from the dissociation of water.

For a solution of a strong base, such as sodium hydroxide, that is:

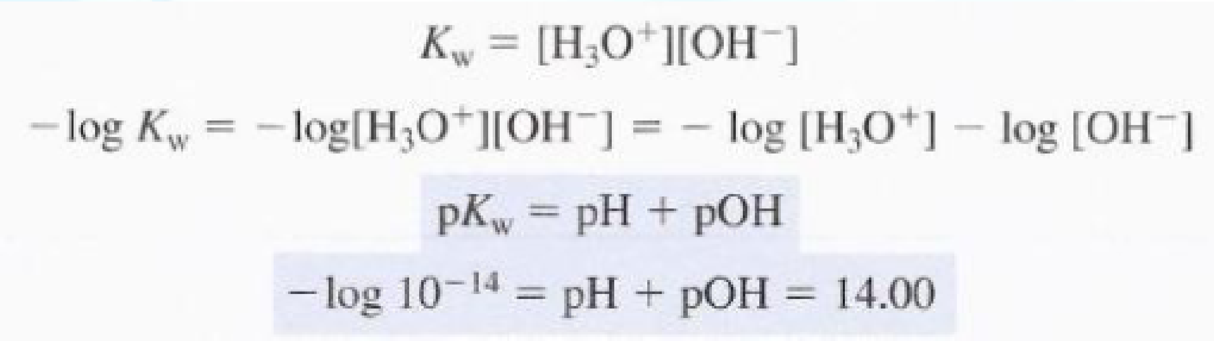
$$[OH^-] = c_{NAOH} + [H_3O^+] \approx c_{NAOH}$$

In solutions of a strong acid that are more concentrated than about 1×10^{-6} M, we can assume that the equilibrium concentration of H_3O^+ is equal to the analytical concentration of the acid. The same is true for $[OH^-]$ in solutions of strong bases.

14B-1 Titrating a Strong Acid with a Strong Base

Three types of calculations must be done to construct the hypothetical curve for titrating a solution of a strong acid with a strong base.

1. Pre-equivalence; compute the concentration of the acid from its starting concentration and the amount of base added.
2. Equivalence: the hydronium ion concentration can be calculated directly from the ion-product constant for water, K_w. The solution is neutral, and pH = pOH, both pH and pOH = 7.00 at 25°C.
3. Post-equivalence: the analytical concentration of the excess base is computed, and the hydroxide ion concentration is assumed to be equal to or a multiple of the analytical concentration. We first calculate pOH and then pH, pH = 14.0 – pOH at 25°C.



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

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

$$pK_w = pH + pOH$$

$$-\log 10^{-14} = pH + pOH = 14.00$$

Ex. 14-1 Derive a titration curve for the titration of 50.00 mL of 0.0500 M HCl with 0.1000 M NaOH. Calculate the pH after the addition of **1) 0 ml NaOH addition 2) 10.0 ml 3) 25.0 ml 4) 25.1 ml**

$$HCl + NaOH \rightarrow NaCl + H_2O$$

a) At 0 ml addition of NaOH we only have HCl; strong acid with a concentration of 0.0500 M; **Then pH = 1.3**;

b) At 10 ml addition
mole HCl = 2.5 x 10^{-3}; mole NaOH added = 1 x 10^{-3}; after the titration reaction
mole HCl = 1.5 x 10^{-3}; M [HCl] = 1.5 x 10^{-3}/ (0.06L (**total volume after mixing**) = **0.025 M**
pH = 1.6

c) At 25ml addition; mole HCl = 2.5 x 10^{-3}; mole NaOH added = 2.5 x 10^{-3}; after the titration reaction; 0ml of both **(Equivalence point); but** H2O is present with Kw;
$\mathbf{K_w = 1.0 \times 10^{-14} = X^2}$; then x = $[H^+]$ = $[OH^-]$ = 1.0 x10^{-7} M; **pH = 7.0**

d) After 25.1 ml addition; mole HCl = 2.5 x 10^{-3}; mole NaOH added = 2.51 x 10^{-3}
mole NaOH remains = 1 x 10^{-5} ; **$[OH^-]$ = 1.333 x 10^{-4} M**
pOH = 3.88; **pH = 10.12**

- **Note that addition of 0.1ml of NaOH increases the pH from 7 to 10**

- **See next table**

Table 14-2 Changes in pH during the titration of a strong acid with a strong base

Volume of NaOH, mL	pH	
	50.00 mL of 0.0500 M HCl with 0.1000 M NaOH	50.00 mL of 0.000500 M HCl with 0.001000 M NaOH
0.00	1.30	3.30
10.00	1.60	3.60
20.00	2.15	4.15
24.00	2.87	4.87
24.90	3.87	5.87
25.00	7.00	7.00
25.10	10.12	8.12
26.00	11.12	9.12
30.00	11.80	9.80

Before equivalence point (1.30–3.87)

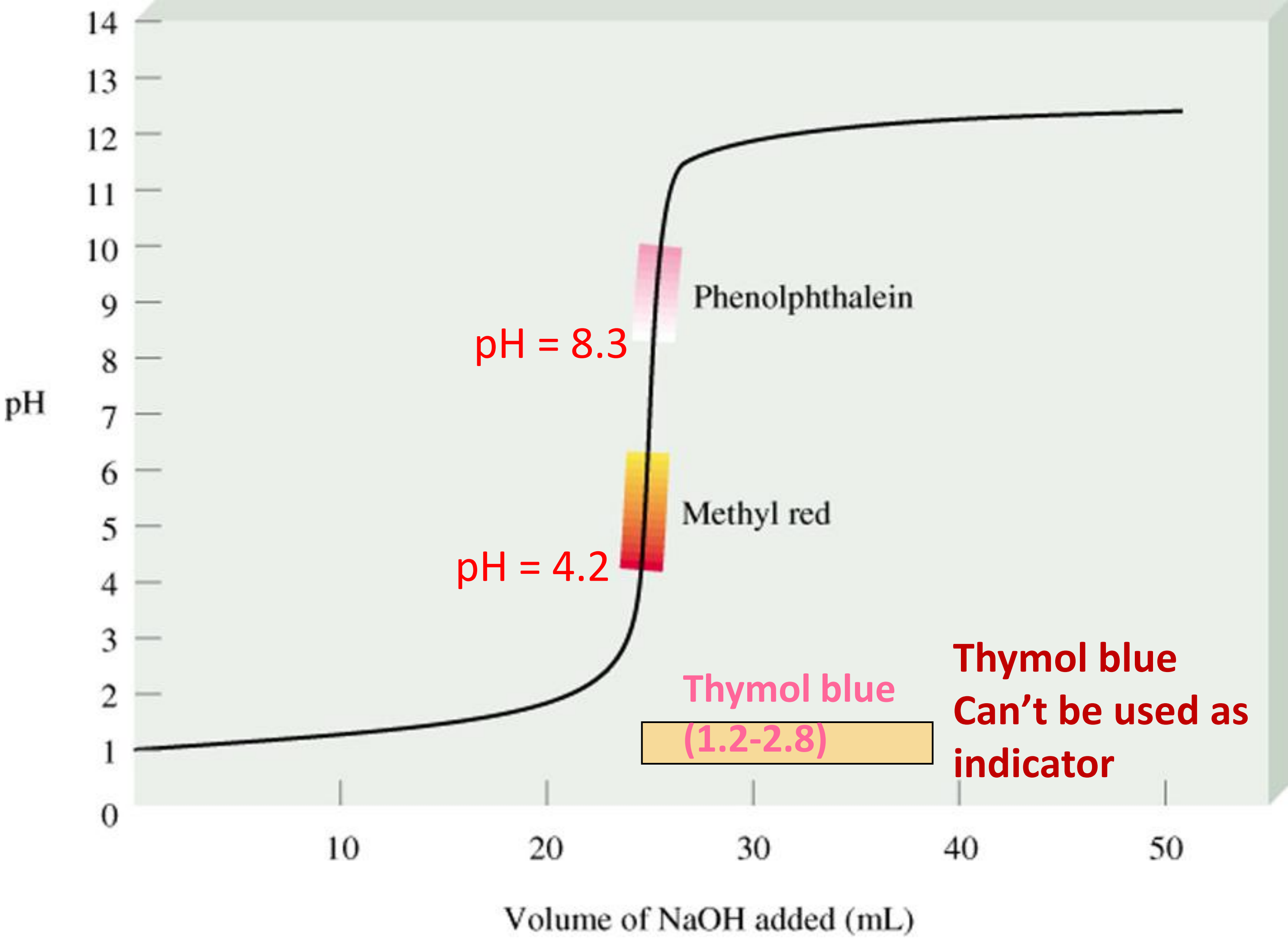
at equivalence point (7.00)

after equivalence point (10.12–11.80)

Sharp end point (3.87–11.12)

Not sharp end point (5.87–8.12)

The titration curve of a strong acid with a strong base.



pH = 8.3

pH = 4.2

Thymol blue
(1.2-2.8)

**Thymol blue
Can’t be used as
indicator**

The Effect of Concentration

The effects of reagent and analyte concentration on the neutralization titration curves for strong acids are shown. Note that with 0.1 M NaOH as the titrant, the change in pH in the equivalence-point region is large (curve A). With 0.001 M NaOH, the change is markedly less but still pronounced (curve B).

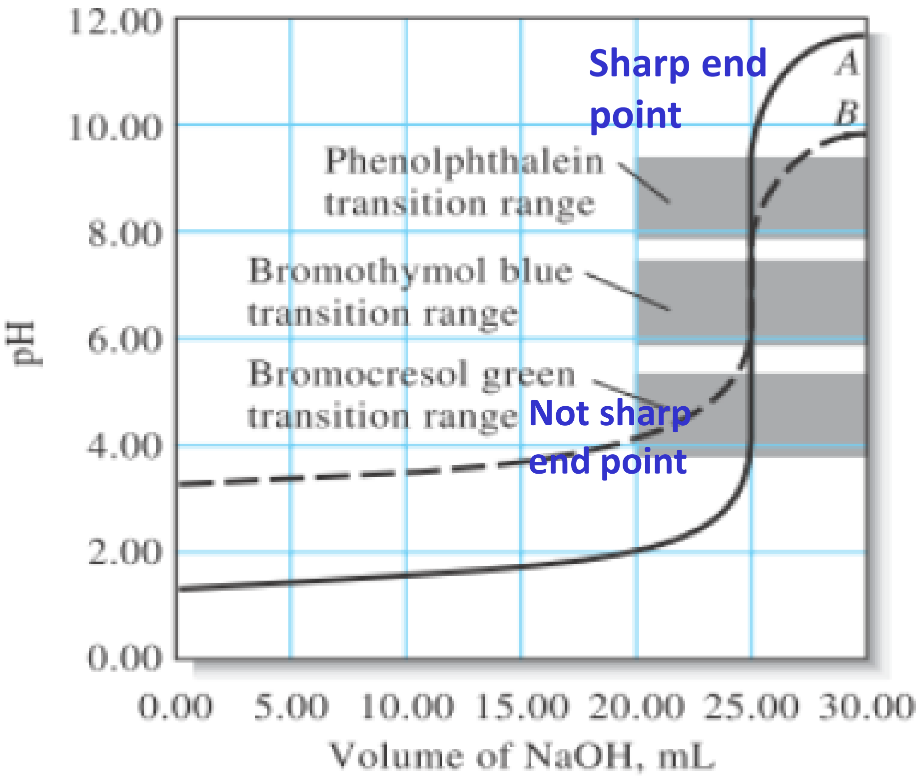
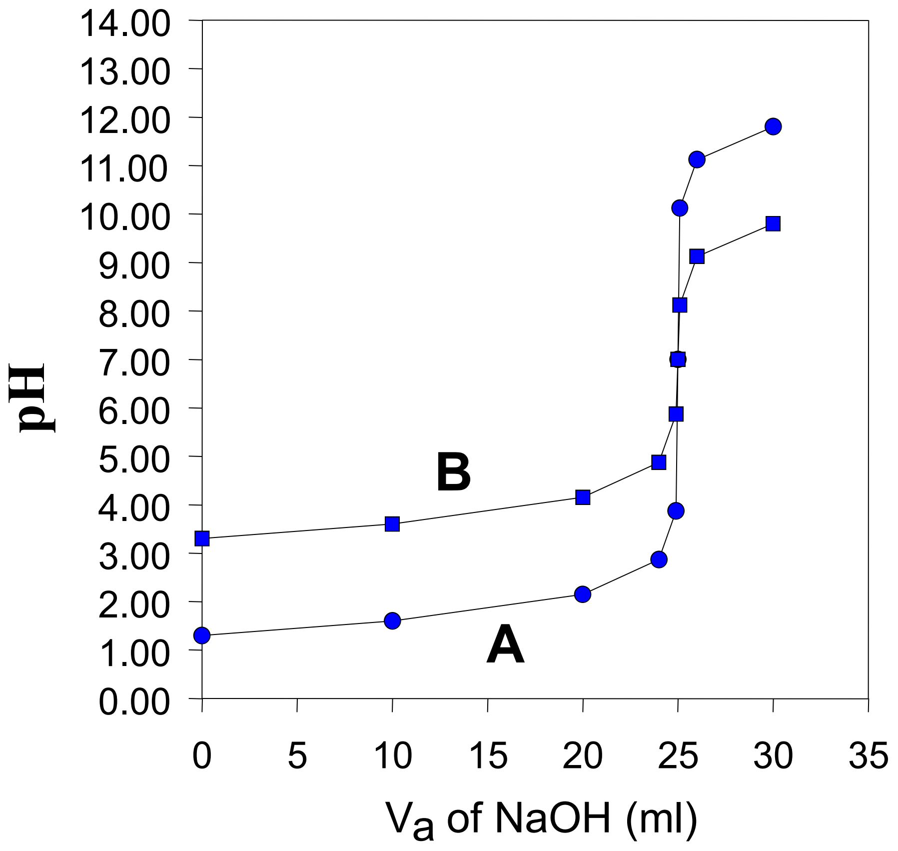


Figure 14-3 Titration curves for HCl with NaOH.

Choosing an Indicator

- Figure 14-3 shows that the selection of an indicator is not critical when the reagent concentration is approximately 0.1 M. The volume differences in titrations with the three indicators shown are of the same magnitude as the uncertainties associated with reading the buret and so are negligible.
- But bromocresol green is unsuited for a titration involving the 0.001 M reagent because the color change occurs over a 5-mL range well before the equivalence point. The use of phenolphthalein is subject to similar objections. Of the three indicators, then, only bromothymol blue provides a satisfactory end point with a minimal systematic error in the titration of the more dilute solution (0.001 M NaOH).



Changes in pH during the titration of Strong acid with strong base

The effects of titrant and analyte concentrations on neutralization titration curves.

For the titration with diluted concentrations, the change in pH in equivalence point region is markedly less than concentrated solution

A: 50 ml of **0.0500M HCl vs 0.1000M NaOH**

B: 50 ml of **0.000500M HCl vs 0.001000M NaOH**

14B-2. Titrating a Strong Base with a Strong Acid

14-2 Calculate the pH during the titration of 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

(a)At 24.50 mL added

$$[OH^-] = C_{NaOH} = \frac{(50.0 \times 0.0500) - (24.50 \times 0.1000)}{(50.0 + 24.50)} = 6.71 \times 10^{-4}\,M$$

pOH = -log(6.71×10^{-4}) = 3.17,   pH= 14 - 3.17 = 10.83

(b) Equivalence point: $[H_3O^+]=[OH^-]$

$$[H_3O^+] = \sqrt{K_w} = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7};\quad pH = 7.00$$

(c) At 25.50 mL added

$$[H_3O^+] = C_{HCl} = \frac{(25.50 \times 0.100) - (50.00 \times 0.0500)}{75.50} = 6.62 \times 10^{-4}\,M$$

pH = -log (6.62×10^{-4}) = 3.18

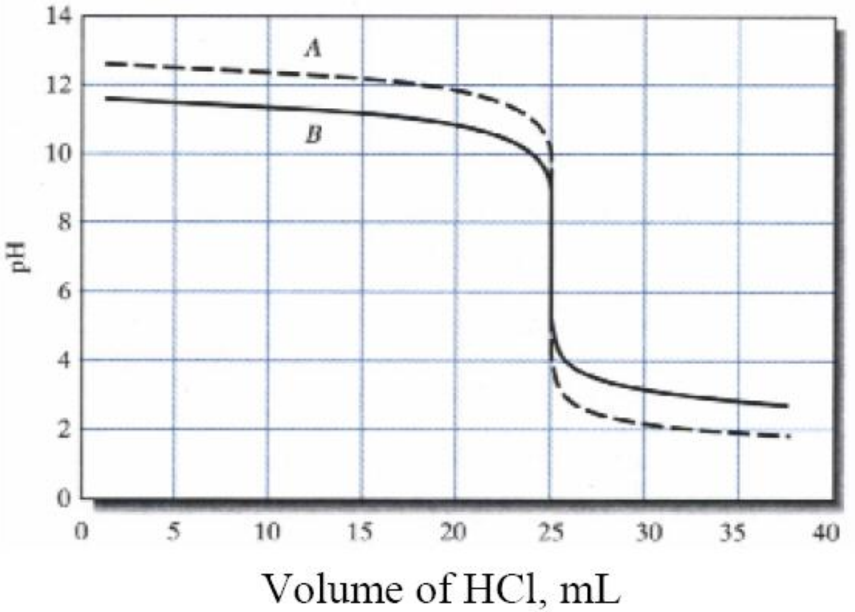


Fig. 14-4. Titration curves for NaOH with HCl.

Curve A (----): 50.00 mL of 0.0500 M NaOH with 0.1000 M HCl.

Curve B (—): 50.00 mL of 0.00500 M NaOH with 0.01000 M HCl.

14 C Titration curves for weak acids

Four distinctly different types of calculations are needed to compute values for a weak acid (or a weak base) titration curve:

1. At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that solute and its dissociation constant.
2. After various increments of titrant have been added (up to, but not including, the equivalence point), the solution consists of a series of buffers. The pH of each buffer can be calculated from the analytical concentrations of the conjugate base or acid and the concentrations of the weak acid or base that remains.
3. At the equivalence point, the solution contains only the conjugate of the weak acid or base being titrated (that is, a salt), and the pH is calculated from the concentration of this product.
4. Beyond the equivalence point, the excess of strong acid or base titrant suppresses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

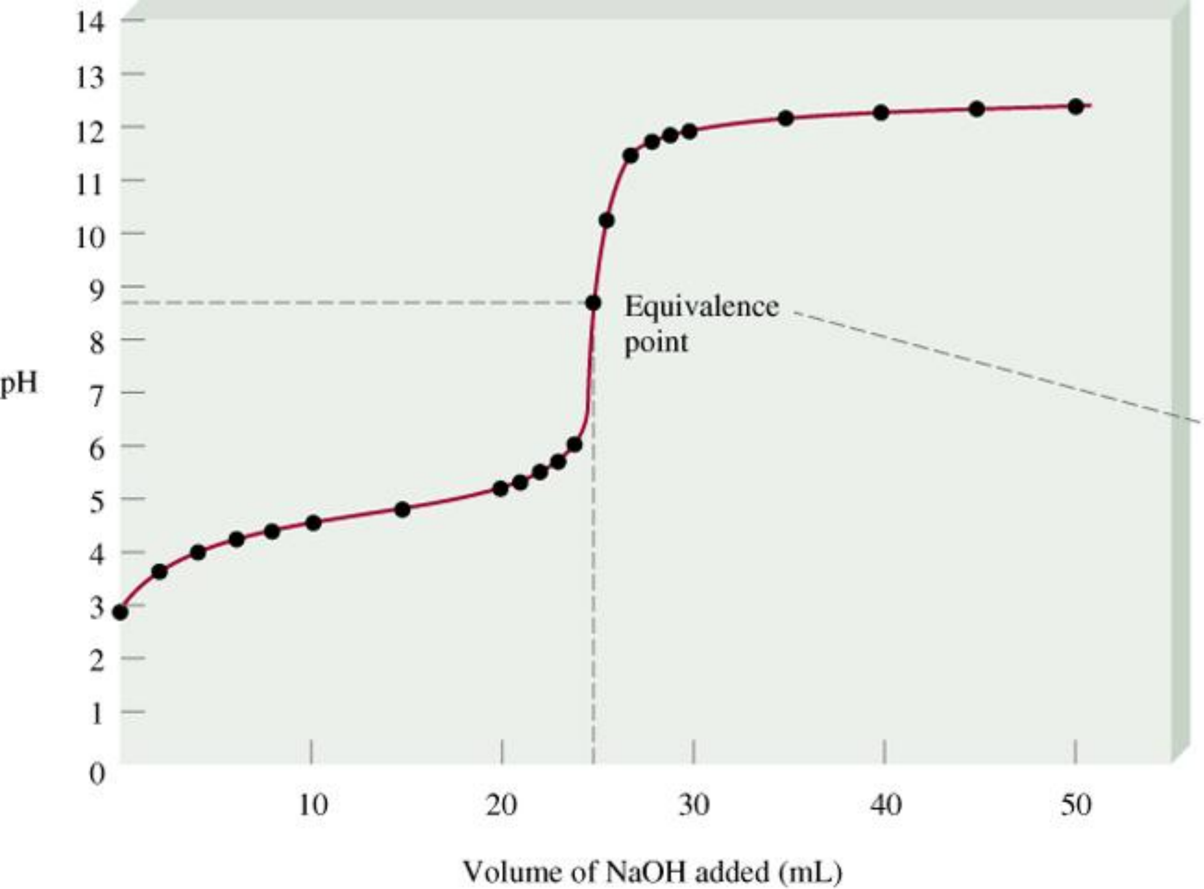
Weak Acid-Strong Base Titrations

$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (l)$

$CH_3COOH\ (aq) + OH^-\ (aq) \longrightarrow CH_3COO^-\ (aq) + H_2O\ (l)$

At equivalence point (pH >7; result from the hydrolysis of CH_3COO^-)

$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + CH_3COOH\ (aq)$



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Ex. 14-2 Generate a curve for the titration of 50.00 mL of 0.1000 M acetic acid ($K_a = 1.75 \times 10^{-5}$) with 0.1000 M NaOH.

1) 0 ml Addition 2) 10.0 ml 3) 50.0 ml 4) 50.10 ml

a) At 0 ml addition of NaOH we only have CH_3COOH (HA); a weak acid; conc. of **0.100 M**;

$$[H_3O^+] = \sqrt{K_a C_{HA}}$$

$[H_3O^+] = 1.32 \times 10^{-3}$; Then pH = 2.8

b) At 10 ml addition $CH_3COOH\,(aq) + NaOH\,(aq) \rightarrow CH_3COONa\,(aq) + H_2O\,(l)$

mole HA = 5.0×10^{-3}; mole NaOH added = 1×10^{-3}; **after the titration reaction**

mole HA = 4.0×10^{-3}; M [HA] = 4.0×10^{-3}/0.06L **(total volume)** = **0.067M**

mole CH_3COONa (A^-) = 1×10^{-3}; M [A] = 1.0×10^{-3}/ 0.06L = **0.0167M**

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

Then we have a buffer; pH = 4.16

$CH_3COOH\,(aq)$	$+ NaOH\,(aq) \rightarrow$	$CH_3COONa\,(aq)$	$+ H_2O\,(l)$
5×10^{-3}	1×10^{-3}	0	0
4×10^{-3}	0	1×10^{-3}	

c) **At 50 ml addition**; mole HA = 5.0×10^{-3}; mole NaOH added = 5.0×10^{-3}; after the titration reaction; 0ml of HA and NaOH **(Equivalence point);**

$CH_3COOH\,(aq)$	$+ NaOH\,(aq) \rightarrow$	$CH_3COONa\,(aq)$	$+ H_2O\,(l)$
5×10^{-3}	5×10^{-3}	0	0
0	0	5×10^{-3}	

mole CH_3COONa (A^-) = 5×10^{-3}; M [A] = 5.0×10^{-3}/ 0.1L = 0.05 M

Then we have weak base;

$$[OH^-] = \sqrt{K_b C_B}$$

Kb = Kw/Ka = 5.71×10^{-10}

$[OH^-] = 5.34 \times 10^{-6}$ M; pH= 8.73

Cont. ……

d) After 50.10 ml addition; mole HA = 5.0 x 10^{-3}; mole NaOH added = 5.01 x 10^{-3}

mole NaOH remains = 1 x 10^{-5} ; M NaOH = 1 x 10^{-5} / 0.1001 = 1 x 10^{-4}

pOH = 4.0; **pH = 10.0**

a) Weak acid
b) Buffer
c) Weak base
d) Strong base

Fig 14-5: The effect of concentration on titration curve

Curve of titration of acetic acid and NaOH;

Curve A: 0.1000M acetic acid and 0.1000M NaOH

Curve B: 0.001000M acetic acid and 0.001000M NaOH

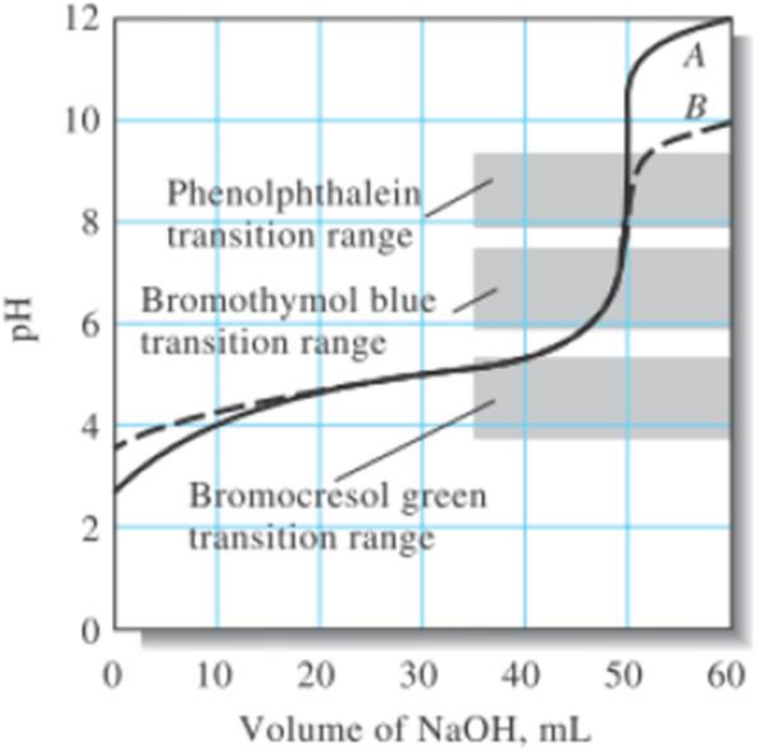


Figure 14-5

14C-2 The Effect of Reaction Completeness

Figure 14-6 The effect of acid strength (dissociation constant) on titration curves.

Titration curves for 0.1000 M solutions of acids with different dissociation constants are shown.

The pH change in the equivalence-point region becomes smaller as the acid becomes weaker, that is, as the reaction between the acid and the base becomes less complete.

Titration of 50.00 ml of 0.1000 M acid with 0.1000 M base.

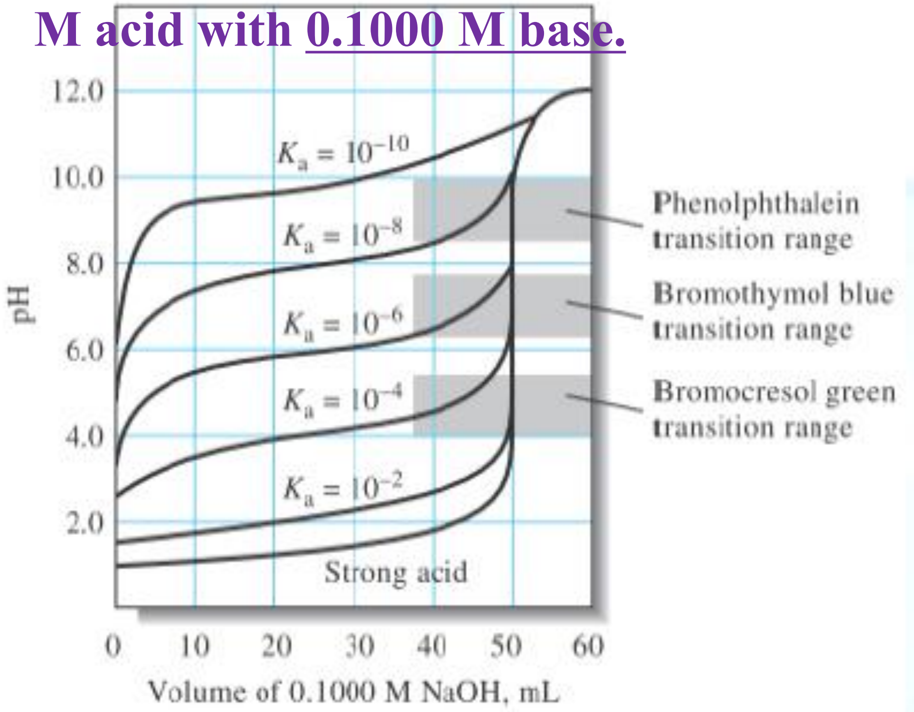


Figure 14-6

The effect of acid strength (dissociation constant) on titration curves. Each curve represents the titration of 50.00 ml of 0.1000 M acid with 0.1000 M base.

14D. Titration Curves for Weak Bases

Ex. 14-4 A 50.00-mL aliquot of 0.0500 M NaCN is titrated with 0.1000 M HCl.

The reaction is $CN^- + H_3O^+ \Leftrightarrow HCN + H_2O$

Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00 and (d) 26.00 mL of acid.

(a) Initial pH $CN^- + H_2O \Leftrightarrow HCN + OH^-$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{K_w}{K_a} = \frac{1.00\times10^{-14}}{6.2\times10^{-10}} = 1.61\times10^{-5}$$

$$[OH^-] = [HCN], \quad [CN^-] = C_{NaCN} - [OH^-] \cong 0.0500\ M$$

$$[OH^-] = \sqrt{K_b C_{NaCN}} = \sqrt{1.61\times10^{-5}\times0.0500} = 8.97\times10^{-4}\ M$$

$pH = 14.00 - (-\log 8.97 \times 10^{-4}) = 10.95$

(b) 10.00 mL of reagent

$$C_{NaCN} = \frac{50.00\times0.0500 - 10.00\times0.100}{60.00} = \frac{1.500}{60.00} M$$

$$C_{HCN} = \frac{10.00\times0.1000}{60.00} = \frac{1.000}{60.00} M$$

$$pH = pK_a + \log\frac{[CN^-]}{[HCN]}$$

$$pH = 9.21 + \log\frac{0.025}{0.0167} = 9.21 + 0.176 = 9.39$$

$$[H_3O^+] = 6.2\times10^{-10}\times\frac{1.000/60.00}{1.500/60.00} = 4.13\times10^{-10}$$

$pH = -\log (4.13 \times 10^{-10}) = 9.38$

(c) 25.00 mL of reagent

$$C_{HCN} = \frac{25.00\times0.1000}{75.00} = 0.03333M$$

$$[H_3O^+] = \sqrt{K_a C_{HCN}} = \sqrt{6.2\times10^{-10}\times0.03333} = 4.45\times10^{-6}$$

$pH = -\log (4.55 \times 10^{-6}) = 5.34$

(d) 26.00 mL of reagent

$$[H_3O^+] = C_{HCl} = \frac{26.00\times0.1000 - 50.00\times0.0500}{76.00} = 1.32\times10^{-3} M$$

$pH = -\log (1.32 \times 10^{-3}) = 2.88$

- Figure 14-7 shows hypothetical titration curves for a series of weak bases of different strengths.
- The curves show that indicators with mostly acidic transition ranges must be used for weak bases.
- When you titrate a weak base, use an indicator with an acidic transition range. When titrating a weak acid, use an indicator with a basic transition range.

Titration of 50.00 ml of 0.1000 M of different bases with 0.1000 M acid.

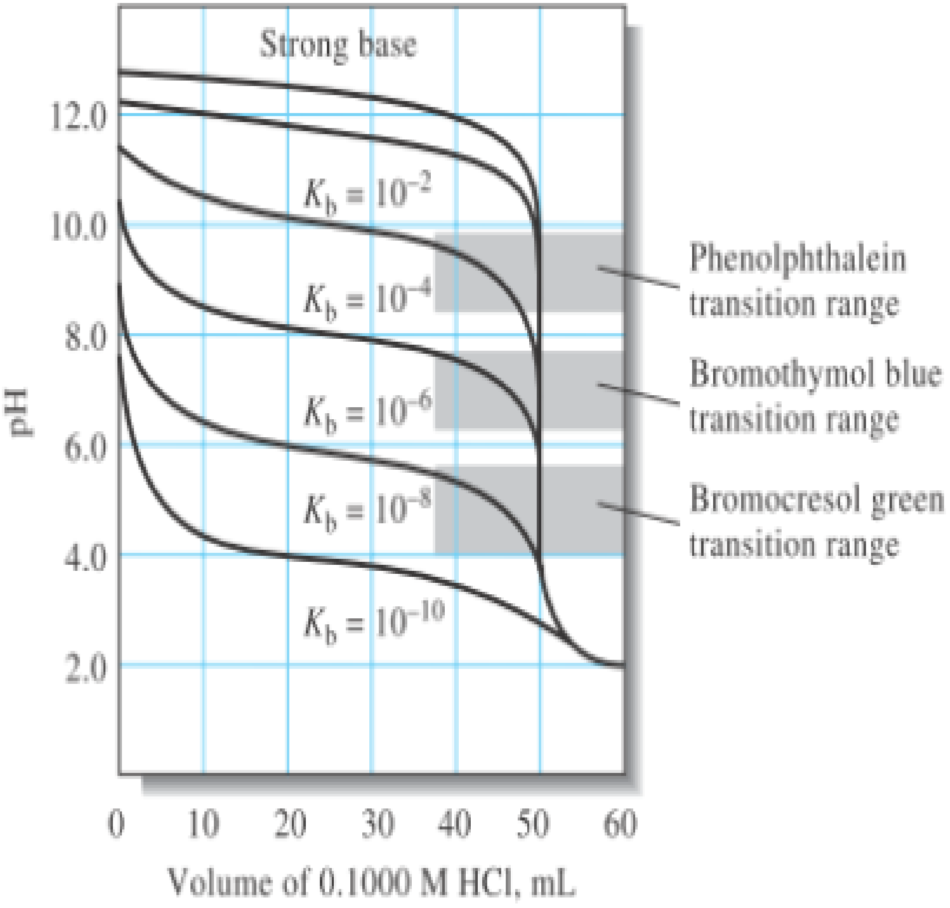


Figure 14-7

14E The Composition of Solutions During Acid/Base Titration

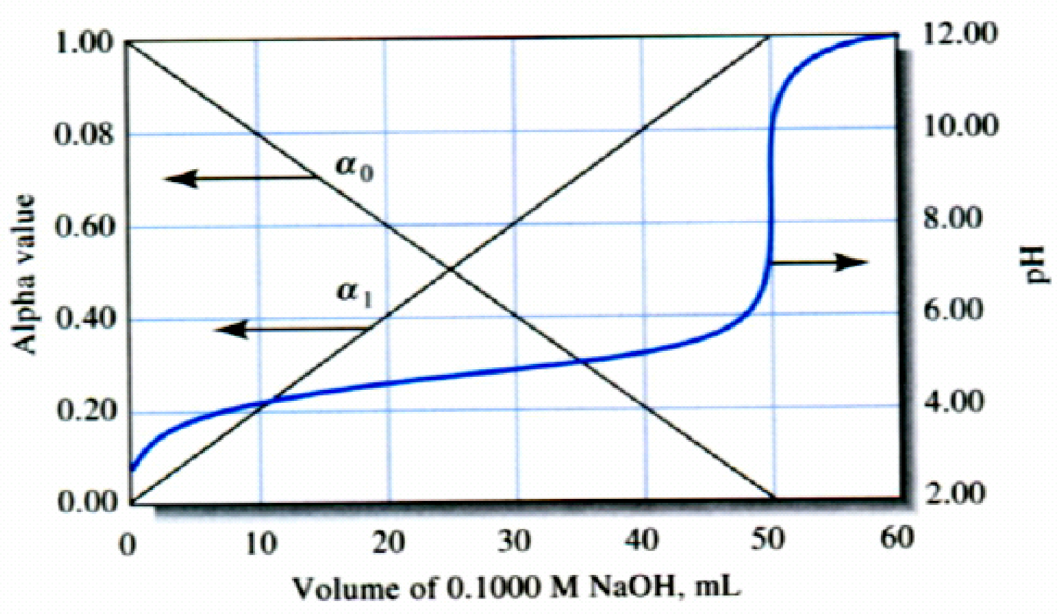


Fig. 14-8 Plots of relative amount of HOAc and OAc^- during a titration. The straight lines show the change in relative amounts of HOAc (α_0) and OAc^- (α_1) during the titration of 50.00 mL of 0.1000 M HOAc. The curved line is the titration curve for the system.

- Before NaOH titration α_o almost equal 1; **only weak acid determines pH**
- **When NaOH added slowly** α_o decreases and α_1 increases gradually **(Buffer)**
- around half titration point (around 25.00ml) $\alpha_o \approx \alpha_1 \approx 0.5$ **(Buffer)**
- At equivalence point (50ml) α_o approach zero and α_1 approach 1; **only weak base determines the pH**
- After end point (after 50 ml) the important species that determines the pH is **NaOH**


Any
Question?

Modified by Dr. Mohammed Rasheed

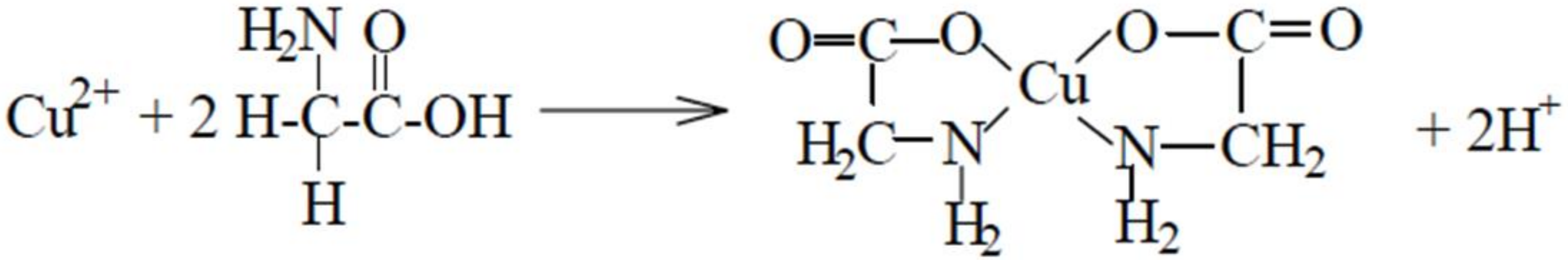
Chapter 17

Complexometric titrations

& Precipitation titrations

- ✓ **Formation of complex**
- ✓ Many metal ions can accept unshared pairs of electrons from an anion or molecule to **form coordinate covalent bonds**.
- ✓ The molecule or ion species containing atom which donates the electrons is called a ***ligand*** or ***complexing agent***.
- ✓ The ion which accepts the donated electrons is called the **central ion or central atom**. And the product resulting from a reaction between a metal ion and a ligand is referred to as a ***coordination compound* or *complex ion*.**

- ➢ W**ater, ammonia and halide ions are common inorganic ligand**.
- ➢ **Coordination number**: the no. of covalent bonds it tends to form with electron donor species.
- ➢ **Chelate**: formed when a metal ion coordinates with two or more donor group of a single ligand to form five or six-member heterocyclic ring



- The ***coordination number*** is the maximum of atoms or groups that can combine, in the coordination sphere, with central atom.

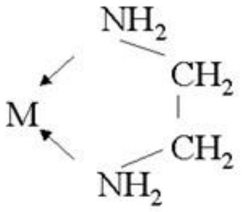
- Ligands containing a single donor atom are called ***monodentate***; those which shares more than one pair of electrons are said to be ***bi-, tri-, poly-dentate***.

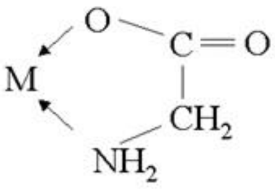
- The complex can have either a positive or a negative charge, or it can be neutral.

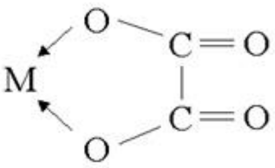
Ex. **Monodentate:** **NH_3 is mono dentate**

$[Cu(H_2O)_4]^{2+} + 4\ NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + 4\ H_2O$

Bidentate Ligand


ethylenediamine


glycinato

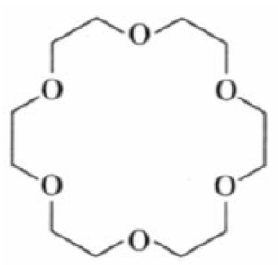

oxalato complex
stable

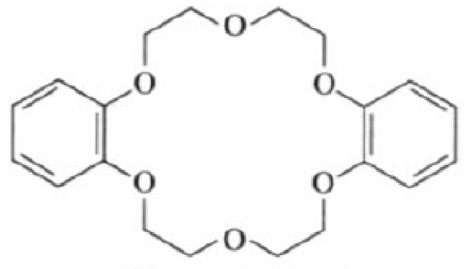
Tetradentate & hexadentate ligands are more satisfactory as titrants than ligands with a lesser no. of donor groups for two reasons:

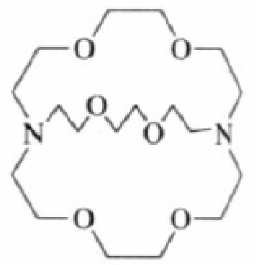
a. react more completely & sharper end points

b. tend to form 1:1 complexes

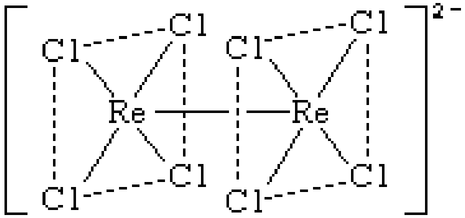
macrocycle: Metal ion-cyclic organic compound


18-crown-6


dibenzo-18-crown-6


cryptand 2,2,2

- ➢A complex can contain more than one central metal ion. In such a case a ligand attached to **two or more metal ions**.
- ➢A **mononuclear complex** contains a single metal ion ; a **binuclear complex** contains two central metal ions, and so forth.


complex with metal-metal bond (Re is rhenium)

Titrations with Inorganic Complexing Agents

Complexometric titrations: a metal ion reacts with a suitable ligand to form a complex, and the equivalence point is determined by an indicator. The formation of soluble inorganic complexes is not widely used for titrations, but **the formation of precipitates**, particularly with silver nitrate ($AgNO_3$) as the titrant, is the basis for important determinations.

Complexometric titrations

- **a plot of pM = -log [M] as a function of the volume of titrant added.**
- **In the titrations, the ligand is usually the titrant, and the metal ion is the analyte.**
- **Most simple inorganic ligands are unidentate, which can lead to low complex stability and indistinct titration end points.**
- **As titrants, multidentate ligands, those having four or six donor groups, have two advantages.**

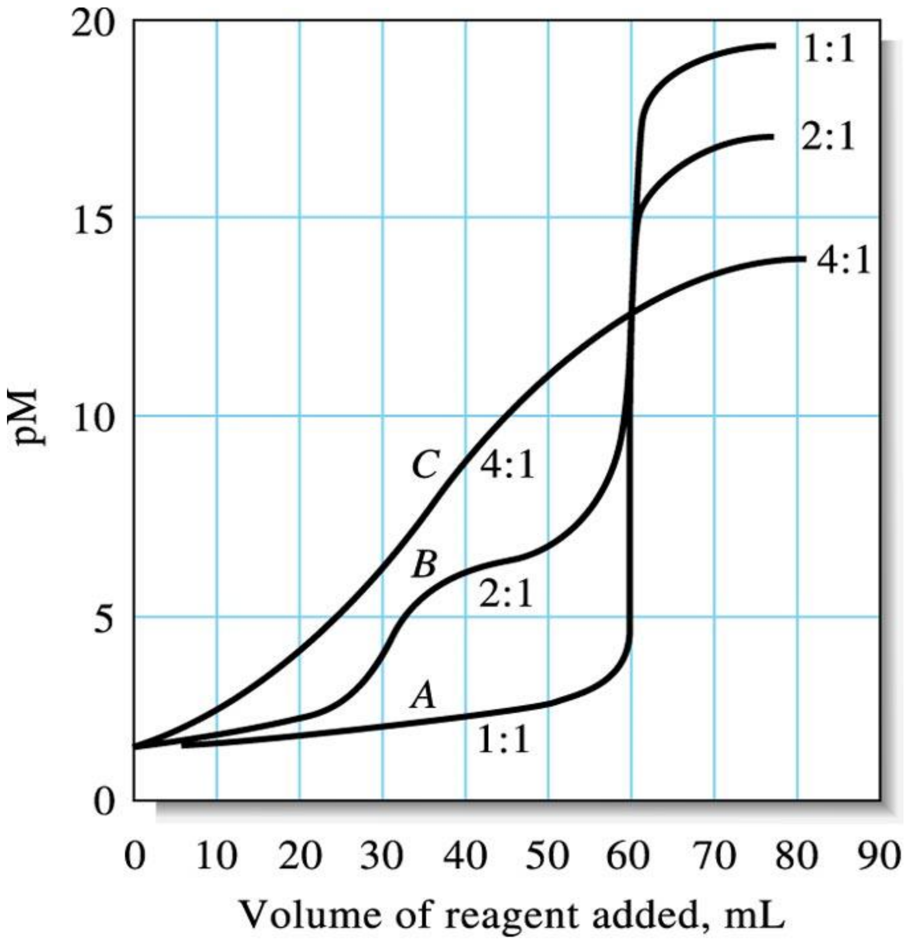
✓ **First, they generally react more completely with cations and thus provide sharper end points.**

✓ **Second, they ordinarily react with metal ions in a single-step process, whereas complex formation with unidentate ligands usually involves two or more intermediate species.**

Titrations with Inorganic Complexing Agents

- Curve *A* is computed for a reaction in which **a metal ion M** having a coordination number of 4 reacts with a **tetradentate ligand D** to form the complex of **MD**.

- Curve *B* is for the reaction of M with a **bidentate ligand B** to give **MB_2** in **two steps.** The formation constant for the first step is 1012 and for he second 108.



- Curve C involves **a unidentate ligand A** that forms **MA_4** in four steps with successive formation constants of 108, 106,104, and 102.

❖ These curves demonstrate that a much sharper end point is obtained with a reaction that takes place in a single step. For this reason, **multi dentate ligands** are ordinarily preferred for complexometric titrations.

Table 17-1 Typical Inorganic Complex-Formation Titration

Titrant	Analyte	Remarks
$Hg(NO_3)_2$	Br^-, Cl^-, SCN^-, CN^-, thiourea	Products are neutral Hg(II) complexes; various indicators used
$AgNO_3$	CN^-	Product is $Ag(CN)_2^-$; indicator is I^-; titrate to first turbidity of AgI
$NiSO_4$	CN^-	Product is $Ni(CN)_4^{2-}$; indicator is I^-; titrate to first turbidity of AgI
KCN	Cu^{2+}, Hg^{2+}, Ni^{2+}	Products are $Cu(CN)_4^{2-}$, $Hg(CN)_2$, $Ni(CN)_4^{2-}$; various indicator used

17C Organic Complexing Agents

$$nHX(org) + M^{n+}(aq) \Leftrightarrow MX_n(org) + nH^+(aq)$$

- Organic complexing agent is useful in precipitating metals to prevent interferences
- Many organic reagents are used to convert metal ions into forms that can be readily extracted from water **into an immiscible organic phase**.
- Masking Agent: is the formation of stable complexes that bind a metal and prevent it from interfering in a determination of another metal.

Table 17-2 Organic reagents for extracting metals

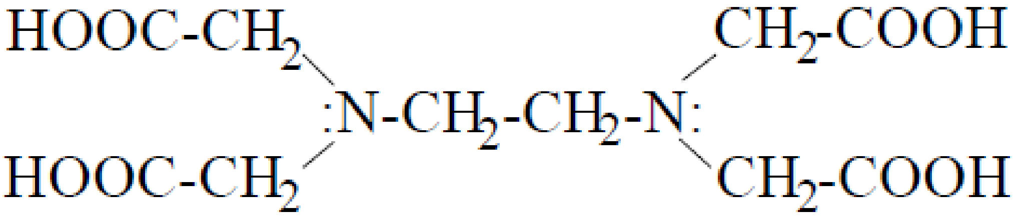
Reagent	**Metal Ions extracting Metals**	**Solvents**
8-Hydroxyquinoline	Zn^{2+}, Cu^{2+}, Ni^{2+}, Al^{3+}, many others	Watetr → Chloroform ($CHCl_3$)
Diphenylthiocarbazone (dithizone)	Cd^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, many others	Watetr → $CHCl_3$ or CCl_4
Acetylacetone	Fe^{3+}, Cu^{2+}, Zn^{2+}, U(VI), many others	Watetr → $CHCl_3$ or CCl_4 C_6H_6
Ammonium pyrrolidine dithiocarbamate	Transition metals	Watetr → Methyl isobutyl ketone
Tenoyltrifluoroacetone	Ca^{2+}, Sr^{2+}, La^{3+}, Pr^{3+}, other rare earths	Watetr → Benzene
Dibenzo-18-crown-6	Alkali metals, some alkaline earths	Watetr → Benzene

17D Aminocarboxylic acid titrations

- Tertiary amines that also contain carboxylic acid groups form remarkably stable chelates with many metal ions.
- Ethylenediaminetetraacetic Acid (EDTA) is the most widely used complexometric titrant. It has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups.
- **EDTA is a hexadentate ligand.**

17D-1 Ethylenediaminetetraacetic acid (EDTA)

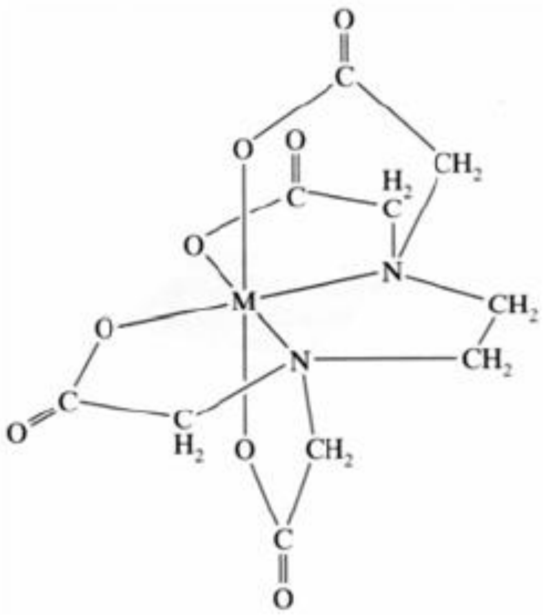
(ethylenedinitrilo)tetraacetic acid → hexadentate ligand



$$\begin{array}{ccc} \mathrm{HOOC{-}CH_2} & & \mathrm{CH_2{-}COOH} \\ & :\mathrm{N{-}CH_2{-}CH_2{-}N}: & \\ \mathrm{HOOC{-}CH_2} & & \mathrm{CH_2{-}COOH} \end{array}$$

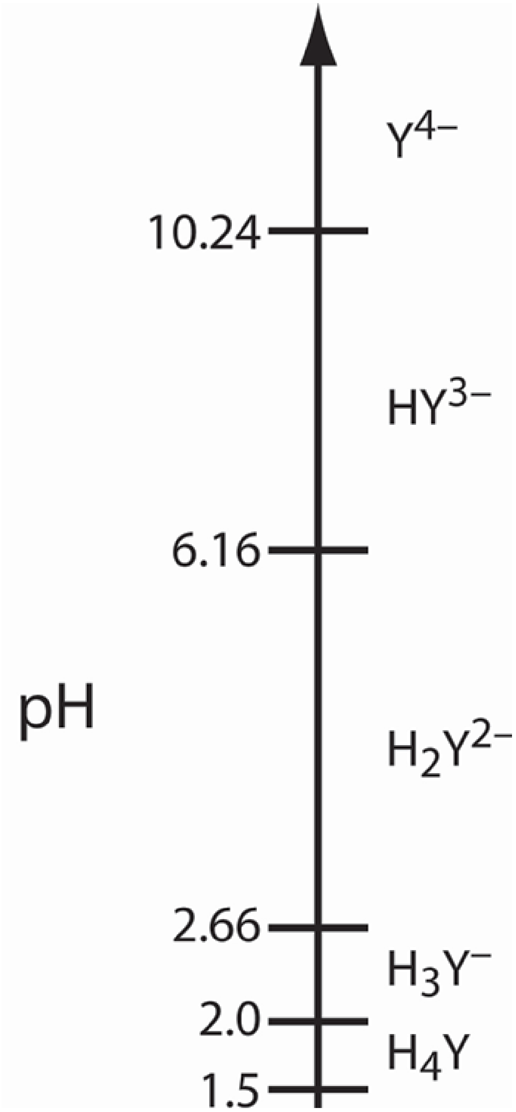
(H_4Y)

Fig. 17-3 Structure of a metal/EDTA complex. (Hexadentate ligand)



Hexadentate ligand

$$C_{EDTA} = [H_4Y]+[H_3Y^-]+[H_2Y^{2-}]+[HY^{3-}]+[Y^{4-}]$$



EDTA is a tetrabasic acid The component distribution of the acid (%) depends on pH

H_4Y α_0

$\downarrow$ $K_1 = 1.02 \times 10^{-2}$

H_3Y^- α_1

$\downarrow$ $K_2 = 2.14 \times 10^{-3}$

H_2Y^{2-} α_2

$\downarrow$ $K_3 = 6.92 \times 10^{-7}$

HY^{3-} α_3

$\downarrow$ $K_4 = 5.50 \times 10^{-11}$

Y^{4-} α_4

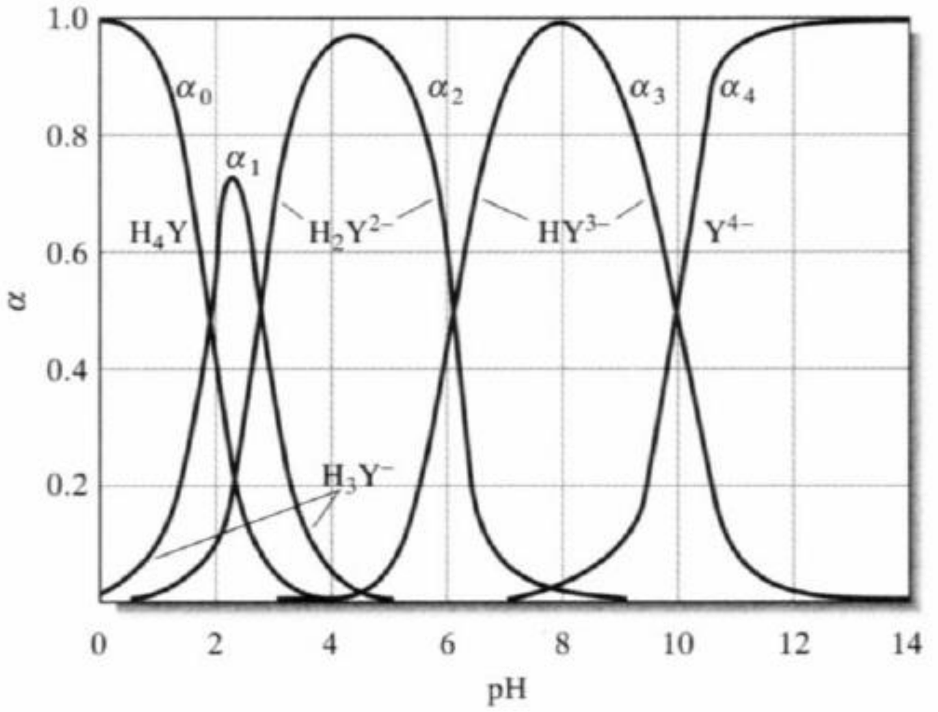


Fig. 17-2 Composition of EDTA solution as a function of pH.

- The Fully protonated form H_4Y is only a major component in very acidic solution pH<3.
- In the pH range of 3-10 H_2Y^{2-} and HY^{3-} are dominant.
- Y_4^- is a significant component only in very basic solution (pH>10)

EDTA Complex

- **EDTA combines with metal ions in a 1:1 ratio regardless of the charge on the cation.**
- It forms chelates with all cations (**except alkali metals**); most of these chelates are sufficiently stable for titrations. EDTA behaves as **a hexa-dentate ligand.**
- The equilibrium constant for the reaction of a metal with a ligand is called **the formation constant, K_f,** or the **stability constant**

Formation constant:

$$Ag^{+} + Y^{4-} \Leftrightarrow AgY^{3-}$$

$$Al^{3+} + Y^{4-} \Leftrightarrow AlY^{-}$$

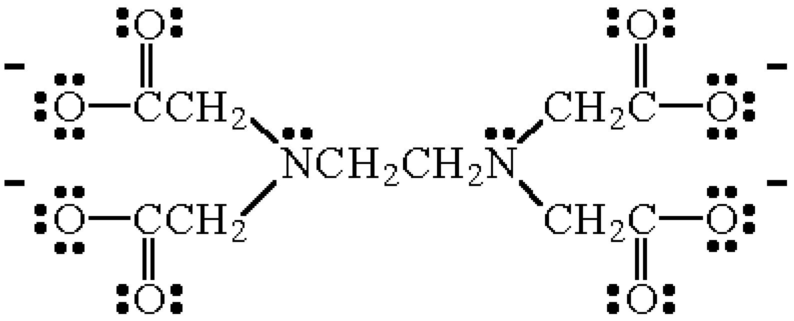
$$M^{n+} + Y^{4-} \leftrightarrow MY^{n-4} \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

- **Note that K_f for EDTA is defined in terms of the species Y^{4-} reacting with the metal ion. The equilibrium constant could have been defined for any of the other six forms of EDTA in the solution.**

Table 17-3 Formation constants for EDTA complexes

Cation	K_{MY}	LogK_{MY}	Cation	K_{MY}	logK_{MY}
Ag^+	2.1×10^7	7.32	Cu^{2+}	6.3×10^{18}	18.80
Mg^{2+}	4.9×10^8	8.69	Zn^{2+}	3.2×10^{16}	16.50
Ca^{2+}	5.0×10^{10}	10.70	Cd^{2+}	2.9×10^{16}	16.46
Sr^{2+}	4.3×10^8	8.63	Hg^{2+}	6.3×10^{21}	21.80
Ba^{2+}	5.8×10^7	7.76	Pb^{2+}	1.1×10^{18}	18.04
Mn^{2+}	6.2×10^{13}	13.79	Al^{3+}	1.3×10^{16}	16.13
Fe^{2+}	2.1×10^{14}	14.33	Fe^{3+}	1.3×10^{25}	25.1
Co^{2+}	2.0×10^{16}	16.21	V^{3+}	7.9×10^{25}	25.9
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}	23.2

- Note the large K_f for most metals



- **Y^{4-}** is hexadentate ligand forms very stable complexes (usually octahedral structures) with most of the transition metals. The donor atoms in **$EDTA^{4-}$** are the two N atoms, and the four, negatively charged O atoms.

17D-3 Equilibrium calculations involving EDTA

- **Calculate Y^{-4} to calculate M^{n+}**
- **in the equation** $M^{n+} + Y^{4-} \leftrightarrow MY^{n-4}$ $\quad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$

C_T: [*uncomplexed* EDTA]

$$C_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y]$$

Conditional Formation Constants

Substitute $\alpha_4 c_T$ for Y^{4-}

$$M^{n+} + Y^{4-} \Leftrightarrow MY^{(n-4)+} \qquad K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\alpha_4 c_T}$$

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

only at the pH for which α_4 is applicable **See Fig 17-2**

(When pH > 10)

Table: Values of α_4 for EDTA in Solutions of Various pH

pH	α_4	pH	α_4	pH	α_4	pH	α_4
2.0	3.71×10^{-14}	5.0	3.54×10^{-7}	8.0	5.39×10^{-3}	11.0	0.85
3.0	2.51×10^{-11}	6.0	2.25×10^{-5}	9.0	5.21×10^{-2}	12.0	0.98
4.0	3.61×10^{-9}	7.0	4.8×10^{-4}	10.0	0.35	13.0	1.00

Ex. 17-1 Calculate the molar Y^{4-} conc. in a 0.0200 M EDTA solution that has been buffered to a pH of 10.00.

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$

At pH 10.00, α_4 is 0.35

$$[Y^{4-}] = \alpha_4 C_T = (0.35)(0.0200) = 7.0 \times 10^{-3}\ M$$

Ex. 17-2 Calculate the equilibrium conc. of Ni^{2+} in a solution with an analytical NiY^{2-} conc. of 0.0150 M at pH (a) 3.0 and (b) 8.0.

$$Ni^{2+} + Y^{4-} \Leftrightarrow NiY^{2-} \qquad K_{NiY} = \frac{[NiY^{2-}]}{[Ni^{2+}][Y^{4-}]} = 4.2 \times 10^{18}$$

$$K'_{MY} = \alpha_4 K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]c_T}$$

a) At pH = 3; $K'_{NiY} = \alpha_4 K_{NiY}$, ($\alpha_4 = 2.51 \times 10^{-11}$) then $K'_{NiY} = 1.05 \times 10^{8}$

as in Ksp; the complex will dissociate to form Ni^{2+} and Y^{4-}; then
$NiY^{2-} \leftrightarrow Ni^{2+} + Y^{4-}$ $K = 1/1.05 \times 10^{8} = 9.52 \times 10^{-9}$;

$NiY^{2-}(aq) \leftrightarrow Ni^{2+}(aq) + Y^{4-}(aq)$ $K = 9.52 \times 10^{-9}$

$NiY^{2-}(aq)$	$Ni^{2+}(aq)$	$Y^{4-}(aq)$
0.0150	0	0
-x	+x	+x
0.0150-x	x	x

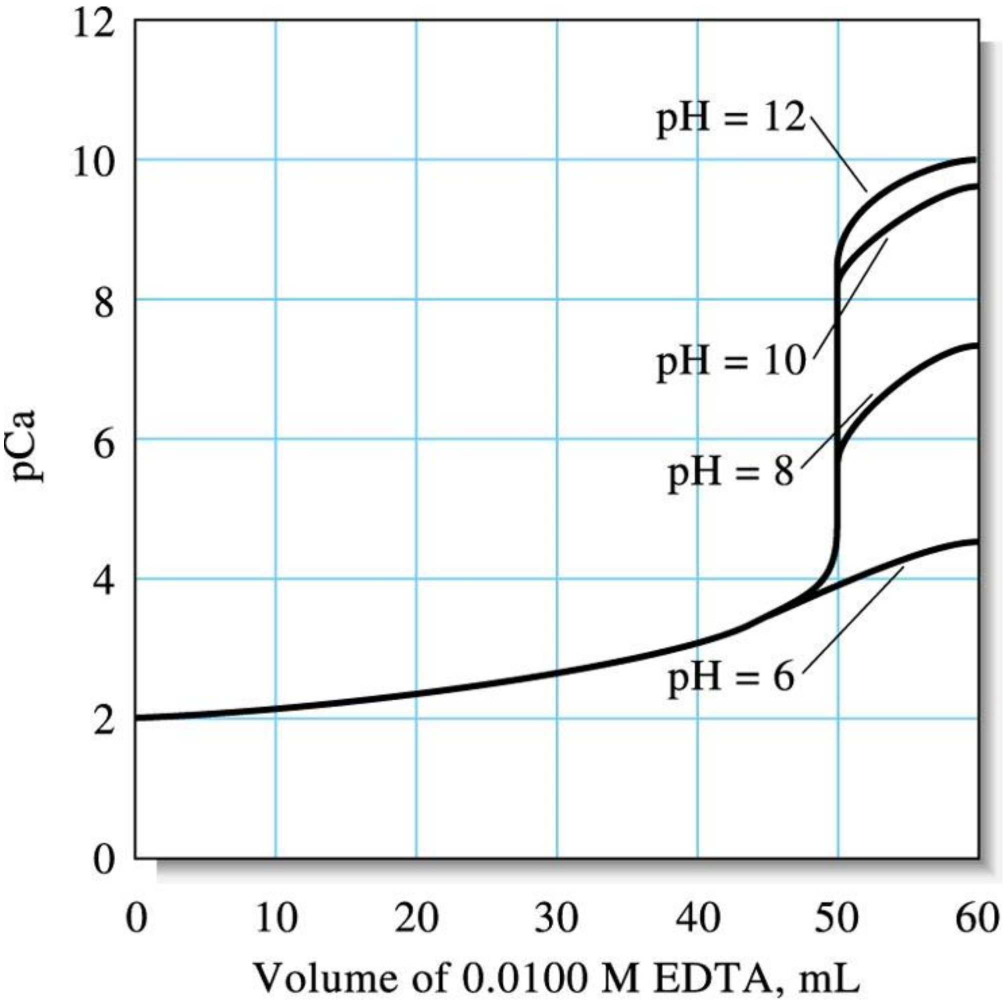
After appromixation $x = Ni^{2+} = 1.2 \times 10^{-5}$

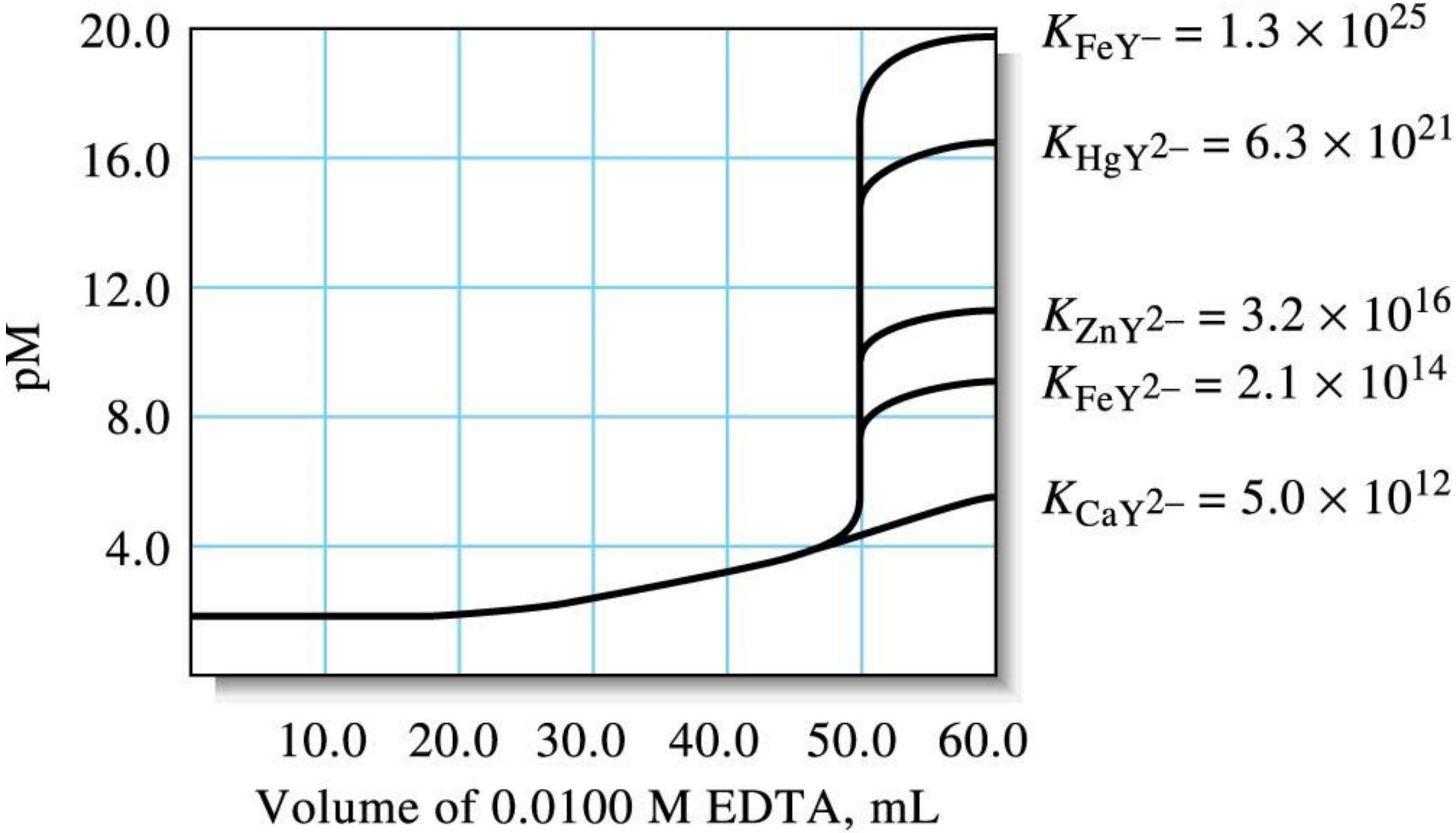
b) At pH = 10; $K'_{NiY} = \alpha_4 K_{NiY}$ ($\alpha_4 = 0.35$);
$Ni^{2+} = 8.1 \times 10^{-10}$ M

Influence of pH on the titration of 0.0100M Ca^{2+} with 0.0100M EDTA.

Note that the end point becomes less sharp as the pH decreases because the complex formation reaction is less complete under these conditions.

At high pH $\alpha_4 \rightarrow 1$



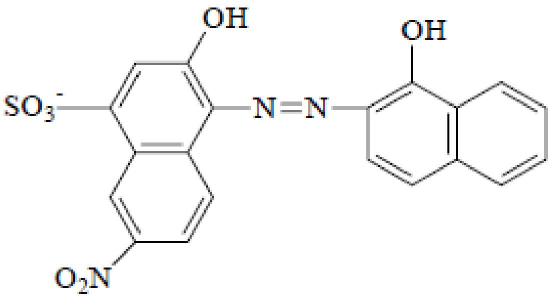


- Titration curves for 50.0 ml 0f 0.0100 M solutions of various cations at pH 6.0.

17D-6 Indicator for EDTA titration

The most common indicators are those that form colored chelates with metal ion in a pM range that is speciall for the particulate cation and dye.

***Eriochrome Black T (EBT)**



- **Its behavior as a weak acid is shown below (can be used as acid/base indicator**

$H_2O + H_2In^- \Leftrightarrow HIn^{2-} + H_3O^+ \qquad K_1 = 5 \times 10^{-7}$

red blue

$H_2O + HIn^{2-} \Leftrightarrow In^{3-} + H_3O^+ \qquad K_2 = 2.8 \times 10^{-12}$

blue orange

$MIn^- + HY^{3-} \Leftrightarrow HIn^{2-} + MY^{2-}$

red **blue**

Metal complex is red, after the end point the color is blue

➢ EDTA titration Curve

Because of the large formation constant, the reaction of calcium with EDTA is more complete, and a large change occurs in the equivalence point region, **the shaded area shows the transition range for the indicator Eriochrome Black T**

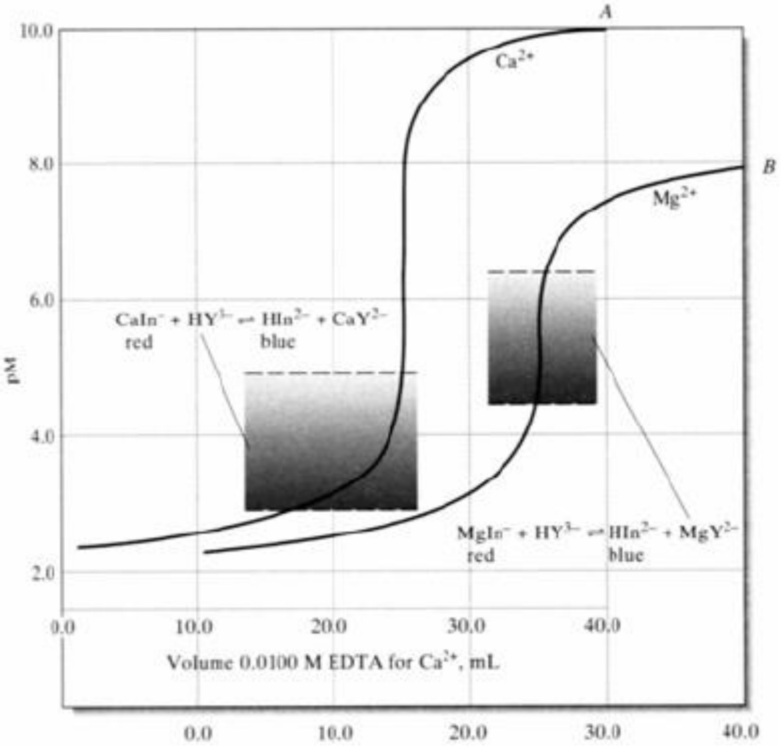
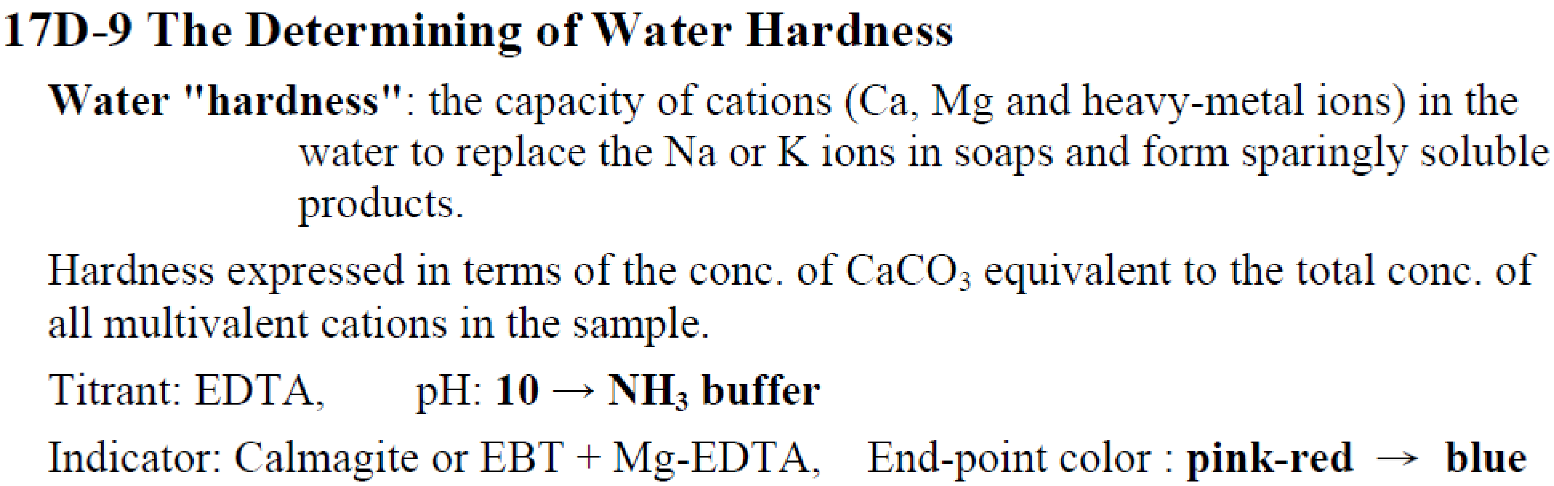


Fig. 17-6 EDTA titration curves for 50.00 mL of 0.00500 M Ca^{2+} ($K'_{CaY}=1.75\times10^{10}$) and Mg^{2+} ($K'_{MgY}=1.72\times10^{8}$) at pH 10.0.

A typical titration is illustrated by the reaction of Mg^{2+} with EDTA, using Eriochrome black T as the indicator.

$$\underset{\text{(red)}}{\text{MgIn}} + \underset{\text{(colorless)}}{\text{EDTA}} \rightarrow \underset{\text{(colorless)}}{\text{MgEDTA}} + \underset{\text{(blue)}}{\text{In}}$$



17D-9 The Determining of Water Hardness

Water "hardness": the capacity of cations (Ca, Mg and heavy-metal ions) in the water to replace the Na or K ions in soaps and form sparingly soluble products.

Hardness expressed in terms of the conc. of $CaCO_3$ equivalent to the total conc. of all multivalent cations in the sample.

Titrant: EDTA, pH: **10 → NH_3 buffer**

Indicator: Calmagite or EBT + Mg-EDTA, End-point color : **pink-red** → **blue**

Ex. A 50.00-mL water sample requires 12.00 mL of 0.0100 M EDTA. Calculate the hardness of this sample as ppm $CaCO_3$ (100.1 g/mol).

From titn. (1:1 reaction); mole EDTA = mole Ca^{2+}.

g $CaCO_3$ = 1. 201 x 10^{-2} g

- ppm $CaCO_3$ = 12.01 mg/0.0500 L = 240.2 ppm

17D-5 The effect of other complexing agents on EDTA titration curves

Auxiliary complexing agents must be used in EDTA titrations to prevent precipitation of the analyte as a hydrous oxide. Such reagents cause end points to be **less sharp**.

Ammonia is an auxiliary complexing agent

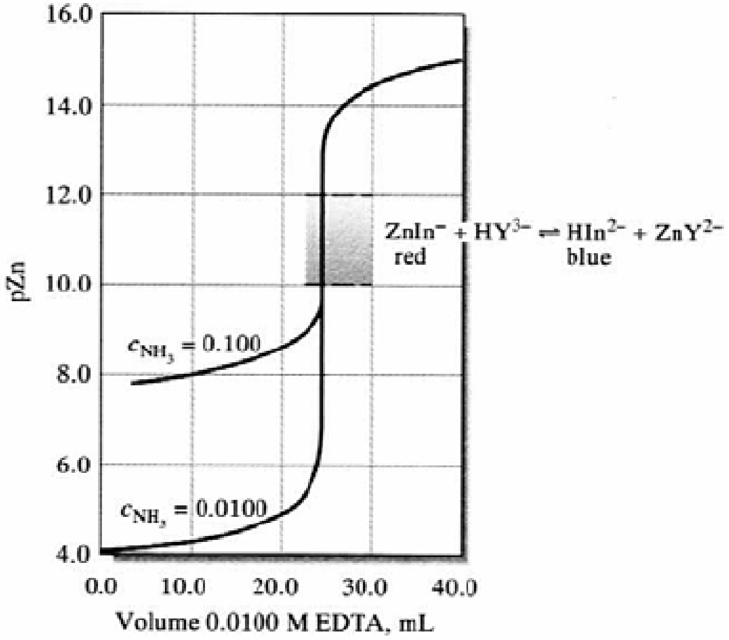
ex: Zn ion in NH_3 solution (buffer soln)

in basic : $Zn^{2+} + 2OH^- \Leftrightarrow Zn(OH)_2(s)$

$Zn(NH_3)_3^{2+} + HY^{3-} \Leftrightarrow ZnY^{2-} + 3NH_3 + NH_4^+$

$Zn(NH_3)_3^{2+}$, $Zn(NH_3)_2^{2+}$, and $Zn(NH_3)^{2+}$

Fig. 17-10 Influence of ammonia conc. on the end point for the titration of 50.0 mL of 0.00500 M Zn^{2+}. Solutions are buffered to pH 9.00.



The concentration of the auxiliary complexing agent should be minimum to lower the impact on the end point sharpness.

Note that the aux. agent does not effect beyond the equivalence point