Section 11

Potentiometry

Potentiometric Electrodes

- Potentiometric electrodes measure:
- Activity not concentration
- Concepts to review:
- Activity and affect factors

Potentiometric Electrodes

- **Electrode of the First Kind**:
- Metal in contact with Cation: M/M^{n+}
- Example: Ag/Ag^{+}
- $Ag^{+} + 1\ e^{-} \leftrightarrow Ag_{(s)}$
- Nernst Equation:
- $E = E^{o}_{Ag+/Ag} - 2.303RT/nF(\log 1/a_{Ag+})$
- Where a_{Ag+} = activity of silver ion
- $E_{measured} = E_{cell} = E_{ind\ vs\ NHE} = E_{ind} - E_{NHE}$
- Why does $E_{cell} = E_{ind}$?
- E_{ref} | solution | E_{ind}

Potentiometric Electrodes

- **Electrode of the Second Kind**:
- General Form: $M \mid MX \mid X^{n-}$
- Example: $Ag \mid AgCl_{(S)} \mid Cl^-$
- $AgCl + 1\ e^- \leftrightarrow Ag_{(s)} + Cl^-$
- Nernst Equation:
- $E = E^o_{AgCl/Ag} - 2.303RT/nF(\log a_{Cl-})$
- What observation can you make about potential for this electrode?

Potentiometric Electrodes

- Can the previous electrode be utilized to measure a_{Ag+} ?

Potentiometric Electrodes

- **Electrode of the Second Kind**:
- General Form: $M \mid MX \mid X^{n-}$
- Example: Calomel Electrode
- $Hg, Hg_2Cl_{2(S)} \mid Cl^-$
- $Hg_2^{2+} + 2e^- \leftrightarrow Hg_{(s)}$
- $E = E^o_{Hg22+/Hg} - 2.303RT/nF(\log 1/a_{Hg22+}$
- $Hg_2Cl_{2(s)} + 2e^- \leftrightarrow 2\,Hg + 2\,Cl^-$
- $E = E^o_{Hg2Cl2/Hg} - 2.303RT/nF(\log a_{Cl-})^2$
- $K^o_{sp} = a_{Hg} \cdot (a_{Cl-})^2$

Potentiometric Electrodes

- REDOX ELECTRODES:
- Inert Metal Electrode: Platinum, Pt
- $M^{a+} + n\ e^- \leftrightarrow M^{(a-n)+}$
- $E = E^o_{Ma+/M(a-n)+} - 2.303RT/nF\ (\log a_{M(a-n)+} / a_{Ma+}$
- Example:
- $MnO^-_4 + 8\ H^+ + 5e^- \leftrightarrow Mn^{2+} + 4\ H_2O$
- Can you write the potential for this half cell?

Potentiometric Electrodes

- Normal Hydrogen Electrode:
- $H^+ + e^- \leftrightarrow \frac{1}{2} H_{2(g)}$
- Can you write the Nernst Equation for this half cell?

$H^+ + e^- = \frac{1}{2}H_2$

$E = E^o - 2.303RT/F \log (P_{H2})^{1/2}/a_{H+}$

$E^o = 0.000$ V. If $P_{H2} = 1$ atm., $E = -2.303RT/F$ pH

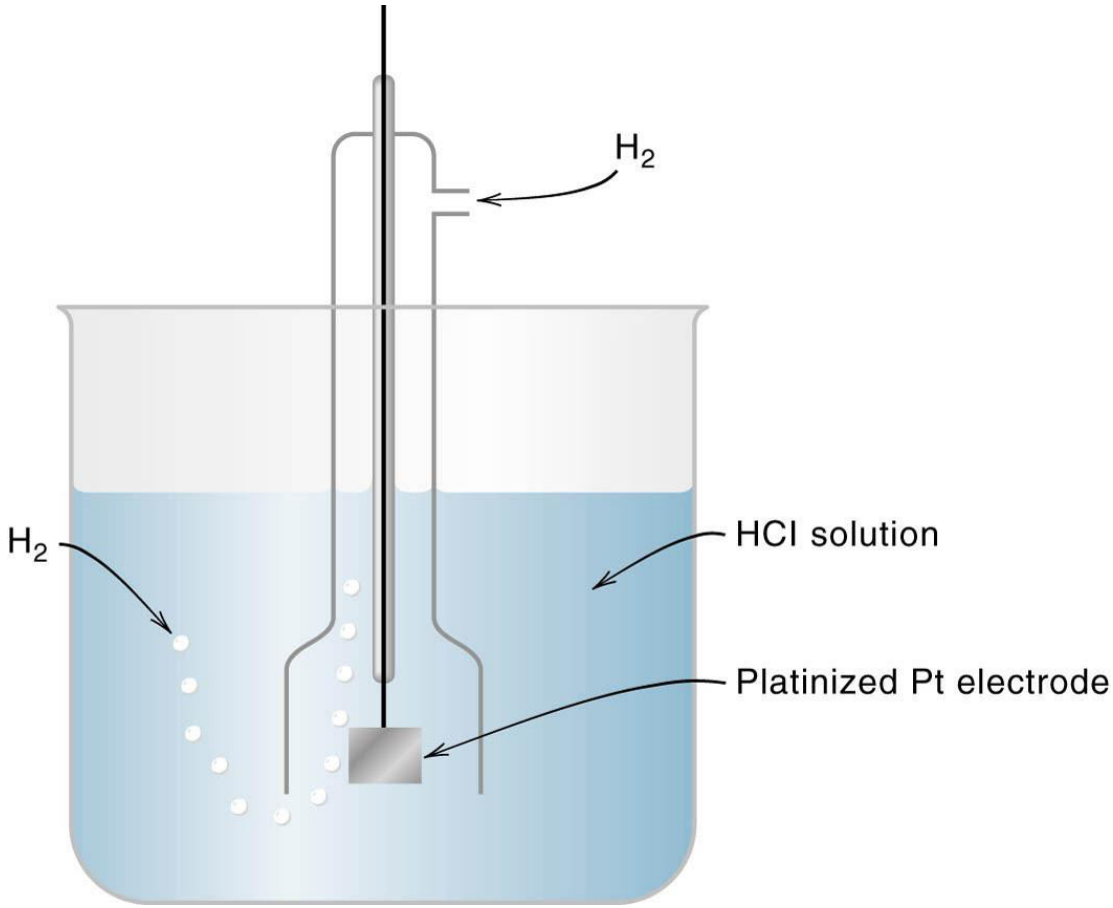

Fig. 13.1. Hydrogen electrode.

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Potentiometric Electrodes

- Cells Without Liquid Junction:
- Two Half Cells Required
- Indicator Electrode
- Reference Electrode
- Example: Pt | $H_{2(g)}$, HCl (solution) | $AgCl_{(s)}$ | Ag
- Can you write the cell potential E_{cell} for this electrode system?

Potentiometric Electrodes

- Cells With Liquid Junction:
- Two Half Cells Required
- Indicator Electrode
- Reference Electrode
- Example:
- $Hg \mid Hg_2Cl_{2(s)} \mid KCl_{(saturated)} \mid\mid HCl_{(solution)}, H_{2(g)} \mid Pt$
- Can you write the cell potential E_{cell} for this electrode system?
- $E_{cell} = (E_{right} - E_{left}) + E_j$

E_j is due to unequal migration of cations and anions at the boundary of a liquid junction, e.g., at a salt bridge interface.

This charge separation results in a potential at steady state.

E_j is minimized by a high concentration of a salt with nearly equal mobilities of cation and anion in the salt bridge, e.g., saturated KCl.

The flux of the migration of this electrolyte is much greater than more dilute ones, and largely determines E_j.

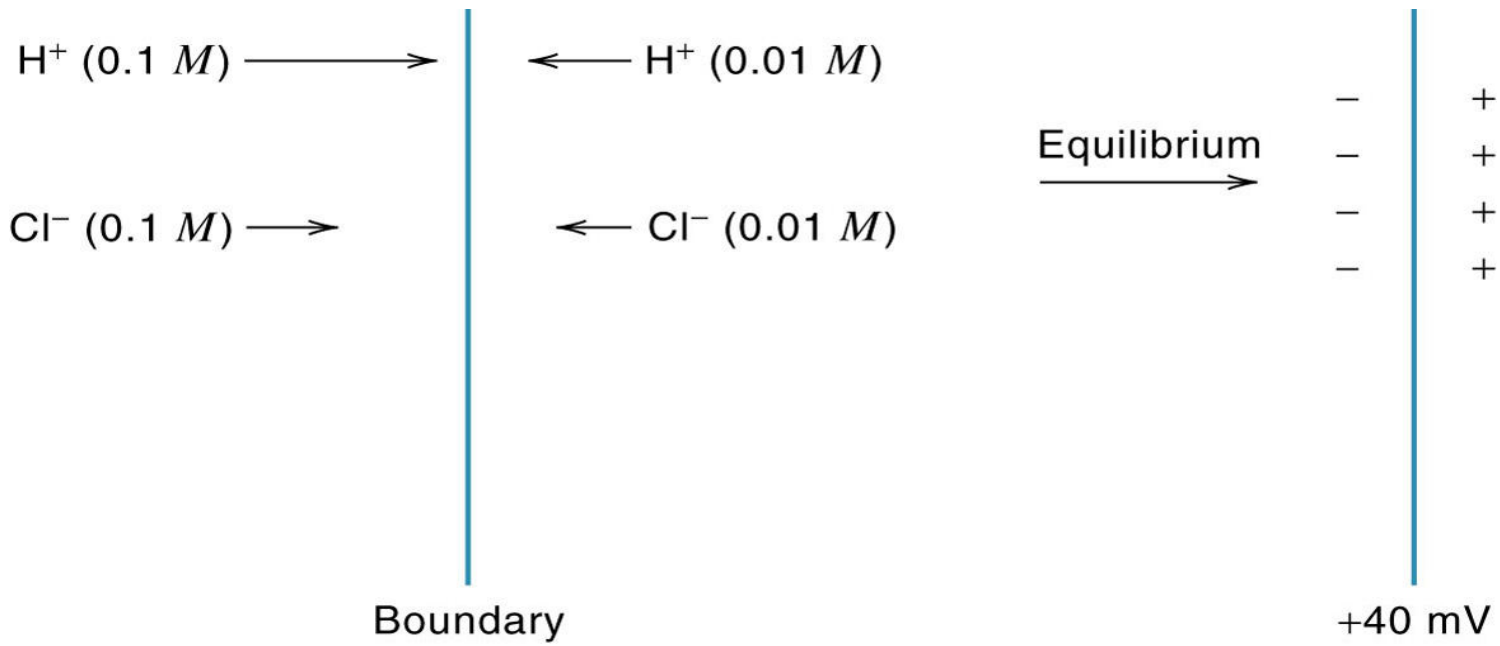

Fig. 13.2. Representation of liquid-junction potential.

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H^+ and OH^- have high mobilities and so pH markedly affects E_j.

Therefore, pH electrode calibration should be done near the sample pH.

Table 13.1

Some Liquid-Junction Potentials at 25°C[a]

Boundary	E_j(mV)
0.1 *M* KCl‖0.1 *M* NaCl	+6.4
3.5 *M* KCl‖0.1 *M* NaCl	+0.2
3.5 *M* KCl‖1 *M* NaCl	+1.9
0.01 *M* KCl‖0.01 *M* HCl	−26
0.1 *M* KCl‖0.1 *M* HCl	−27
3.5 *M* KCl‖0.1 *M* HCl	+3.1
0.1 *M* KCl‖0.1 *M* NaOH	+18.9
3.5 *M* KCl‖0.1 *M* NaOH	+2.1
3.5 *M* KCl‖1 *M* NaOH	+10.5

[a]Adapted from G. Milazzo, *Electrochemie*. Vienna: Springer, 1952; and D. A. MacInnes and Y. L. Yeh, *J. Am. Chem. Soc.*, **43** (1921) 2563.

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The S.C.E. is a common reference electrode.

The cell half-reaction is: $\frac{1}{2}Hg_2Cl_2 + e^- = Hg + Cl^-$.

$E = E^o - 0.0592 \log 1/a_{Cl^-} = 0.242$ V for saturated KCl.

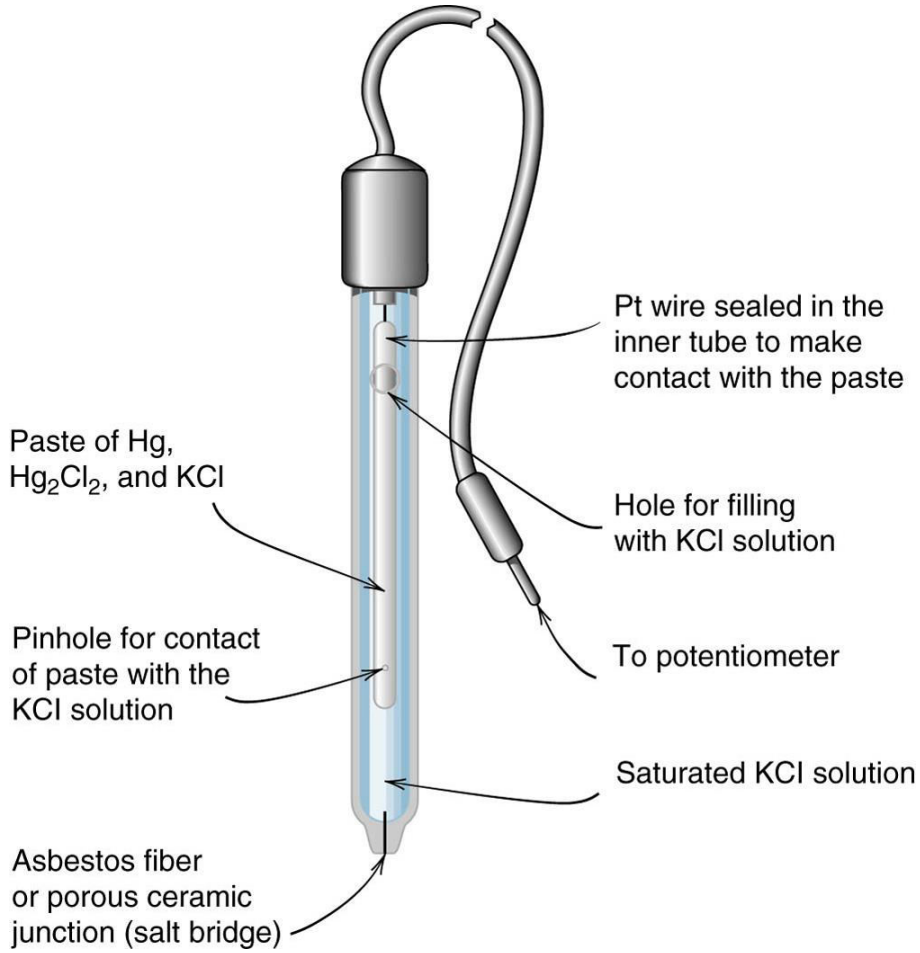

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Fig. 13.3. Commercial saturated calomel electrode.

Reference electrode potentials are all relative.

The measured cell potential depends on the one used.

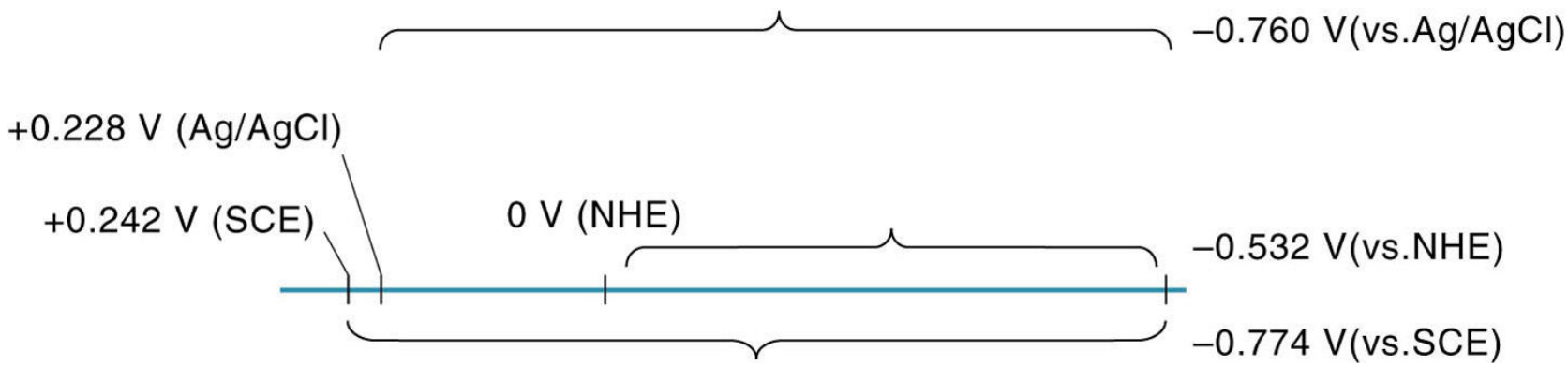

Fig. 13.4. Schematic representation of electrode potential relative to different reference electrodes.

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A complete cell consists of an indicating electrode that responds to the analyte and a reference electrode of fixed potential.

The potential difference between the two is measured.

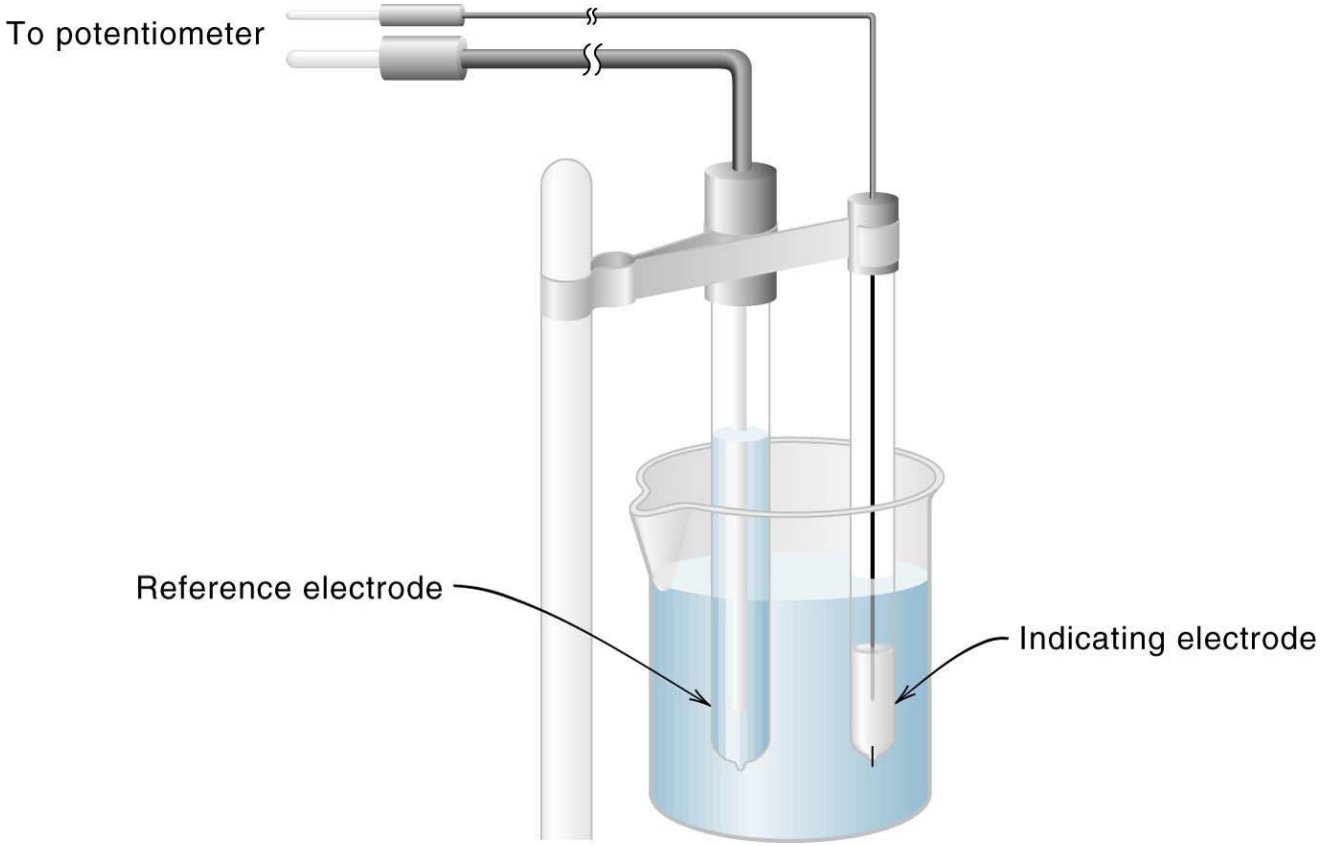

Fig. 13.5. Cell for potentiometric measurements.

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E_{glass} = constant – 2.303RT/F log ($a_{H+\ int}$/ $a_{H+\ ext}$)

The hydrated glass responds to a_{H+}.

The asymmetry potential of the glass membrane is unknown, so the electrode must be calibrated with a standard buffer.

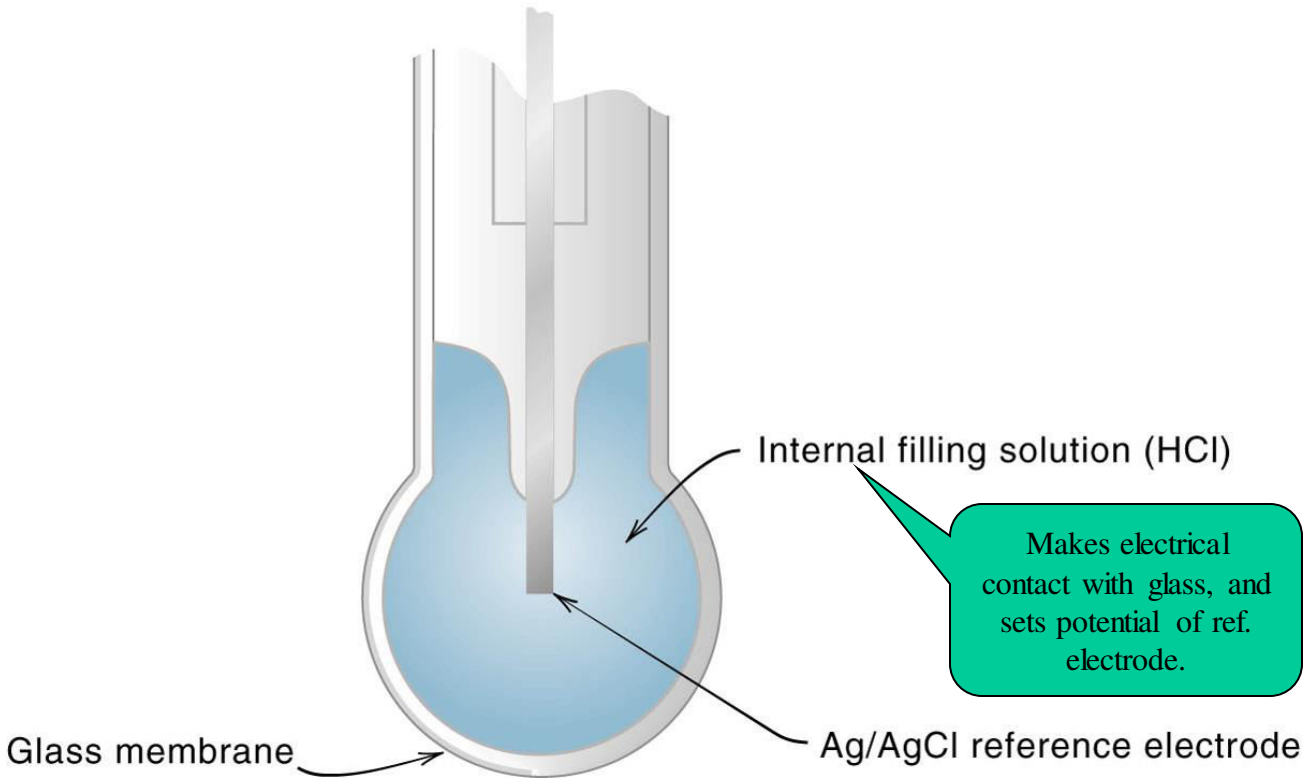

Fig. 13.6. Glass pH electrode.

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This is two electrodes in one.

The porous plug salt bridge must be immersed in the solution.

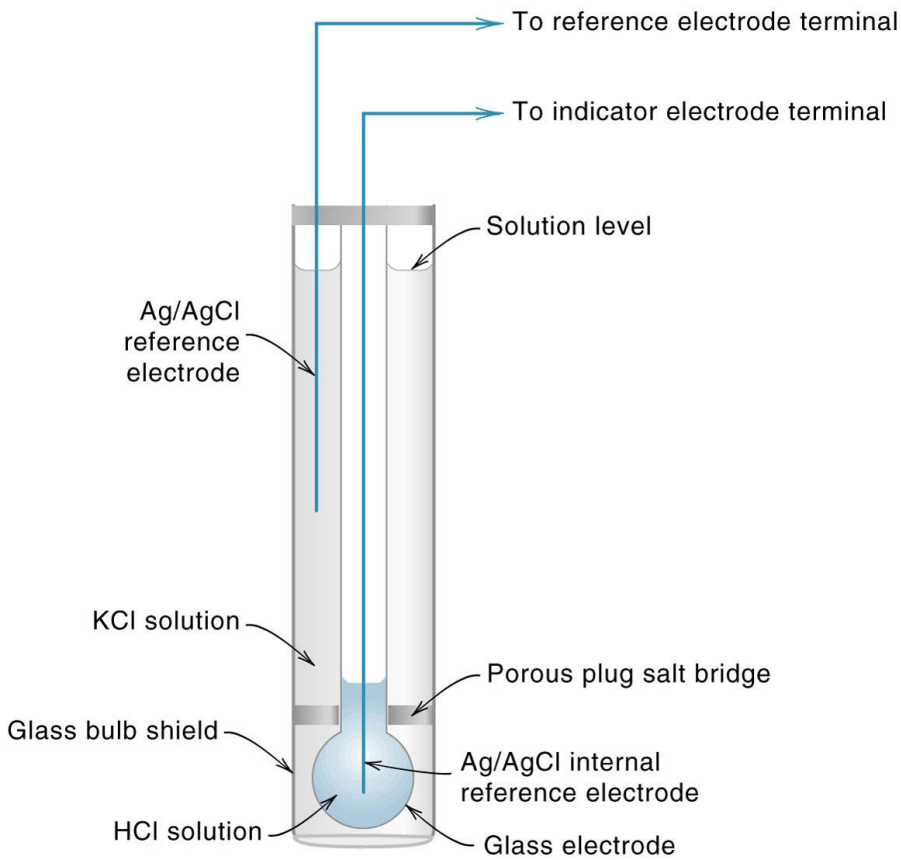

Fig. 13.7. Combination pH-reference electrode.

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When a_{H+} is very small, the glass electrode senses other cations. The solution appears more acidic than it really is.

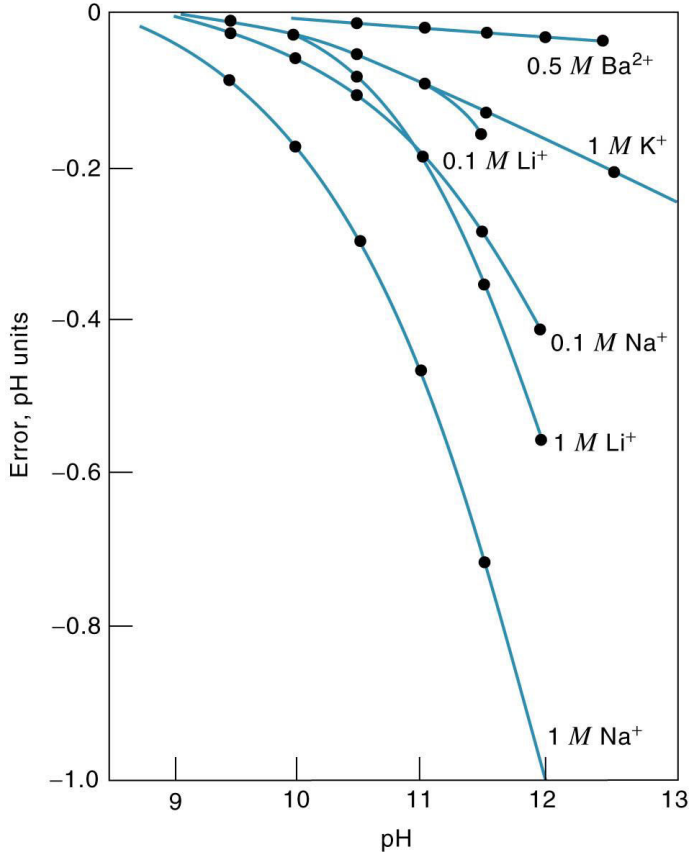

Fig. 13.8. Error of Corning 015 glass electrode in strongly alkaline solutions containing various cations.

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In very acid solutions, the activity of water is less than unity (it solvates the proton).

The a_{H+} is decreased, and the pH reading is increased.

High concentrations of dissolved salts or adding a nonaqueous solvent does the same.

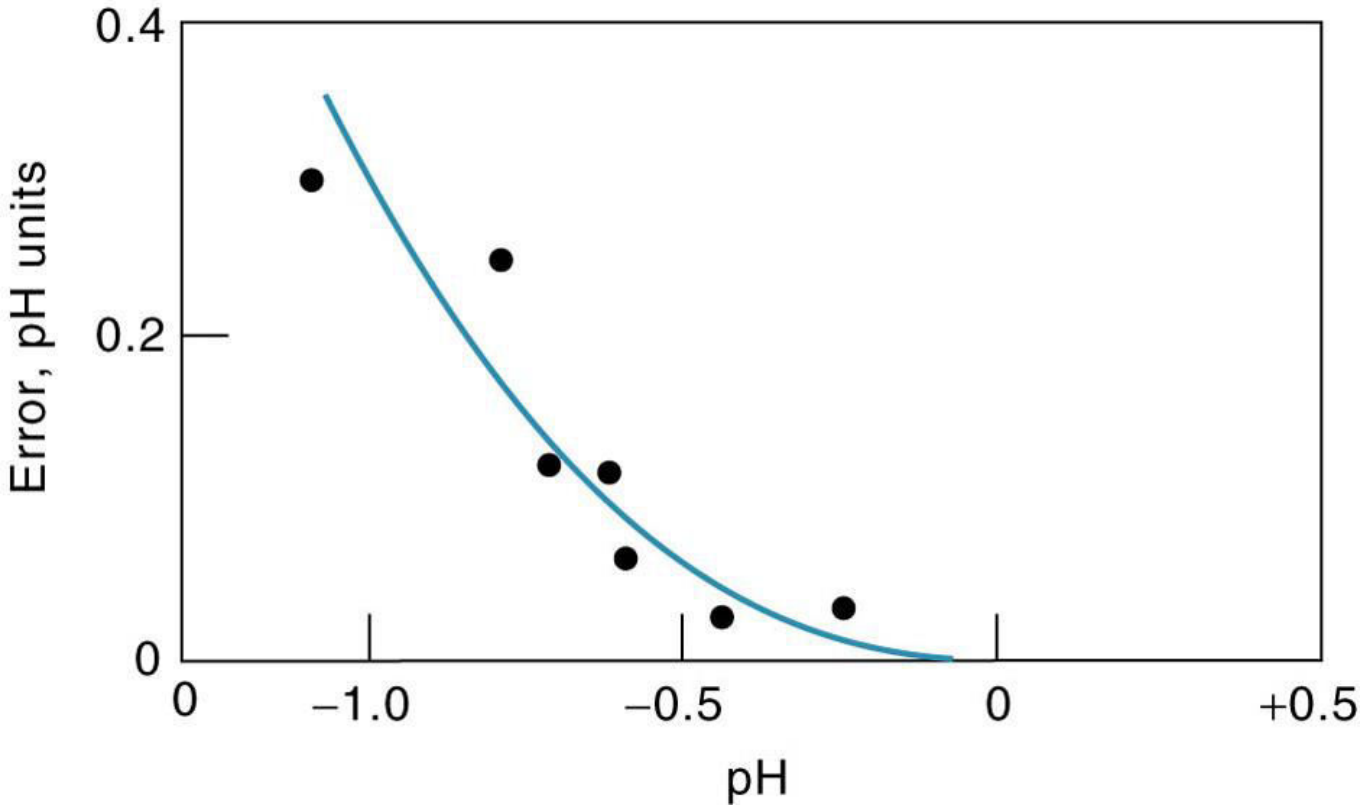

Fig. 13.9. Error of glass electrode in hydrochloric acid solutions.

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These are really accurate to 0.01 pH, due to Debye-Huckel limitations in calculating activity of the chloride ion in the Ag/AgCl reference electrode used in measurements.

But they are reproducible to 0.001 pH unit.

Only the phosphate mixtures are really buffers.

K_a values change with temperature, and so the pH changes.

Table 13.2

pH Values of NIST Buffer Solutions[a]

	Buffer						
t (°C)	Tetroxalate[b]	Tartrate[c]	Phthalate[d]	Phosphate[e]	Phosphate[f]	Borax[g]	Calcium Hydroxide[h]
0	1.666	—	4.003	6.984	7.534	9.464	13.423
5	1.668	—	3.999	6.951	7.500	9.395	13.207
10	1.670	—	3.998	6.923	7.472	9.332	13.003
15	1.672	—	3.999	6.900	7.448	9.276	12.810
20	1.675	—	4.002	6.881	7.429	9.225	12.627
25	1.679	3.557	4.008	6.865	7.413	9.180	12.454
30	1.683	3.552	4.015	6.853	7.400	9.139	12.289
35	1.688	3.549	4.024	6.844	7.389	9.102	12.133
38	1.691	3.549	4.030	6.840	7.384	9.081	12.043
40	1.694	3.547	4.035	6.838	7.380	9.068	11.984
45	1.700	3.547	4.047	6.834	7.373	9.038	11.841
50	1.707	3.549	4.060	6.833	7.367	9.011	11.705
55	1.715	3.554	4.075	6.834	—	8.985	11.574
60	1.723	3.560	4.091	6.836	—	8.962	11.449
70	1.743	3.580	4.126	6.845	—	8.921	—
80	1.766	3.609	4.164	6.859	—	8.885	—
90	1.792	3.650	4.205	6.877	—	8.850	—
95	1.806	3.674	4.227	6.886	—	8.833	—

[a] From R. G. Bates, *J. Res. Natl. Bur. Std.*, **A66** (1962) 179. (Reprinted by permission of the U.S. Government Printing Office.)
[b] 0.05 *m* potassium tetroxalate (*m* refers to molality, but only small errors result if molarity is used instead).
[c] Satd. (25°C) potassium hydrogen tartrate.
[d] 0.05 *m* potassium hydrogen phthalate.
[e] 0.025 *m* potassium dihydrogen phosphate, 0.025 *m* disodium monohydrogen phosphate.
[f] 0.008695 *m* potassium dihydrogen phosphate, 0.03043 *m* disodium hydrogen phosphate.
[g] 0.01 *m* borax.
[h] Satd. (25°C) calcium hydroxide.

Only the phosphate mixtures are really buffers. The pH values change with temperature due to the temperature dependence of the K_a values.

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The potential scale is calibrated in pH units (59.16 mV/pH at 25° C).

A temperature adjustment feature changes the slope by 2.303RT/F.

Fig. 13.10. Typical pH meter.

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The isopotential point (usually at pH 7) of a glass electrode is temperature insensitive.

The potential is set at zero here (if different than zero, this is the offset).

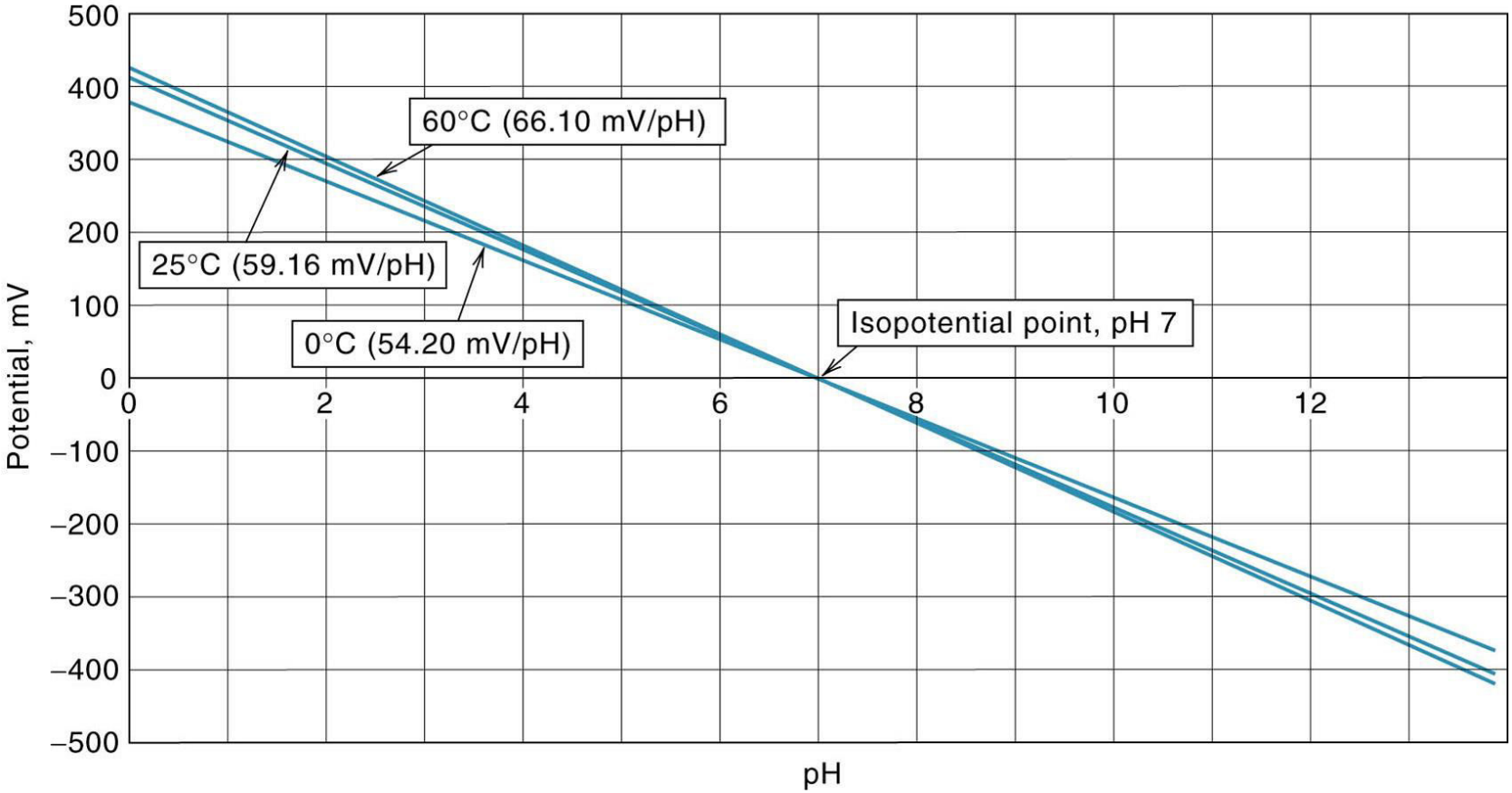

Fig. 13.11. Isopotential point.

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The most common ion-selective electrode of this type is the fluoride electrode: LaF_3 crystal doped with Eu(II) to increase conductivity.

Plastic membrane-ionophore electrodes have a similar design, with a soft plastic PVC membrane containing a neutral lipophilic ionophore that selectively complexes with the test ion.

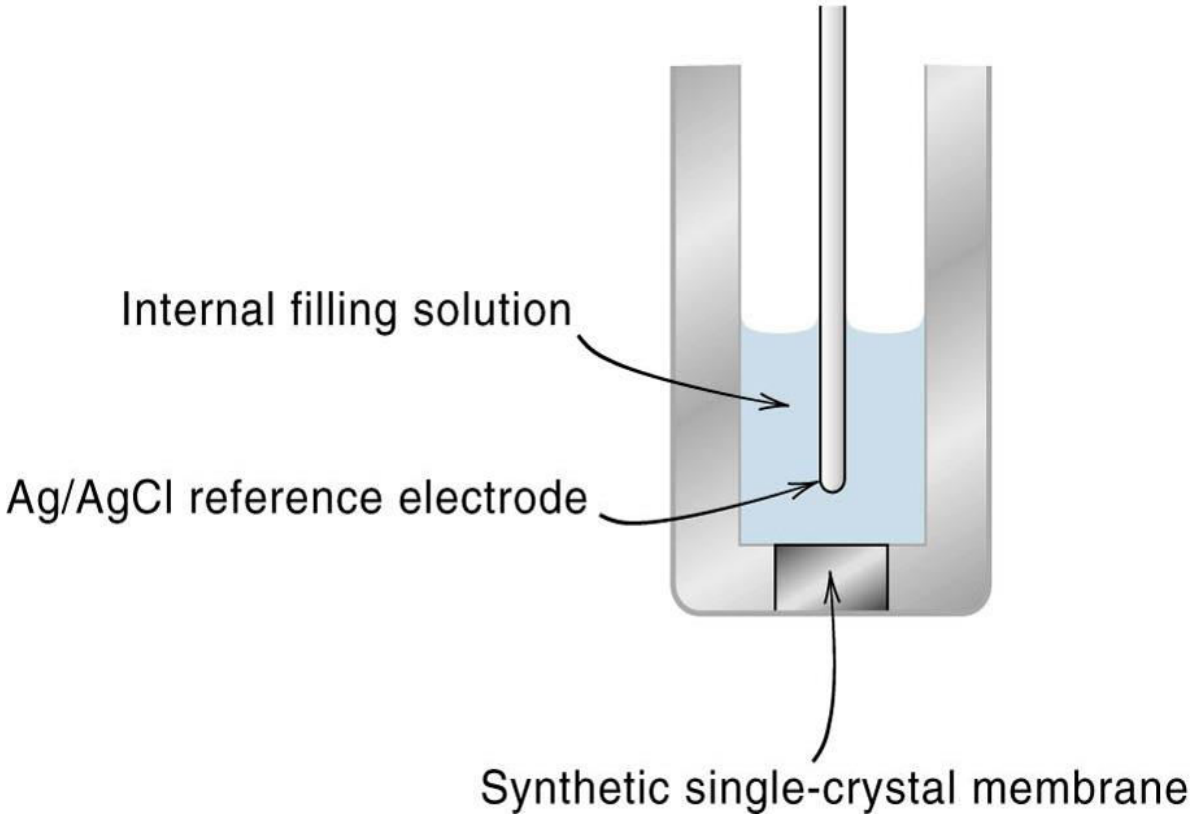

Fig. 13.12. Crystal membrane electrode.

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The potential determining "membrane" is a layer of water-immiscible liquid ion exchanger at the porous membrane face.

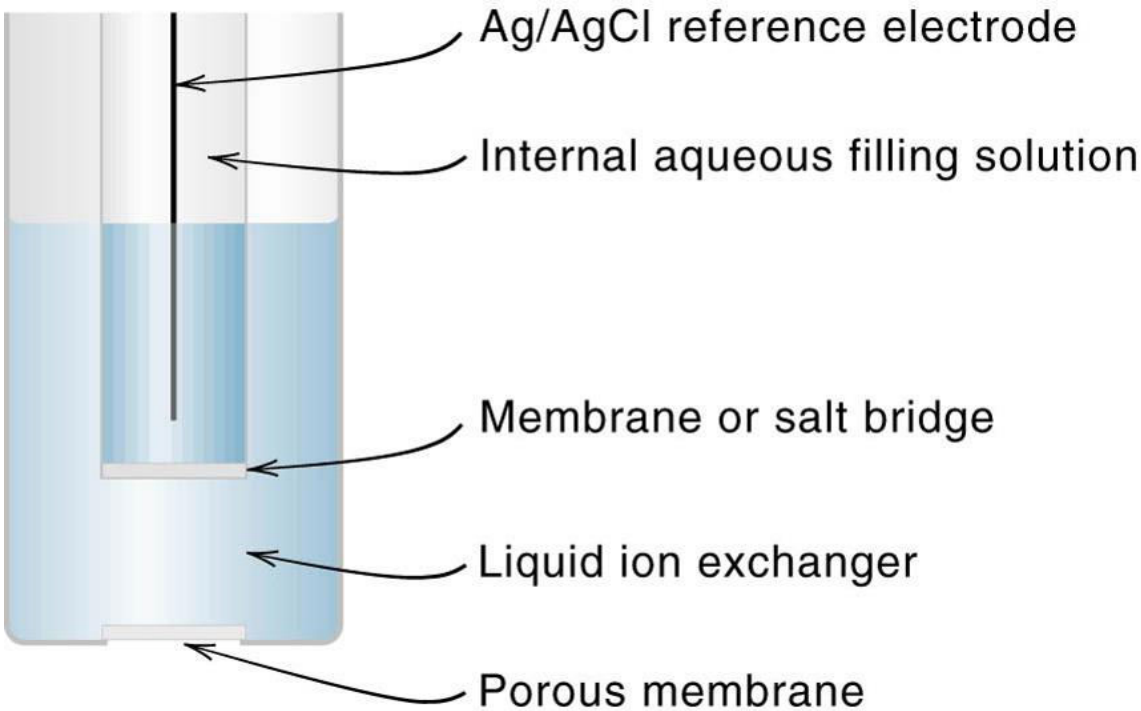

Fig. 13.13. Liquid-membrane electrode.

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There are numerous plastic membrane-ionophore electrodes also, e.g., for Na^+, K^+, Li^+, and Ca^{2+}.

Table 13.3

Typical Properties of Some Commercial Ion-Selective Electrodes

Electrode	Concentration Range (M)	Principal Interferences[a]
Liquid–liquid ion exchange electrodes		
Ca^{2+}	10^0–10^{-5}	Zn^{2+}(3); Fe^{2+}(0.8); Pb^{2+}(0.6); Mg^{2+}(0.1); Na^+(0.003)
Cl^-	10^{-1}–10^{-5}	I^-(17); NO_3^-(4); Br^-(2); HCO_3^-(0.2); SO_4^{2-}, F^-(0.1)
Divalent cation	10^0–10^{-8}	Fe^{2+}, Zn^{2+}(3.5); Cu^{2+}(3.1); Ni^{2+}(1.3); Ca^{2+}, Mg^{2+}(1); Ba^{2+}(0.94); Sr^{2+}(0.54); Na^+(0.015)
BF_4^-	10^{-1}–10^{-5}	NO_3^-(0.1); Br^-(0.04); OAc^-, HCO_3^-(0.004); Cl^-(0.001)
NO_3^-	10^{-1}–10^{-5}	ClO_4^-(1000); I^-(20); Br^-(0.1); NO_2^-(0.04); Cl^-(0.004); CO_3^{2-}(0.0002); F^-(0.00006); SO_4^{2-}(0.00003)
ClO_4^-	10^{-1}–10^{-5}	I^-(0.01); NO_3^-, OH^-(0.0015); Br^-(0.0006); F^-, Cl^-(0.0002)
K^+	10^0–10^{-5}	Cs^+(1); NH_4^+(0.03); H^+(0.01); Na^+(0.002); Ag^+, Li^+(0.001)
Solid–state electrodes[b]		
F^-	10^0–10^{-6}	Maximum level: $OH^- < 0.1\ F^-$
Ag^+ or S^{2-}	10^0–10^{-7}	$Hg^{2+} < 10^{-7}\ M$

[a] Number in parentheses is the relative selectivity for the interfering ion over the test ion (see The Selectivity Coefficient below).
[b] Interference concentrations given represent maximum tolerable concentrations.

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The crown ether cavity size is just right for complexing lithium ion. It is placed in a PVC plastic membrane.

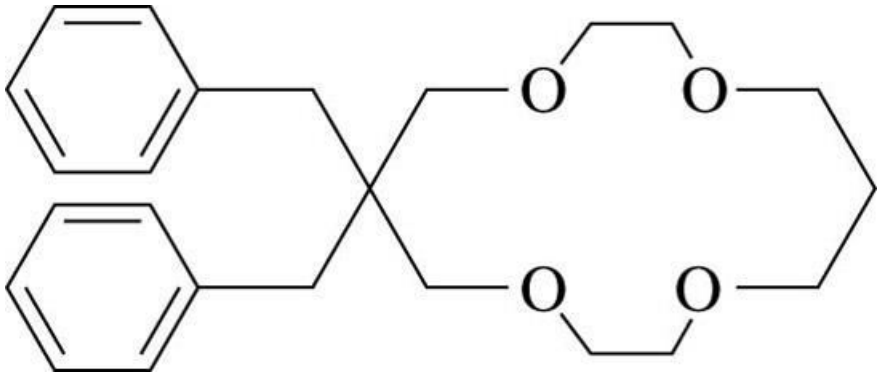

Fig. 13.14. 14-Crown-4 ether that selectively binds lithium ion.

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Amide-based ionophores in PVC membranes are good complexers of these ions.

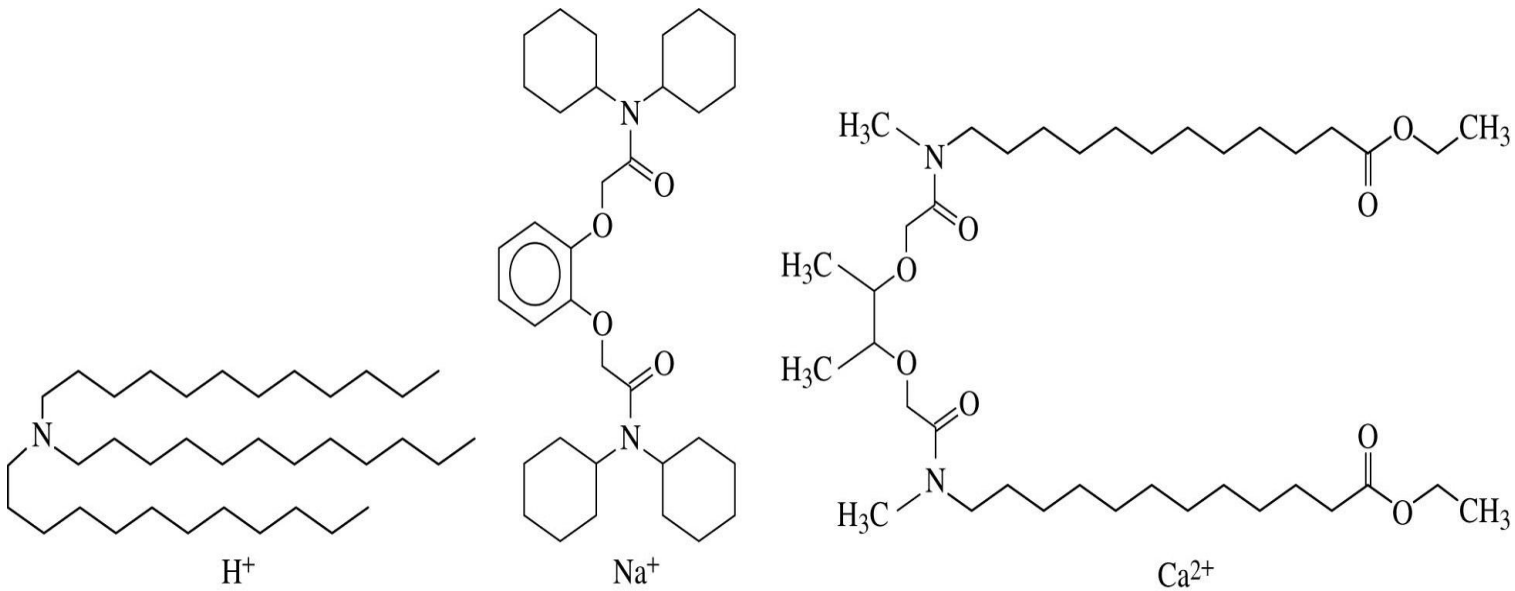

Fig. 13.15. Ionophores for H^+, Na^+, and Ca^{2+}.

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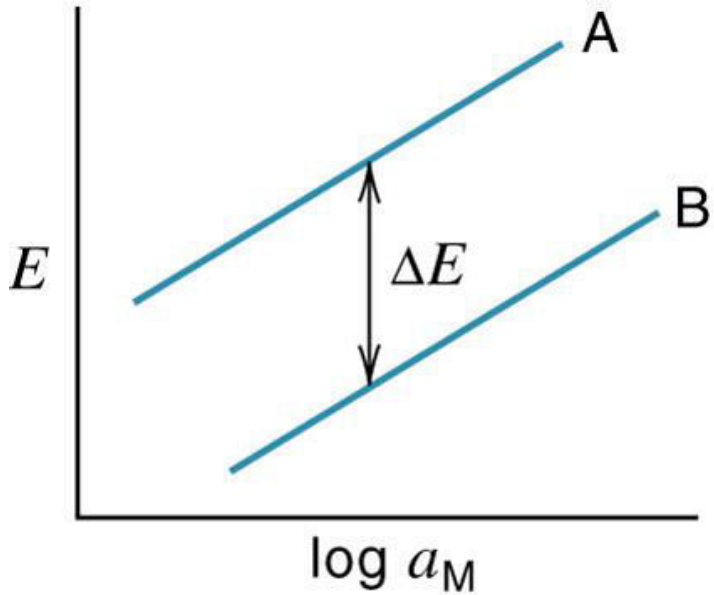
The larger the potential difference, the more selective the electrode.



$$-\log K_{AB} = \Delta E/S$$

The separate solution method of determining selectivity coefficient for ion A with respect to ion B.

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The calibration curve for A is prepared in the presence of fixed activity of interfering ion.

z_A and z_B are the charges of the ions.

The intersection is where the electrode responds equally to both ions.

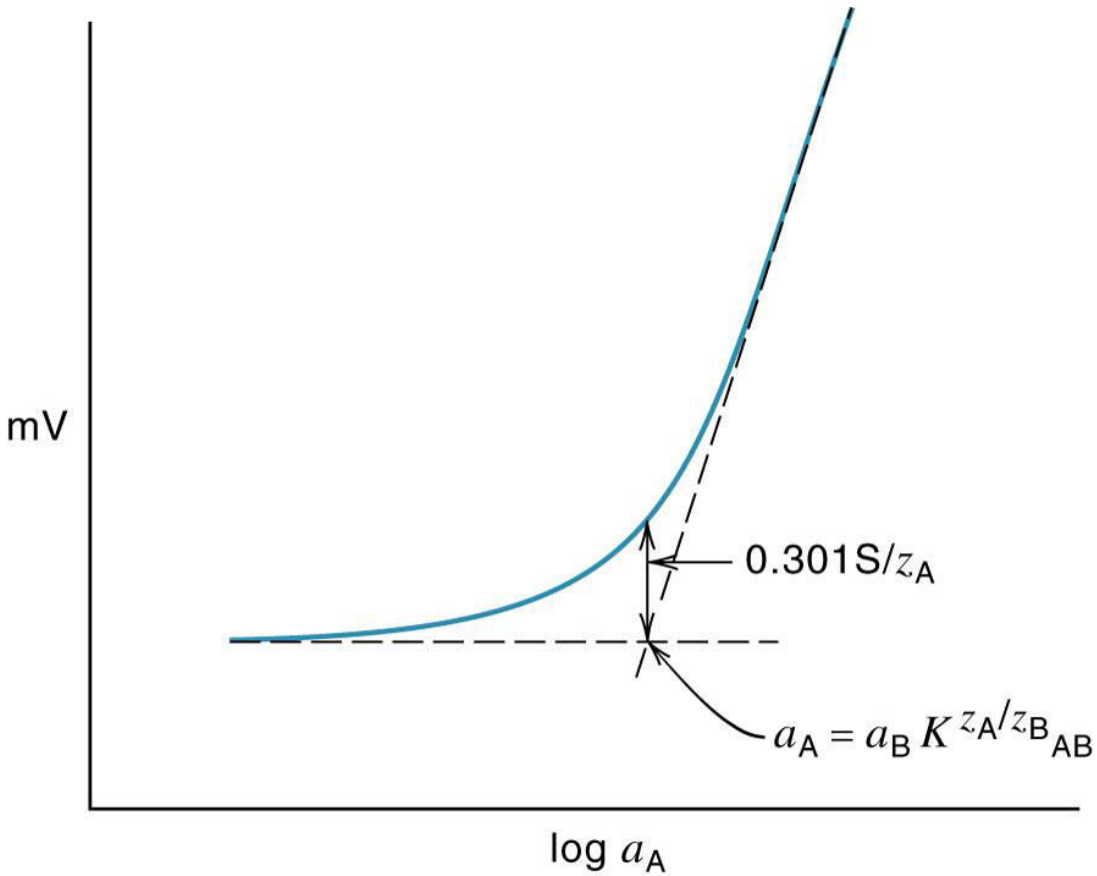

Fig. 13.16. Fixed interference calibration curve.

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These are ion-selective field-effect transistor electrodes.

A semiconductor transistor serves as the base for electrical contact.

It is coated with insulating layers of SiO_2 and Si_3N_4, and then an ion-sensitive membrane.

This one is a non-glass ISFET pH electrode.

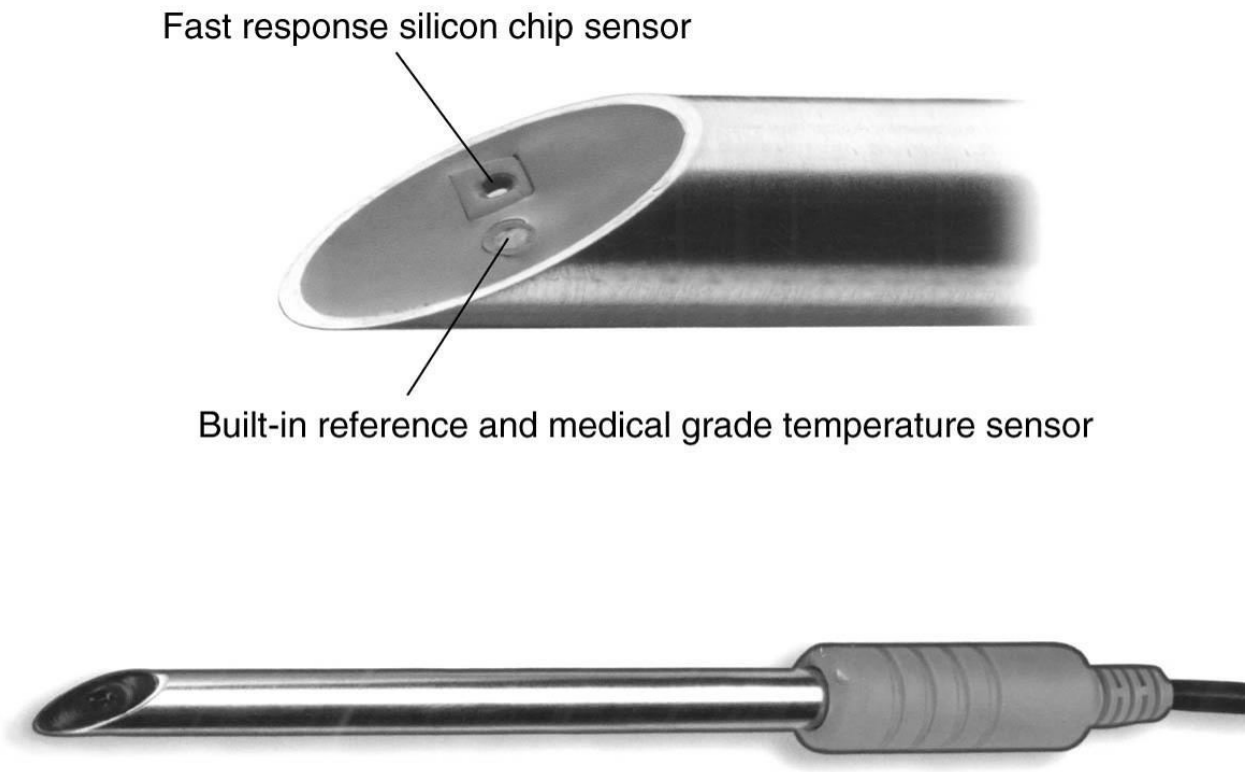

Fig. 13.17. Solid-state ISFET electrode.

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Redox Titrimetry and Potentiometry

Redox Titrations

- Titrate 50.0mL of 0.050 M Fe^{2+} vs 0.100M Ce^{4+}
- How do we observe the end point?
- Is the equilibrium constant large enough?
- To Observe End Point:

Redox Titrations

Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

- Use Pt Indicator Electrode:
- $E_{pt} = E_{Fe3+/Fe2+} = E_{Ce4+/Ce3+}$ at Equilibrium
- <u>a) Add 10.0 mL Ce^{4+}:</u>

Redox Titrations

Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

- <u>b) At 50% of Titration (12.50 mL Ce^{4+})</u>

Redox Titrations

Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

- <u>c) Just Before Equivalence Point (24.90 mL Ce^{4+})</u>

Redox Titrations

Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

- <u>d) Just Beyond Equivalence Point (25.10 mL Ce^{4+})</u>

Redox Titrations

Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

- <u>e) Equivalence Point Potential (25.00 mL Ce^{4+})</u>

Redox Titrations

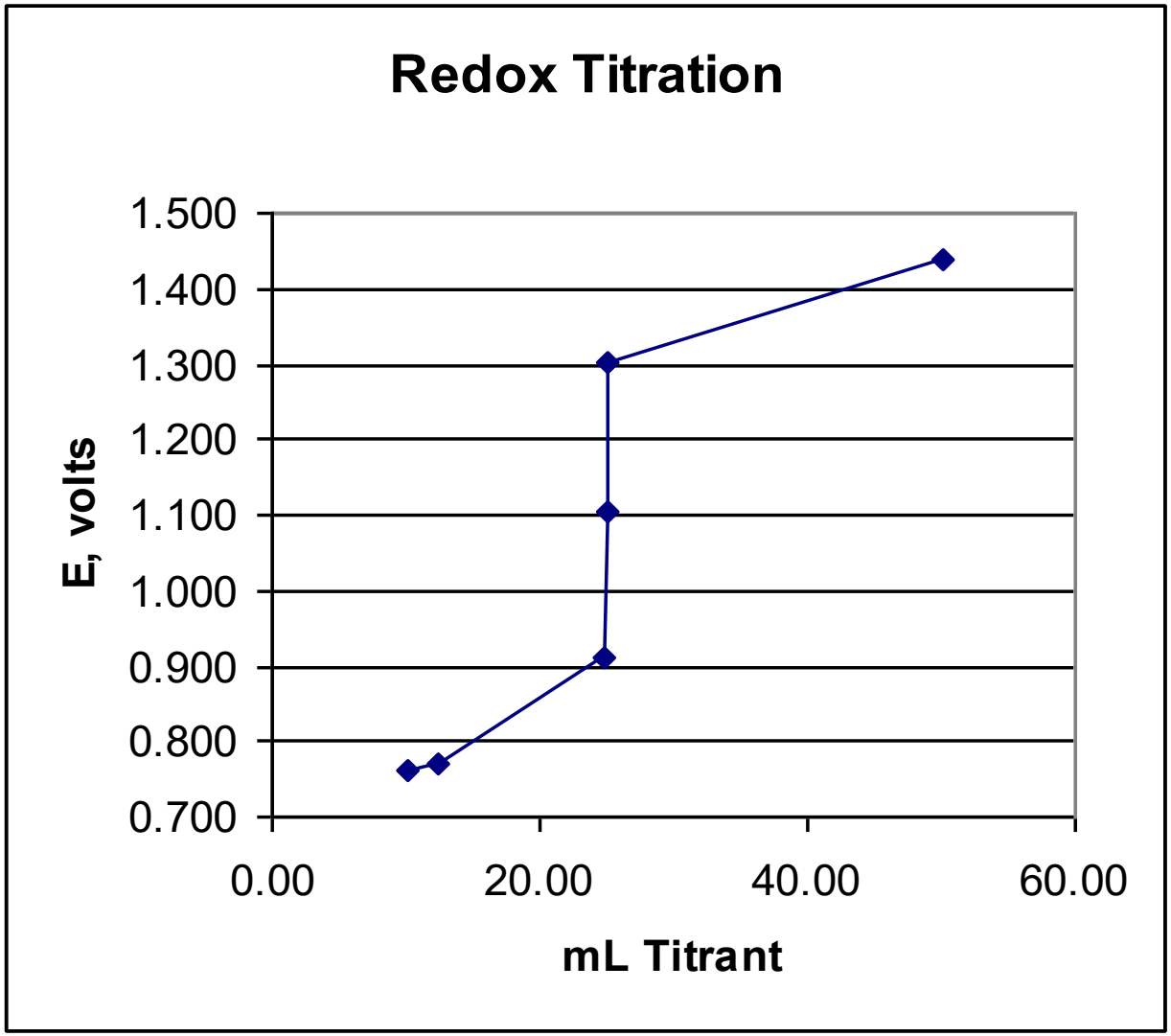
Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

- <u>e) Equivalence Point Potential (25.00 mL Ce^{4+})</u>

Redox Titrations

Titrate 50.0 mL 0.050 M Fe^{2+} vs 0.100 M Ce^{4+}

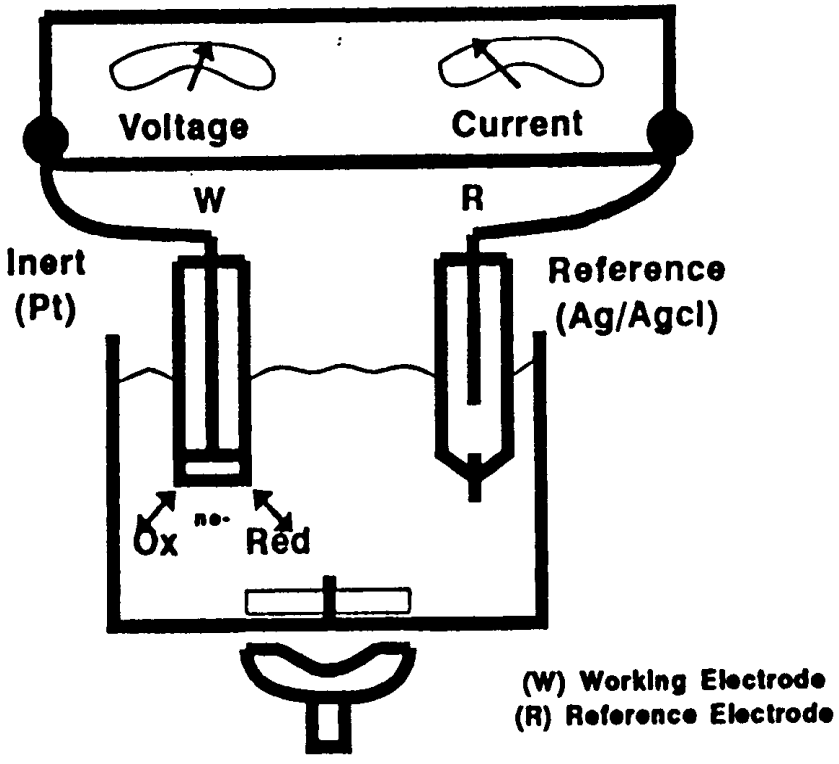
mL Titrant	E(V. vs NHE)
0.00	----
10.00	0.761
12.50	0.771
24.90	0.912
25.00	1.106
25.10	1.300
50.00	1.440



Section 13

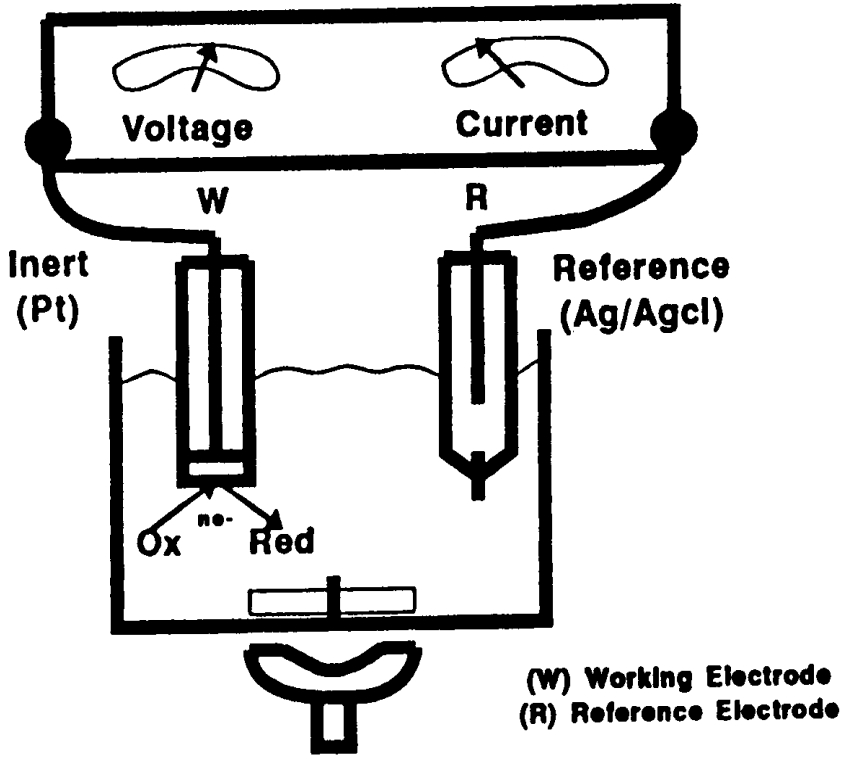
Analytical Voltammetry

Potentiometry & Voltammetry



Potentiometry

- Control cell current (= 0)
- Measure cell potential



Voltammetry

- Control cell potential
- Measure cell current

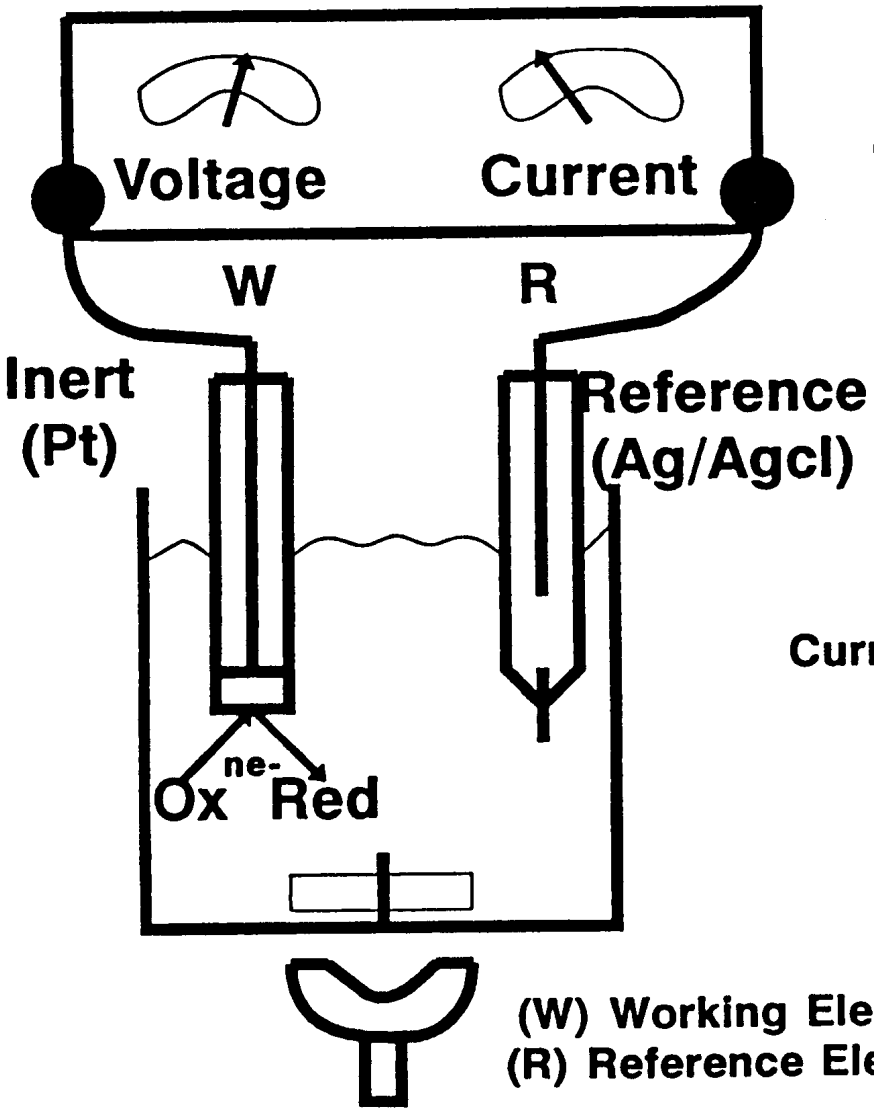
Analytical Voltammetry

Description of the Technique

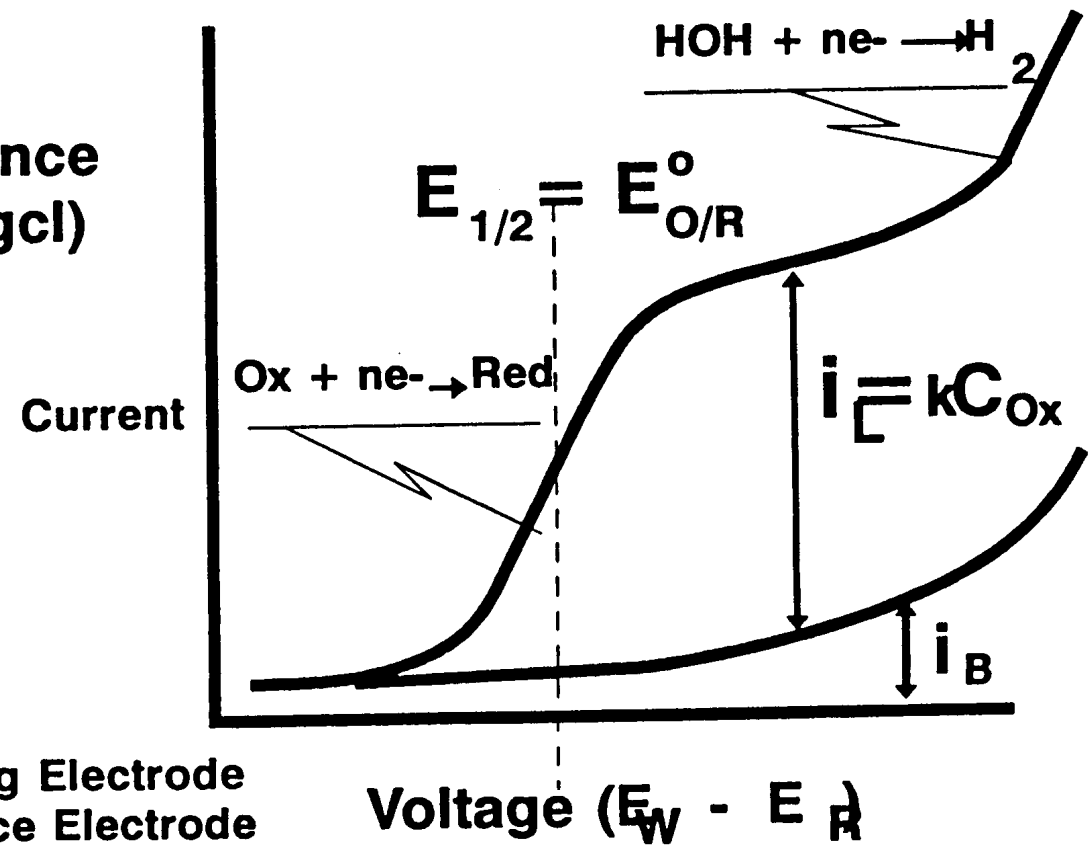
- o Electrolytic cells
- o Micro–electrodes
- o Controlled potential
- o Measure "micro" currents "Amperometry"
- o Current levels proportional to analyte concentration

Analytical Voltammetry

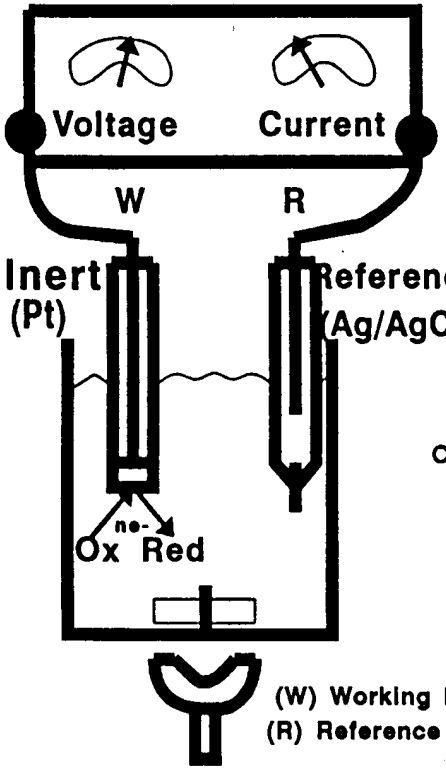
Description of the Technique



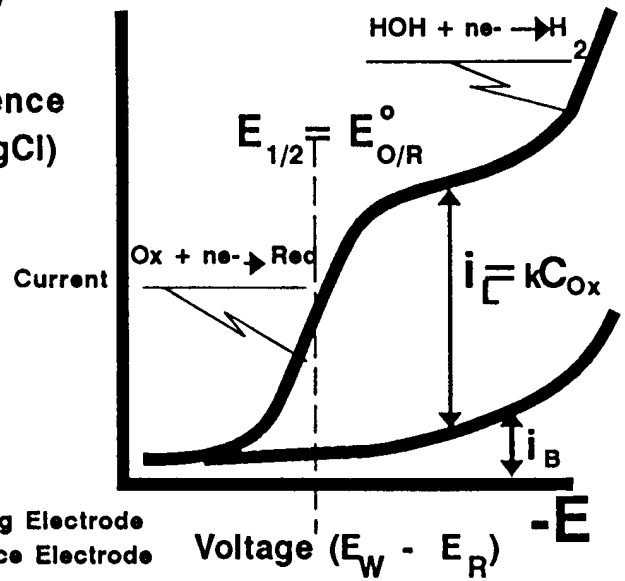
Voltammetry in Stirred Solutions



Analytical Voltammetry



Voltammetry in Stirred Solutions



Note:

Dissolved Oxygen interferes
$O_2 + ne^- + 4H^+ \rightarrow 2HOH$

O_2 removed w/ bubbling N_2

Solvent reduction limits voltage
Voltage limit is ~-2V.

Added inert electrolyte needed to provide conducting solution

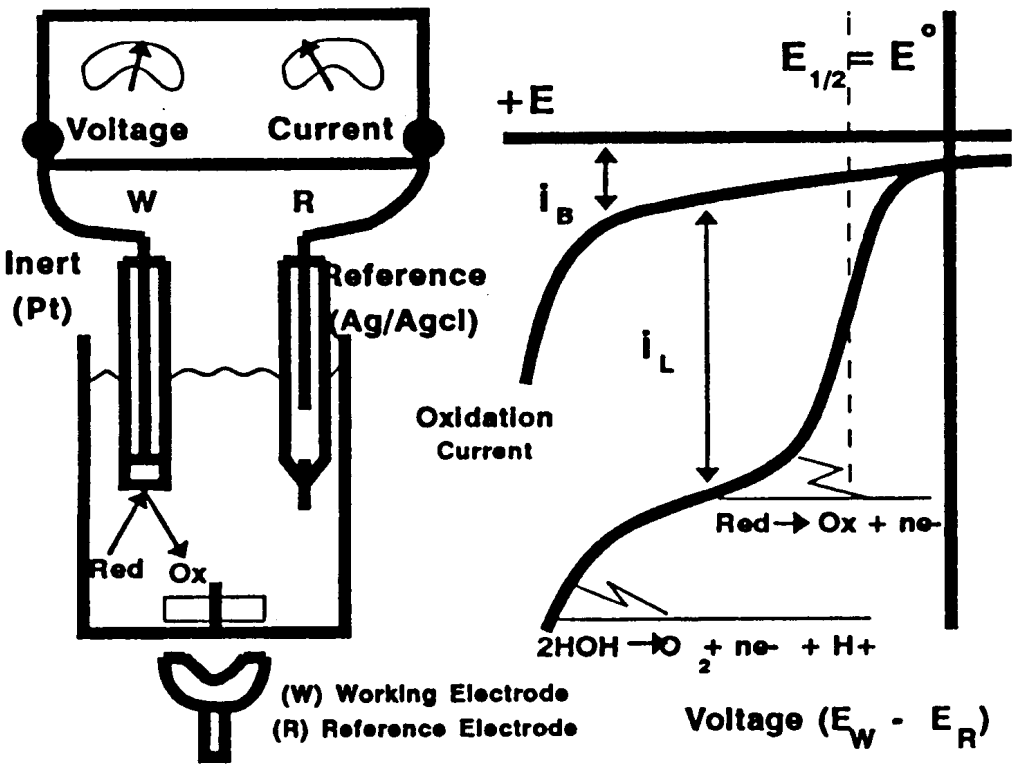
Current depends on stirring rate, concentration

Typical Reducible Analytes:

Soluble inorganics: Fe(III), Ti(IV), U(VI), ...
Solid Product: Cd(II), Hg(II), Zn(II), Tl(I), Pb(II).....
Organics: aromatic ketones, acids, nitro compounds, etc.
Biol. & Pharm. Vitamins (B, C), amino acids, narcotics, ...

Analytical Voltammetry

Oxidation Reactions



Note:

Oxygen doesn't interfere

Solvent oxidation limits range

Electrodes may oxidize

$Pt \xrightarrow{HOH} PtO, PtO_2 + ne-$

Voltage limit is ~ +2V.

Typical Oxidizable Analytes:

Inorganics: Fe(II), Sn(II), I^-, NO_2^-

Organics: aromatic amines, phenols, poly-aromatics,....

Biol. & Pharm: vitamin C, neural transmitters, ...

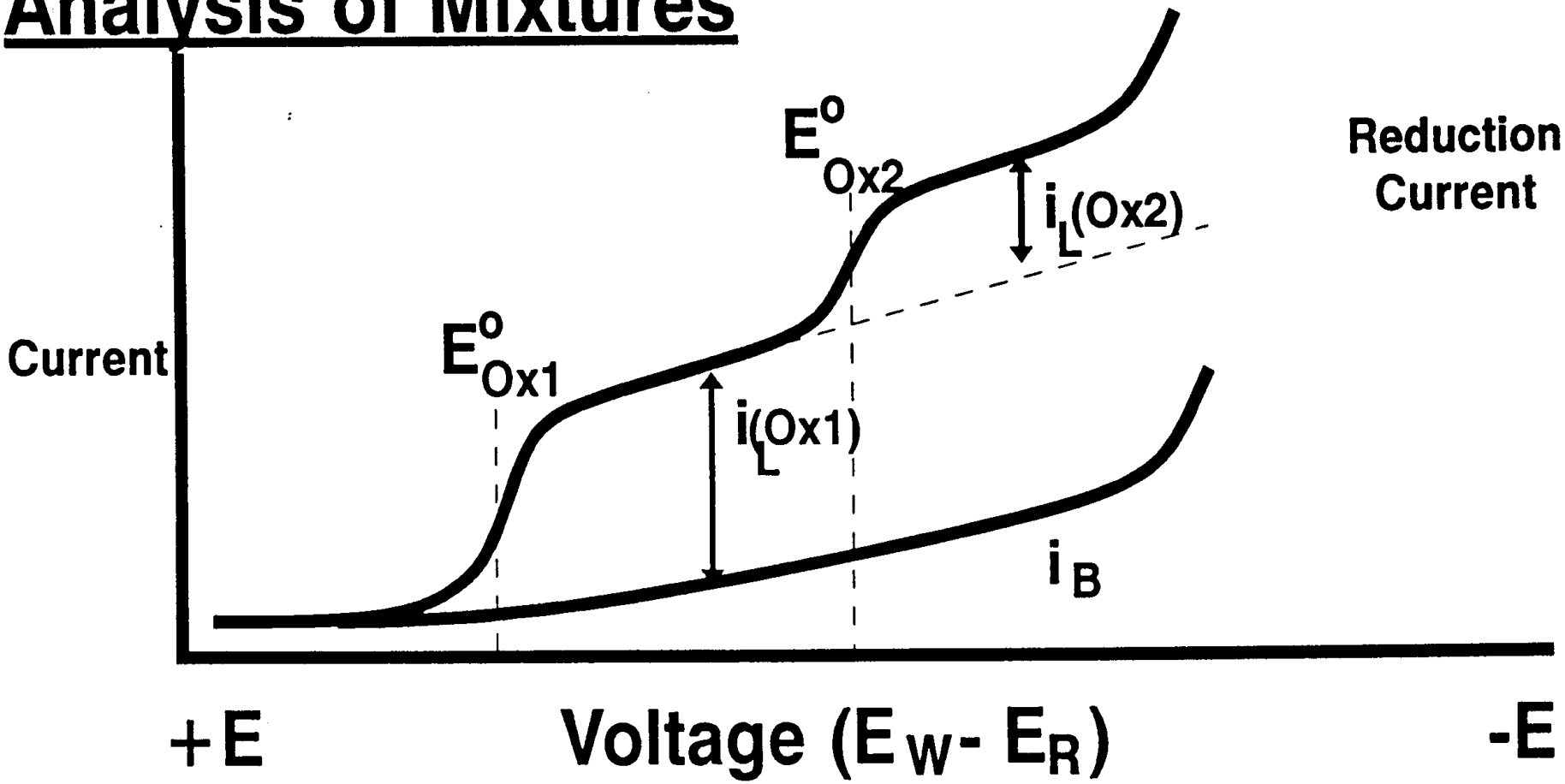
Analytical Voltammetry

Summary of Properties w/ Stirred Solutions

- o Typical electrodes: Pt, Au, Hg, C
- o Electrode areas: $< 1\ mm^2$ to $\sim 1\ cm^2$
- o $i = knAC$
  - k depends on stirring, mass transport
  - n = no. of electrons transferred/molecule
  - A = electrode area
  - C = analyte concentration (Ox or Red)
- o Analyte concentration: 10^{-6} to 10^{-3} M
- o Currents: 10^{-9} to 10^{-3} Amp

Analytical Voltammetry

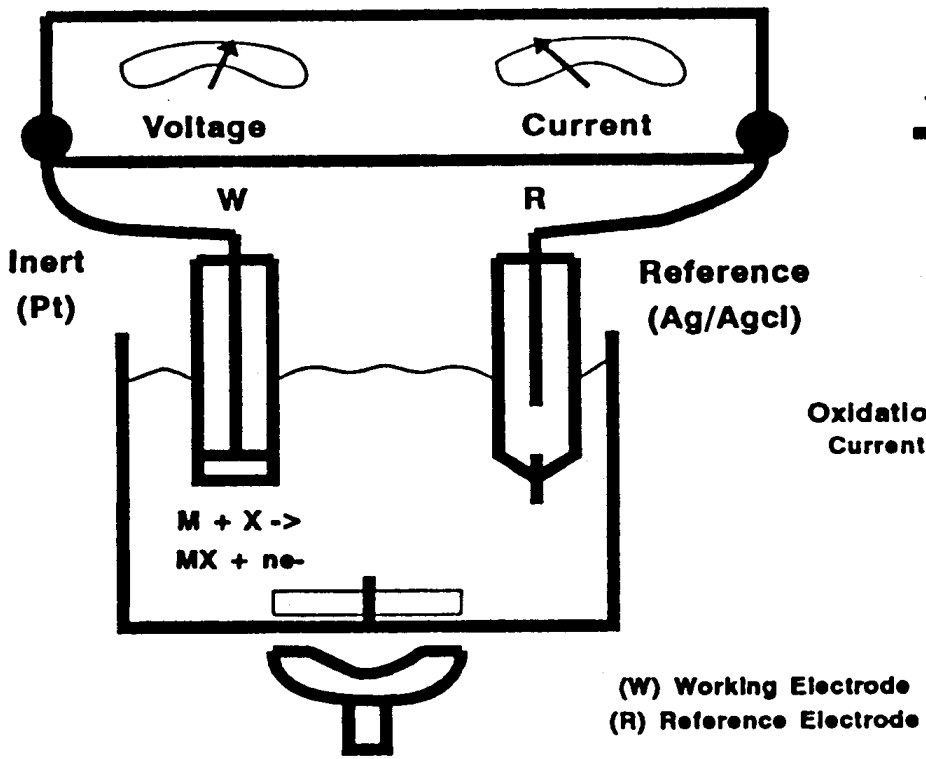
Analysis of Mixtures

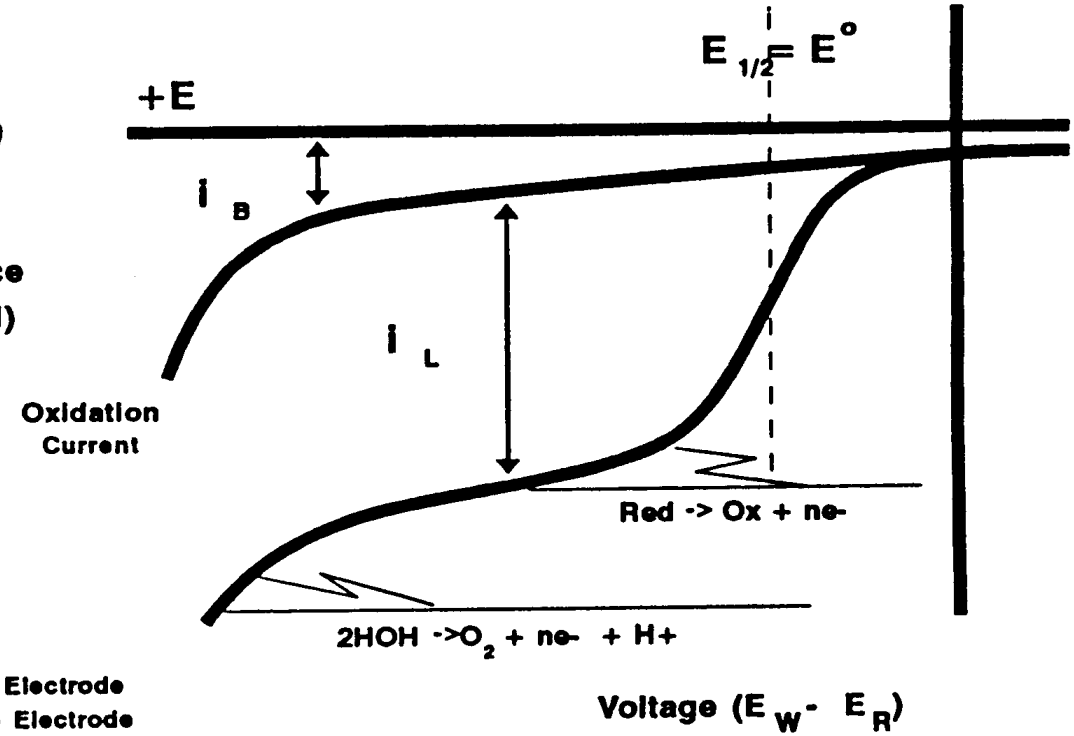


- o Currents are additive
- o Resolution requires $(E^o_2 - E^o_1) > 240/n$ mV

Analytical Voltammetry

Use of "Active" Electrodes





Applications:

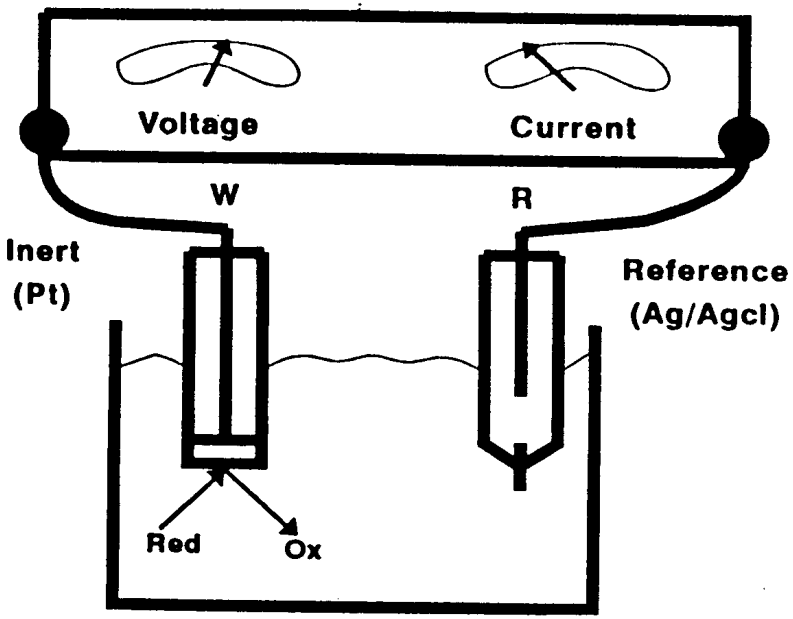
$Ag + I^- \rightarrow AgI + e^-$ [Iodide, Halide determinations]

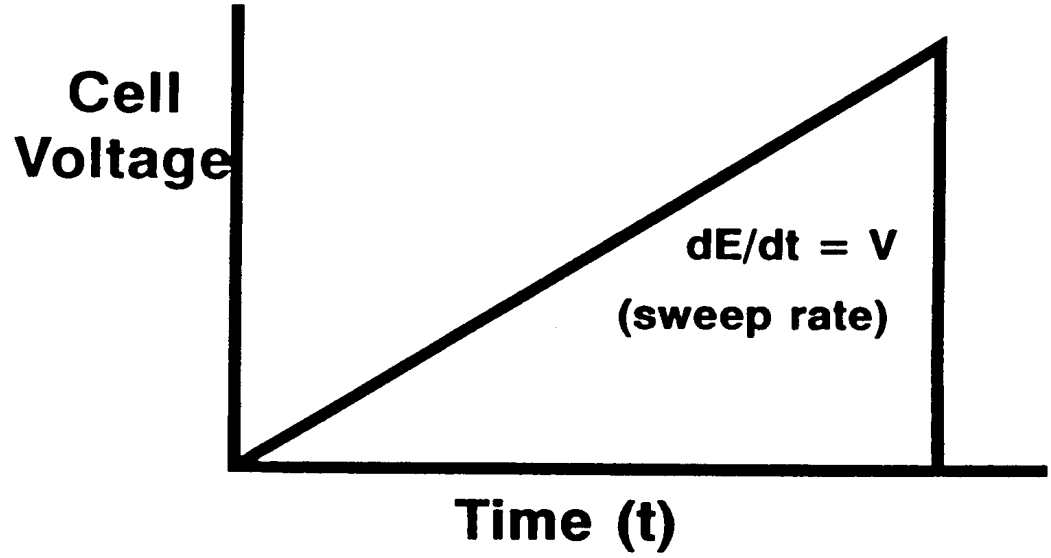
$2Hg + 2Cl^- \rightarrow Hg_2Cl_2 + 2e^-$ [" " "]

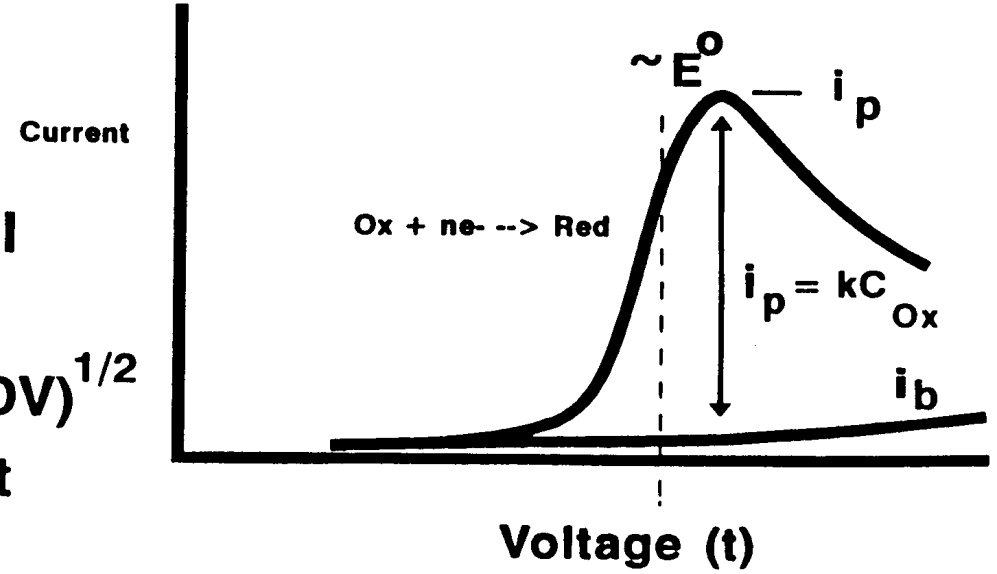
$Hg + S^{2-} \rightarrow HgS + 2e^-$ [Sulfide determination]

Analytical Voltammetry

Voltammetry in Unstirred Solutions







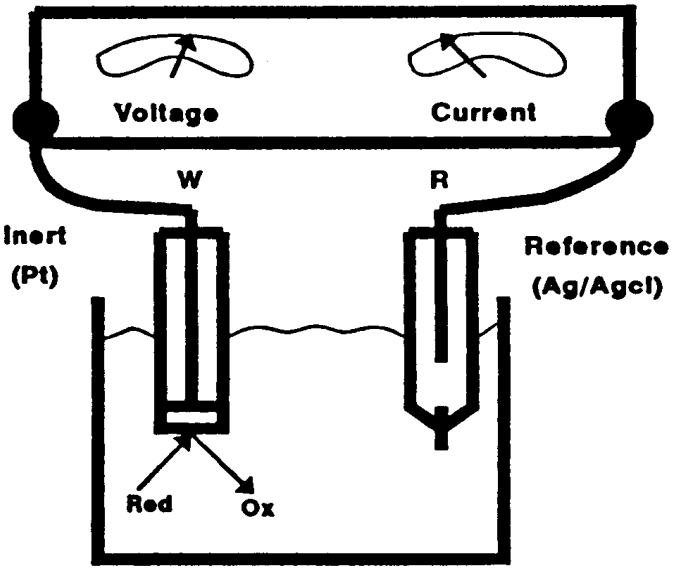
- Apply voltage sweep to cell
- Measure dynamic current

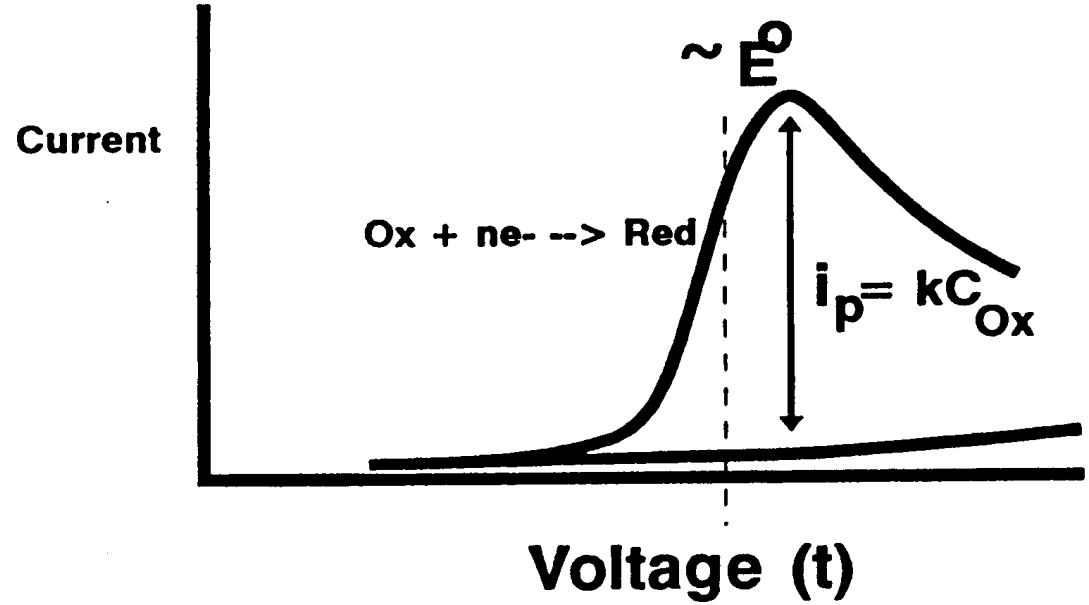
$$i_p(\text{net}) = i_p - i_b = kn^{3/2}AC_{ox}(DV)^{1/2}$$

D = diffusion coefficient
V = sweep rate

Analytical Voltammetry

Voltammetry in Unstirred Solutions





Analytical Characteristics

Concentration range: 10^{-3} to 10^{-7} M

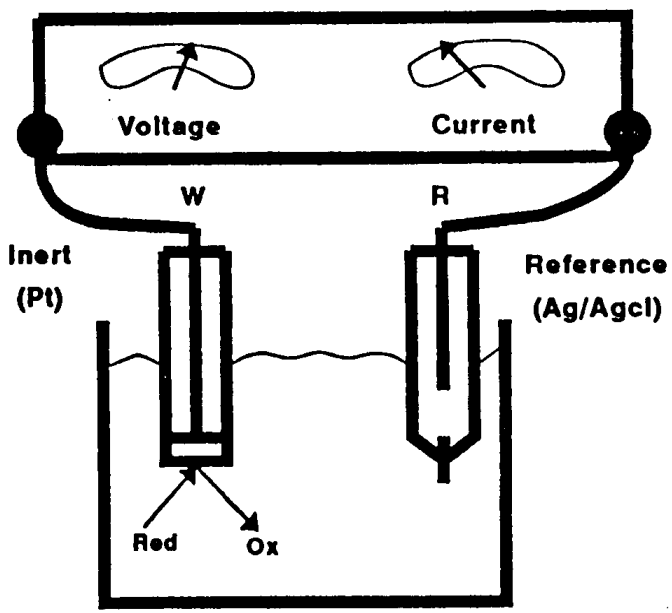
Rapid experiments: microsecs. to secs.

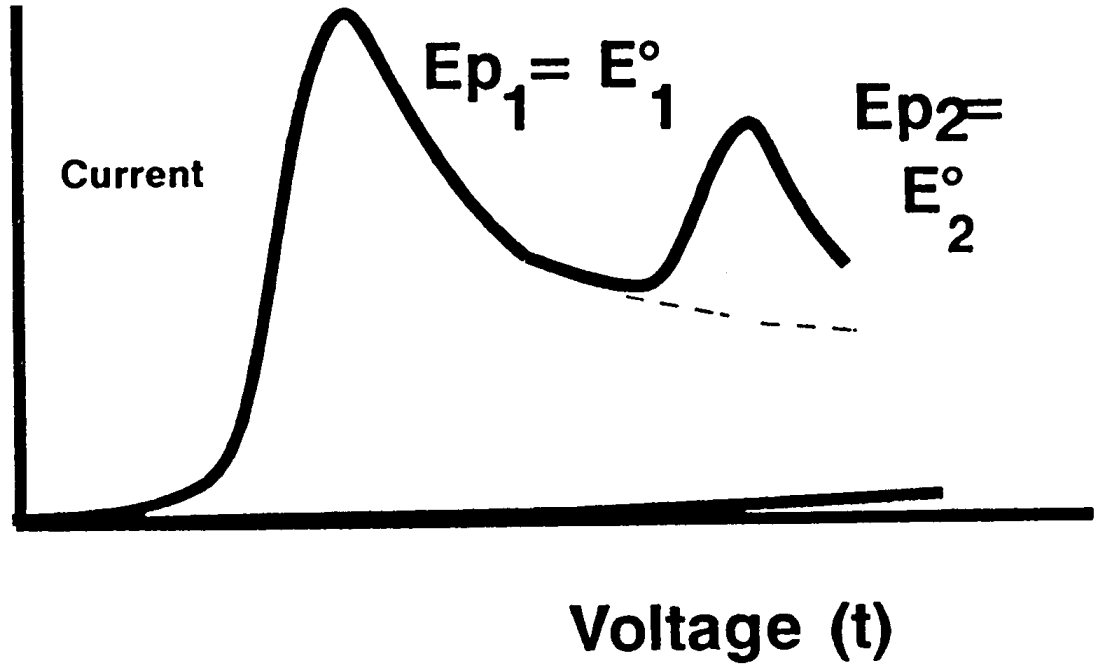
Same voltage range limits as stirred voltammetry

Mixture currents are additive

Analytical Voltammetry

Voltammetry of Mixtures in Unstirred Solutions





Analytical Characteristics

Concentration range: 10^{-3} to 10^{-7} M

Mixture currents are additive

Non-linear background currents

Quantitative Analysis with Voltammetric Measurements

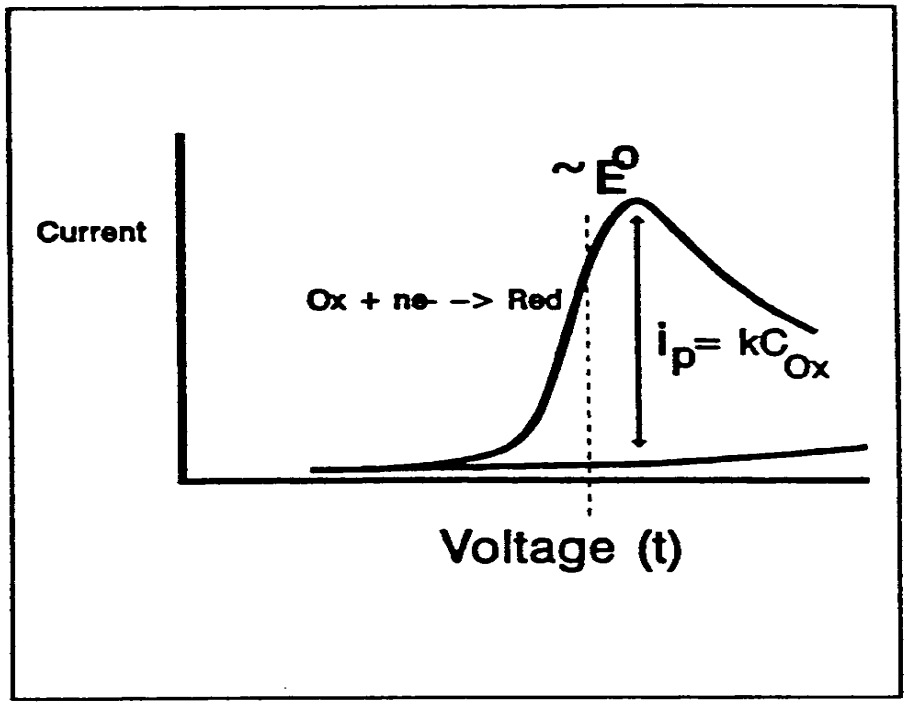
Let $C_{OX} = 6.0 \times 10^{-4}$ M
$i_p = 5.0\ \mu$Amp
$i_b = 0.2\ \mu$Amp

$i_p(\text{net}) = i_p - i_b$

$= 4.8\ \mu$Amp

$i_p(\text{net}) = kC_{OX}$

$k = 4.8/(6.0 \times 10^{-4})$



$k = 8.0 \times 10^3\ \mu$A/M

If $C_{OX} = 1.0 \times 10^{-3}$ M, $i_p = ?$

$i_p(\text{net}) = (8.0 \times 10^3)(1.0 \times 10^{-3}) = 8.0\ \mu$Amp

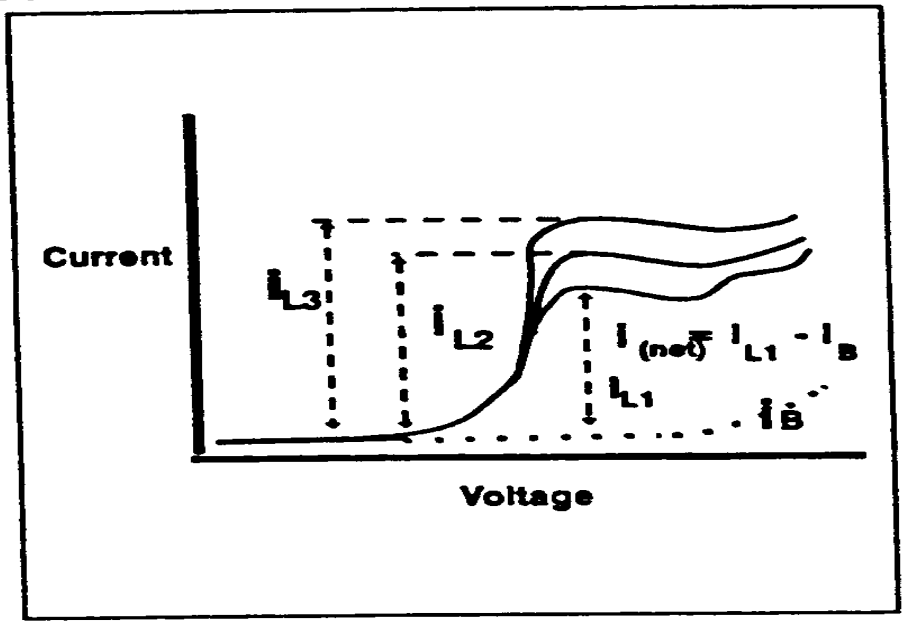
$i_p = i_p(\text{net}) + i_b = 8.0 + 0.2 = 8.2\ \mu$Amp

Quantitative Analysis with Voltammetric Measurements (Standard Addition Experiments)

For 100.0 mL of unknown solution of reducible analyte (Ox):

$i_{L1} = 1.25\mu A.$

$i_B = 0.10\mu A.$



$i_{L1}(net) = 1.15\mu A = kC_{OX}$

When 2.00 mL of Ox Stndrd (C_S=4.0 x 10^{-4}M) is added:

$i_{L2} = 2.45\ \mu A.$

$i_{L2}(net) = 2.35\ \mu A.$

$C_{OX} = ?$

$i_{L2}(net) = kC_2 = k[C_{OX}V_o + C_s\Delta V]/(V_o+\Delta V)$

V_o = 100.0mL; ΔV = 2.00mL. Thus, for $i_{L2}(net)/i_{L1}(net)$, solving for C_{OX}:

$C_{OX} = (i_{L1}(net)C_s\Delta V)/[i_{L2}(net)(V_o+\Delta V) - i_{L1}(net)V_o]$

$C_{OX}=(1.15)(4\times10^{-4})(2.0)/[(2.35)(102)-(1.15)(100)=$

$C_{OX} = 7.3 \times 10^{-6}M$

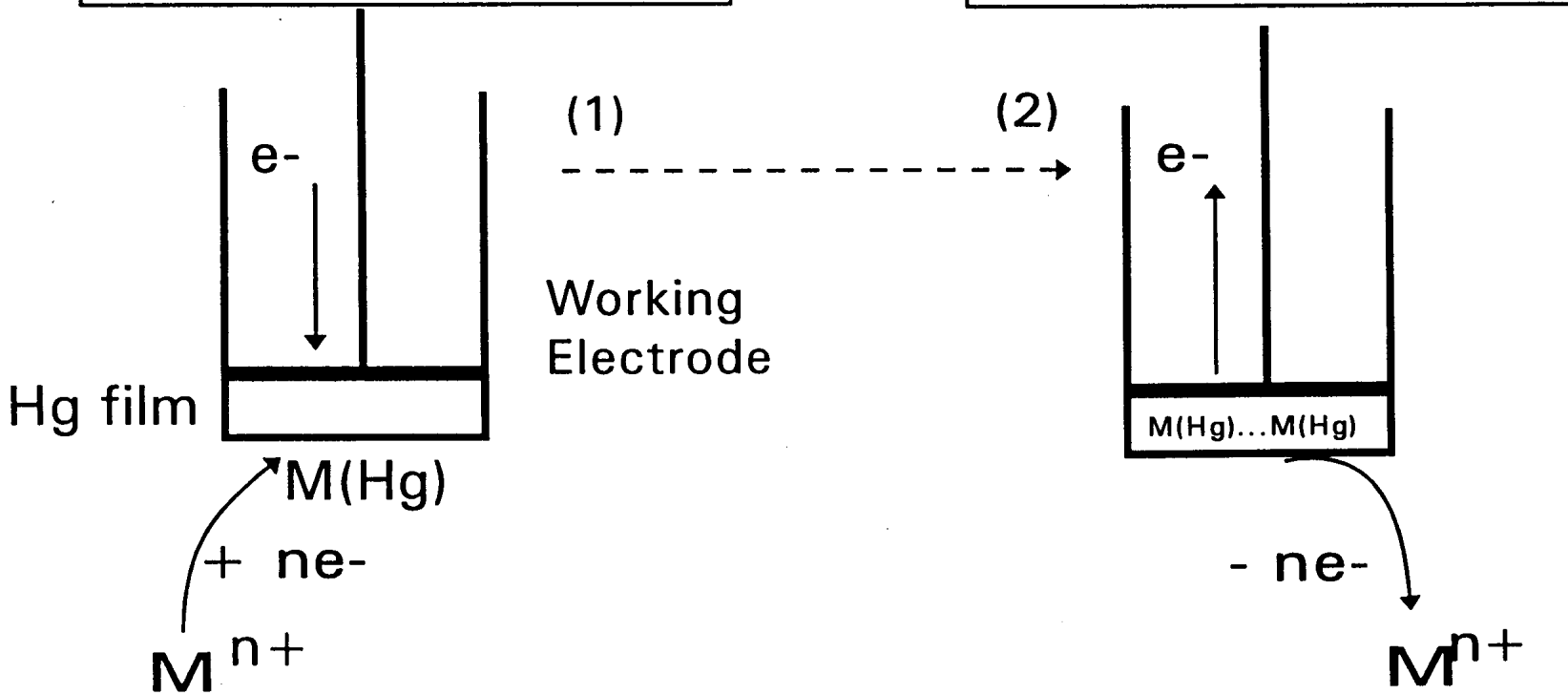
wph21.55ecvg13

Anodic Stripping Voltammetry (ASV)

Trace metal analysis

(1) Pre-concentration Electrolysis (with stirring) for time, t.

(2) Anodic stripping step (w/o stirring)



$$[M(Hg)] = k*[M(n+)]*t$$

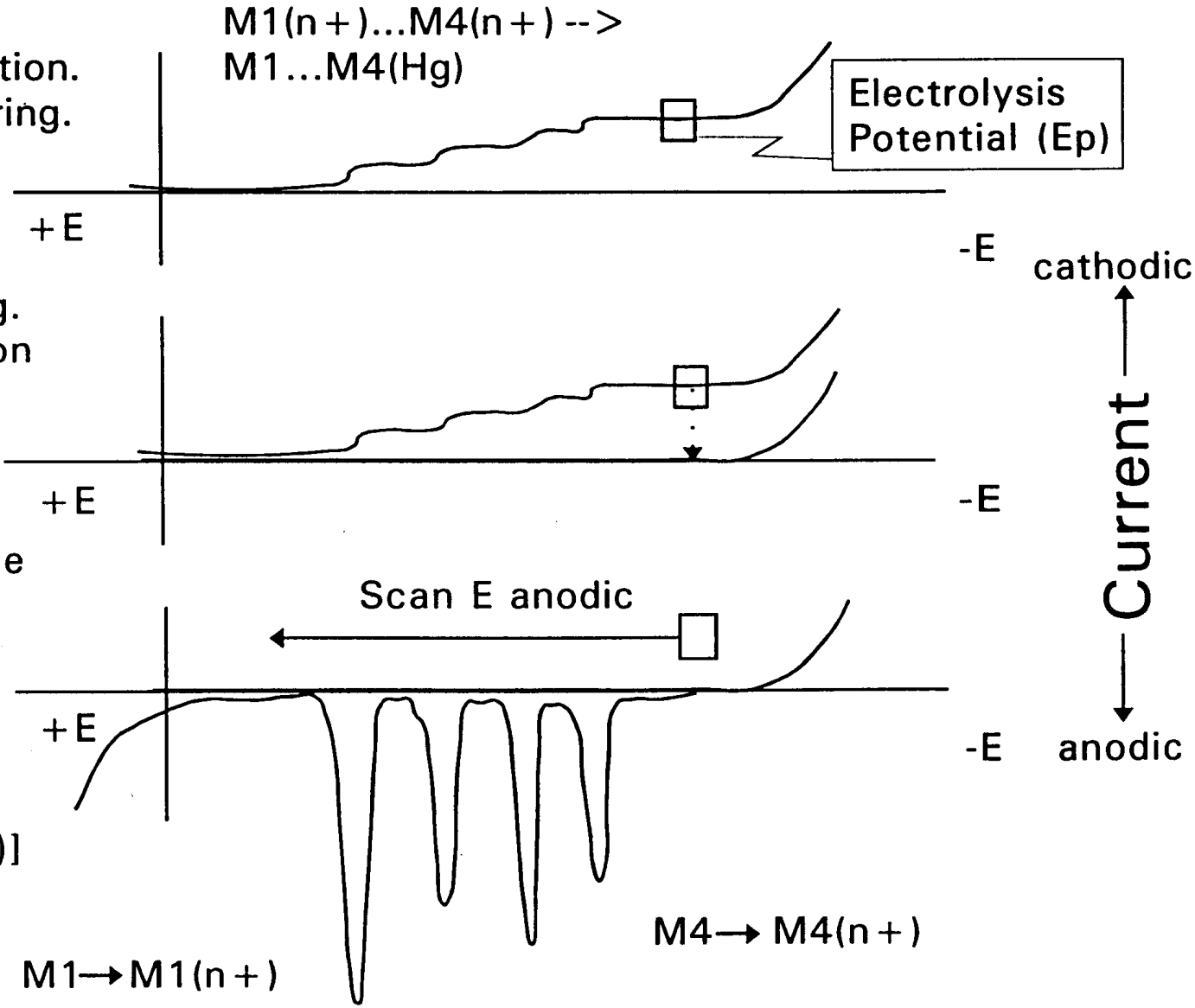
$$i = K*[M(Hg)] = ß*[M(n+)]$$

$$ß = K*k*t$$

Anodic Stripping Voltammetry (ASV)

Trace metal analysis (4-component mixture)

(1A) Pre-concentration. Electrolysis w/ stirring.



(1B) Stop stirring. Keep reduction potential

(2) Sweep voltage anodic. Strip metals.

(3) $I_p = \beta[M(n+)]$

Anodic Stripping Voltammetry (ASV)

Summary of Properties

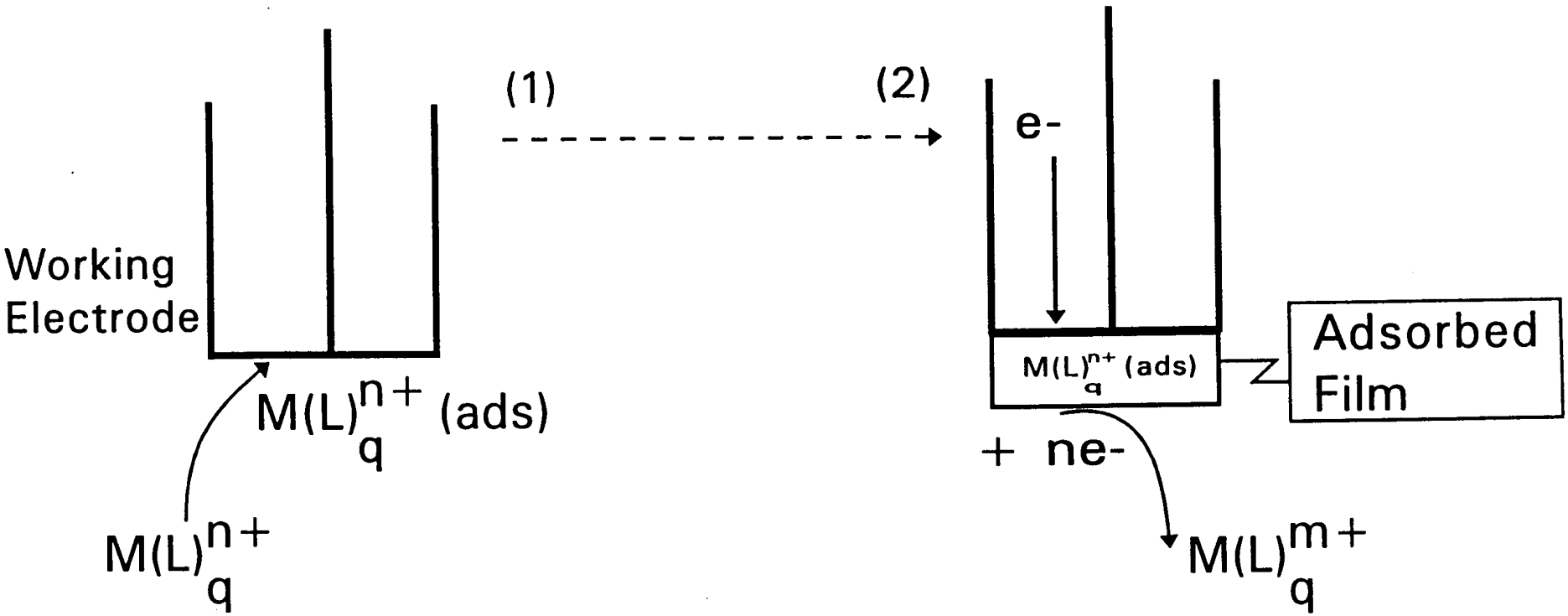
- Pre-concentration of normally undetectable analytes, [M(n+)], by electrolysis for time, t; forming concentrated amalgams.
- Anodic limiting current = ß*[M(n+)]; ß= K*k*t (i.e., sensitivity depends on electrolysis time, t)
- Typical analytes (Pb, Cd, Zn, In, Tl, Cu, Sb, Sn)
- Analytical range (~10^{-4} **M** to 10^{-10} **M**)
- Detection Limit (~5 x 10^{-11} **M**; ~.005 ppb; ~5 ppt)
- Use solid electrodes (Au, Pt, C) to extend to other analytes (e.g., Ni, Ag, Hg); stripping of metal deposits.
- Can be extended to nearly any metal ion, using adsorption to pre-concentrate ion on electrode surface (usually a metal complex). [Stripping by a cathodic voltage sweep, "Cathodic Stripping Voltammetry", CSV]

Cathodic Stripping Voltammetry (CSV)

Adsorption-dependent trace metal analysis

(1) Pre-concentration Adsorption (with stirring) for time, t.

(2) Cathodic stripping step (w/o stirring)



$[M(Ads)] = k*[M(n+)]*t$

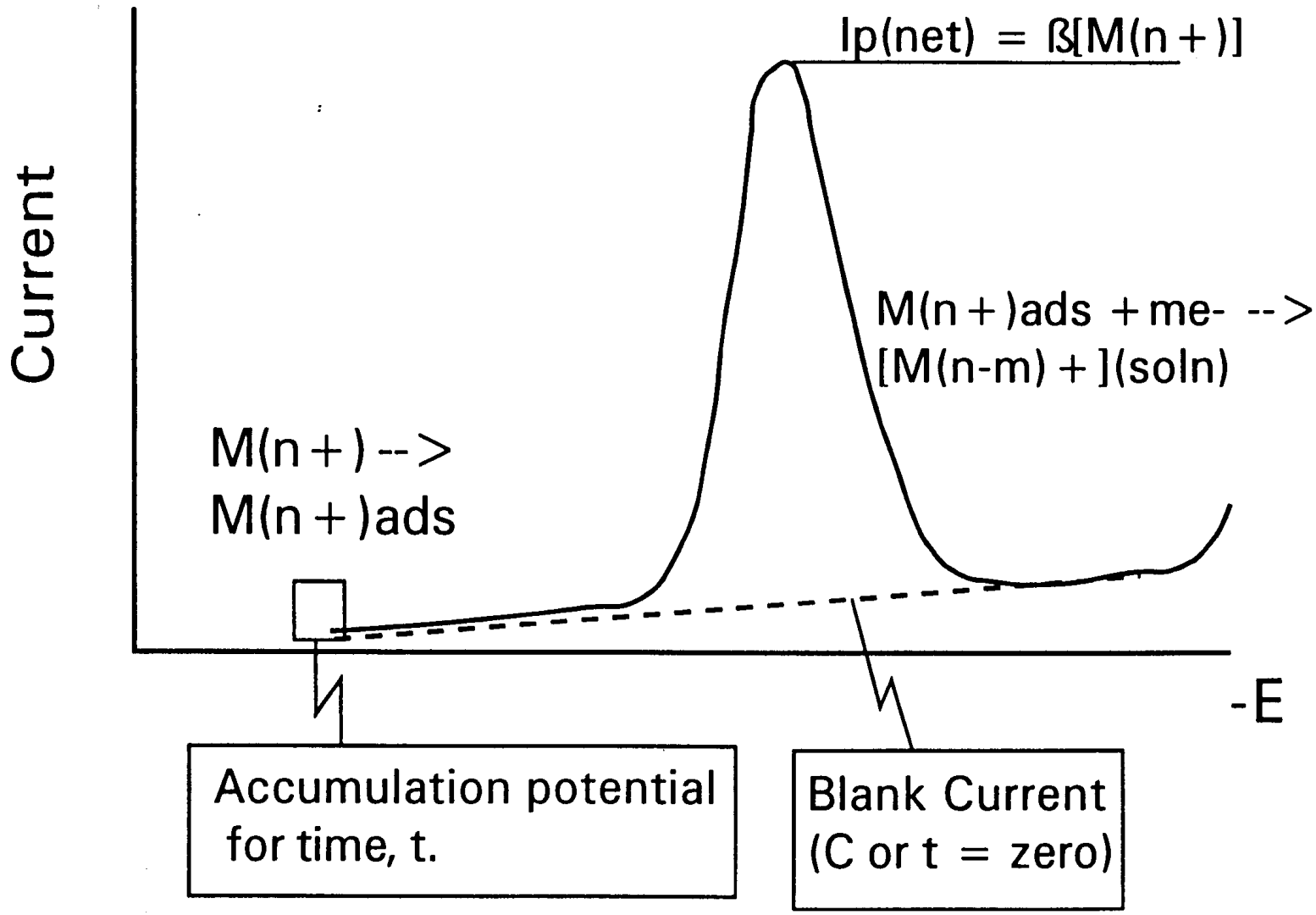
for $[M(ads)] = 0$ to Ã

$i = K*[M(ads)] = ß*[M(n+)]$

$ß = K*k*t$

Cathodic Stripping Voltammetry (CSV)

Adsorption-dependent trace metal analysis



There is a micro working electrode, a reference electrode, and an auxiliary electrode.

Current flows between the working and auxiliary electrodes.

The voltage between the working and reference electrodes is recorded.

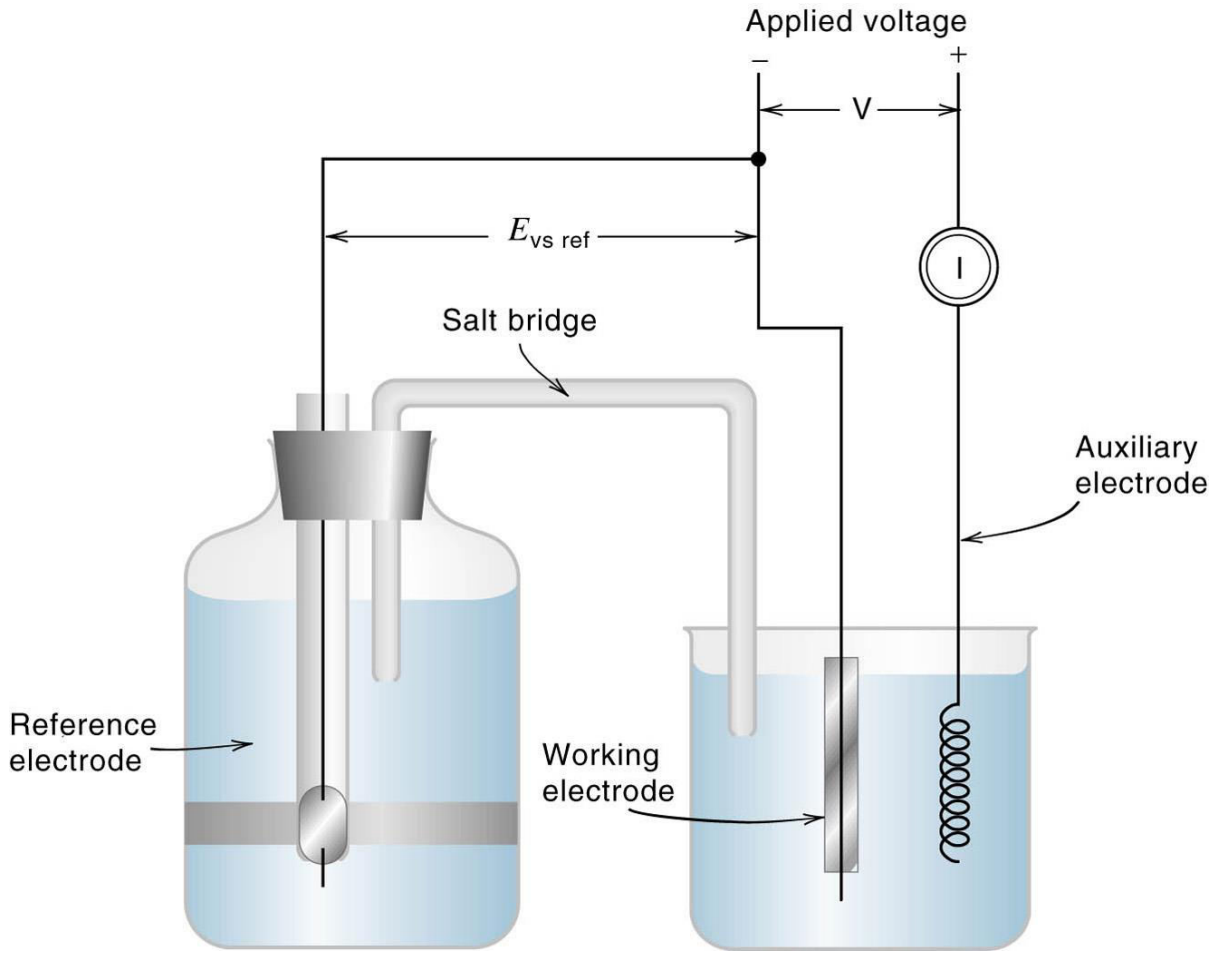


Fig. 15.1. Setup for voltammetric measurements.

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When the decomposition potential for reduction or oxidation of the analyte is reached, electrolysis begins.

A limiting current is reached when the rate of electrolysis equals the rate of diffusion.

In an unstirred solution, the diffusion layer extends futher into the solution with time, so the limiting current decreases exponentially.

Stepwise electrolysis occurs for species with different oxidation states, or for mixtures.

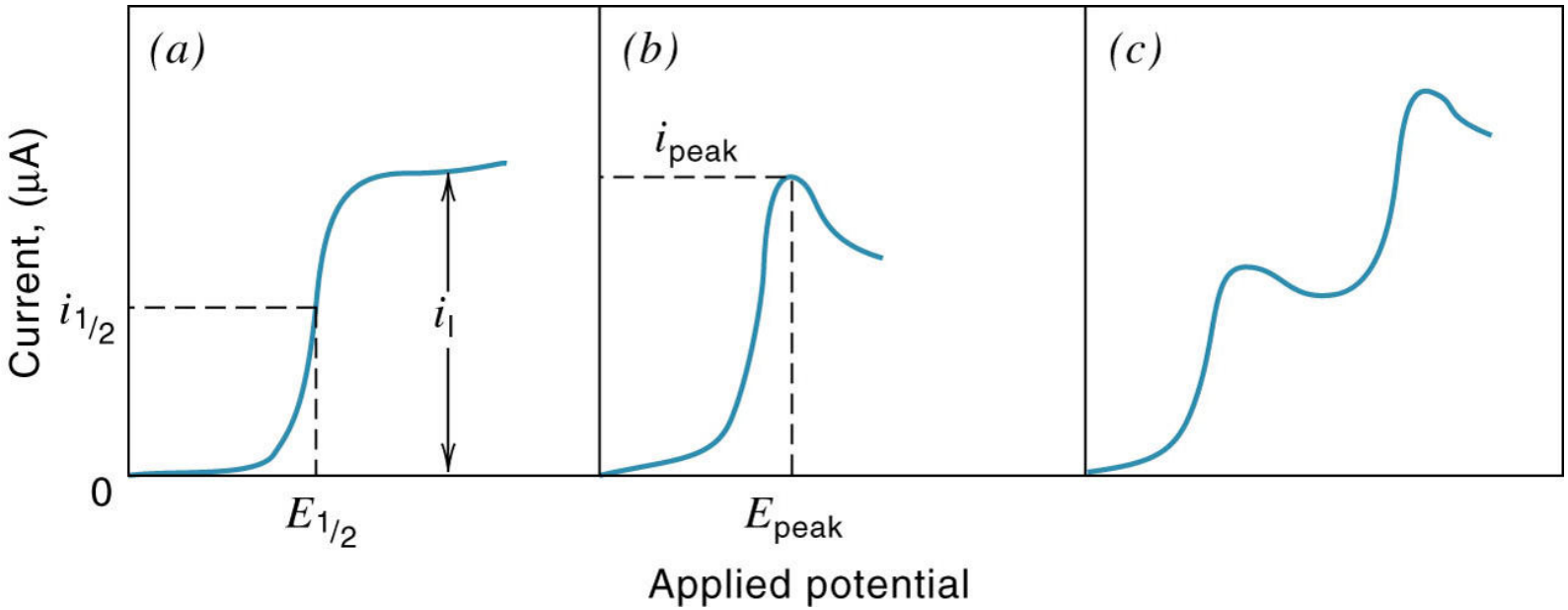

Fig. 15.2. Different types of voltammetric curves. *(a)* Stirred solution or rotated electrode. *(b)* unstirred solution, and *(c)* stepwise reduction (or oxidation) of analyte or of a mixture of two electroactive substances (unstirred solution).

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This is a complete cell.

Oxygen diffuses through the membrane and is reduced at the platinum cathode ring.

The anode coil is a Ag/AgCl reference electrode.

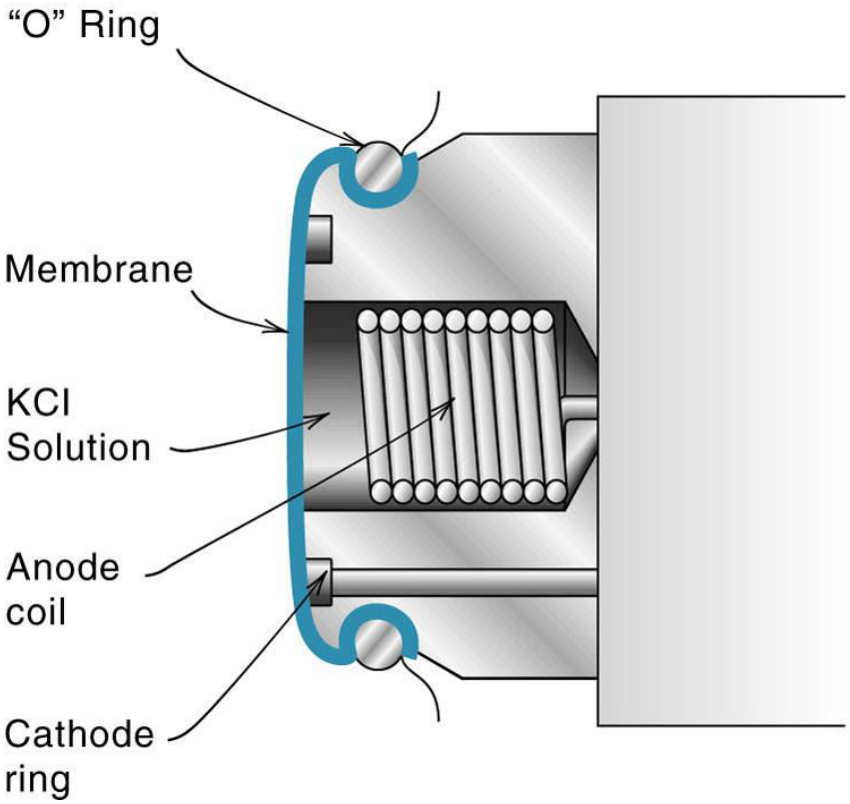

Fig. 15.3. Construction of an oxygen electrode.

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Glucose oxidase is immobilized on the Pt electrode.

This catalyzes reaction of glucose with oxygen:

$$\text{glucose} + O_2 = \text{gluconic acid} + H_2O_2$$

The H_2O_2 is oxidized at the Pt electrode by applying +0.6 V vs. Ag/AgCl:

$$H_2O_2 = O_2 + 2H^+ + 2e^-$$

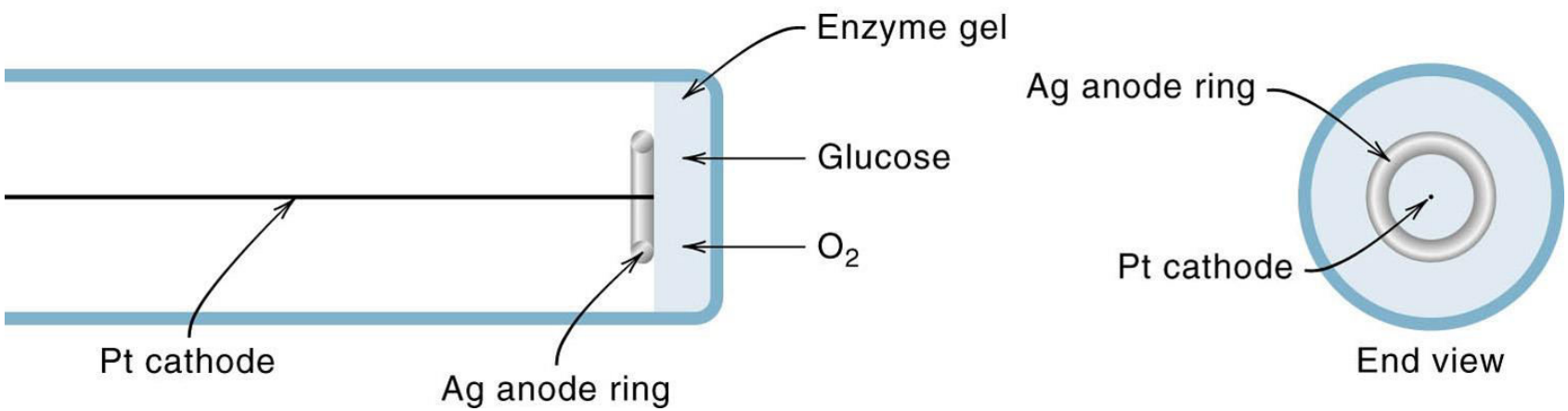

Fig. 15.4. Amperometric glucose electrode.

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The mediator layer, M_{ox}, acts as an electrocatalyst for the electrooxidation of an analyte with slow electron transfer.

So a smaller potential needs to be applied, giving better selectitvity.

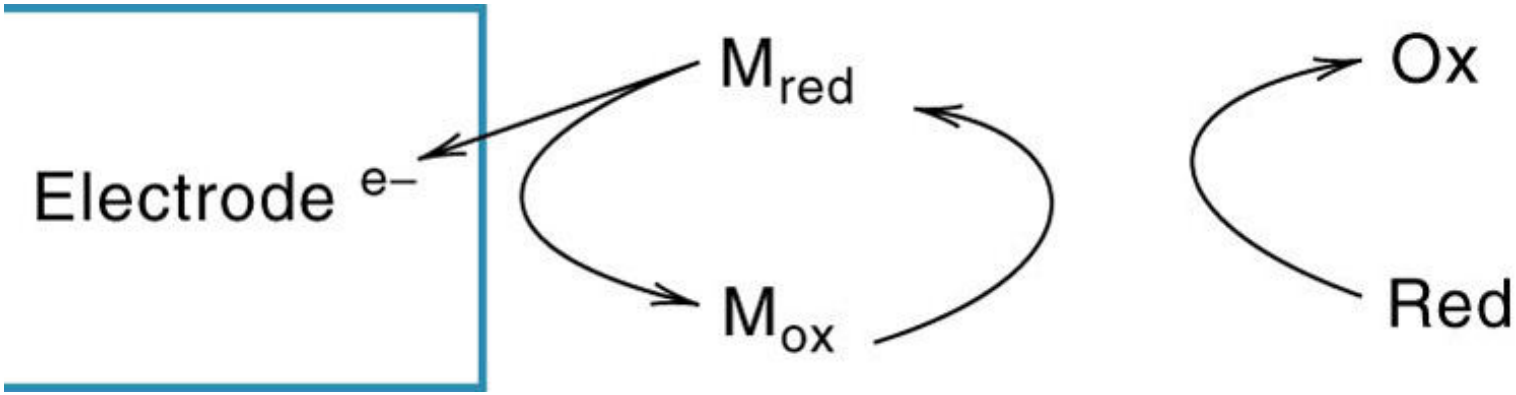

Fig. 15.5. Redox modified electrode.

Red is the analyte being measured, in the reduced form.

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The microdisk electrode is about 5-30 μm.

This smaller than the diffusion layer thickness.

This results in:

- **enhanced mass transfer**
- **independence on flow**
- **increased signal-to-noise ratio**
- **S-shaped curve in an unstirred solution**
- **can measure in nonaqueous solvents**

$i_l = 2nFDCd$

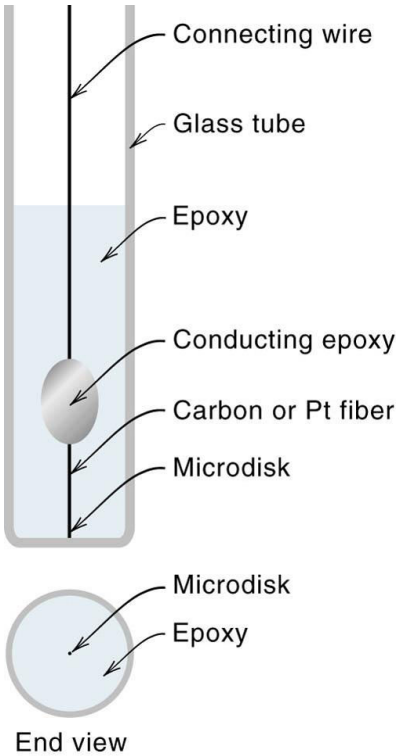

Fig. 15.6. Ultramicro electrode.

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Chemistry 5

The Art and Science of
Chemical Analysis

Introduction to Chemical Analysis

- Chemical analysis includes any aspect of the chemical characterization of a sample material.

- Analytical Chemistry?
  - “Science of Chemical Measurements”

Areas of Chemical Analysis and Questions They Answer

- Quantitation:
  - How much of substance X is in the sample?
- Detection:
  - Does the sample contain substance X?
- Identification:
  - What is the identity of the substance in the sample?
- Separation:
  - How can the species of interest be separated from the sample matrix for better quantitation and identification?

What do Chemical Analyst Do?

- Analyst:
- Applies known measurement techniques to well defined compositional or characterization questions.
- Research Analytical Chemist

What do Chemical Analyst Do?

- Senior Analyst:
- Develops new measurement methods on existing principles to solve new analysis problems.

What do Chemical Analyst Do?

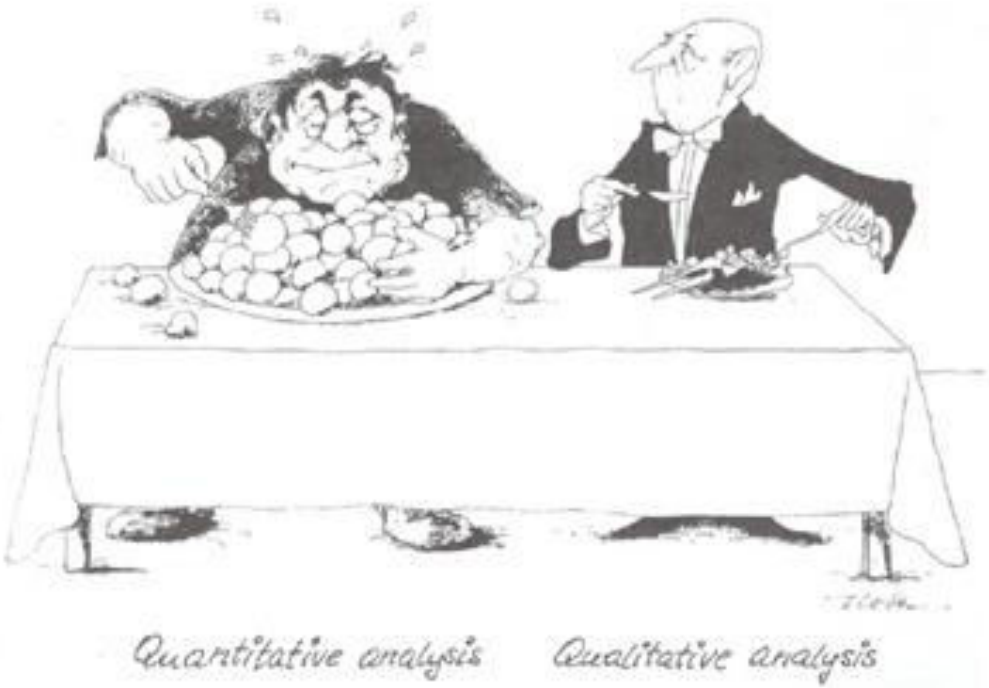
- Research Analytical Chemist:
- Creates and /or investigates novel techniques or principles for chemical measurements.
- or
- Conducts fundamental studies of chemical/physical phenomena underlying chemical measurements.

What is Analytical Science?

- Analytical Chemistry provides the methods and tools needed for insight into our material world…for answering four basic questions about a material sample?
- What?
- Where?
- How much?
- What arrangement, structure or form?
- Fresenius' J. Anal. Chem. 343 (1992):812-813

Qualitative analysis is what.

Quantitative analysis is how much.



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An analysis involves several steps and operations which depend on:

- **the particular problem**
- **your expertise**
- **the apparatus or equipment available.**

The analyst should be involved in every step.

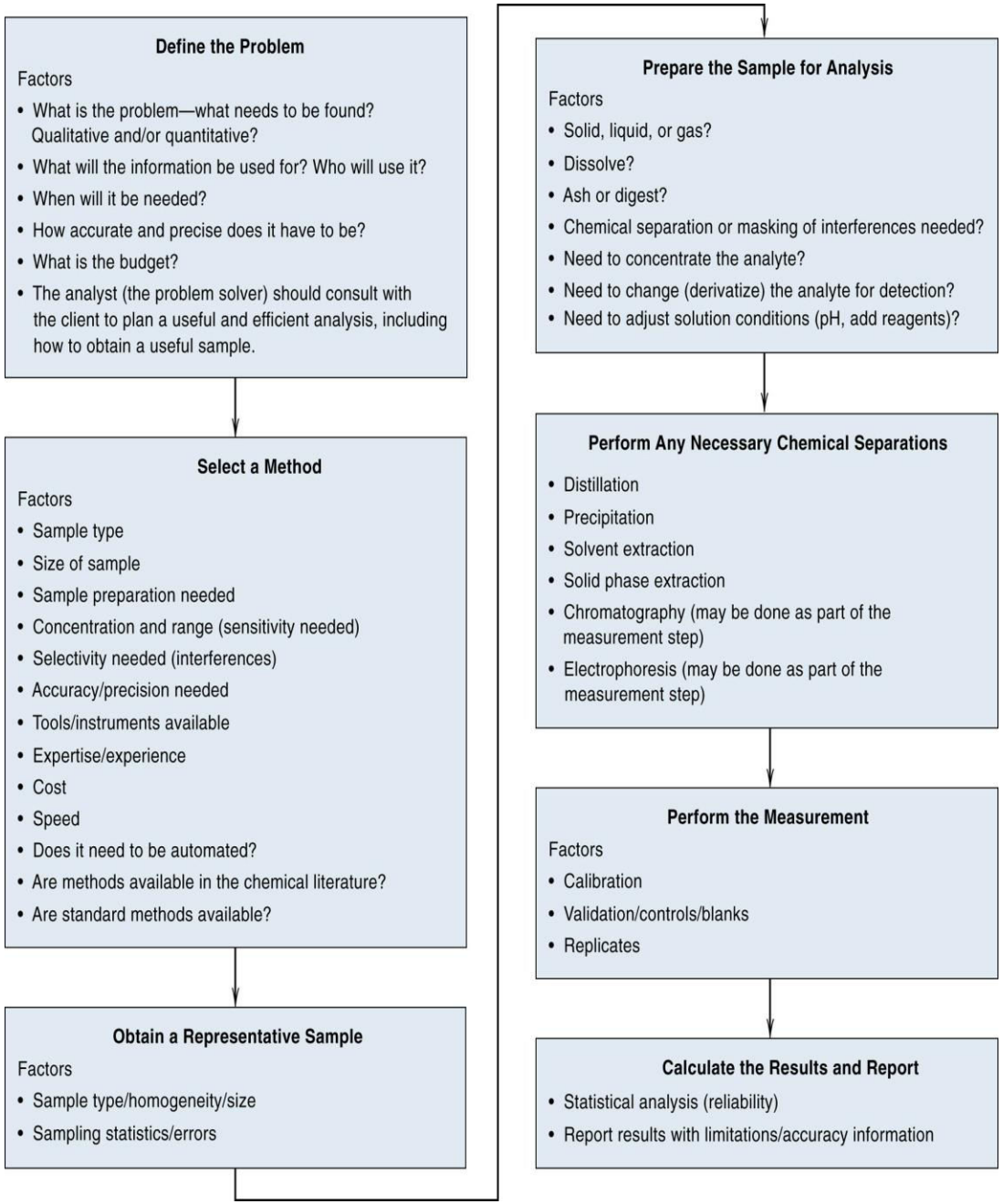

Fig. 1.1. Steps in an analysis

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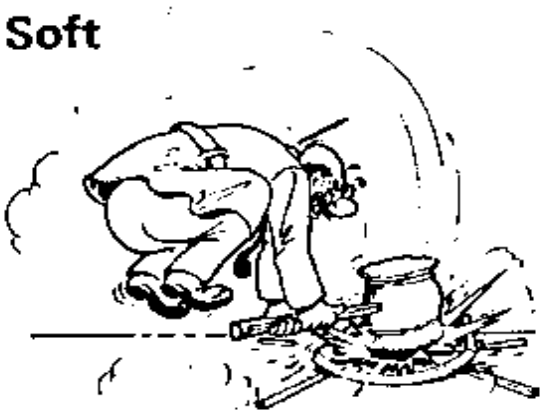
Measurement science

Provides the "tools" and the "eyes" scientists and engineers require

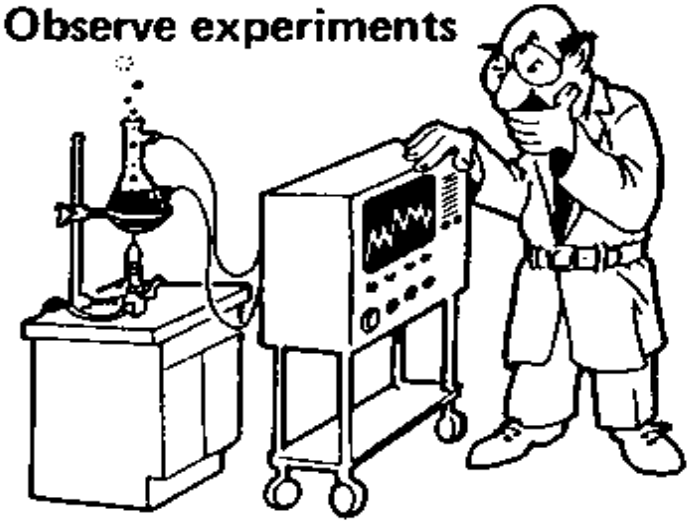
1 Characterize materials

Soft



Brittle

2 Observe experiments



Different methods provide a range of precision, sensitivity, selectivity, and speed capabilities.

Table 1.1

Comparison of Different Analytical Methods

Method	Approx. Range (mol/L)	Approx. Precision (%)	Selectivity	Speed	Cost	Principal Uses
Gravimetry	10^{-1}–10^{-2}	0.1	Poor–moderate	Slow	Low	Inorg.
Titrimetry	10^{-1}–10^{-4}	0.1–1	Poor–moderate	Moderate	Low	Inorg., org.
Potentiometry	10^{-1}–10^{-6}	2	Good	Fast	Low	Inorg.
Electrogravimetry, coulometry	10^{-1}–10^{-4}	0.01–2	Moderate	Slow–moderate	Moderate	Inorg., org.
Voltammetry	10^{-3}–10^{-10}	2–5	Good	Moderate	Moderate	Inorg., org.
Spectrophotometry	10^{-3}–10^{-6}	2	Good–moderate	Fast–moderate	Low–moderate	Inorg., org.
Fluorometry	10^{-6}–10^{-9}	2–5	Moderate	Moderate	Moderate	Org.
Atomic spectroscopy	10^{-3}–10^{-9}	2–10	Good	Fast	Moderate–high	Inorg., multielement
Chromatography	10^{-3}–10^{-9}	2–5	Good	Fast–moderate	Moderate–high	Org., multicomponent
Kinetic methods	10^{-2}–10^{-10}	2–10	Good–moderate	Fast–moderate	Moderate	Inorg., org., enzymes

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The sample size dictates what measurement techniques can be used.

Table 1.2

Classification of Analytical Methods According to Size of Sample

Method	Sample Weight (mg)	Sample Volume (μL)[a]
Meso	>100	>100
Semimicro	10–100	50–100
Micro	1–10	<50
Ultramicro	<1	

[a] μL = Microliter. Sometimes the symbol l(lambda) is used in place of m L.

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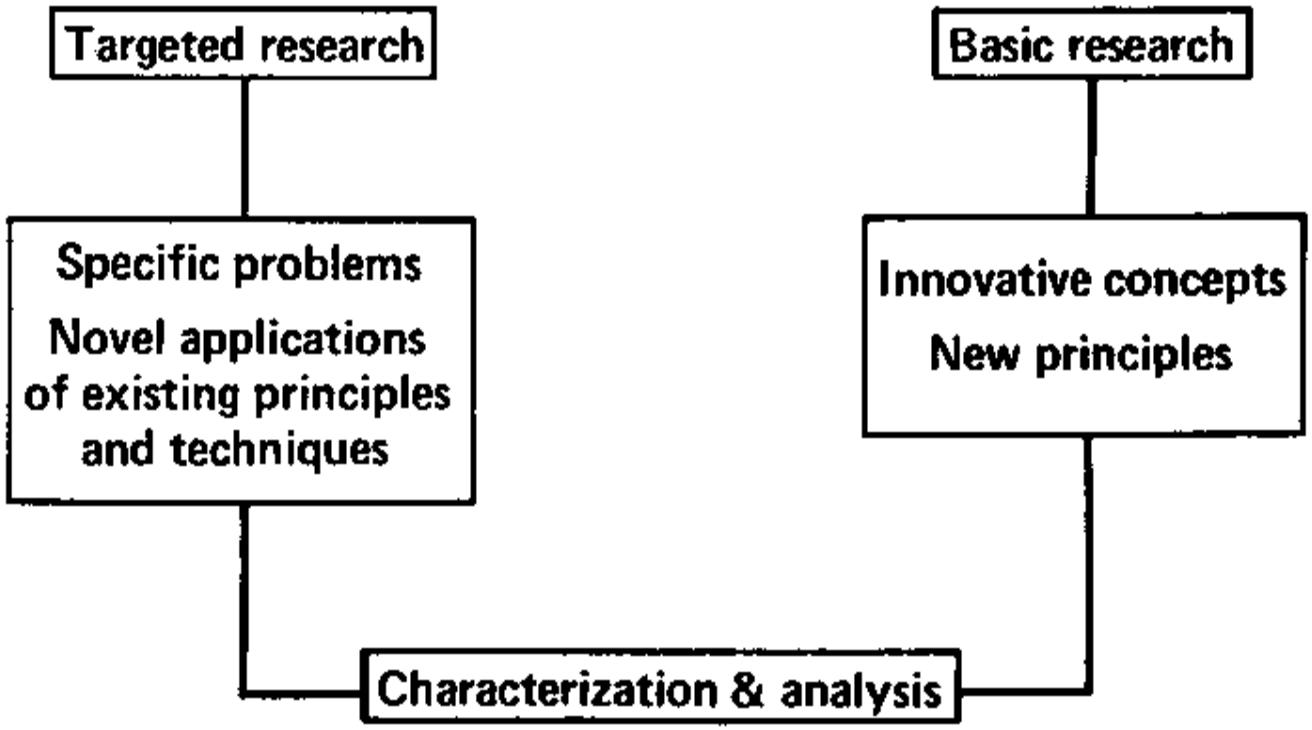
Measurement science

Progress in measurement science involves both targeted and basic research



Training of Chemical Analysts (Analytical Chemists)

- Training focuses on principles and techniques for solving measurement problems … but…
- Chemical analysts interface multiple disciplines to the solution of chemical measurement problems
  - Physical-, organic-, inorganic-, bio-chem-, physics, math, biology, electronic, computers

Chemistry 5
Training Focuses on

- Underlying principles of chemical measurements (integrating all chemistry fields, math, physics, biology, electronics, and computers).
- Developing proficiency with quantitative analysis laboratory procedures
- Exposure to role of chemical analysis in a broad range of modern science.

Chemical Analysis Affects Many Fields

- Physical-, Organic-, …, Chemistry:
  - "Theory guides but Experiment decides"
- Biotechnology:
  - Distinguishing isomers with differing bioactivities.
  - Biosenors
- Materials Science:
  - High-temperature superconductors

Chemical Analysis Affects Many Fields

- Manufacturing:
  - Quality control of packaged foods specifications
- Forensics:
  - Chemical features for criminal evidence

Role of Analytical Chemistry in Modern Science

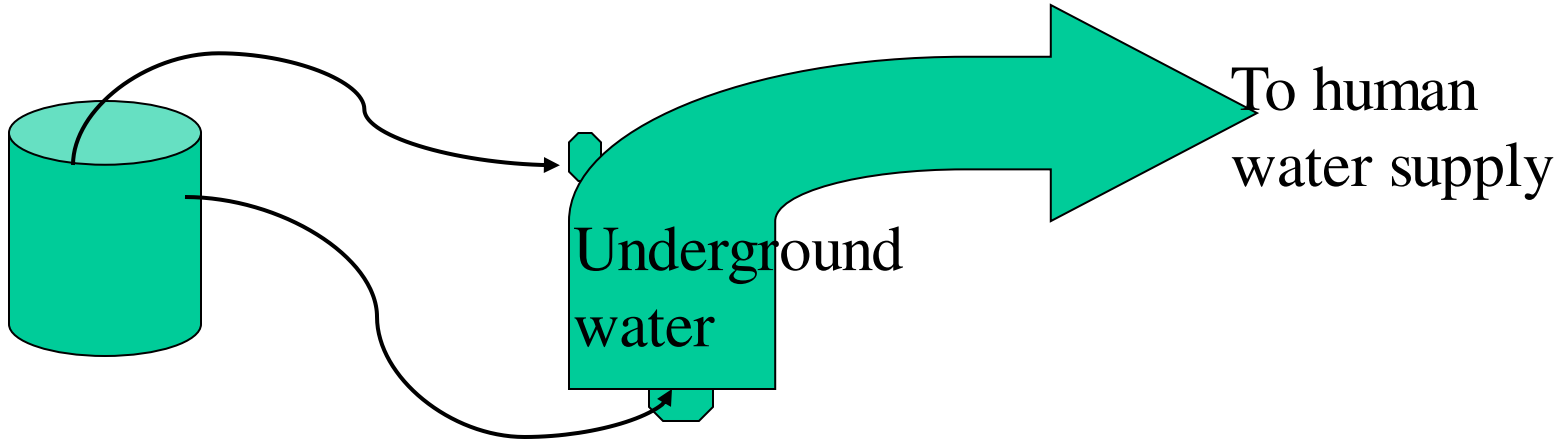
- Case Study 1.
- Nuclear Waste Disposal
  - Nuclear Power Plants
  - Nuclear Reactors
  - Weapons Processing
  - Weapons Disposal

Nuclear Waste Disposal Case Study

- **One Disposal Plan:**
  - ✓ **seal waste in corrosion-resistant containers**
  - ✓ **bury 1000's of feet underground (rocky strata above water table)**
  - ✓ **Must remain contained for> 20,000 years**

Nuclear Waste Disposal Case Study

- Technical Problems:
- Metal Package Corrosion:
  - M + water, oxygen, oxidizers →M ions + products



Nuclear Waste Disposal Case Study

- Repository above water table, but some water present
- Model exists for chemical reactions, rates, and time-dependent dispersion of products and waste
- Predicted containment time depends on very accurate measurements of microscopic corrosion processes over short periods (weeks, months)

Nuclear Waste Disposal Case Study

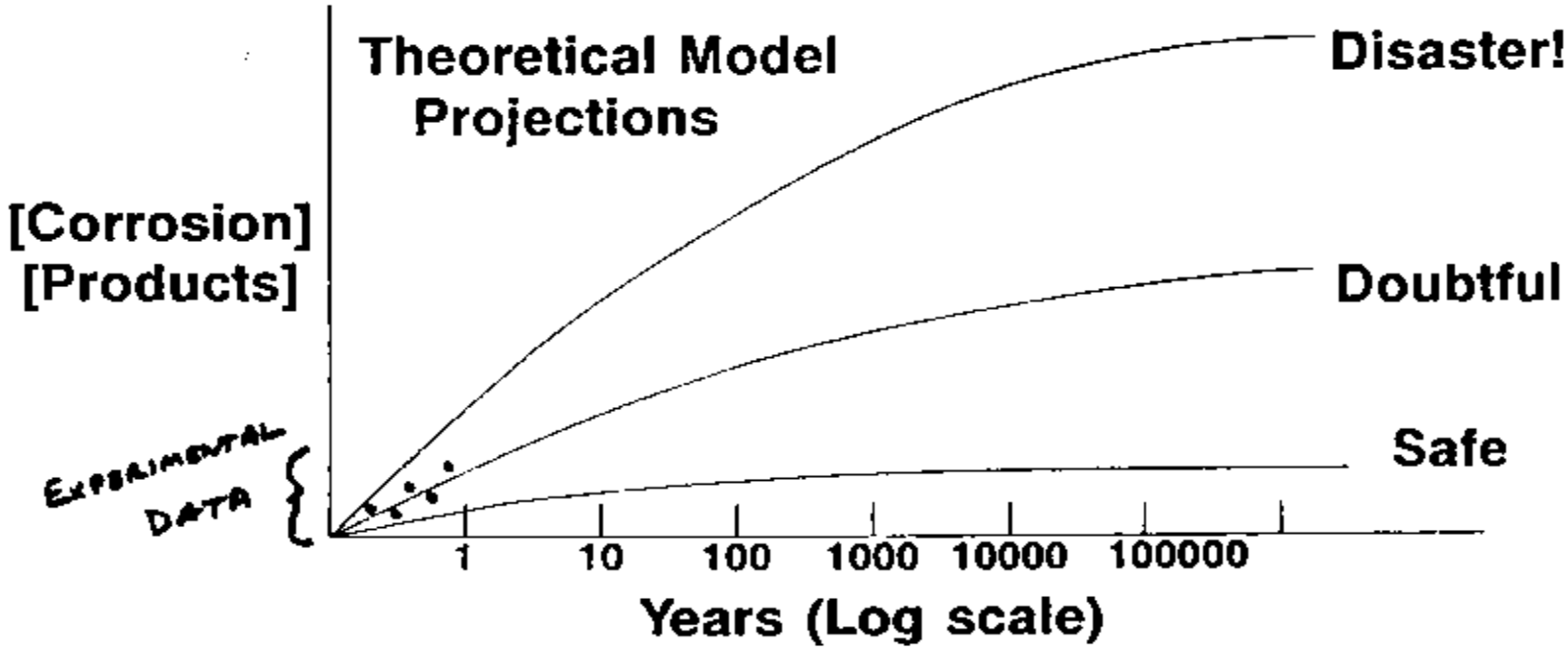
- **Corrosion Model:**
- $M + H_2O, SO_4^{2-}, O_2 \rightarrow M^+ + OH^-, H_2$
- $CO_3^{=}, H^+, F^-, Cl^-, \rightarrow MXn^+$:
- $NO_2^-, NO_3^-, S^{=}$,etc.$\rightarrow MYm^+, MZj$ + Prod.

Nuclear Waste Disposal Case Study

- What Do We Need To Know?
- Laboratory Simulation Studies
- Water Composition at site before container placement.
- Water Composition after exposure to container
  - **Time dependence (rate of product growth over weeks/months)**
  - **Small changes must be measured very precisely**

Nuclear Waste Disposal Case Study

Need for Precise Measurements:

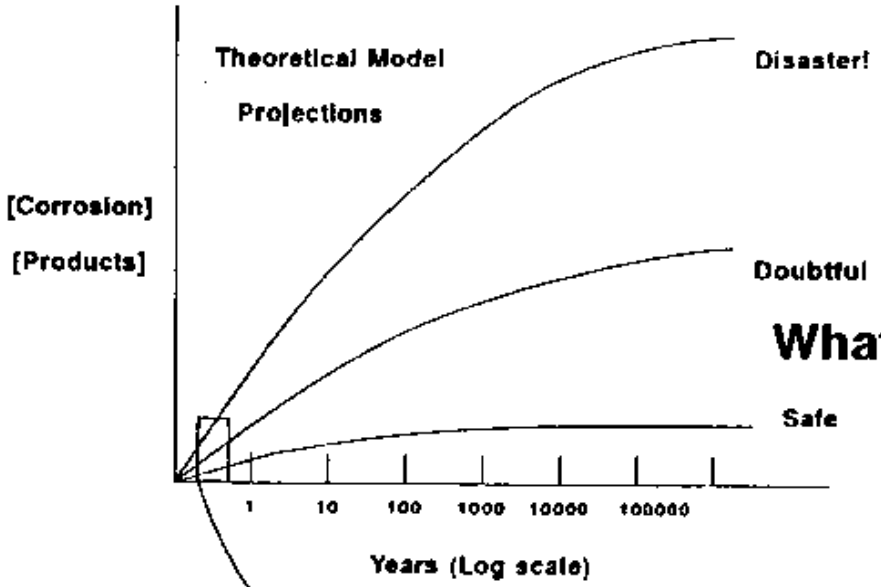


NOTE: Short–term lab measurements are made at high temperatures to accelerate corrosion processes.

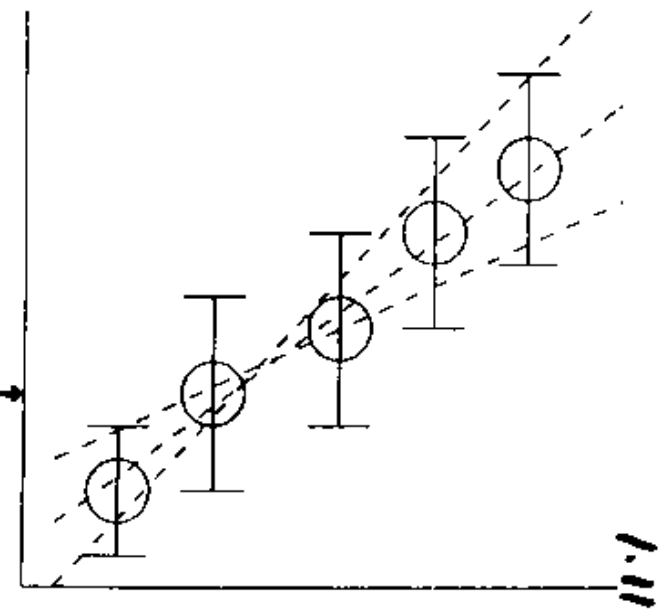
Model projections are corrected to the ambient temperature of the repository.

Nuclear Waste Disposal Case Study

Need for Precise Measurements:



What is impact of data range?



How can we narrow the range?

Nuclear Waste Disposal Case Study Analytical Chemistry Issues:

- What species to be measured?
- What precision is required?
- What measurement technique?
- What are the sources of error?

Nuclear Waste Disposal Case Study Analytical Chemistry Issues:

- Example: $CO_3^{=}$ Analysis
- Species? $CO_3^{=}$, HCO_3^{-}, H_2CO_3 ?
- Precision? +/- (0.1%, 0.01%, 10%)
- Technique?
  - +/- 1-2% Ion Chromatography
  - +/- 0.1% Acid-Base Titration
- Error Sources?
  - Acid-Base (Other Bases Interfer)
  - Ion Chromatography (pH – Dependent Results)

Nuclear Waste Disposal Case Study Analytical Chemistry Issues:

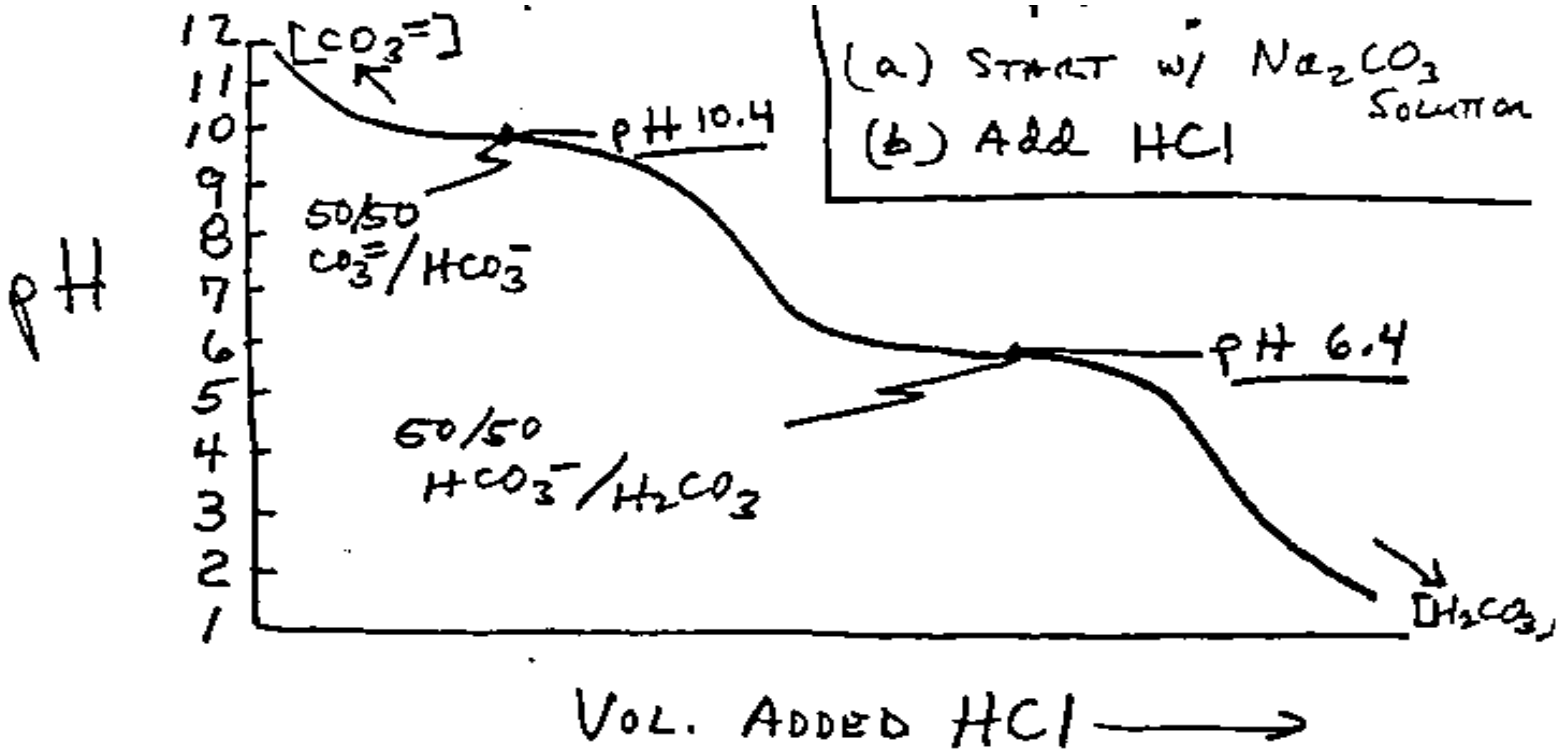
- What Carbonate Species?
- $CO_3^{=} + H_2O \leftrightarrow HCO_3^- + OH^-$
- $HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$
- $H_2CO_3 \leftrightarrow CO_{2(g)} + H_2O$
- Temperature, Pressure Dependence

Nuclear Waste Disposal Case Study Analytical Chemistry Issues:

- If Need $[CO_3^{=}]$ only
  - Specify pH, Temperature, Pressure
  - Use Technique Selective for $CO_3^{=}$
    - (Ion Chromatography)
- If Need $\Sigma\ [CO_3^{=}] + [HCO_3^{-}] + [H_2CO_3]$
  - Remove Interferences
  - Acid-Base Titration

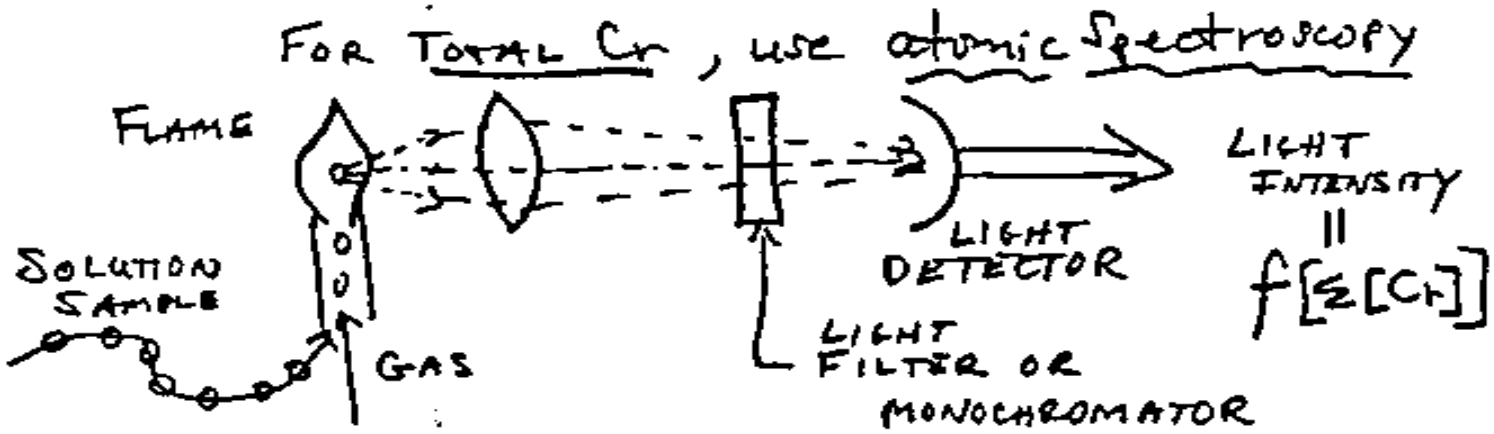
Nuclear Waste Disposal Case Study Analytical Chemistry Issues:

What carbonate species is present as a function of pH?



Nuclear Waste Disposal Case Study Analytical Chemistry Issues: (Cont.)

- Other Chemical Measurements:
- Chromium: Cr^{2+}, Cr^{3+}, $Cr_2O_7^{=}$, $CrO_4^{=}$, etc.



PROBLEM: PRECISION = ± 1-5 %

Nuclear Waste Disposal Case Study Analytical Chemistry Issues: (Cont.)

- What does the Analytical Chemist need to know to solve these problems?
- Measurement Techniques Available
  - Titrations, Optical Spectroscopy, Chromatography; etc.
- Strengths/Weaknesses of Techniques
  - Accuracy, Precision, Interferences, Range, Detection Limits, etc.

Nuclear Waste Disposal Case Study Analytical Chemistry Issues: (Cont.)

- Underlying Chemistry/Physics of the Sample Material
  - Solution Chemistry (Acid/Base)
  - Solids Homogeneity, Structure
- Error Analysis
  - Sources
  - Solutions

Deer Kill

- Case Study # 2: Deer Kill
- Problem: Dead whitetail deer near pond in the Land Between the Lakes State Park in south central Kentucky.
- Chemist state veterinary diagnostic laboratory helped find the cause

Site Investigation

- Careful visual observation of a two acre area around the site:
- Observation: grass around nearby power-poles was wilted and discolored.
- Speculation: Herbicide used on grass.
- Ingredient: Arsenic in a variety of forms
  - $CH_3AsO(OH)_2$ very soluble in water.

Select Method

- Association of Official Analytical Chemists (AOAC)
- Distillation of arsenic as arsine which is then determined by colorimetric measurements.

Representative Sample

- Dissect both deer. Removed kidneys for analysis.
- Laboratory Sample. Preparation
- Cut kidney into pieces and blend in a high speed blender to homogenize the sample.

Defining Replicate Samples

- Three 10-g samples of the homogenized tissue were placed in porcelain curcibles and dry ashed. Dry ashing serves to free the analyte from organic material and convert the arsenic present to As_2O_5. Samples of the discolored grass were treated in a similar manner.

Dissolving the Samples

- The dry solid in each of the sample crucibles was dissolved in dilute HCl, which converted the As_2O_5 to soluble H_3AsO_4.

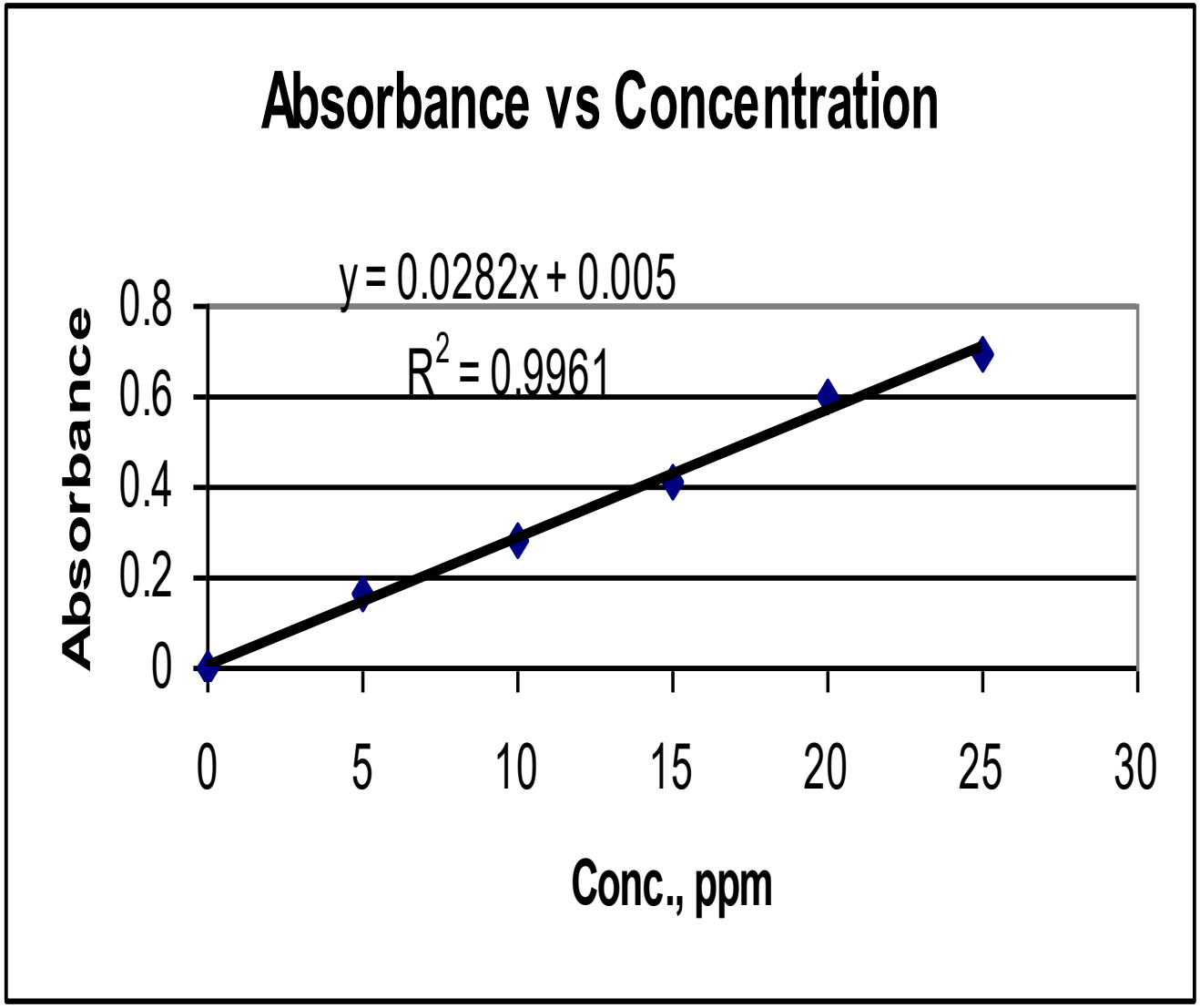
Eliminating Interferences

- Reactions to Eliminate Interferences:
- $H_3AsO_4 + SnCl_2 + 2HCl \rightarrow H_3AsO_3 + SnCl_2 + H_2O$
- $H_3AsO_3 + 3Zn + 6HCl \rightarrow AsH_{3(g)} + 3ZnCl_2 + 3H_2O$
- Bubble gas into collectors with silver diethyldithiocarbamate to form a colored complex compound shown below.

Measuring the Amount of Analyte

- Spectrophotometer: Highly colored complex of arsenic was found to absorb light at a wavelength of 535 nm.

Conc.	Absorbanc
ppm	
0	0
5	0.16
10	0.28
15	0.41
20	0.595
25	0.7
deer 1	0.61
deer 2	0.43



Calculating the Concentration

- ppm = (Absorbance -.005)/0.0282
- Deer 1: (0.61 - 0.005)/0.0282 = 22 ppm
- Deer 2: (0.43 -0.005)/0.0282 = 15 ppm
- Arsenic in the kidney tissue of animals is toxic at levels above about 10 ppm.
- Grass Samples showed about 600 ppm arsenic.

Reliability of the Data

- The data from these experiments could be analyzed using the statistical methods we will describe in Section 3.

Where Do We Begin?

- Review of Basic Tools and Operations of Analytical Chemistry
  - The Laboratory Notebook
  - Analytical Balances, Volumetric Glassware
  - Laboratory Safety
- Error Analysis
  - Concepts
  - Terminology
  - Evaluation of Data
  - Experimental Design
- Review of Solution Chemistry
  - Units
  - Concentration Calculations
  - Stoichiometry
  - Balanced Chemical Reactions

Laboratory safety is a must!

Learn the rules.

See Appendix D.

Always wear eye protection in the laboratory!

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Chapter Two

Basic Tools and Operations of Analytical Chemistry

The Laboratory Notebook

- Your Critical Record
- Why must all data be recorded in ink when they are collected?
- Saving Time:
  - don't have to reorganize and rewrite data
  - more organized and prepared to carry out the analysis
- Immediate record:
  - detect possible errors in measurements and calculations
  - data will not be lost or transferred incorrectly
  - Legal records

Laboratory Notebook Documentation

- Hardcover Notebook (no loose leafs)
- Number pages consecutively.
- Record only in ink.
- Never tear out pages.
- Date each page, sign it, and have it signed and dated by someone else, stating
- “Read and Understood by”
- Record the name of the project, why it is being done and any literature references.
- Record all data on the day you obtain it.

Borosilicate glassware (Pyrex, Kimax) is normally used because it is thermally stable.

Table 2.1

Properties of Laboratory Materials

Material	Max. Working Temperature (°C)	Sensitivity to Thermal Shock	Chemical Inertness	Notes
Borosilicate glass	200	150°C change OK	Attacked somewhat by alkali solutions on heating	Trademarks: Pyrex (Corning Glass Works); Kimax (Owens-Illinois)
Soft glass		Poor	Attacked by alkali solutions	Boron-free. Trademark: Corning
Alkali-resistant glass		More sensitive than borosilicate		
Fused quartz	1050	Excellent	Resistant to most acids, halogens	Quartz crucibles used for fusions
High-silica glass	1000	Excellent	More resistant to alkalis than borosilicate	Similar to fused quartz Trademark: Vycor (Corning)
Porcelain	1100 (glazed) 1400 (unglazed)	Good	Excellent	
Platinum	ca. 1500		Resistant to most acids, molten salts. Attacks by aqua regia, fused nitrates, cyanides, chlorides at >1000°C. Alloys with gold, silver, and other metals	Usually alloyed with iridium or rhodium to increase hardness. Platinum crucibles for fusions and treatment with HF
Nickel and iron			Fused samples contaminated with the metal	Ni and Fe crucibles used for peroxide fusions
Stainless steel	400–500	Excellent	Not attacked by alkalis and acids except conc. HCl, dil. H_2SO_4, and boiling conc. HNO_3	
Polyethylene	115		Not attacked by alkali solutions or HF. Attacked by many organic solvents (acetone, ethanol OK)	Flexible plastic
Polystyrene	70		Not attacked by HF. Attacked by many organic solvents	Somewhat brittle
Teflon	250		Inert to most chemicals	Useful for storage of solutions and reagents for trace metal analysis.

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Modern balances are electronic. They still compare one mass against another since they are calibrated with a known mass. Common balances are sensitive to 0.1 mg.

Fig. 2.1. Electronic analytical balance.

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Electronic balances operate on the principle of emf compensation – the compensation current to bring the pan back to its original position is proportional to the sample weight.

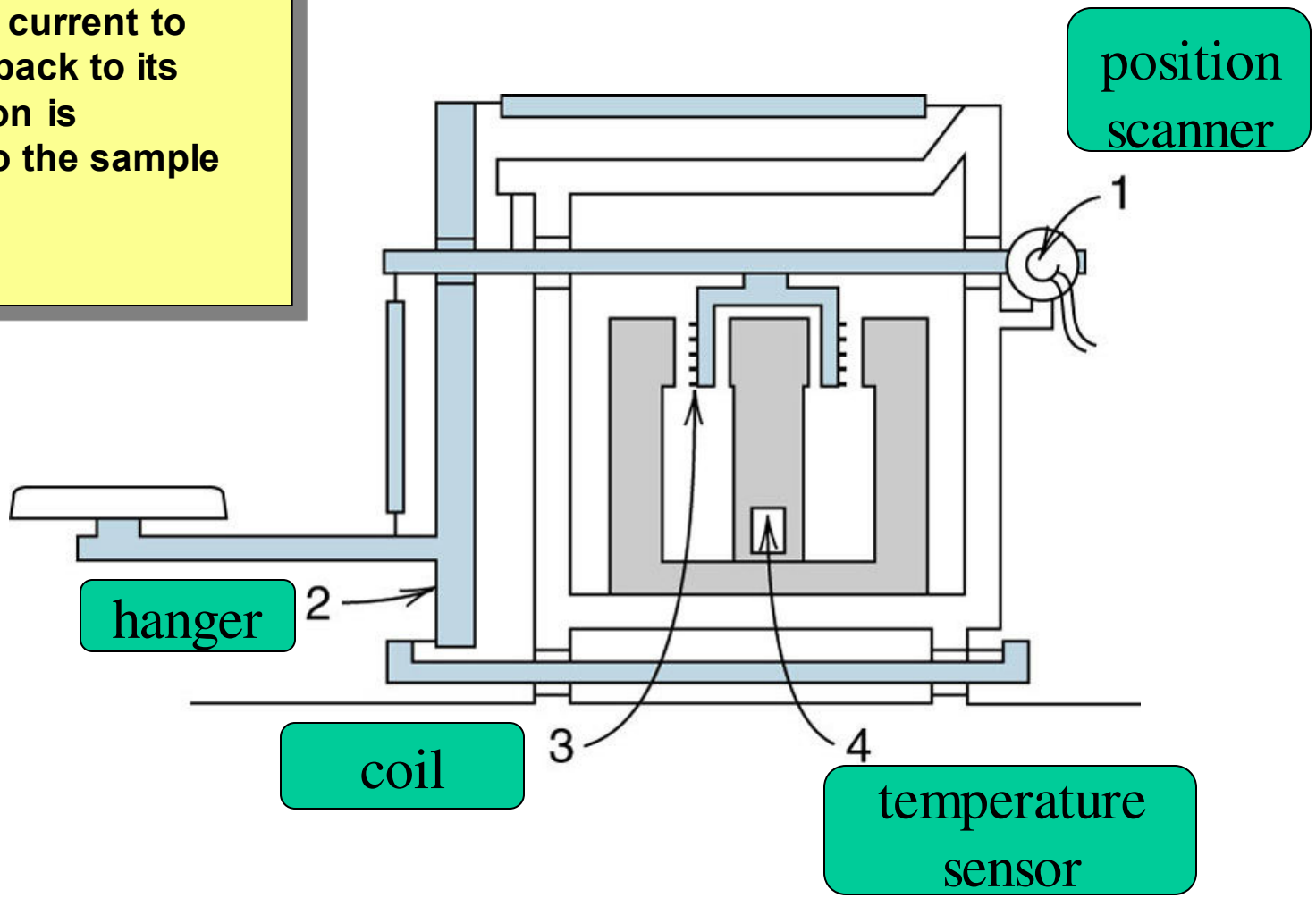

Fig. 2.2. Operating principle of electronic balance.

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Mechanical balances operate as first class levers.
$M_1L_1 = M_2L_2$

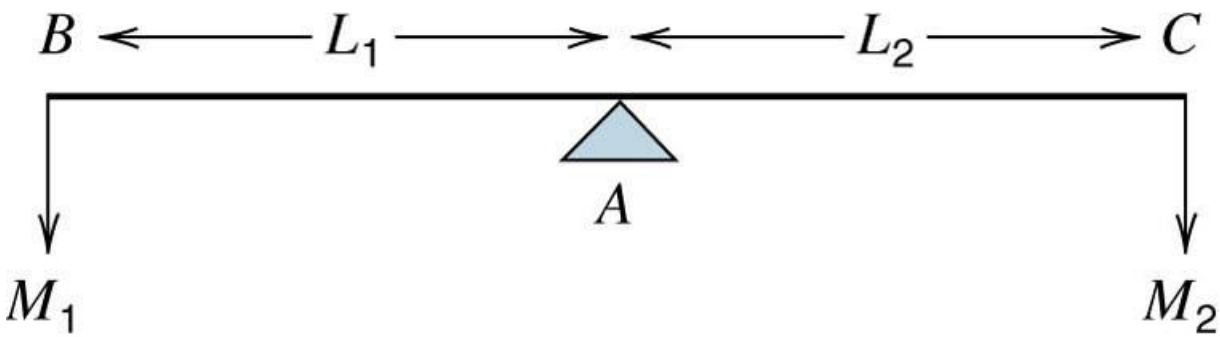

Fig. 2.3. Principle of analytical balance.

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The single pan balance operates by removing weights equal to the mass of the sample. Small residual imbalances are read optically from the deflection of the beam.

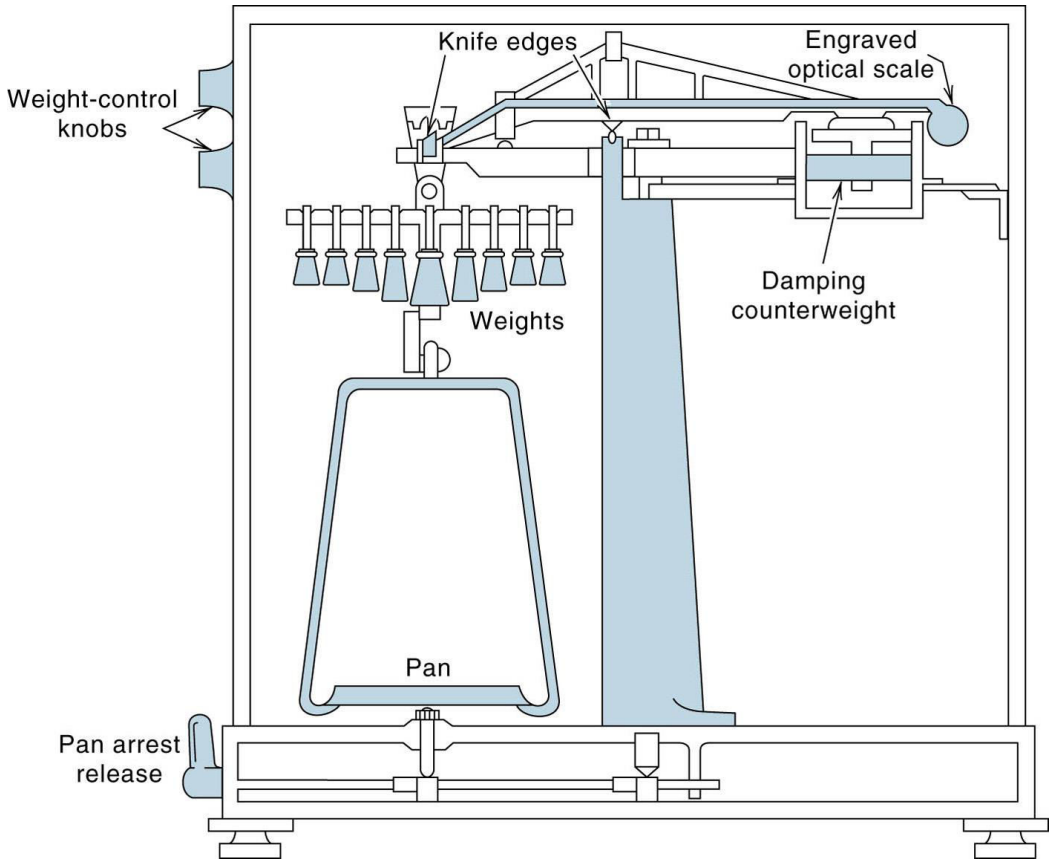

Fig. 2.4. Schematic diagram of a typical single-pan balance.

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The single-pan balance is as accurate as electronic balances, and almost as fast.

But it can't be interfaced to a computer to collect and process data.

And you have to read a scale instead of a digital number.

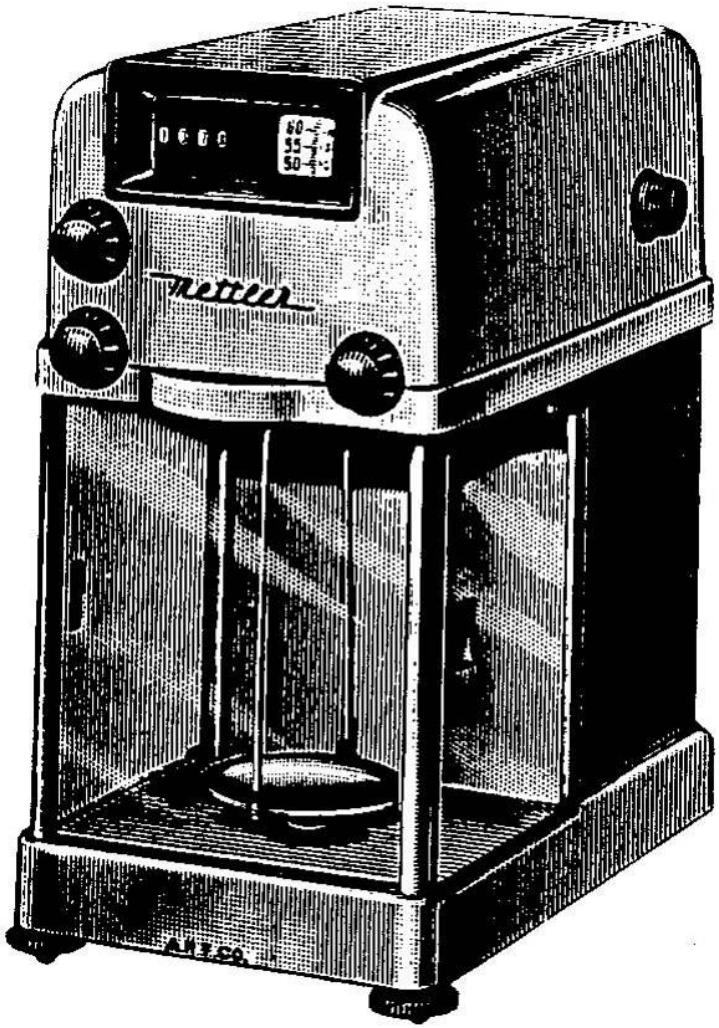

Fig. 2.5. Typical single-pan balance.

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Weight in a Vacuum
This is the Most Accurate

- Weights of objects in air can be corrected to the weight in vacuum by
- $W_{vac} = W_{air} + W_{air}((0.0012/D_o)-(0.0012/D_w))$
- W_{vac} = weight in vacuum, g
- W_{air} = weight in air, g
- D_o = density of object
- D_w = density of weights
- 0.0012 = density of air

Weighing bottles are used for drying samples. Hygroscopic samples are weighed by difference, keeping the bottle capped except when removing the sample.

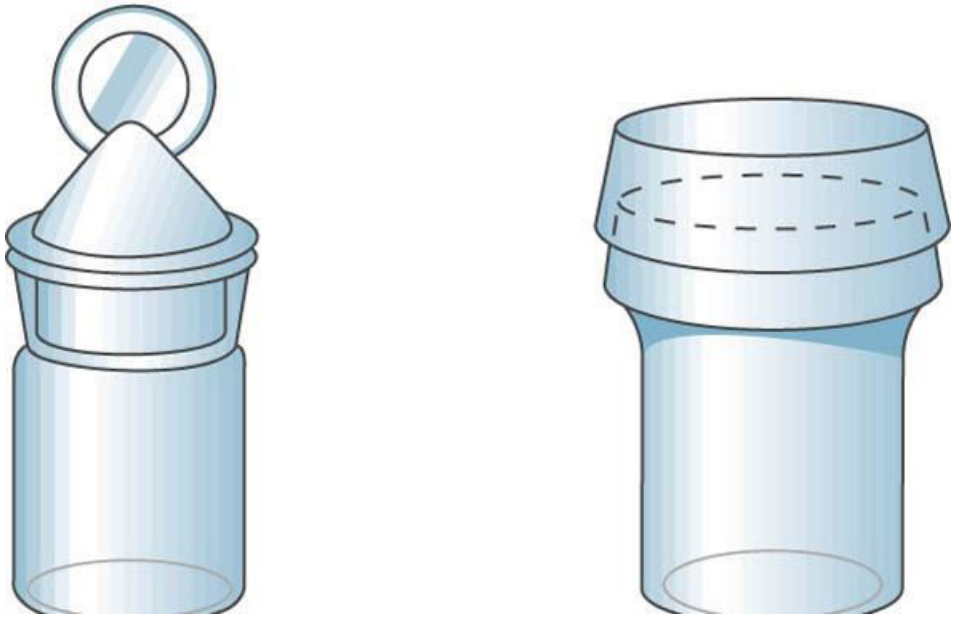

Fig. 2.6. Weighing bottles.

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A weighing dish or boat is used for direct weighing of samples.

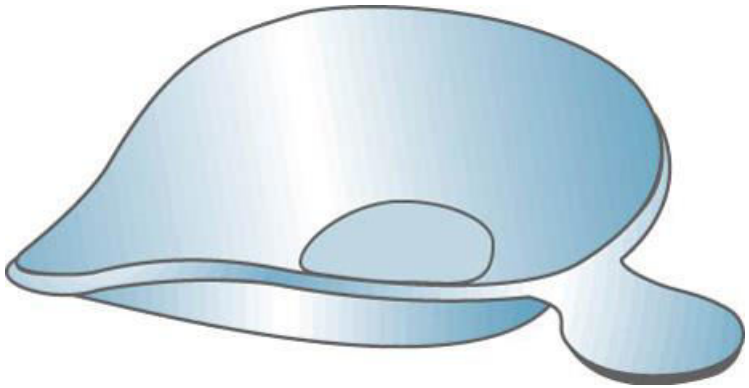

Fig. 2.7. Weighing dish.

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Volumetric flasks are calibrated to contain an accurate volume. See the inside back cover of the text for tolerances of Class A volumetric glassware.

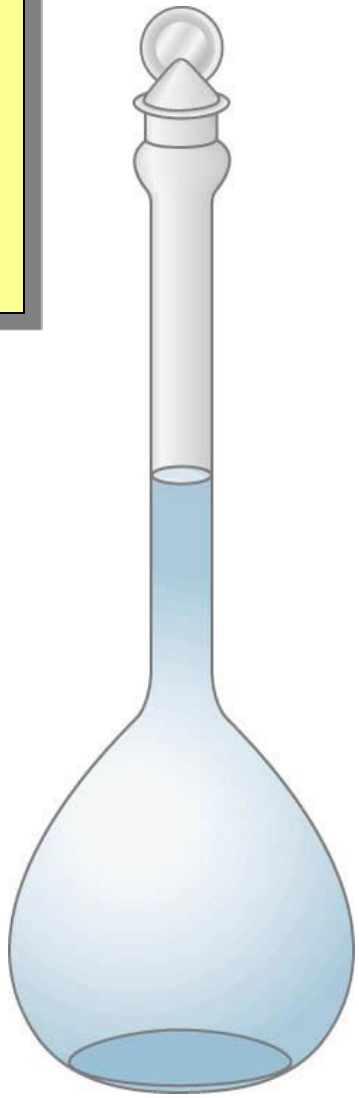

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Fig. 2.8. Volumetric flask.

Volumetric pipets accurately deliver a fixed volume.

A small volume remains in the tip.

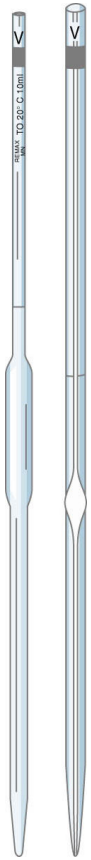

Fig. 2.9. Transfer or volumetric pipets.

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Measuring pipets are straight-bore pipets marked at different volumes.

They are less accurate than volumetric pipets.

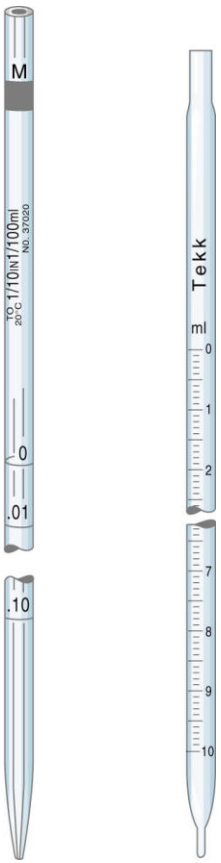

Fig. 2.10. Measuring pipets.

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Syringe pipets precisely deliver microliter volumes.

They are commonly used to introduce samples into a gas chromatograph.

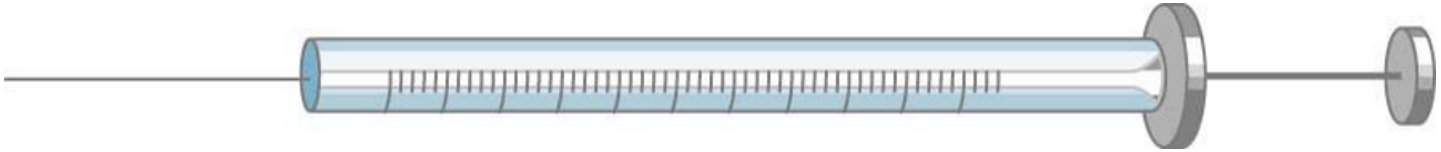

Fig. 2.11. Hamilton microliter syringe.

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These syringe pipets can reproducibly deliver a selected volume.

They come in fixed and variable volumes. The plastic tips are disposable.

Fig. 2.12 Single-channel and multichannel digital displacement pipets and microwell plates.

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The DIN error gives the range for which we are 95% confident the delivery will fall.

Table 2.2

DIN 12650 Error Limits for Single Channel Air Displacement Pipets[a]

Nominal Volume (m L)	Maximum Error (m L)	Relative Error (%)
1	±0.15	±15.0
2	±0.20	±10.0
5	±0.30	±6.0
10	±0.30	±3.0
20	±0.40	±2.0
50	±0.80	±1.6
100	±1.50	±1.5
200	±2.00	±1.0
500	±5.00	±1.0
1000	±10.00	±1.0
2000	±20.00	±1.0
5000	±50.00	±1.0
10000	±100.00	±1.0

[a]These limits apply to manufacturers with a controlled environment. If the tests are performed by a user in a normal laboratory environment, the limits in the table may be doubled.

Courtesy of Thermo Labsystems Oy, Finland.

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These accuracies and precisions are typical for single channel pipets.

Table 2.3

Accuracy and Precision for Single Channel Digital Finnpipettes

Range (m L)	Increment (m L)	Volume (m L)	Accuracy (m L)	Accuracy (%)	Precision[a] s.d. (m L)	Precision[a] CV (%)
0.2–2	0.01	2	±0.050	±2.5	0.040	2.0
		0.2	±0.024	±12.0	0.020	10.0
0.5–10	0.1	10	±0.100	±1.0	0.050	0.5
		1	±0.025	±2.5	0.020	2.0
0.5–10	0.1	10	±0.100	±1.0	0.080	0.8
		1	±0.035	±3.5	0.030	3.0
2–20	0.1	20	±0.200	±1.0	0.080	0.4
		2	±0.060	±3.0	0.030	1.5
5–40	0.5	40	±0.240	±0.6	0.120	0.3
		5	±0.100	±2.0	0.100	2.0
10–100	1.0	100	±0.80	±0.8	0.20	0.2
		10	±0.30	±3.0	0.10	1.0
20–200	1.0	200	±1.20	±0.6	0.40	0.2
		20	±0.36	±1.8	0.14	0.7
200–1000	5.0	1000	±6.00	±0.6	2.00	0.2
		200	±1.80	±0.9	0.60	0.3
100–1000	5.0	1000	±6.00	±0.6	2.00	0.2
		100	±1.00	±1.0	0.60	0.6

[a]s.d. = standard deviation, CV = coefficient of variation.
Courtesy of Thermo Labsystems Oy, Finland.

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A 50-mL buret is marked in 0.1 mL increments.

You interpolate to 0.01 mL, good to about ±0.02 mL.

Two readings are taken for every volume measurement.

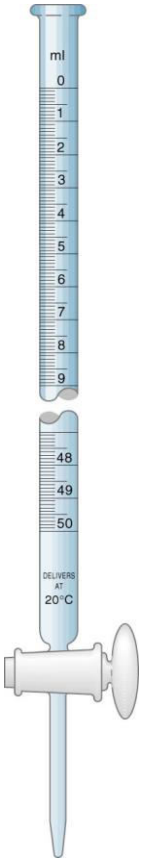

Fig. 2.13. Typical buret.

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Position the black field just below the meniscus.

Avoid parallax error by reading at eye level.

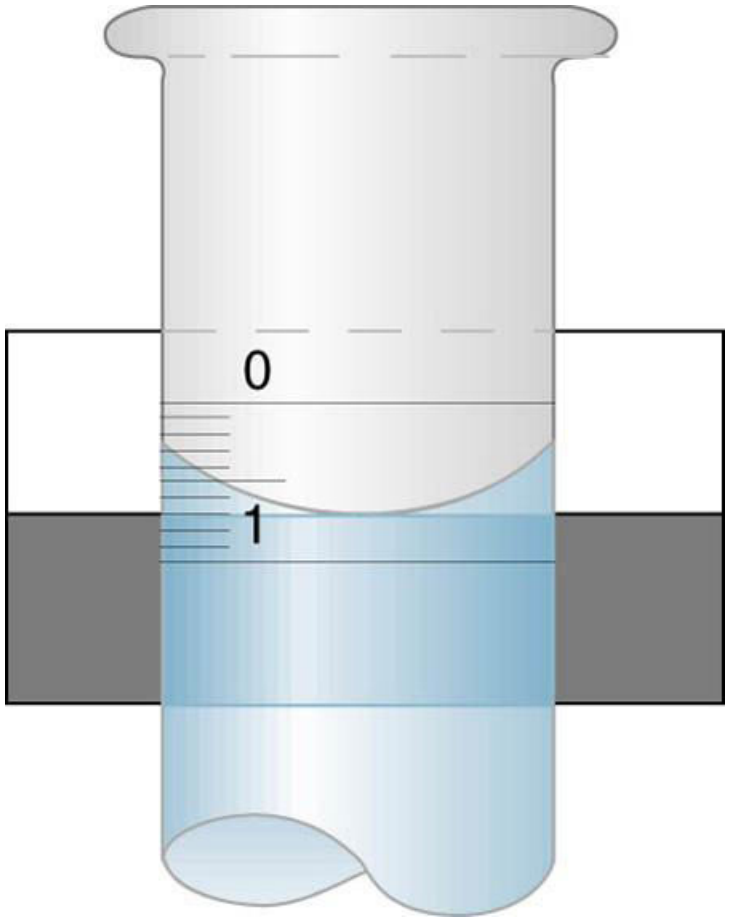

Fig. 2.14. Meniscus illuminator.

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Place the flask on a white background.

Place the buret tip in the neck of the flask while your swirl.

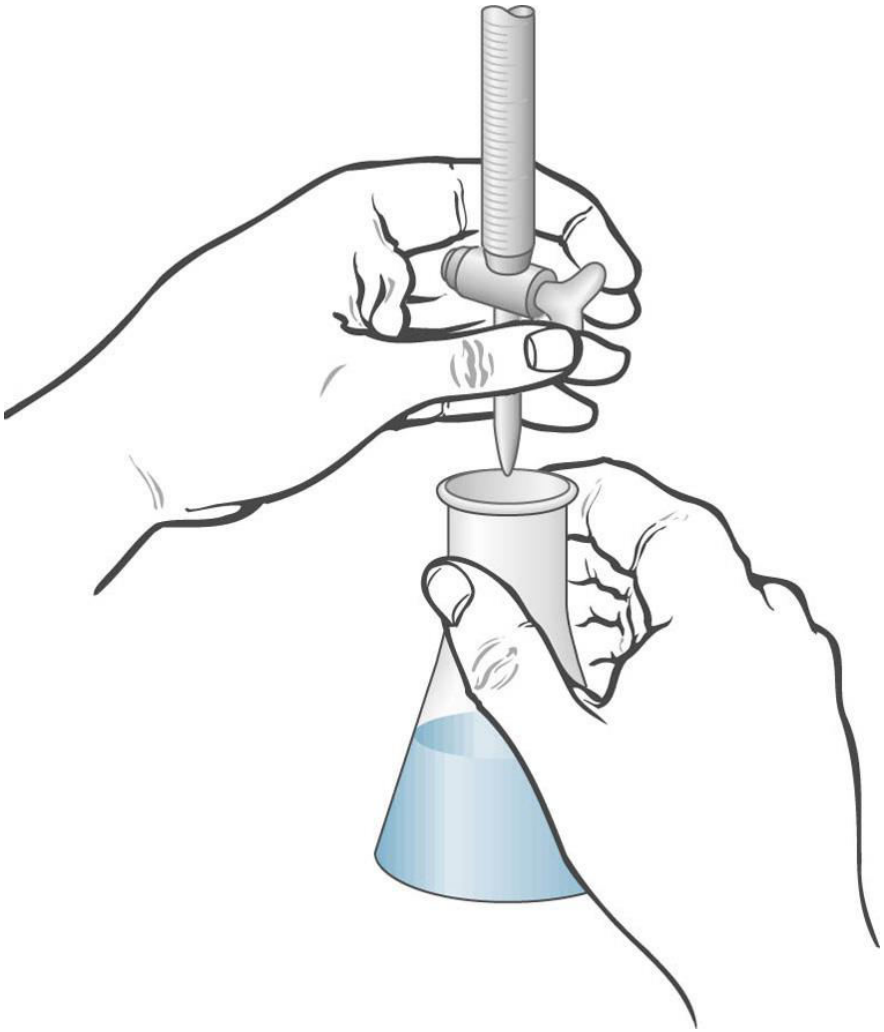

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Fig. 2.15. Proper technique for titration.

These are calculated volumes for 1 gram of water in air at atmospheric pressure, corrected for buoyancy with stainless steel weights.

You can substitute a specific weight in column B to obtain the corresponding volume (CD spreadsheet).

Table 2.4

Glassware Calibration

	A	B	C	D	E	F	G	H
1	**Table 2.4 Glassware Calibration**							
2	Weight in vacuum assuming stainless steel weights, density 7.8 g/mL.							
3	Glass expansion for borosilicate glass, 0.000025 mL/mL/ °C.							
4								
5	Save this spreadsheet contained in your CD, Chapter 2, to your desktop, and use it to calculate							
6	calibrated volumes of glassware. Substitute into the appropriate Cell B, at temperature T, the							
7	weight of water in air, obtained from the glassware at the temperature of the measurement (Cell A).							
8	The calibration volume at the temperature, T (Cell D), and at 20°C (Cell F), is calculated.							
9	Round the calculated values to the appropriate number of significant figures, usually							
10	four or five.							
11								
12	**T, °C**	**Wt. H_2O**	**Wt. in**	**Vol. at T,**	**Glass expansion,**	**Vol. at 20°,**	**Density,**	
13		**in air, g**	**vacuum, g**	**mL**	**at 20°C, mL**	**mL**	**g/mL**	
14	10	1.0000	**1.0010**	**1.0013**	**-0.000250**	**1.0016**	0.9997026	
15	11	1.0000	1.0010	1.0014	-0.000225	1.0017	0.9996081	
16	12	1.0000	1.0010	1.0015	-0.000200	1.0017	0.9995004	
17	13	1.0000	1.0010	1.0017	-0.000175	1.0018	0.9993801	
18	14	1.0000	1.0010	1.0018	-0.000150	1.0020	0.9992474	
19	15	1.0000	1.0010	1.0019	-0.000125	1.0021	0.9991026	
20	16	1.0000	1.0010	1.0021	-0.000100	1.0022	0.9989460	
21	17	1.0000	1.0010	1.0023	-0.000075	1.0023	0.9987779	
22	18	1.0000	1.0010	1.0025	-0.000050	1.0025	0.9985896	
23	19	1.0000	1.0010	1.0026	-0.000025	1.0027	0.9984082	
24	20	1.0000	1.0010	1.0028	0.000000	1.0028	0.9982071	
25	21	1.0000	1.0010	1.0031	0.000025	1.0030	0.9979955	
26	22	1.0000	1.0010	1.0033	0.000050	1.0032	0.9977735	
27	23	1.0000	1.0010	1.0035	0.000075	1.0034	0.9975415	
28	24	1.0000	1.0010	1.0038	0.000100	1.0037	0.9972995	
29	25	1.0000	1.0010	1.0040	0.000125	1.0039	0.9970479	
30	26	1.0000	1.0010	1.0043	0.000150	1.0041	0.9967867	
31	27	1.0000	1.0010	1.0045	0.000175	1.0044	0.9965162	
32	28	1.0000	1.0010	1.0048	0.000200	1.0046	0.9962365	
33	29	1.0000	1.0010	1.0051	0.000225	1.0049	0.9959478	
34	30	1.0000	1.0010	1.0054	0.000250	1.0052	0.9956502	
35								
36	Formulas are entered into the boldface cells above as indicated below. They are							
37	copied down for all temperatures. See Chapter 3 for setting up a spreadsheet.							
38	**Cell C14:** $W_{vac} = W_{air} + W_{air}(0.0012/D_o - 0.0012/D_w) = W_{air}(0.0012/1.0 + 0.0012/7.8)$							
39			= B14+B14*(0.0012/1.0-0.0012/7.8)			Copy down		
40	**Cell D14:** V_T (mL)= $W_{vac,T}$(g)/D_T(g/mL)							
41			= C14/G14			Copy down		
42	**Cell E14:** Glass expans. = (T - 20) (deg) x 0.000025 (mL/mL/deg) x W_{air} (g)							
43			= (A14-20)*0.000025*B14			Copy down		
44	**Cell F14:** $V_{20o} = V_T$ - $Glass_{exp}$ =			D14-E14		Copy down		

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Temperature Dependence of Molarity

- The Molarity of a solution is temperature dependent, therefore when preparing or standardizing solutions you have to record the temperature of solutions.
- Conversion Formula:
- $M_{new\ temp} = M_{old\ temp} x (D_{new\ temp}/D_{old\ temp})$
- See Exam 2.4 in Text

Calibration of Glassware

- The Ultimate Accuracy

Techniques for Calibrating Glassware
Volumetric Flask Calibration

1. Weigh the clean, dry flask and stopper.
2. Fill to mark with distilled water.
    1. No droplets on the neck, blot dry
3. Flask and water should be equilibrated to room temperature.
4. Weigh the filled flask, and record the temperature of the water to 0.1^{o}C.
5. The increase in weight represents the weight in air of the water contained by the flask.
6. Use speadsheet on CD or see table 2.4 page 39

Techniques for Calibrating Glassware
Pipet Calibration

1. Weigh a clean, dry conical flask with a rubber stopper or a weighing bottle with a glass stopper or cap.
2. Fill pipet with distilled water and deliver the water into the flask or bottle, stopper container to avoid evaporation loss.

   Record temperature to 0.1^{o}C
3. Reweigh the container to obtain the weight in air of the water delivered by the pipet.
4. Use either Equation 2.1 page 29 or spreadsheet see table 2.4 page 39

Techniques for Calibration of Glassware
Buret Calibration

1. Weigh a clean, dry conical flask.
2. Take the volume at 20% full-volume increments by filling the buret each time and then delivering the nominal volume into a dry flask.
3. Alternative: make successive deliveries into same flask, filling the buret only once.
4. The delivered volume does not have to be exact, but close to the nominal volume, you can make fairly fast deliveries, but wait 10 to 20s for film drainage.
5. Prepare a plot of volume correction versus nominal volume and draw straight lines between each point. Interpolation is made at intermediate volumes from the lines.

Use a desiccator to cool a dried or ignited sample.

Cool a red hot vessel before placing in the desiccator.

Do not stopper a hot weighing bottlle (creates a partial vacuum on cooling).

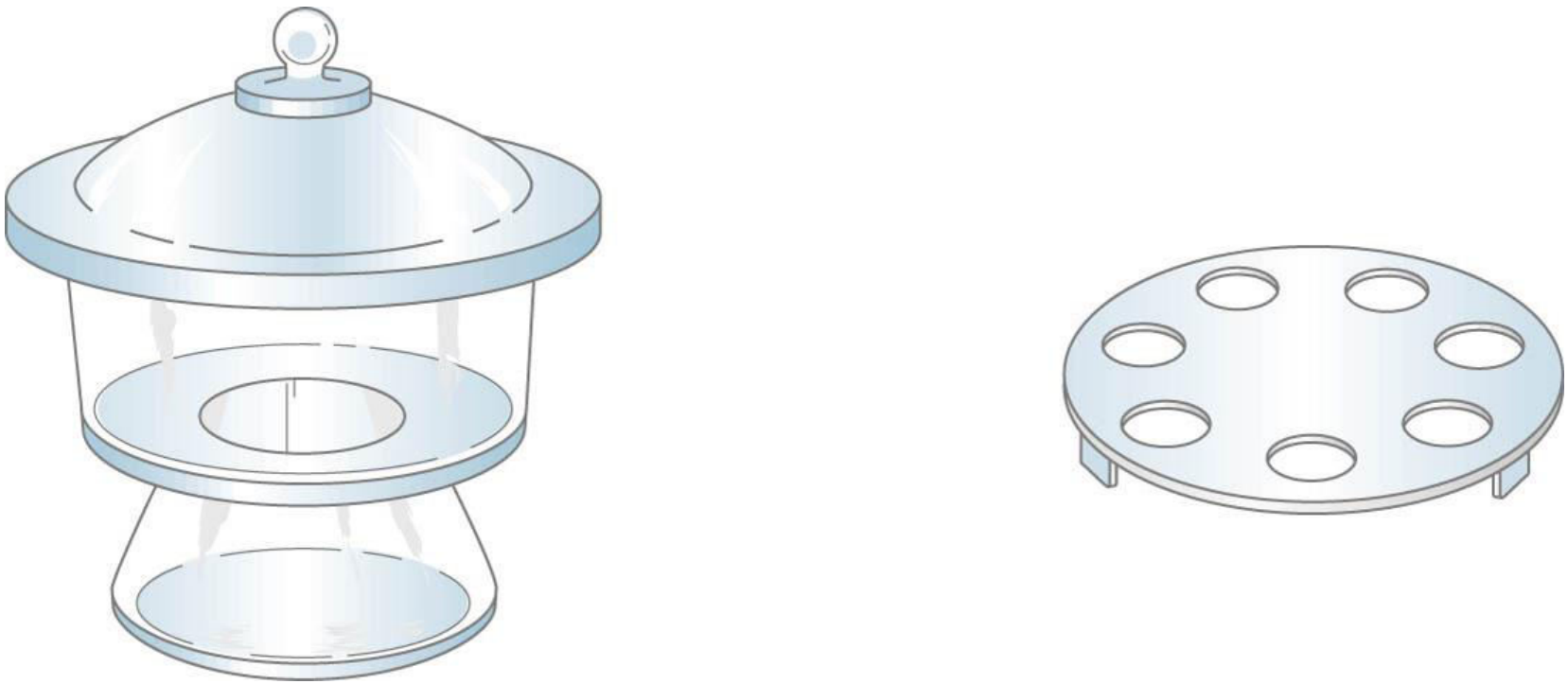

Fig. 2.16. Desiccator and desiccator plate.

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$CaCl_2$ is commonly used.

It needs periodic replacement when wet or caked.

Table 2.5

Some Common Drying Agents

Agent	Capacity	Deliquescent[a]	Trade Name
$CaCl_2$ (anhydrous)	High	Yes	
$CaSO_4$	Moderate	No	Drierite (W. A. Hammond Drierite Co.)
CaO	Moderate	No	
$MgClO_4$ (anhydrous)	High	Yes	Anhydrone (J. T. Baker Chemical Co.); Dehydrite (Arthur H. Thomas Co.)
Silica gel	Low	No	
Al_2O_3	Low	No	
P_2O_5	Low	Yes	

[a] Becomes liquid by absorbing moisture.

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Used to ignite samples at high temperatures, e.g., to dry ash organic matter.

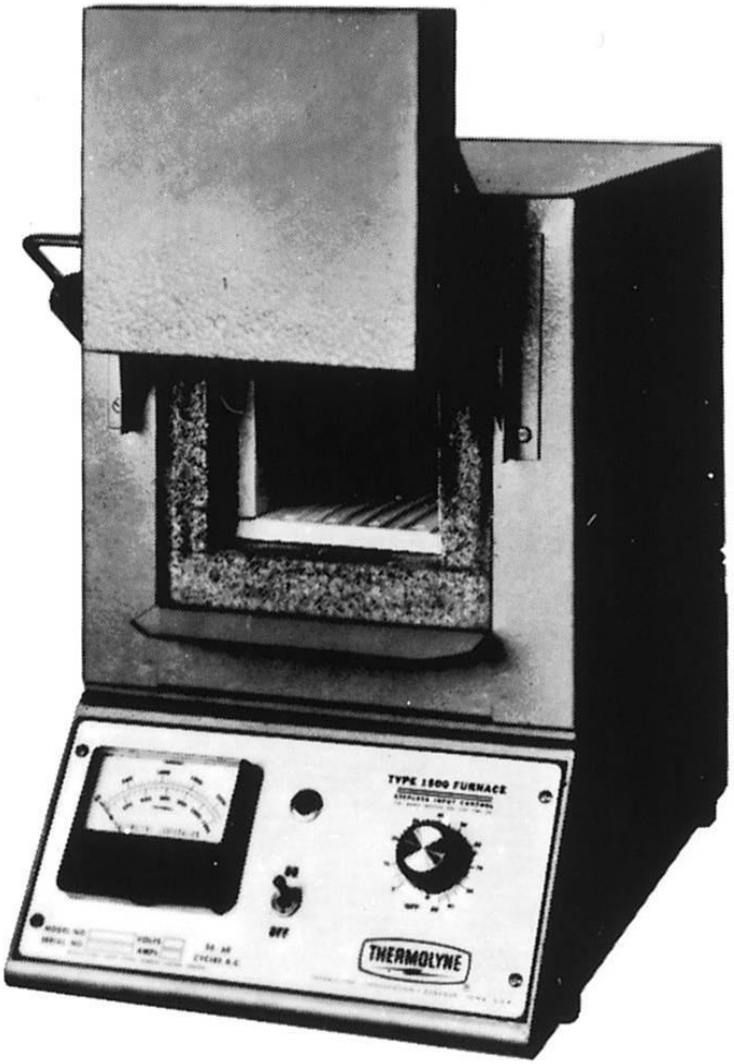

Fig. 2.17. Muffle furnace.

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Used to dry samples before weighing.

Usually 110° C used.

Fig. 2.18. Drying oven.

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A fume hood is "dirty" since it draws in laboratory air.

A laminar-flow hood filters air (0.3 μm HEPA filter) and flows it out into the room.

Use it as a workstation for trace analysis.

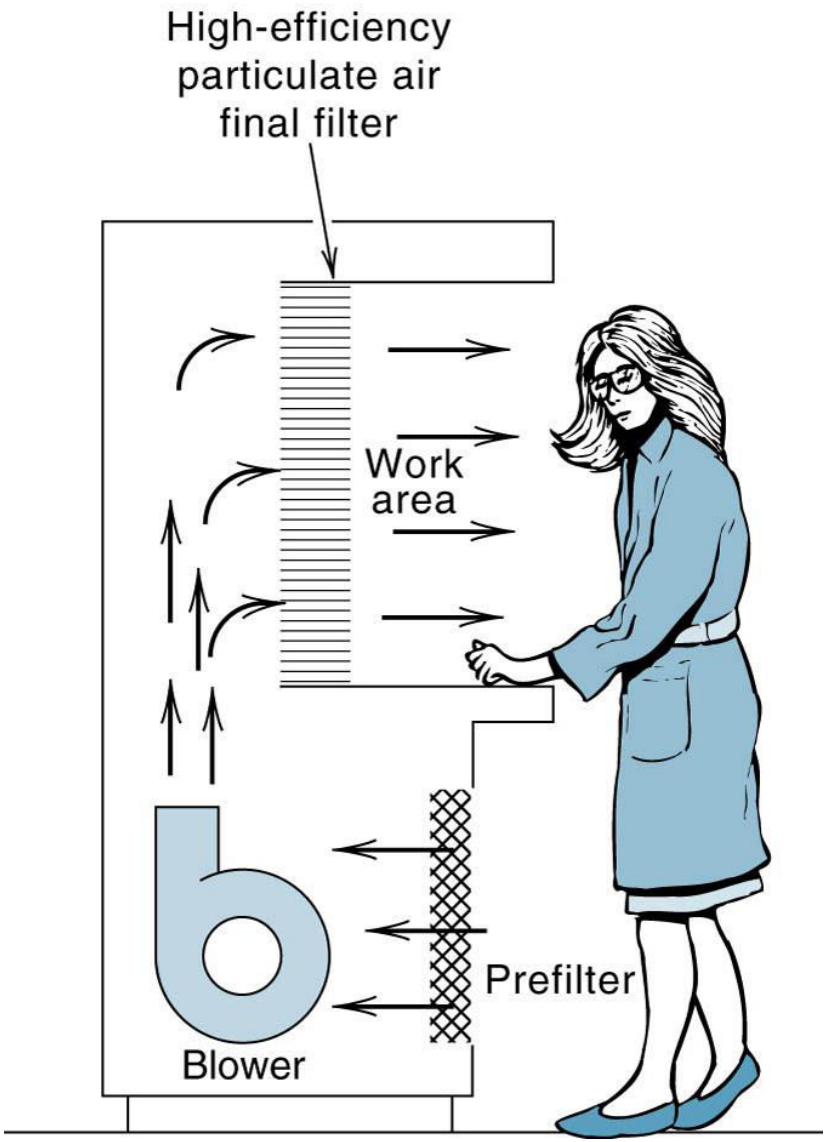

Fig. 2.19. Laminar-flow workstation.

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Use these for quantitative transfer of precipitates and solutions, and for washing precipitates.

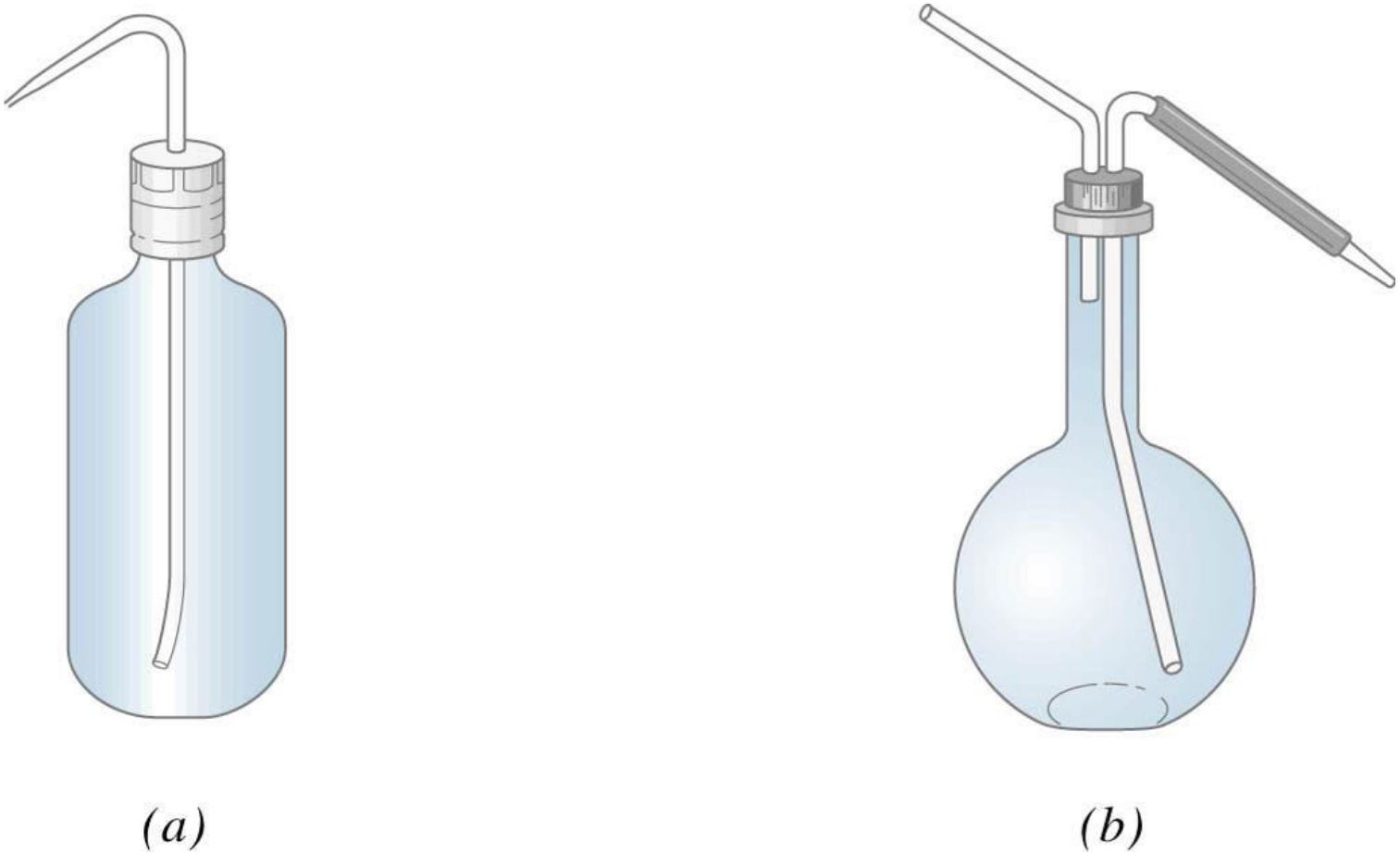

Fig. 2.20. Wash botltles: (a) polyethylene, squeeze type; (b) glass, blow type.

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Use for filtering non-gelatinous precipitates.

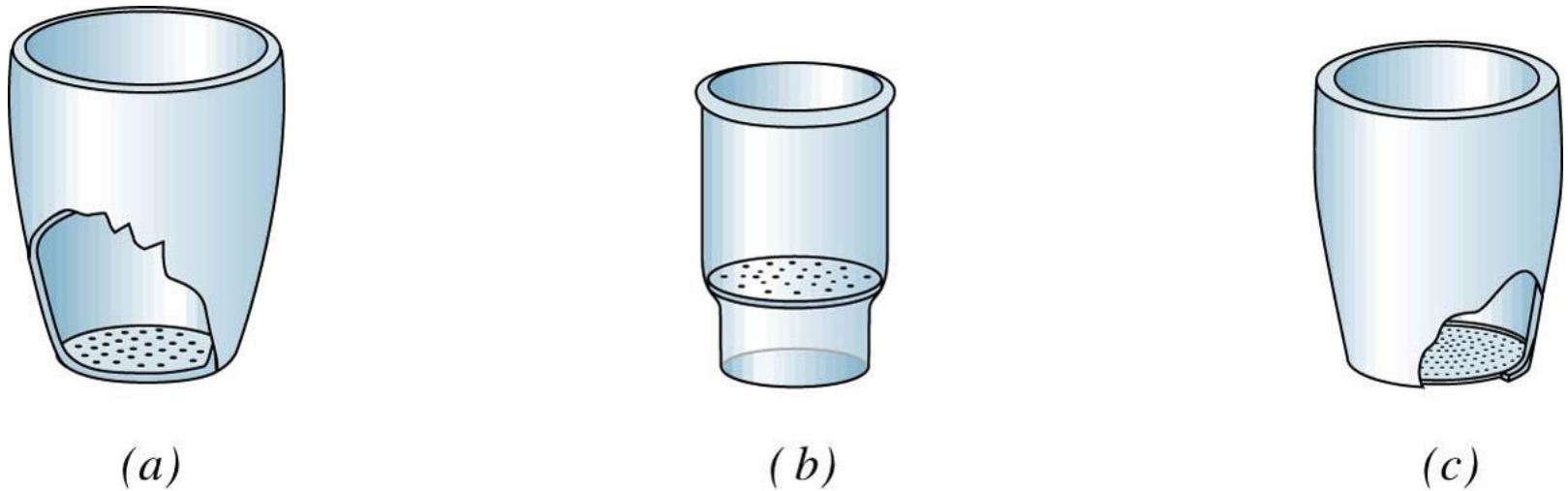

Fig. 2.21. Filtering crucibles: (a) Gooch crucible; (b) sintered-glass crucible; (c) porcelain filter crucible.

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Mount the filtering crucible in a crucible holder and connect the filtering flask to a water aspirator.

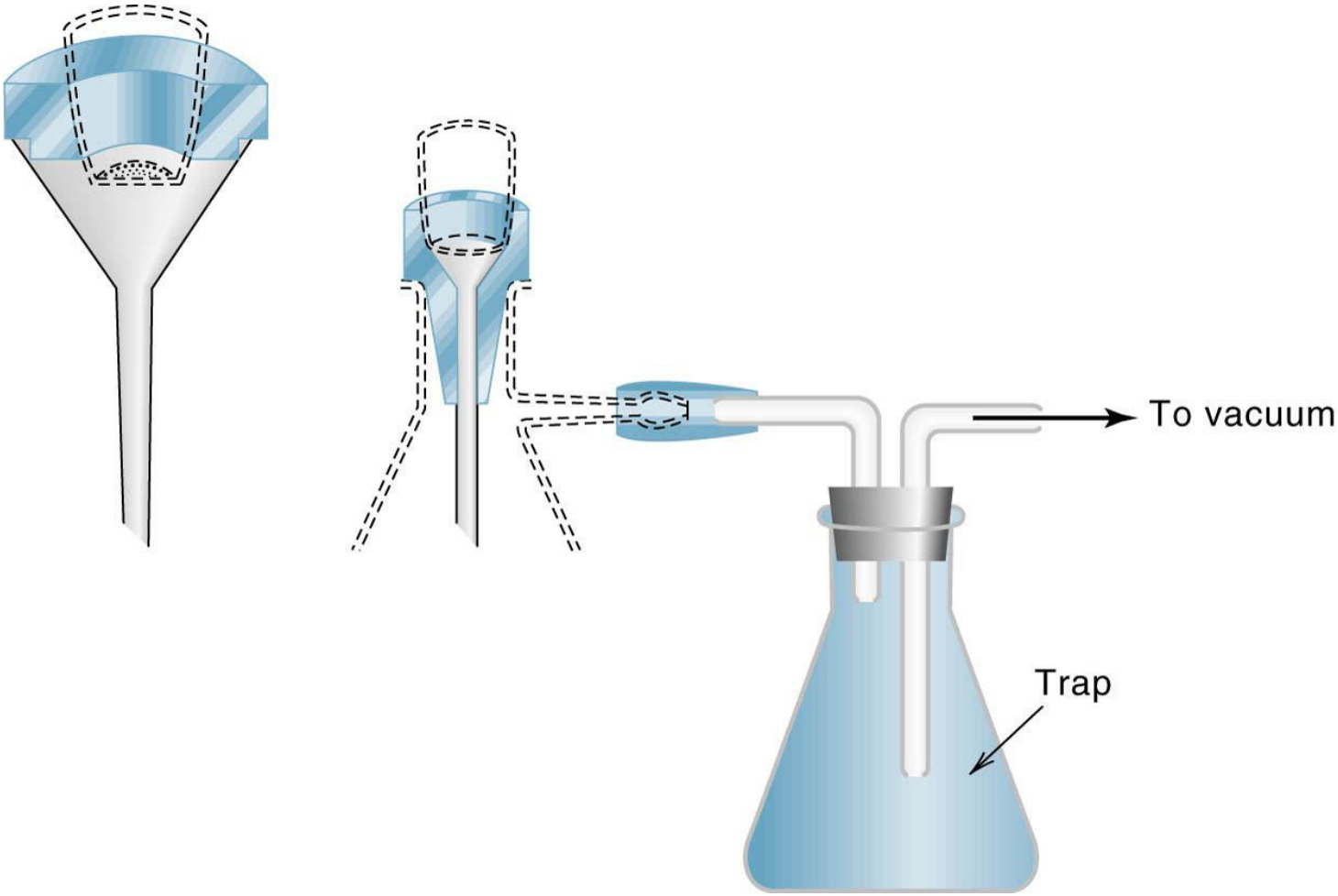

Fig. 2.22. Crucible holders.

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These are ashless filter papers.

They are ignited away after collection of the precipitate.

Use for gelatinous precipitates.

Table 2.6

Types of Filter Papers

Precipitate	Whatman	Schliecher and Schuell
Very fine (e.g., $BaSO_4$)	No. 42 (2.5 m m)	No. 589/2 or 5, Blue or Red Band (2–4 m m)
Small or medium (e.g., AgCl)	No. 40 (8 m m)	No. 589/2, White Band (4–12 m m)
Gelatinous or large crystals (e.g., $Fe_2O_3 \cdot xH_2O$)	No. 41 (20–25 m m)	No. 589/1, Black Band (>12–25 m m)

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This provides a good seal and prevents air bubbles from being drawn in.

Suction from the weight of the water in the stem increases the filtration rate.

Let the precipitate settle in the beaker before beginning filtration.

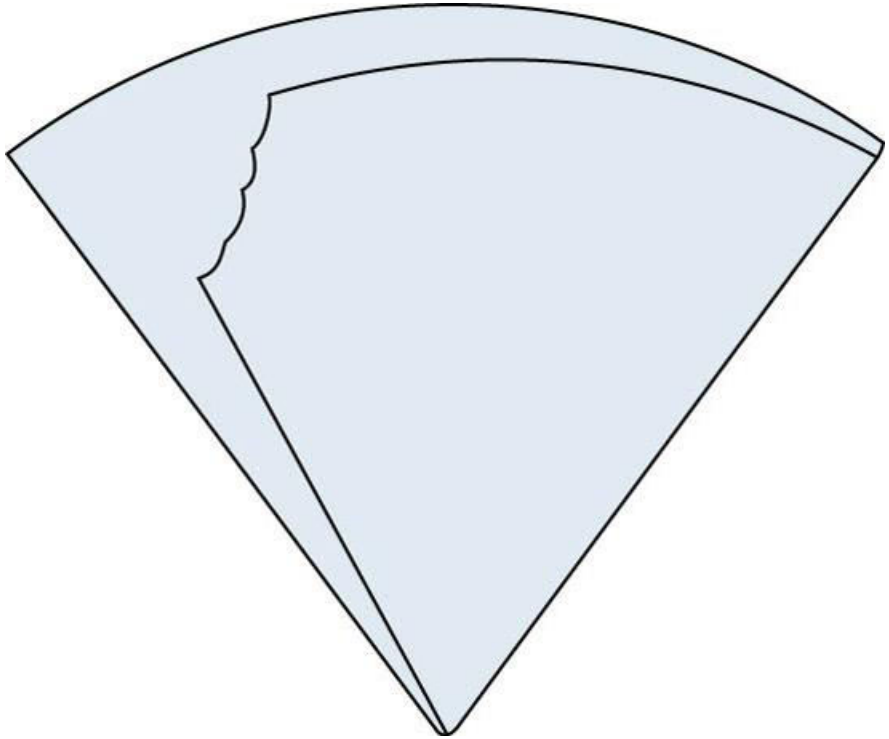

Fig. 2.23. Properly folded filter paper.

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Decant the solution by pouring down the stirring rod.

After decantiing the mother liquor, add wash water to the precipitate and decant again, repeating 2-3 times.

Then wash the precipitate into the filter.

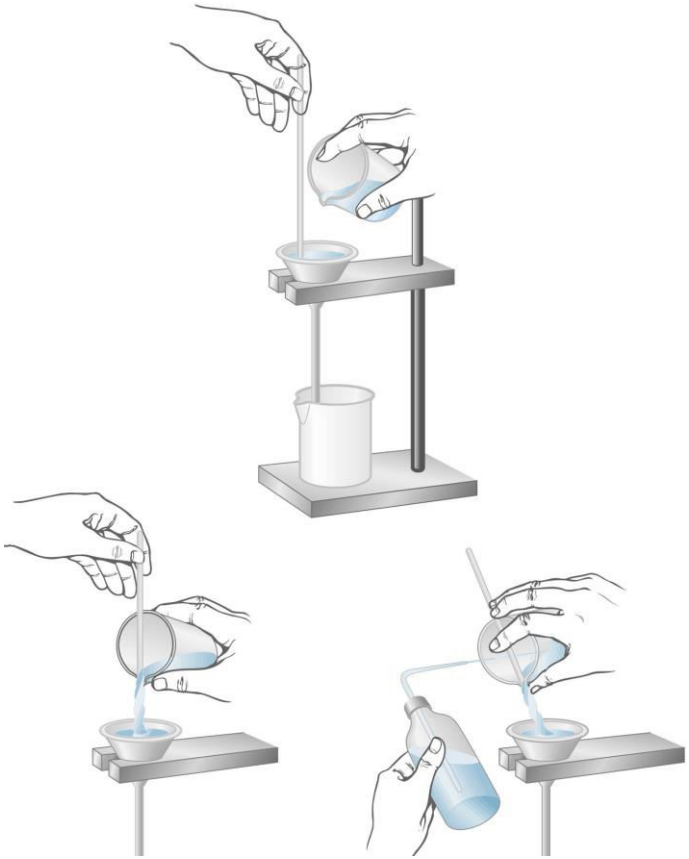

Fig. 2.24. Proper technique for transfer of a precipitate.

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Use this to scrub the walls of the beaker and collect all the precipitate (by washing).

Fig. 2.25. Rubber policeman.

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Heat or ignite the crucible to a constant weight (to 0.3-0.4 mg) before adding the filtered precipitate.

Fold the filter paper over the precipitate.

Drive off moisture at low heat. Then gradually increase heat till the paper begins to char.

After the paper is gone, ignite the precipitate.

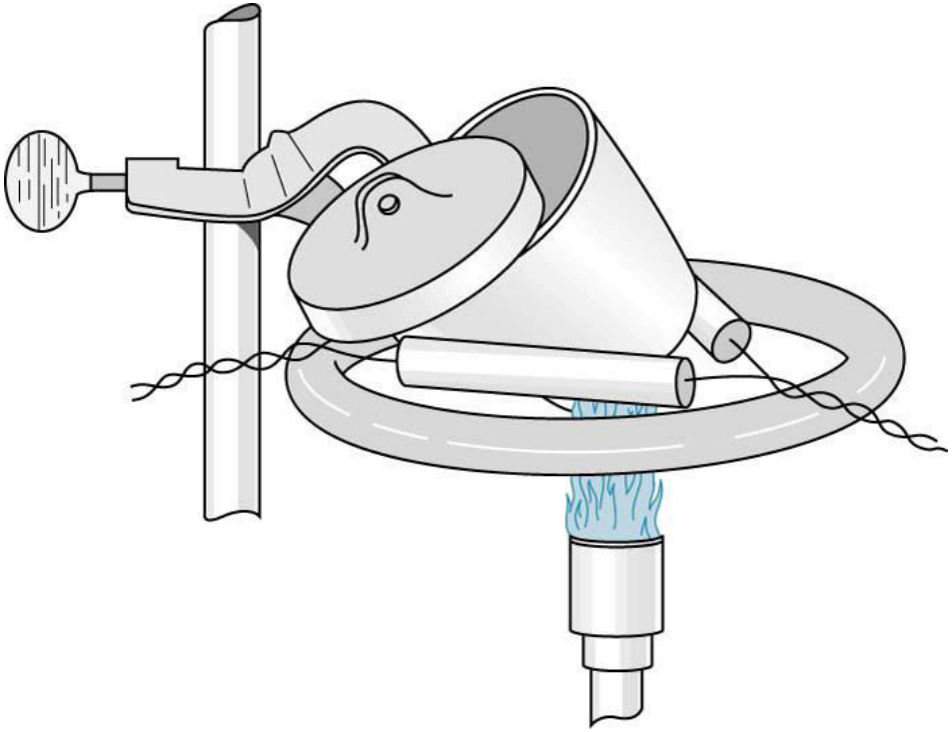

Fig. 2.26. Crucible and cover supported on a wire triangle for charring off paper.

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Obtaining a representative sample is the first step of an analysis.

The *gross sample* is several small portions of the sample.

This is reduced to provide a *laboratory sample*.

An aliquot of this sample is taken for the *analysis sample*.

Sampling

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Microwave ovens provide rapid drying.

Acid decomposition times are reduced from hours to minutes.

Lower blank levels are achieved with reduced amounts of reagents.

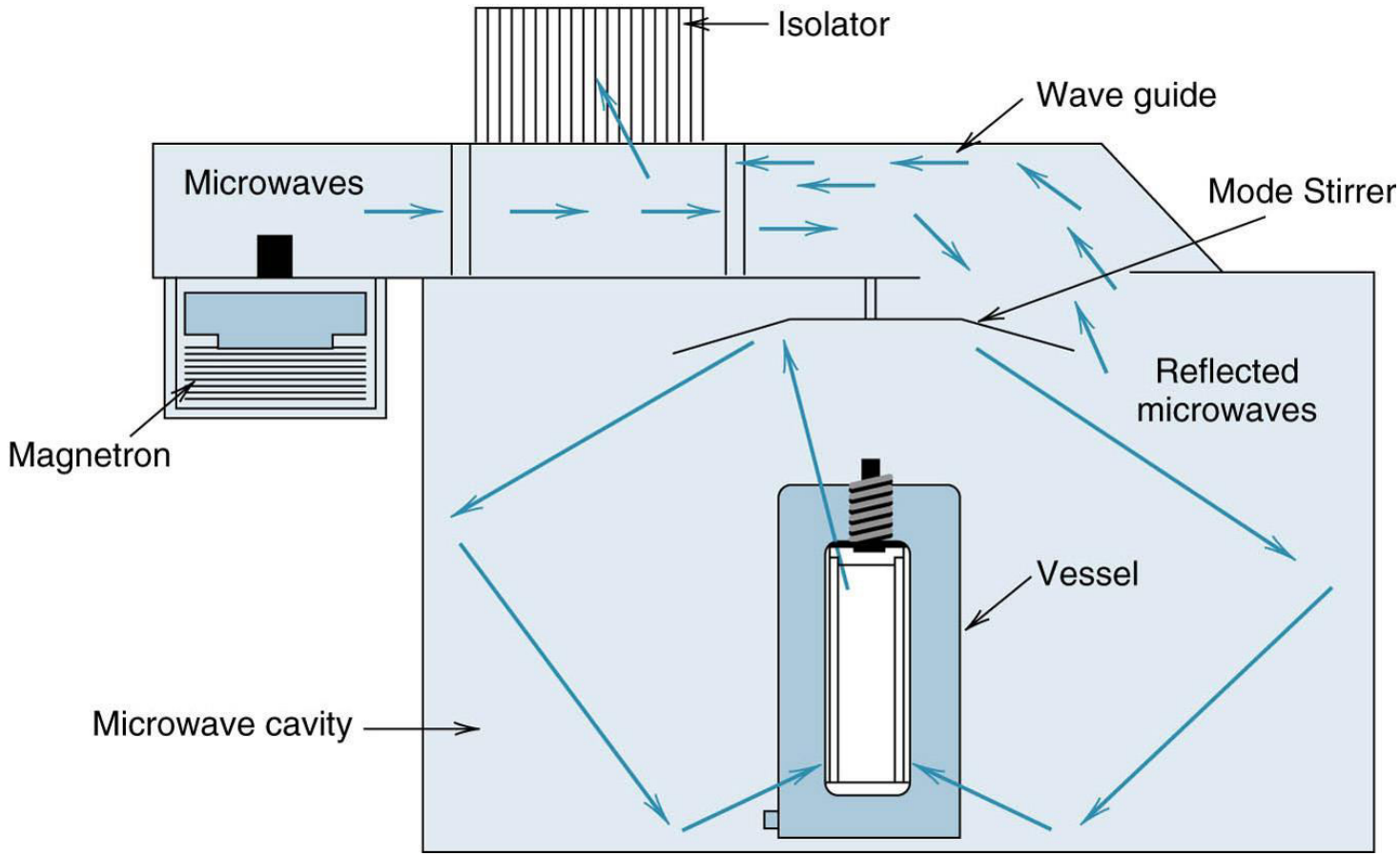

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Fig. 2.27. Schematic of a microwave system.

Use these for acid digestions.

They are tilted while heating to avoid losses from "bumping".

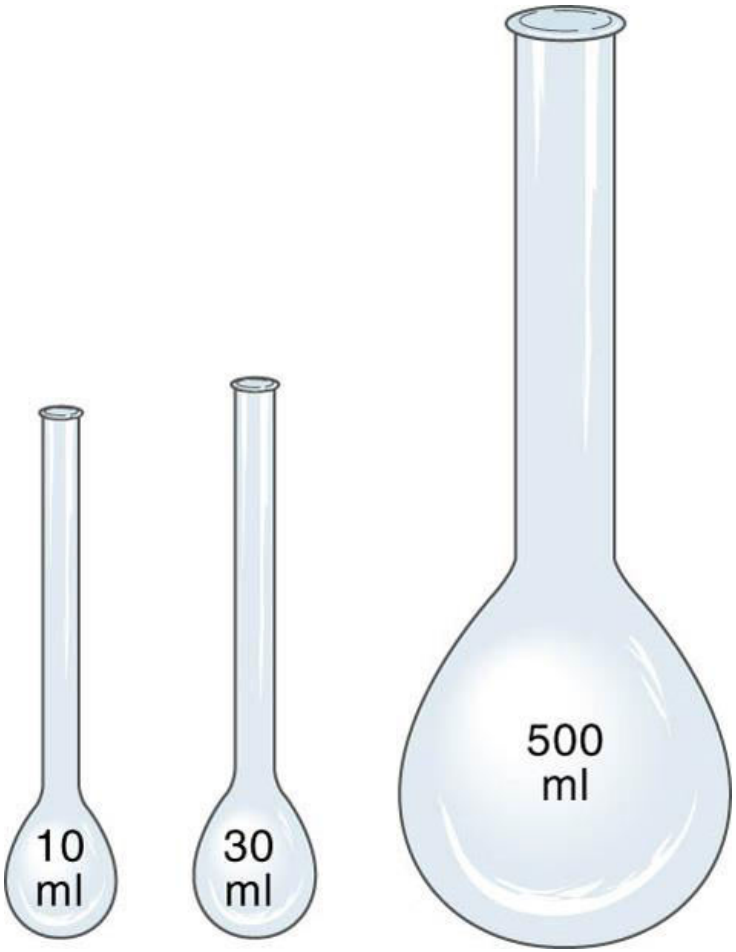

Fig. 2.28. Kjeldahl flasks.

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Laboratory safety is a must!

Learn the rules.

See Appendix D.

Always wear eye protection in the laboratory!

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Section 03

Data Handling and Spreadsheets in Analytical Chemistry

Why do we need statistics in analytical chemistry?

- Scientists need a standard format to communicate significance of experimental numerical data.
- Objective mathematical data analysis methods needed to get the most information from finite data sets
- To provide a basis for optimal experimental design.

What Does Statistics Involve?

- **Defining properties of probability distributions for infinite populations**
- **Application of these properties to treatment of finite (real-world) data sets**
- **Probabilistic approaches to:**
  - **Reporting data**
  - **Data treatment**
  - **Finite sampling**
  - **Experimental design**

Some Useful Statistics Terms

- Mean – Average of a set of values
- Median – Mid-point of a set of values.
- Population – A collection of an infinite munber of measurements. N → infinity
- Sample – A finite set of measurements which represent the population.
- True value (true mean)- (μ), mean value for the population.
- Observed Mean –(x), mean value of the sample set

Accuracy and Precision: Is There a Difference?

- Accuracy: degree of agreement between measured value and the true value.
- Absolute true value is seldom known
- Realistic Definition: degree of agreement between measured value and accepted true value.

Precision

- Precision: degree of agreement between replicate measurements of same quantity.
- Repeatability of a result
- Standard Deviation
- Coefficient of Variation
- Range of Data
- Confidence Interval about Mean Value

You can't have accuracy without good precision.

But a precise result can have a determinate or systematic error.

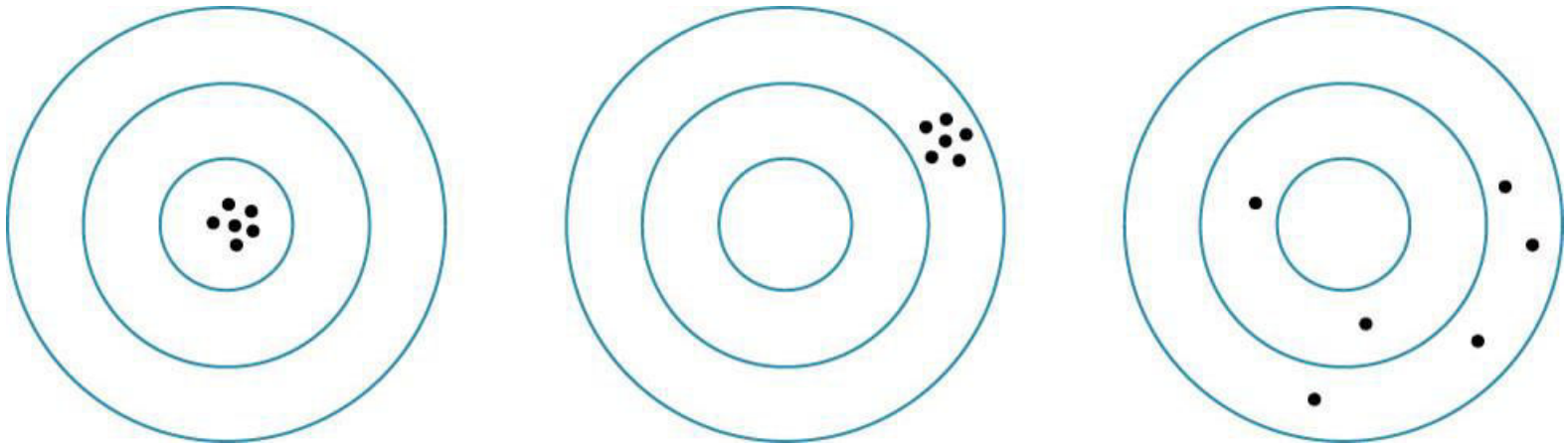

Fig. 3.1. Accuracy and precision.

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Determinate Errors
Are They Systematic?

- Determinate Errors:
- Determinable and either avoided or corrected.
- Constant errors
- Uncalibrated weights
- Burets- volume readings can be corrected
- Concentration variation with temperature

Indeterminate Errors
Are They Random?

- Indeterminate Errors-
  - accidental or random errors
- Represent the experimental uncertainty that occurs in any measurement.
  - Small difference on successive measurements
- Random Distribution
- Mathematical Laws of Probability
- Normal distribution or Gaussian Curve

Random errors follow a Gaussian or normal distribution.

We are 95% certain that the true value falls within 2σ (infinite population), IF there is no systematic error.

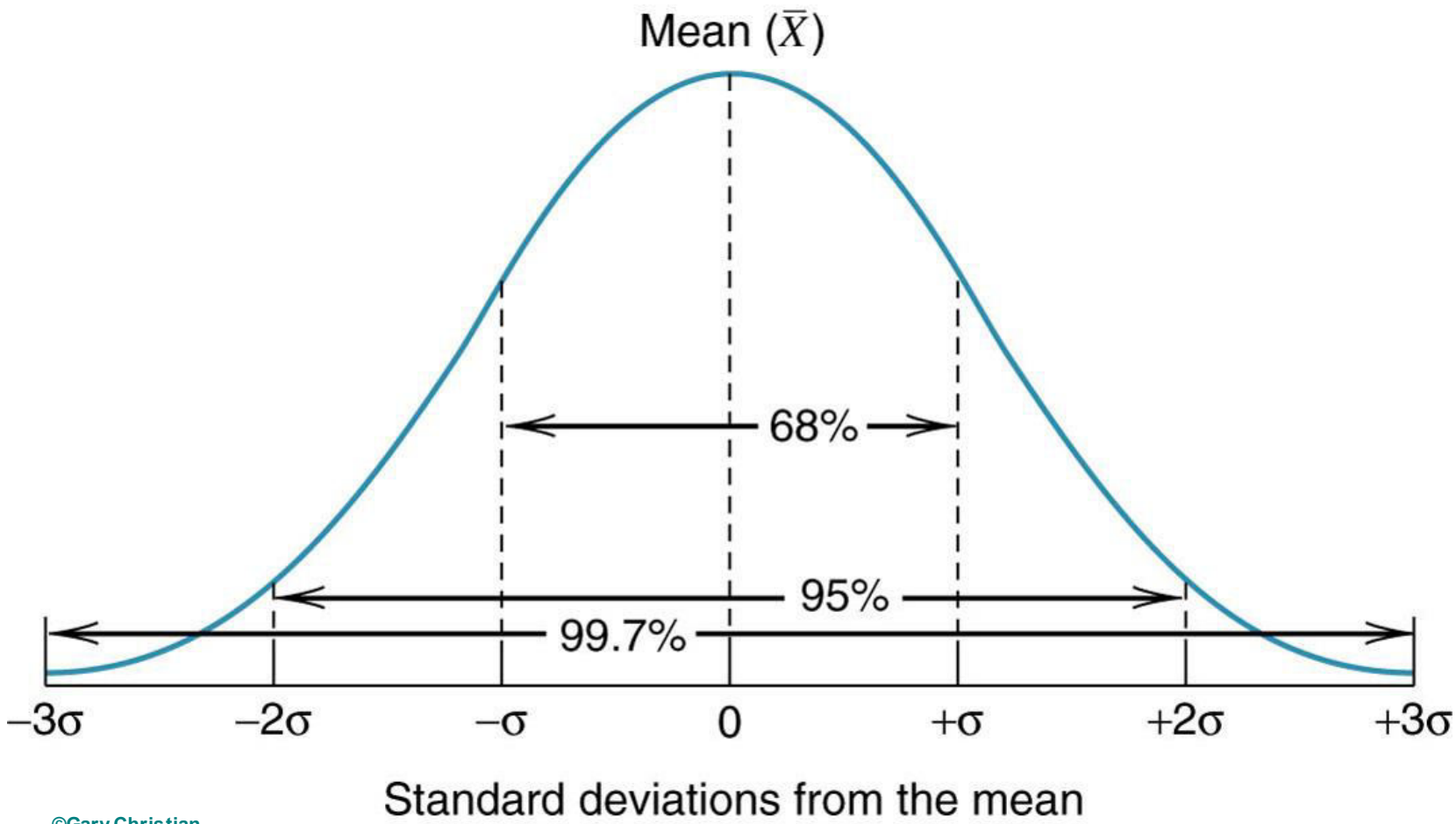

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Fig. 3.2 Normal error curve.

A Review of Significant Figures

How many significant figures in the following examples?

- 0.216 90.7 800.0 0.0670 500
- ((35.63 * 0.5482 * 0.05300)/1.1689)*100%
- 88.5470578%
- 88.55%
- ((97.7/32.42)*100.0)+36.04)/687
- 0.491_1

Ways of Expressing Accuracy

- **Absolute Errors:** difference between true value and measured value
- **Mean Errors:** difference between true value and mean value
- **Relative Error:** Absolute or Mean Errors expressed as a percentage of the true value
  - $((\mu - x)/\mu) * 100 = \%$ Relative Error
- **Relative Accuracy:** measured or mean value expressed as a percentage of true value

  $((x/\mu) * 100 = \%$ Relative Accuracy

Standard Deviation
The Most Important Statistic

- Standard Deviation σ of an intinite set of experimental data is theoretically given by

$$\sigma = \sqrt{\Sigma(x_i - \mu)^2/N}$$

- x_i = individual measurement
- μ = mean of infinite number of measurements (true value)
- N = number of measurements

Standard Deviation of a Finite Set of Experimental Data

- Estimated Standard Deviation, s ($N < 30$)
- $s = \sqrt{(\Sigma(x_i - x)^2/(N-1))}$
- For finite sets the precision is represented by s.
- Standard deviation of the mean s_{mean}
- $S_{mean} = s/\sqrt{N}$
- Relative standard deviation rsd: or coefficient of variation
- (s/mean)*100 = % rsd

Enter text, numbers, or formulas in specific cells.

	A	B	C	D	E
1	A1	B1	C1	etc.	
2	A2	B2	C2	etc.	
3	A3	B3	C3	etc.	
4					
5					

Fig. 3.3. Spreadsheet cells.

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The formula in cell B6 subtracts the weight of the flask from the weight with water.

You can copy the formula to the right by highlighting the cell and dragging it from the lower right corner to the right.

	A	B	C	D
1	Net weights			
2				
3	Pipet	1	2	
4	Weight of flask + water, g	47.702	49.239	
5	Weight of flask, g	27.687	29.199	
6	Weight of water, g	20.015	20.040	
7				
8	cell B6=B4-B5			
9	cell C6=C4-C5			
10				

Fig. 3.4. Filling cell contents.

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We often use relative cell references in formulas.

If a number from a given cell is to be a constant in the formula, place $ in front of that cell's descriptors.

	A	B	C	D
1	Titration means			
2				
3	Titn. No.	Series A, mL	Series B, mL	
4	1	39.27	45.59	
5	2	39.18	45.55	
6	3	39.30	45.63	
7	4	39.22	45.66	
8	Mean:	**39.24**	45.61	
9	Std.Dev.	**0.053150729**	0.047871355	
10				
11	**Cell B8=**	SUM(B4:B7)/$A$7 Copy right to Cell C8.		
12	**Cell B9=**	STDEV(B4:B7) Copy right to Cell C9.		
13	We have boldfaced the cells with formulas entered.			

Fig. 3.5. Relative and absolute cell references.

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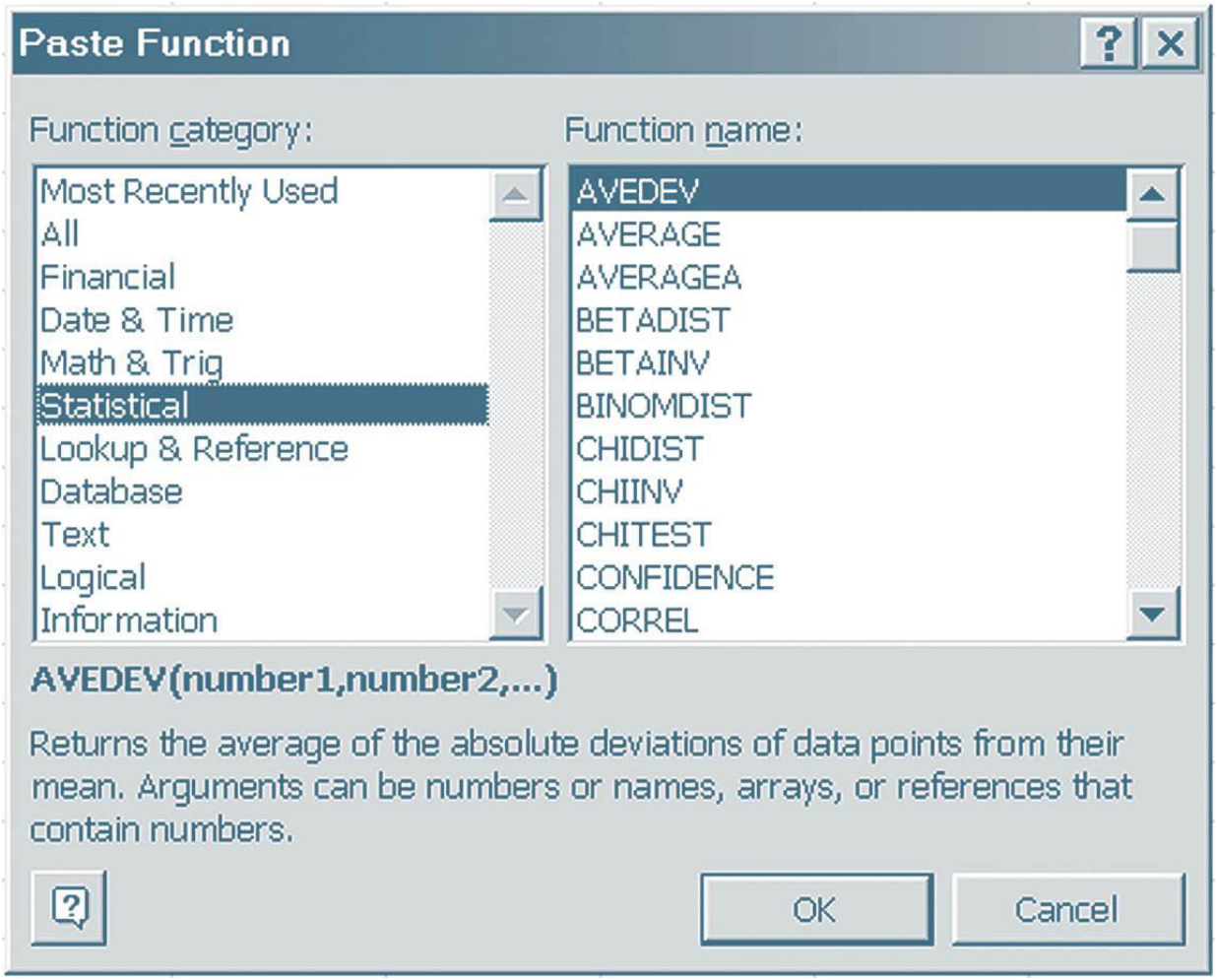
Excel has a number of mathematical and statistical functions.

Click on f_x on the tool bar to open the Paste Function.



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The cell B4 formula calculates the standard deviation of cells B1 to B3.

	A	B
1	N1	0.1167
2	N2	0.1163
3	N3	0.1164
4	STDEV:	0.000208
5	Cell B4:	
6	STDEV(B1:B3)	

Standard deviation calculation.

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Propagation of Errors
Not Just Additive

Computation	Determinate	Indeterminate (Random)
Add/Subtract $R = A+B-C$	$E_R = E_A + E_B - E_C$	$s_R^2 = s_A^2 + s_B^2 + s_C^2$ $s_R = \sqrt{s_A^2 + s_B^2 + s_C^2}$
Multiply/Divide $R = AB/C$	$\frac{E_R}{R} = \frac{E_A}{A} + \frac{E_B}{B} - \frac{E_C}{C}$	$(s_R/R)^2 = (s_A/A)^2 + (s_B/B)^2 + (s_c/C)^2$
General $R = f(A,B,C,\cdots)$		

Control Charts

- Quality control chart: time plot of a measured quantity assumed to be constant.
- Inner and Outer control limits
- Inner control limit: 2σ (1/20)
- Outer control limit: 2.5σ (1/100) or 3σ(1/500)

This is a time plot for analysis of the same sample, assumed to have only random distribution, to check for errors in a method.

At 2σ, there is a 1 in 20 chance a value will exceed this only by chance. At 2.5σ, it is 1 in 100.

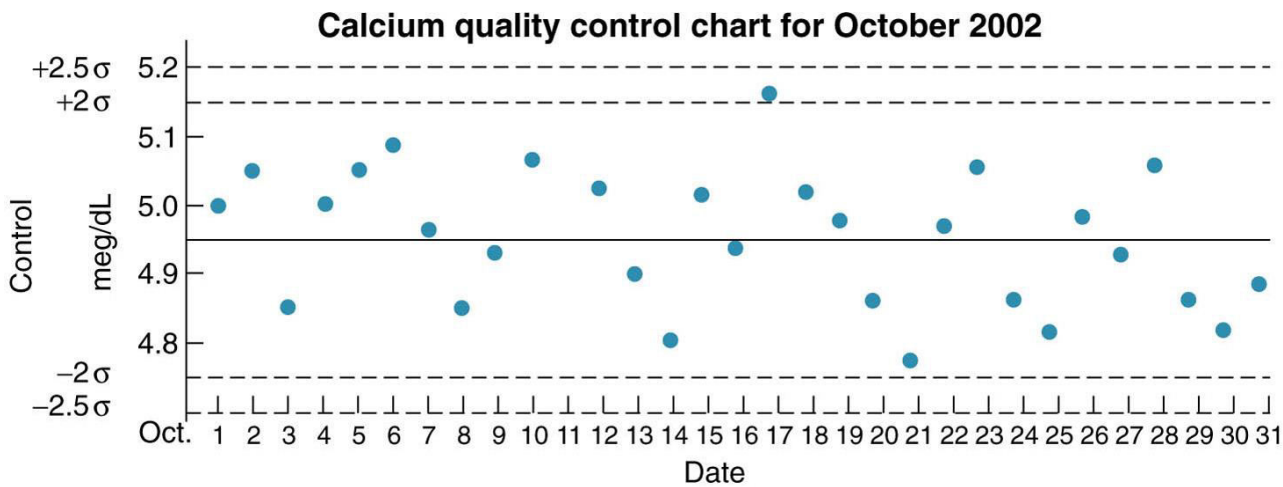

Fig. 3.6. Typical quality control chart.

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Confidence Limit
How sure are you?

- Confidence Limit = $x \pm ts/\sqrt{N}$

t statistical factor that depends on the number of degrees of freedom

ν degrees of freedom = N-1

Values of t at different confidence levels and degrees of freedom are located in table 3.1

Select a confidence level (95% is good) for the number of samples analyzed (= degrees of freedom +1).

Confidence limit = x ± ts/√N.

It depends on the precision, s, and the confidence level you select.

Table 3.1

Values of *t* for ν Degrees of Freedom for Various Confidence Levels[a]

	Confidence Level			
ν	90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

[a] $\nu = N - 1$ = degrees of freedom.

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Tests of Significance
Is there a difference?

- The F Test
- Designed to indicate whether there is a difference between two methods.
- $F = s_1^2/s_2^2$ degrees of freedoms ν_1 and ν_2

If calculated F value exceeds a tabulated F value at a selected confidence level, then there is a significant difference between the variances of the two methods.

$F = s_1^2/s_2^2$.

You compare the variances of two different methods to see if there is a significant difference in the methods, at the 95% confidence level.

Table 3.2

Values of *F* at the 95% Confidence Level

	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20	30
$\nu_2 = 2$	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66	8.62
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80	5.75
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56	4.50
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87	3.81
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44	3.38
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15	3.08
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94	2.86
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77	2.70
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33	2.25
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12	2.04
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93	1.84

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Student T Test
Are there Differences in the Methods?

1. t Test When an Accepted Value is Known

$$\mu = x \pm ts/\sqrt{N}$$

It follows

$$\pm t = (x - \mu)\sqrt{N}/s$$

Select a confidence level (95% is good) for the number of samples analyzed (= degrees of freedom +1).

Confidence limit = x ± ts/√N.

It depends on the precision, s, and the confidence level you select.

Table 3.1

Values of *t* for ν Degrees of Freedom for Various Confidence Levels[a]

	Confidence Level			
ν	90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

[a] $\nu = N - 1$ = degrees of freedom.

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Tests of Significance
Is there a difference?

- **Comparison of the Means of Two Samples**
- $\pm t = ((x_1 - x_2)/s_p)\ \sqrt{(N_1 N_2/(N_1 + N_2))}$

- pooled standard deviation: s_p
- $s_p = \sqrt{(\Sigma(x_{i1} - x_1)^2 + \Sigma(x_{i2} - x_2)^2 + \cdots + \Sigma(x_{ik} - x_k)^2/(N-k))}$

Rejection of a Result: The Q Test

- The Q test is used to determine if an "outlier" is due to a determinate error. If it is not, then it falls within the expected random error and should be retained.
- $Q = a/w$
- a = difference between "outlier" and nearest sorted result
- w = range of results.

Q_{Calc} = outlier difference/range.

If $Q_{Calc} > Q_{Table}$, then reject the outlier as due to a systematic error.

Table 3.3

Rejection Quotient, *Q*, at Different Confidence Limits[a]

No. of Observations	Confidence Level		
	Q_{90}	Q_{95}	Q_{99}
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
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372

[a]Adapted from D. B. Rorabacher, *Anal. Chem.*, **63** (1991) 139.

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Confidence Limits Using Range

- Confidence Limit = $x \pm Rt_r$

The median may be a better indicator of the true value than the mean for small numbers of observations.

And the range times a factor (K) may be a better measure of spread than the standard deviation ($s_r = RK_R$).

Table 3.4

Efficiencies and Conversion Factors for 2 to 10 Observations[a]

No. of Observations	Efficiency		Range Deviation Factor, K_R	Range Confidence Factor (t)	
	Of Median, E_M	Of Range, E_R		$t_{r0.95}$	$t_{r0.99}$
2	1.00	1.00	0.89	6.4	31.83
3	0.74	0.99	0.59	1.3	3.01
4	0.84	0.98	0.49	0.72	1.32
5	0.69	0.96	0.43	0.51	0.84
6	0.78	0.93	0.40	0.40	0.63
7	0.67	0.91	0.37	0.33	0.51
8	0.74	0.89	0.35	0.29	0.43
9	0.65	0.87	0.34	0.26	0.37
10	0.71	0.85	0.33	0.23	0.33
∞	0.64	0.00	0.00	0.00	0.00

[a]Adapted from R. B. Dean and W. J. Dixon, *Anal. Chem.*, **23** (1951) 636.

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A least-squares plot gives the best straight line through experimental points.

Exel will do this for you.

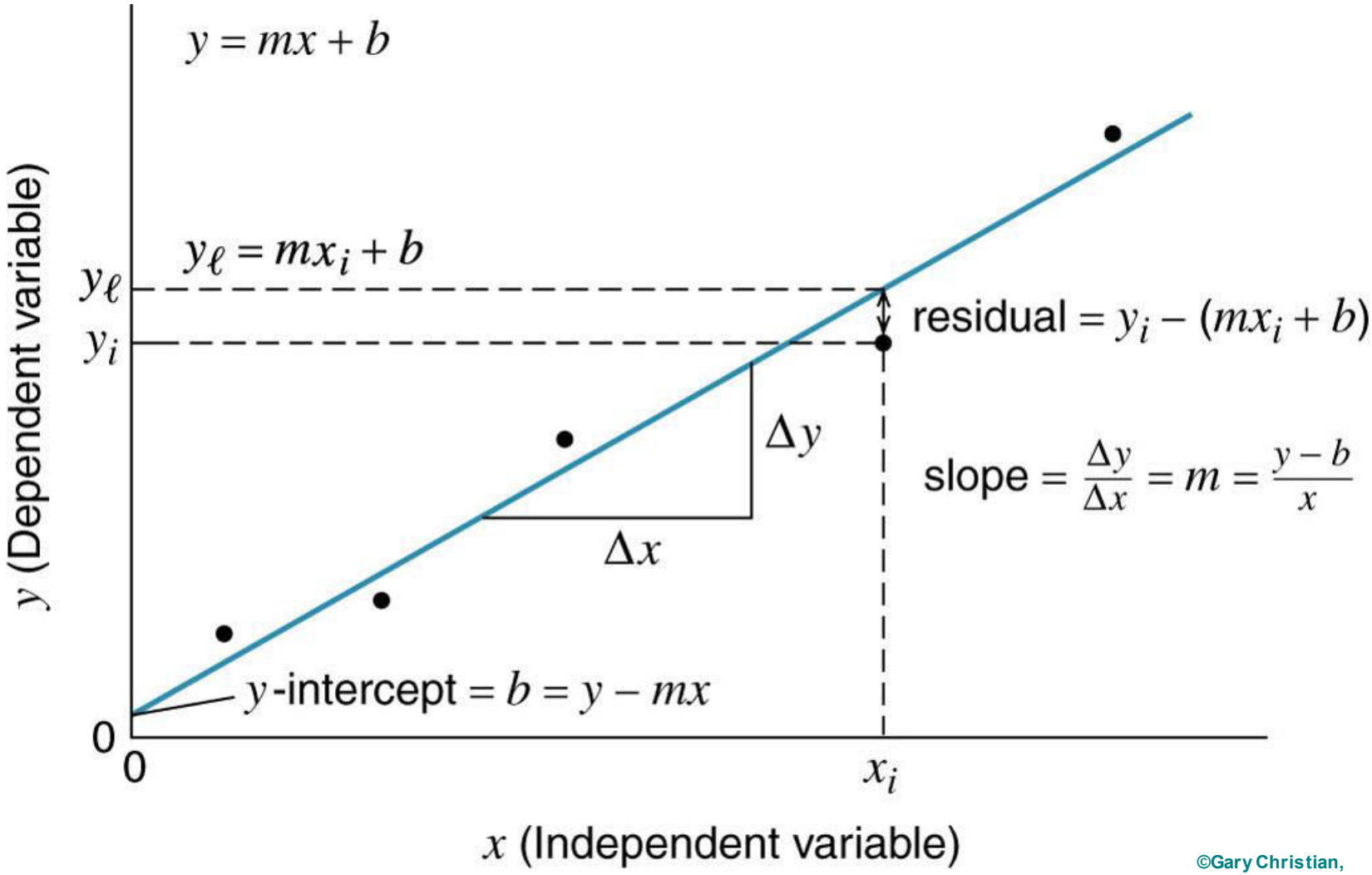

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Fig. 3.7. Straight-line plot.

This Excel plot gives the same results for slope and intercept as calculated in the example.

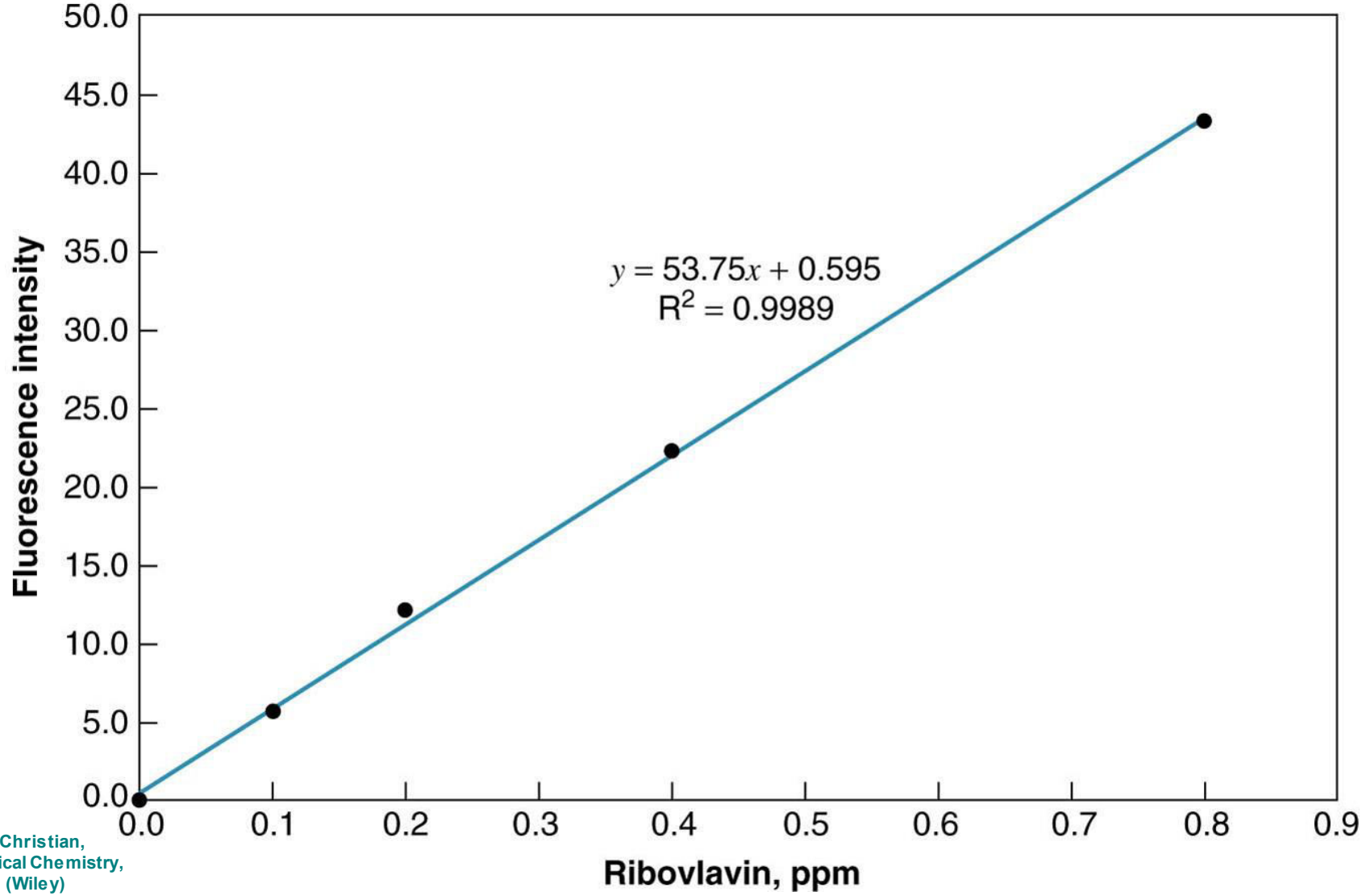

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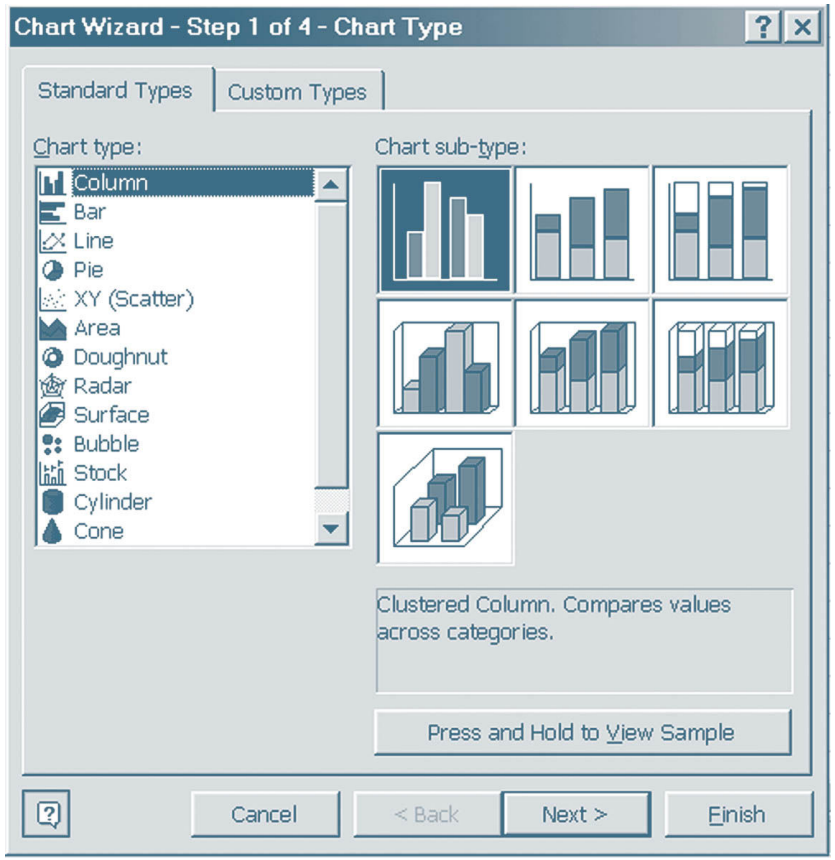
Fig. 3.8. Least-squares plot of data from Example 3.21.

Chart Wizard is on your tool bar (the icon with vertical bars).

Select XY (Scatter) for making line plots.



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You may insert the graph within the data sheet (Sheet 1), or a new Sheet 2.

	A	B	C	D	E	F	G
1	Riboflavin, ppm	Fluorescence intensity					
2							
3	0.000	0.0					
4	0.100	5.8					
5	0.200	12.2					
6	0.400	22.3					
7	0.800	43.3					
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							

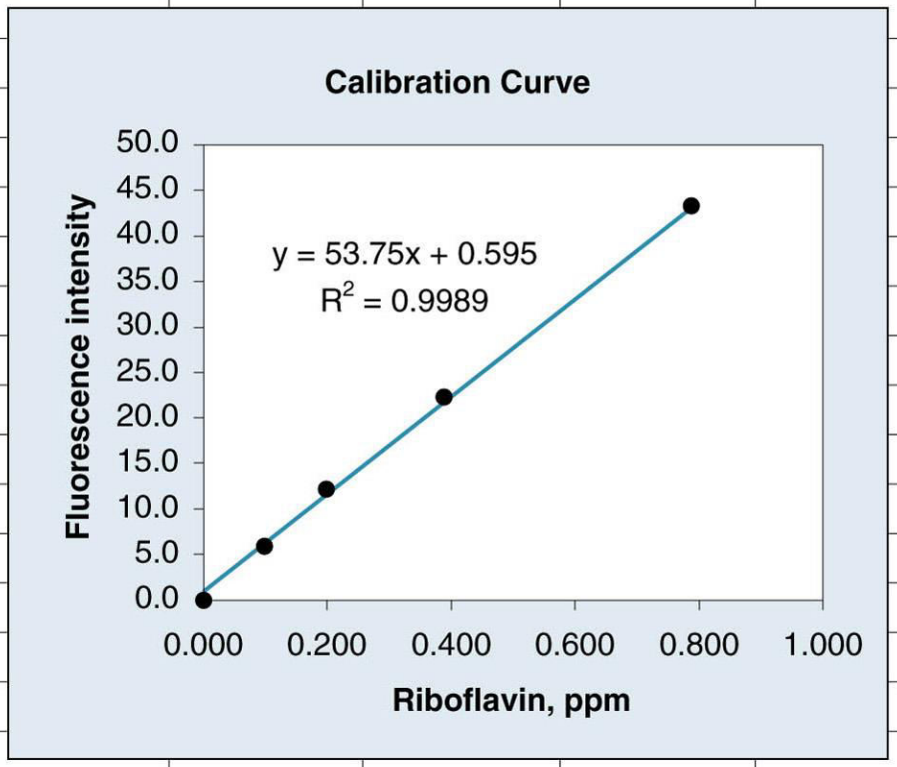

Fig. 3.9. Calibration graph inserted in spreadsheet (Sheet 1).

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Select LINEST from the statistical function list (in the Paste Function window – click on f_x in the tool bar to open).

LINEST calculates key statistical functions for a graph or set of data.

	A	B	C	D	E
1	Riboflavin, ppm	Fluorescence intensity			
2					
3	0.000	0.0			
4	0.100	5.8			
5	0.200	12.2			
6	0.400	22.3			
7	0.800	43.3			
8					
9	slope	53.75	0.595	intercept	
10	std. devn.	1.017759	0.419633	std. devn.	
11	R^2	0.998926	0.643687	std. error of estim.	
12	F	2789.119	3	d.f.	
13	sum sq. regr.	1155.625	1.243	sum sq. resid.	

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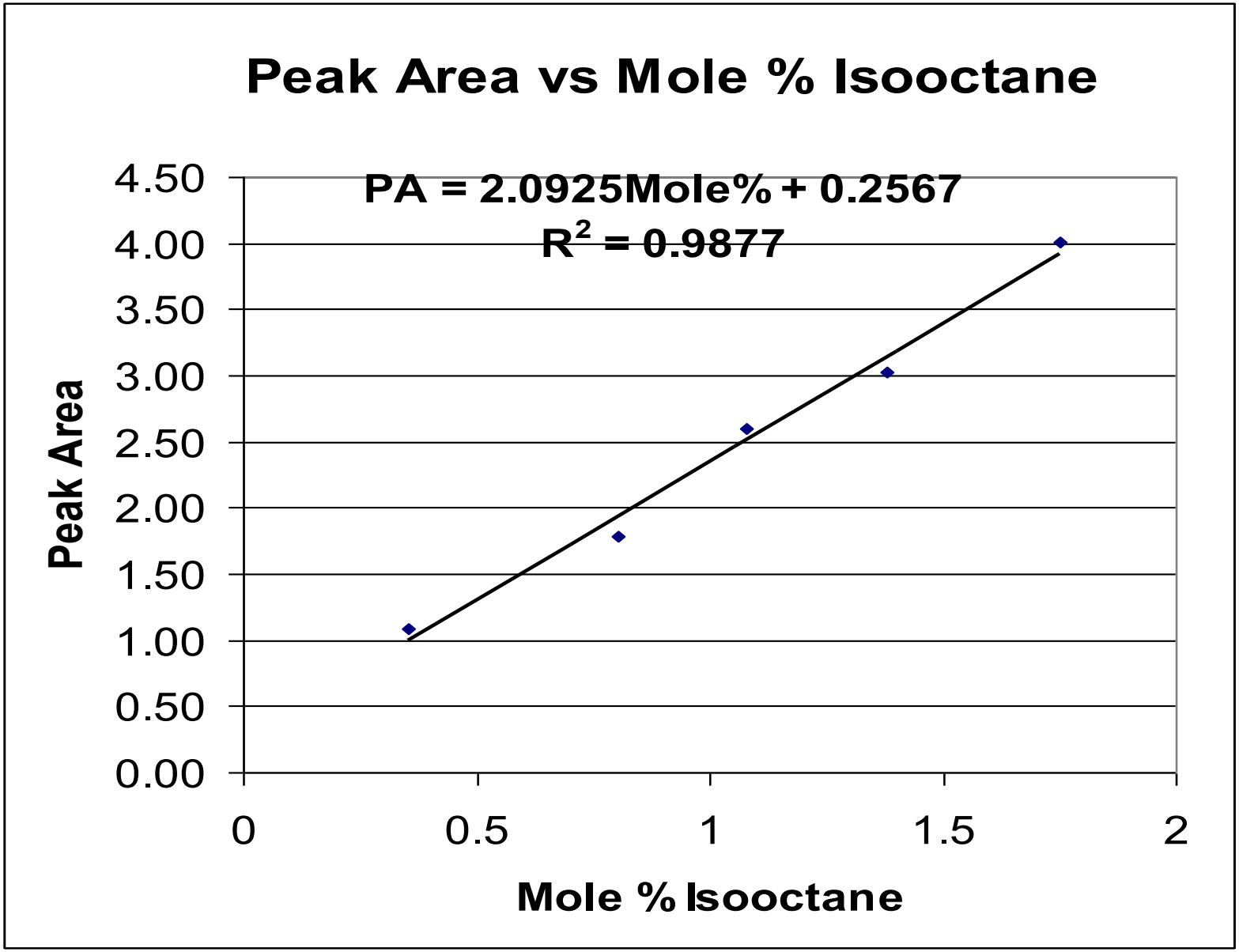
Fig. 3.10. Using LINEST for statistics.

Calibration Data for a Chromatographic Method						
for the Determination of Isooctane in a Hydrocarbon Mixture						
Mole %	Peak					
Isooctane	Area	Statistics				
0.352	1.09	Slope	2.09	0.26	Intercept	
0.803	1.78	Std Dev	0.13	0.16	Std Dev	
1.08	2.60	R^2	0.99	0.14	Std Error of Estimate	
1.38	3.03	F	241.15	3.00	Degree Freedom	
1.75	4.01	Sum sq regression	5.02	0.06	Sum Sq Residuals	


Peak Area vs Mole % Isooctane
PA = 2.0925Mole% + 0.2567
R2 = 0.9877
Peak Area
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
0.5
1
1.5
2
Mole % Isooctane

Detection Limits
There Is No Such Thing as Zero

- All instrumental methods have a degree of noise associated with the measurement that limits the amount of analyte that can be detected.
- Detection Limit is the lowest concentration level that can be determined to be statistically different from an analyte blank.
- Detection Limit is the concentration that gives a signal three times the standard deviation of the background signal.

A "detectable" analyte signal would be 12 divisions above a line drawn through the average of the baseline fluctuations.

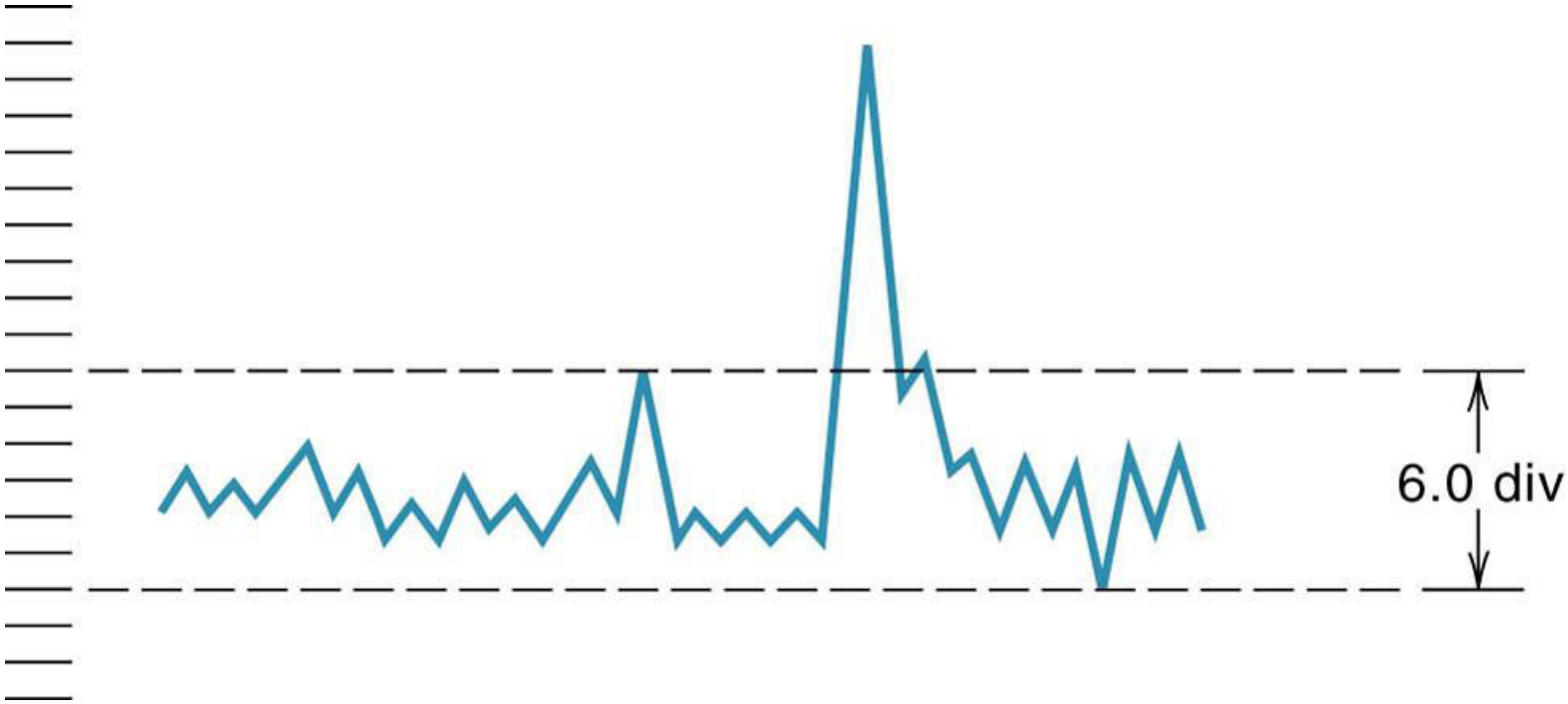


Fig. 3.11. Peak-to-peak noise level as a basis for detection limit.

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ANALYTICAL "SENSITIVITY" AND "DETECTION LIMITS"

DEFINITIONS:

SENSITIVITY ⟹ A MEASURE OF change in RESPONSE OF AN INDICATOR OR SENSOR TO change in THE CONCENTRATION OF ANALYTE.

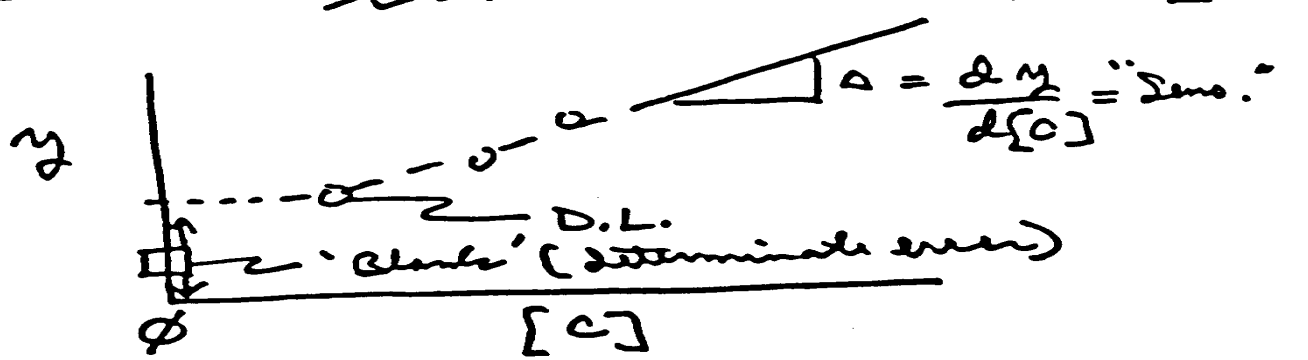
SPECIFICALLY:

$$y = a + b \cdot [C]$$

y = SENSOR MEASUREMENT

$[C]$ = ANALYTE CONC'N

$$\left[b = \text{"SENSITIVITY"} = \frac{dy}{d[C]} \right]$$



DETECTION LIMIT ⟹ Lowest possible analyte conc'n whose SENSOR Level is STATISTICALLY DISTINGUISHABLE FROM THE BACKGROUND (BLANK)

Detection Limit of an Analytical Method

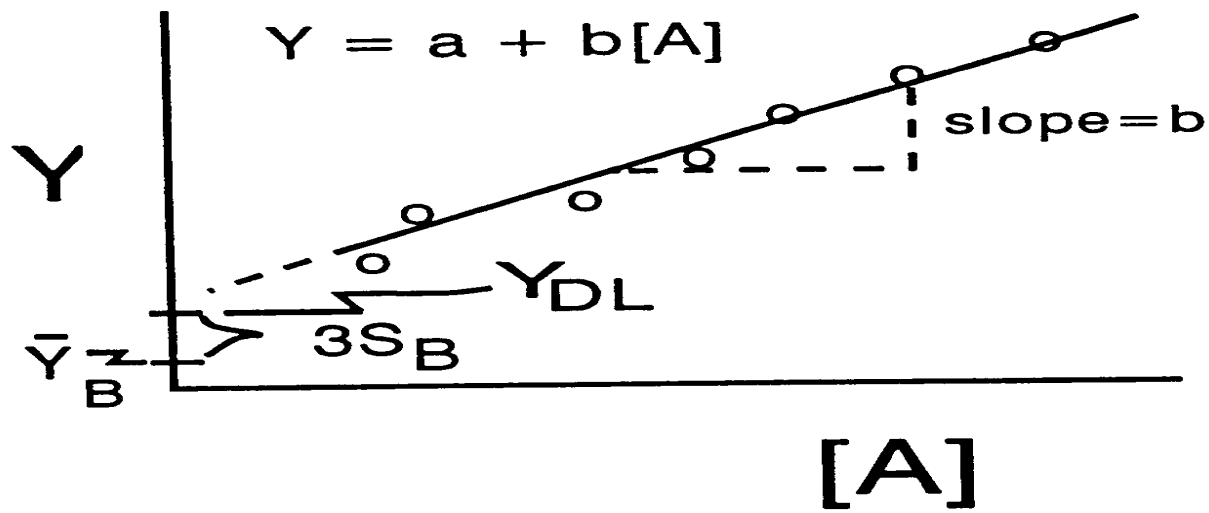
A. Iupac Definition

$Y_{DL} = \bar{Y}_B + 3\sigma_B$

[A] = analyte conc.

$A_{DL} = Y_{DL}$ /(sensitivity)

$A_{DL} = Y_{DL}$ /(b)

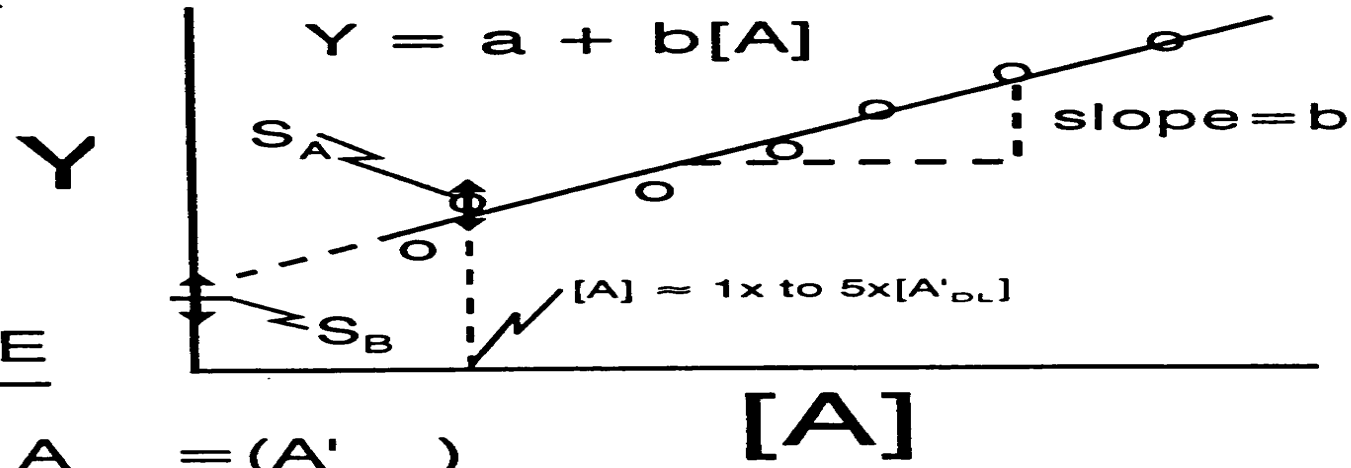


Procedure:

(1) Use S_B to estimate σ_B
OR
(2) Use S_A for low [A] to estimate σ_B
(where [A] ≈ 1x to 5x[A_{DL}])

Detection Limit of an Analytical Method

- CONT -



B. EPA PROCEDURE

(1,) Estimate $A_{DL} = (A'_{DL})$

e.g, $A'_{DL} \approx 3x[S_B / b]$

(2) Prepare standards w/ $[A] \approx 1x$ to $5x[A'_{DL}]$

(3) Analyze at least 7 replicate samples.

(4) Obtain S_A for this low concentration

(5) $A_{DL} = S_A \, t(99\%)$

v	t(99%), one-sided
6	3.143
8	2.896
10	2.484
20	2.528

Section Four

Good Laboratory Practice:

Quality Assurance of Analytical Measurements

What is Good Laboratory Practice (GLP)?

- The goal of GLP is to certify that every step of the analysis is valid.
- Standard Operating Procedures (SOP)
- Quality Assurance Unit (QAU)

Validation of Analytical Methods

	Defintion	Example
Technique	Scientific principle gives compositional information	**Spectrophotometry**
Method	Distinct adaptation of technique selected measurement purpose	Pararosaniline method to determine SO_2
Procedure	Written directions to use a method	**ASTM D2914 Sulfur Dioxide**
Protocol	Set of definitive directions that must be followed, without exception	**EPA Reference Method Determine SO_2 Atmosphere**

Validation involves determining:

- **selectivity**
- **linearity**
- **accuracy**
- **precision**
- **sensitivity**
- **range**
- **limit of detection**
- **limit of quantitation**
- **ruggedness/robustness**

Standard reference materials (SRMs) best for determining accuracy.

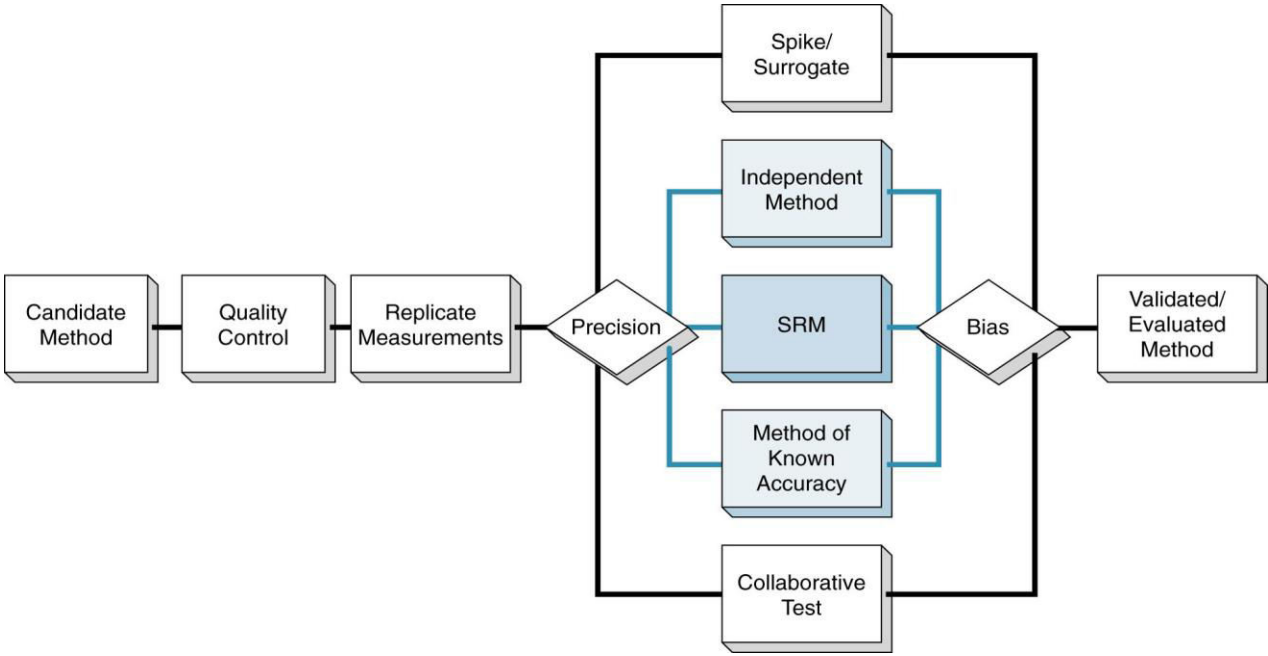


Fig. 4.1. General process for evaluation/validation of methodology.

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RF = (signal – y intercept)/(concentration).

A zero slope indicates linear response over the concentration range selected.

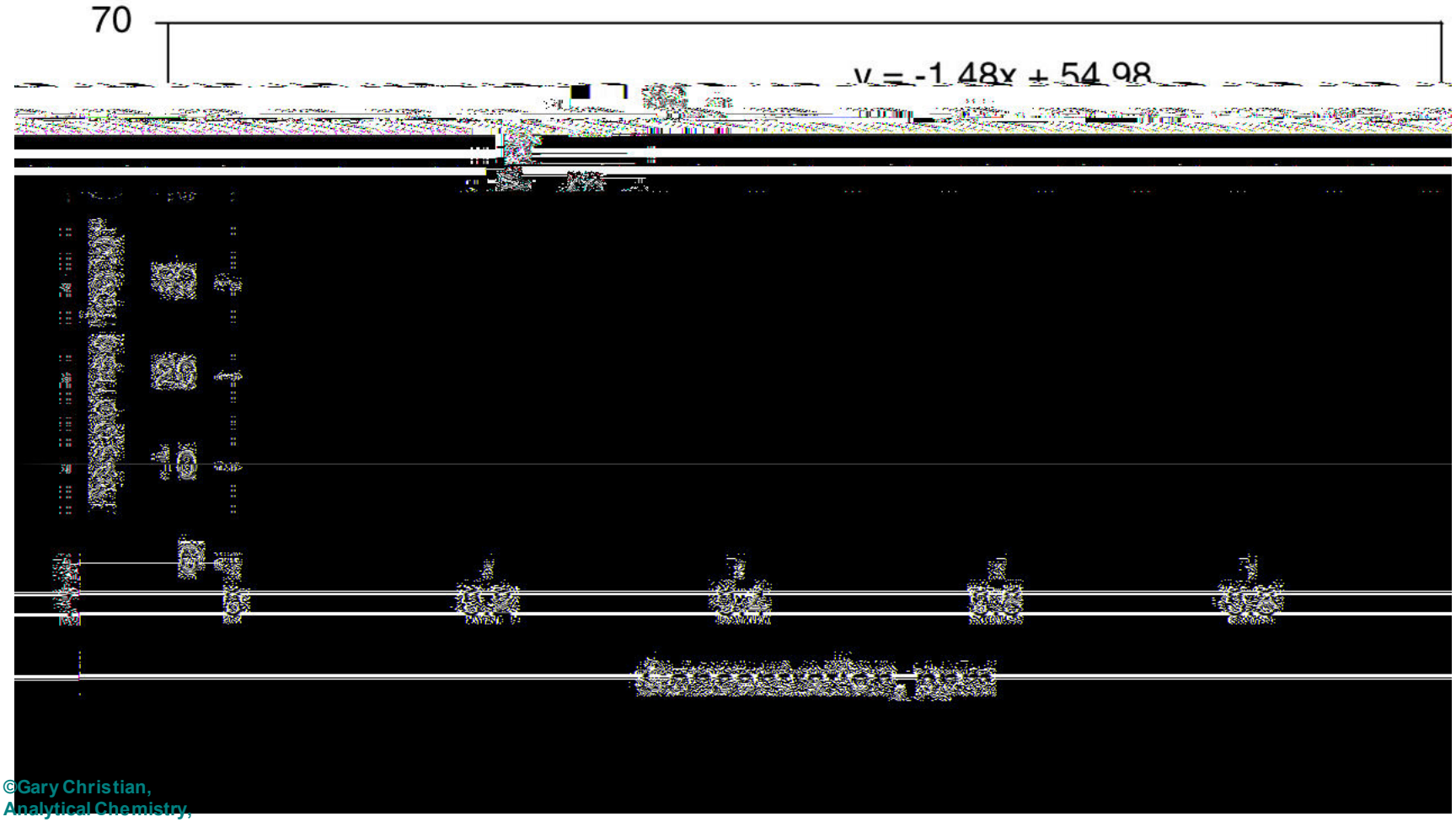

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Fig. 4.2. Response factor plot for Figure 3.8. (p. 104)

The precision becomes poorer at low concentrations.

(Also sometimes at high concentrations, as in spectrophotometric measurements –see spectrometric error, Fig. 16.27.)

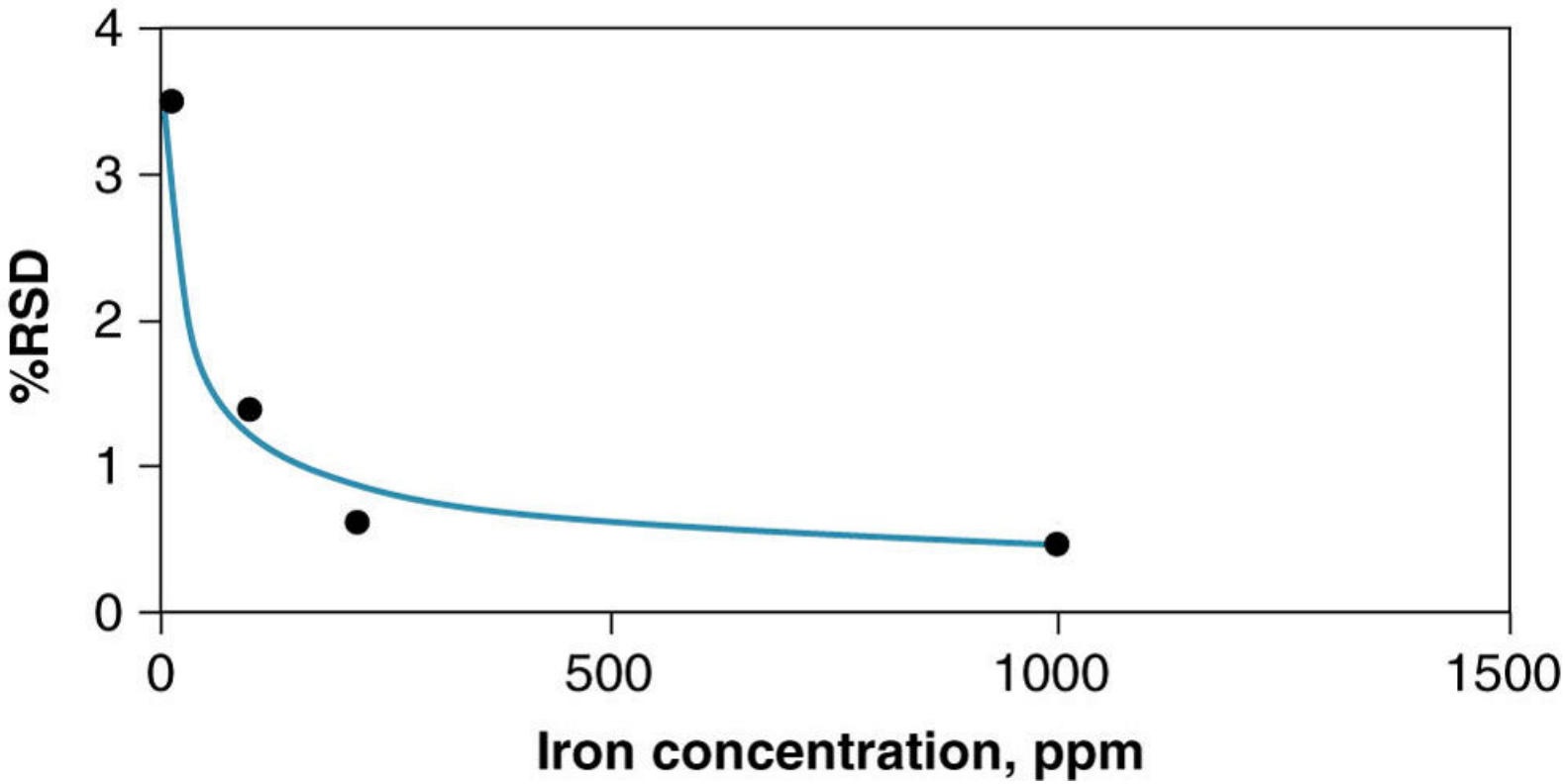

Fig. 4.3. Dependence of relative standard deviation on concentration.

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$Z = (X_i - X)/s$ = (mean conc. of lab – accepted conc.)/(S.D. accepted conc.)

A z-value of 2 means a lab is two S.D. away from the accepted value (95% chance of systematic error).

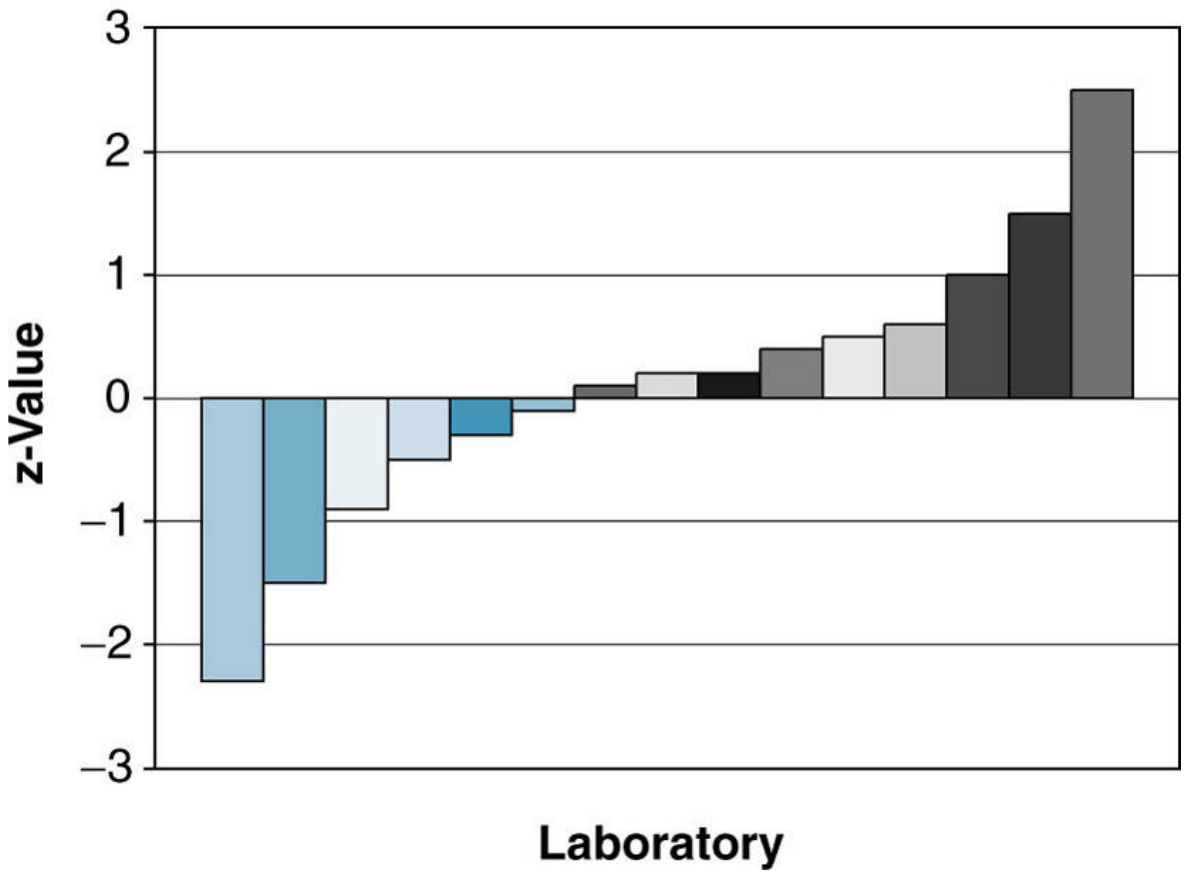

Fig. 4.4. Representative z-value distributions for proficiency tests with a series of laboratories.

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Section Five

Stoichiometric Calculations:
The Workhorse of the Analyst

Review of Fundamentals

- Atomic, Molecular, and Formula Weights

- Moles: 1mole = 6.022×10^{23} (atoms, molecules or formula units)

How Do We Express Concentrations of Solutions?

- Molarity (M)= moles/liter or mmoles/mL
- Normality(N) = equivalence/liter or meq/mL
- Formality(F)= is identical to molarity
- Molality(m) = moles/1000g solvent

In normality calculations, the number of equivalents is the number of moles times the number of reacting units per molecule or atom.

Table 5.1

Reacting Units in Different Reactions

Reaction Type	Reacting Unit
Acid–base	H^+
Oxidation–reduction	Electron

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Density Calculations
How do we convert to Molarity

- Density = mass solute /unit volume
- Specific Gravity = D_{solute}/D_{H20}
- D_{H2O} = 1.00000 g/mL @ 4°C
- D_{H2O} = 0.99821 g/mL @ 20°C

Analytical and Equilibrium Concentrations

- They are not the same!
- Analytical Molarity, C_x = sum of all species of the substance in solution
- Equilibrium Molarity, [X] = concentration of a given dissolved form of the substance

Dilutions
Preparing the Right Concentration

- The millimoles taken for dilution will be the same as the millimoles in the diluted solution.
- $M_{stock} x\ mL_{stock} = M_{diluted}\ x\ mL_{diluted}$

Expression of Analytical Results So Many Ways

- **<u>Solid Samples:</u>**
- %(wt/wt) = (wt analyte/wt sample)x 10^2 %
- pt(wt/wt) = (wt analyte/wt sample)x 10^3 ppt
- ppm(wt/wt) = (wt analyte/wt sample)x 10^6 ppm
- ppb(wt/wt) = (wt analyte/wt sample)x 10^9 ppb

Expression of Analytical Results So Many Ways

- **<u>Liquid Samples</u>**
- %(wt/vol) = (wt analyte/vol sample mL)x 10^2 %
- pt(wt/vol) = (wt analyte/vol sample mL)x 10^3 ppt
- ppm(wt/vol) = (wt analyte/vol sample mL)x 10^6 ppm
- ppb(wt/vol) = (wt analyte/vol sample,mL)x 10^9 ppb
- **<u>Liquid Analyte</u>**
- %(vol/vol) = (vol analyte/vol sample mL)x 10^2 %
- pt(vol/vol) = (vol analyte/vol sample mL)x 10^3 ppt
- ppm(vol/vol) = (vol analyte/vol sample mL)x 10^6 ppm
- ppb(vol/vol) = (vol analyte/vol sample,mL)x 10^9 ppb

The units ppm or ppb are used to express trace concentrations.

These are weigh or volume based, rather than mole based.

Table 5.2

Common Units for Expressing Trace Concentrations

Unit	Abbreviation	wt/wt	wt/vol	vol/vol
Parts per million	ppm	mg/kg	mg/L	m L/L
(1 ppm = 10^{-4}%)		m g/g	m g/mL	nL/mL
Parts per billion	ppb	m g/kg	m g/L	nL/L
(1 ppb = 10^{-7}% = 10^{-3} ppm)		ng/g	ng/mL	pL/mL[a]
Milligram percent	mg%	mg/100 g	mg/100 mL	

[a] pL = picoliter = 10^{-12} L.

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The equivalents (based on charge) of cations and anions are equal.

Table 5.3

Major Electrolyte Composition of Normal Human Plasma[a]

Cations	meq/L	Anions	meq/L
Na^+	143	Cl^-	104
K^+	4.5	HCO^{3-}	29
Ca^{2+}	5	Protein	16
Mg^{2+}	2.5	HPO_4^-	2
		SO_4^{2-}	1
		Organic acids	3
Total	155	Total	155

[a] Reproduced from Joseph S. Annino, *Clinical Chemistry,* 3rd ed., by Boston: LIttle, Brown, 1964.

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Reporting Concentrations as Different Chemical Species

- We may express results in any form of the analyte.
- Example:
- Water Hardness due to calcium ion is expressed as ppm $CaCO_3$.
- Chloride present in AgCl derived from a salt mixture of NaCl and KCl.

Volumetric Analysis - Principles

- "**Titrimetry**" – determination of **analyte** by reaction with measured amount of standard reagent
- "Standard Solution" (**titrant**) – reagent of known concentration
- "**Titration**" – slow addition of titrant to analyte solution from a volumetric vessel (buret)
- "**Equivalence Point**" – reached when amount of added titrant is chemically equivalent to amount of analyte present in the sample.
- "**End Point**" – the occurrence of an observable physical change indicating that the equivalence point is reached. Might differ from Eq.Pt.!

Volumetric Analysis - Principles

How Do We Make Stoichiometric Calculations?

- Titration- What are the requirements?

1. Reaction must be stoichiometric
2. Reaction should be rapid
3. No side reactions
4. Marked change in some property of the solution when reaction is complete
5. Equivalence point
6. Reaction should be quantitative

Volumetric Analysis - Principles
Standard Solutions

- "Primary Standard " –
  - highly purified compound used as a reference material in titrimetry
- <u>Properties:</u>
- High purity
- Stable in air
- Independent of relative humidity
- Readily available
- Reasonable solubility
- Large formula weight

Volumetric Analysis - Principles

Standard Solutions

- "Secondary Standard"
  - do not meet requirements for a primary standard but are available with sufficient purity and properties to be generally acceptable
- Desirable properties of a Standard Solution:
- Prepared from primary standard
- Stable
- Reacts rapidily and completely with analyte
- Reacts selectively with analyte

Volumetric Analysis - Principles
Examples of Standard Materials

- **Primary**
- Potassium Acid Phthalate
- $KHC_8H_4O_4$ (FW 204.23)
- Benzoic Acid
- C_6H_5COOH (FW 122.12)
- Na_2CO_3 , $KH(IO_3)_2$
- Arsenious Oxide (As_2O_3)
- Sodium Oxalate ($Na_2C_2O_4$)
- KI , $K_2Cr_2O_7$, Fe(pure)

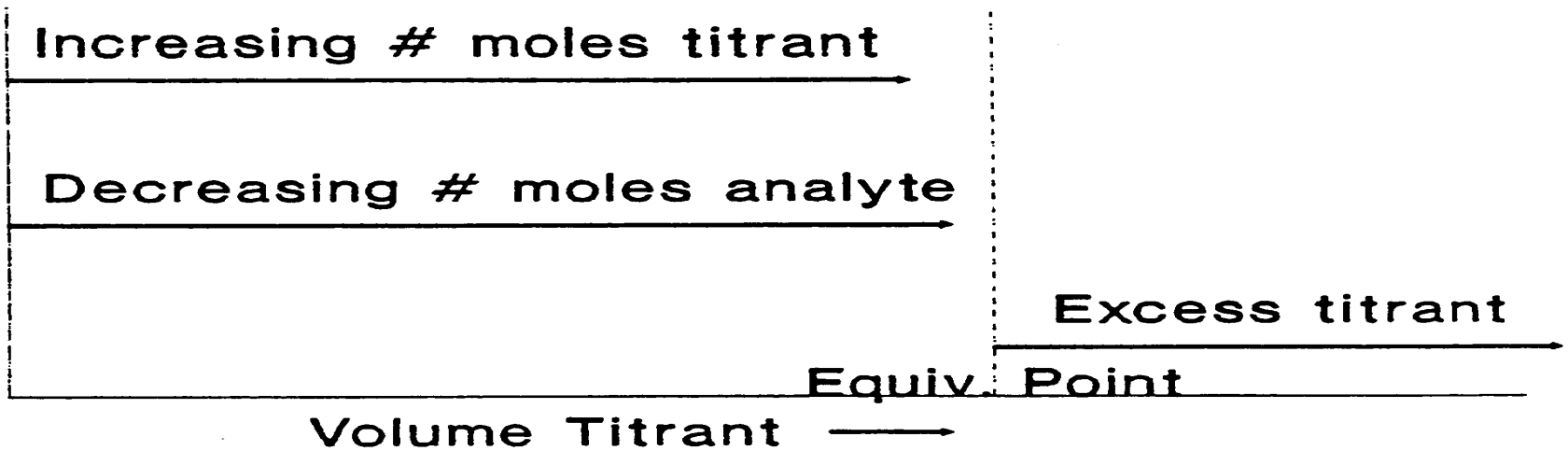
- **Secondary**
- NaOH , KOH , $Ba(OH)_2$
- HCl , HNO_3 , $HClO_4$
- Sulfamic Acid (HSO_3NH_2)
- $KMnO_4$, $Na_2S_2O_3$
- $Ce(HSO_4)_4$ (FW 632.6)

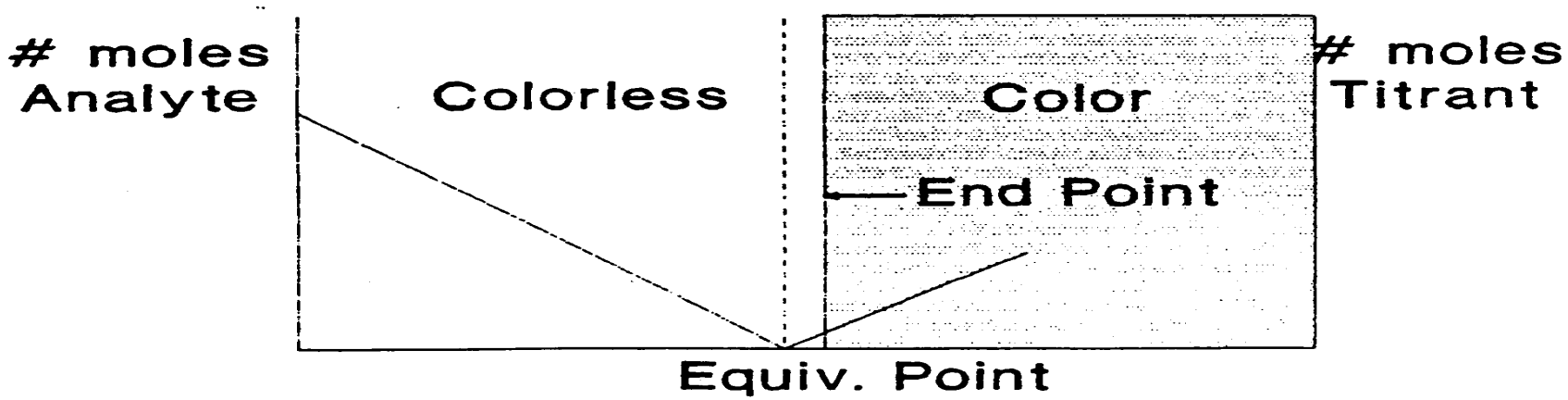
Volumetric Analysis-Principles

- **Standardization** – involves establishing the concentration of a "standard solution"
- **Direct method:**
- dissolve caarefully weighed quantity of primary standard; dilute to known volume
- **Indirect methods:**
- Titrate weighed quantity of primary standard
- Titrate weighed quantity of secondary standard
- Titrate measured volume of other standard solution

Volumetric Analysis
Principles

Titration Characteristics:





Volumetric Analysis - Principles

- **Acid – Base**
- $HA + B \rightarrow BH^+ + A^-$
- **Precipitation**
- $M^{n+} + X^- \rightarrow MX_n$
- **Oxidation-Reduction**
- $Red_1 + Ox_2 \rightarrow Ox_1 + Red_2$
- **Complexation**
- $M^{n+} + Q \rightarrow M(Q)^{n+}$ use standard Q solution

Volumetric Analysis - Principles

- **<u>Dilutions</u>**
- $V_c \times C_c = V_d \times C_d$

- **<u>Stoichiometric Ratios (S.R.) Mole Ratio:</u>**
- What are stoichiometric ratios (mole ratios)?
- $2\ HCl + Ba(OH)_2 \rightarrow 2\ HOH + Ba^{2+} + 2\ Cl^-$

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

Section 06

General Concepts of Chemical Equilibrium

General Concepts: Chemical Equilibrium

- Chemical Reactions: The Rate Concept
- $aA + bB \leftrightarrow cC + dD$
- $Rate_f = k_f[A]^a[B]^b$
- $Rate_r = k_r[C]^c[D]^d$
- $Rate_f = Rate_r$
- $k_f[A]^a[B]^b = k_r[C]^c[D]^d$
- Molar Equilibrium Constant K
- $K = k_f / k_r = ([C]^c[D]^d)/([A]^a[B]^b)$
- Not Generally Valid, because reaction rates depend on mechanisms

The rate of the forward reaction diminishes with time, while that of the backward reaction increases, until they are equal.

A large K means the reaction lies far to the right at equilibrium.

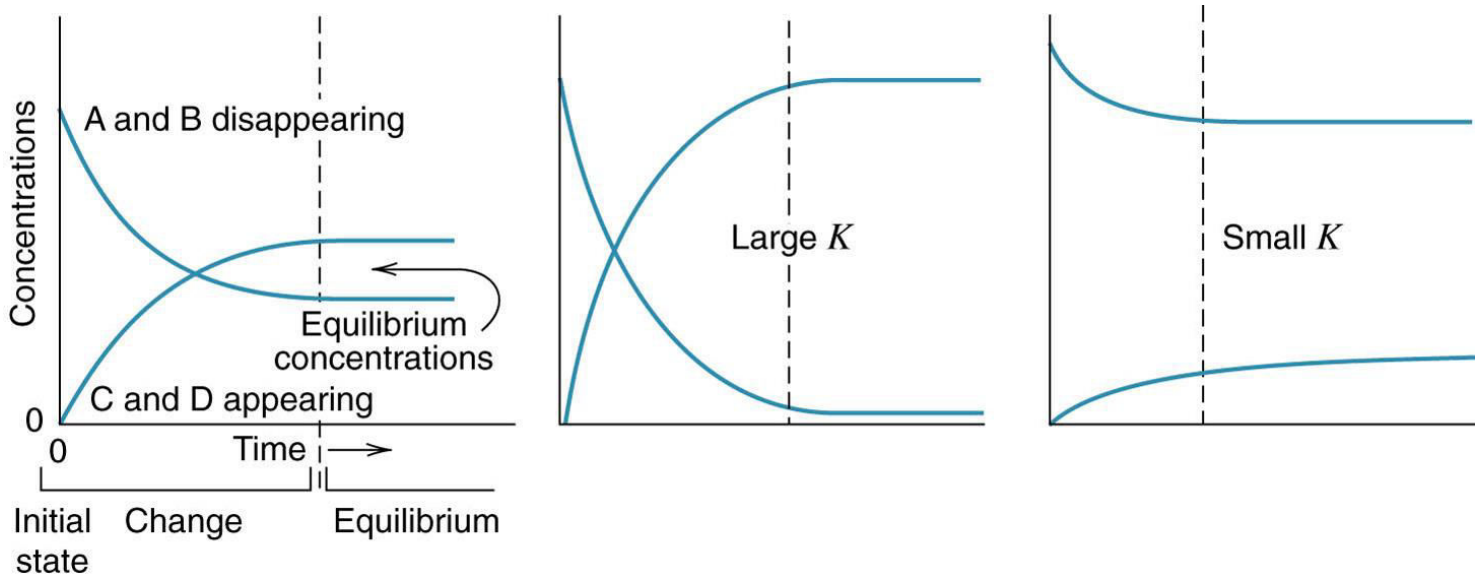


Fig. 6.1. Progress of a chemical reaction.

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Equilibrium constants may be written for dissociations, associations, reactions, or distributions.

Table 6.1

Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acidity constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

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General Concepts: Chemical Equilibrium

- Gibbs Free Energy & Equilibrium Constant
- $G = H - TS$ but $H = E + PV$
  - G = Gibbs Free Energy H = Enthalpy
  - T = Temperature S = Entropy
  - E = Internal Energy P = Pressure V = Volume
- $G = E + PV - TS$ but $E = q - w$
- $G = q - w + PV - TS$
- Derivative
- $dG = dq - dw + PdV + VdP - TdS - SdT$

General Concepts: Chemical Equilibrium

- $dG = dq - dw + PdV + VdP - TdS - SdT$
- Let's Simplify by imposing some conditions on the reaction.
- Constant Temperature: $dT = 0 \rightarrow SdT = 0$
- Reversible Reaction: $dq = TdS$
- Expansion work only: $dw = PdV$
- Then all terms except one cancel
- $dG = VdP$ 1mole of an ideal gas $V = RT/P$
- $dG = RTdP/P$

General Concepts: Chemical Equilibrium

- Now lets integrate: $dG = RTdP/P$
- Result:
- $G_2 - G_1 = RT\ln(P_2/P_1)$
- make state 1 = standard state
- $G - G^o = RT\ln(P/P^o)$ but $P^o = 1$ atm
- Activity is defined: $a = P/P^o$
- $G = G^o + RT\ln(a)$

General Concepts: Chemical Equilibrium

- General Expressions:
- $rR + sS \leftrightarrow tT + uU$
- $\Delta G = tG_T + uG_U - rG_R + sG_S$
- Each Free Energy Term Expressed in Terms of Activity
- $tG_T = tG_T^o + t\,RT \ln a_T$
- $uG_U = uG_U^o + u\,RT \ln a_U$
- $rG_R = rG_R^o + r\,RT \ln a_R$
- $sG_S = sG_S^o + s\,RT \ln a_S$
- $\Delta G = \Delta G^o + RT \ln (a_T^t\, a_U^u / a_R^r\, a_S^s)$

General Concepts: Chemical Equilibrium

- $\Delta G = \Delta G^o + RT \ln (a_T^t\, a_U^u / a_R^r\, a_S^s)$
- At Equilibrium: $\Delta G = 0$
- Reaction quotient $Q = (a_T^t\, a_U^u / a_R^r\, a_S^s) = K^o$
- Where K^o is the thermodynamic equilibrium constant
- $0 = \Delta G^o + RT \ln K^o$
- $\ln K^o = - \Delta G^o / RT$

- $K^o = e^{(- \Delta G^o / RT)}$

Chemical Equilibrium

- Review of Principles
- Chemical reactions are never "complete"
- Chemical reactions proceed to a state where ratio of products to reactants is <u>constant</u>
- $NH_3 + HOH \leftrightarrow NH_4^+ + OH^-$
- $[NH_4^+][OH^-]/[NH_3][HOH] = K_b^o$
- If $K_b << 1$ (little ionization)
- $H_2SO_4 + HOH \rightarrow H_3O^+ + HSO_4^-$
- $[H_3O^+][HSO_4^-] / [H_2SO_4][HOH] = K_a$
- If $K_a >> 1$ (mostly ionized)

Chemical Equilibrium

- Equilibrium
  - is not reached instantaneously
  - can be approached from either direction
  - is a dynamic state
  - amounts of reactants/products can be changed by "mass action"
  - (adding/ deleting products/reactants)
  - $HCO_3^- + H^+ \leftrightarrow CO_{2(g)} + HOH$
  - $K_e = [CO_2][HOH]/[HCO_3^-][H^+]$

Chemical Equilibrium

- <u>Equilibrium Constants</u>
- $2\ A + 3\ B \leftrightarrow C + 4\ D$
- $K_e = [C][D]^4/[A]^2[B]^3$
- Concentrations [ ] :
  - molar for solutes
  - partial pressures (atm) for gases
  - [1.0] for pure liquid, solid, or solvent

Chemical Equilibrium

- Important Equilibria in Analytical Chemistry
- **<u>Solubility:</u>**
- $AgCl(s) \leftrightarrow Ag^+ + Cl^-$
- $Ag_3AsO_4(s) \leftrightarrow 3\ Ag^+ + AsO_4^{3-}$
- $BaSO_4(s) \leftrightarrow Ba^{2+} + SO_4^{2-}$
- $K_{sp}(AgCl) = [Ag^+][Cl^-] = 1.0 \times 10^{-10}$
- $K_{sp}(Ag_3AsO_4) = [Ag^+]^3[AsO_4^{3-}] = 1.0 \times 10^{-22}$
- $K_{sp}(BaSO_4) = [Ba^{2+}][SO_4^{2-}] = 1.0 \times 10^{-10}$

Chemical Equilibrium

- Important Equilibria in Analytical Chemistry
- **<u>Autoprotolysis:</u>**
- $HOH + HOH \leftrightarrow H_3O^+ + OH^-$
- $K_e = [H_3O^+][OH^-]/[HOH]^2$
- $K_e[HOH]^2 = K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ @ 25^oC
- In pure water @ 25^oC $[H_3O^+] = [OH^-] = 10^{-7}$
- **<u>Acid Dissociation:</u>**
- $H_2CO_3 + HOH \leftrightarrow H_3O^+ + HCO_3^-$
- $K_a = [H_3O^+][HCO_3^-]/[H_2CO_3] = 4.3 \times 10^{-7}$

Chemical Equilibrium

- **Important Equilibria in Analytical Chemistry**
- $H_2CO_3 + HOH \leftrightarrow H_3O^+ + HCO_3^-$
- $acid_1$ $base_1$
- **<u>Dissociation of Conjugate Base$_1$:</u>**
- $HCO_3^- + HOH \leftrightarrow H_3O^+ + CO_3^{2-}$
- $K_a(HCO_3^-) = [H_3O^+][CO_3^{2-}]/[HCO_3^-] = 4.8 \times 10^{-11}$
- **<u>Hydrolysis of Conjugate Base$_1$:</u>**
- $HCO_3^- + HOH \leftrightarrow H_2CO_3 + OH^-$
- $K_b(HCO_3^-) = K_w/K_a(H_2CO_3) = 10^{-14}/4.3 \times 10^{-7}$
- $K_b(HCO_3^-) = 2.3 \times 10^{-8}$

Chemical Equilibrium

- Important Equilibria in Analytical Chemistry
- **<u>Base Dissociation:</u>**
- $NH_3 + HOH \leftrightarrow NH_4^+ + OH^-$
- $K_b(NH_3) = [NH_4^+][OH^-]/[NH_3] = 1.75 \times 10^{-5}$
- **<u>Hydrolysis of Salts:</u>**
- $NH_4Cl(s) \rightarrow NH_4^+ + Cl^-$
- $NH_4^+ + HOH \leftrightarrow NH_3 + H_3O^+$
- $K_a(NH_4^+) = K_w/K_b(NH_3) = 10^{-14}/1.75 \times 10^{-5}$
- $K_a(NH_4^+) = 5.7 \times 10^{-10}$

Chemical Equilibrium

- Some Useful Calculations
- **<u>Common Ion Effects on Solubility:</u>**
- What is the solubility of BaF_2 in pure water?

- What is the solubility of BaF_2 in 0.1 M NaF?

Chemical Equilibrium

- Some Useful Calculations
- **<u>pH of Weak Acid or Base Solutions:</u>**

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???**

Activity and Activity Coefficients

- Activity of an ion, $a_i = C_i f_i$
- C_i = concentration of the ion
- f_i = activity coefficient (@ $C_i < 10^{-4}$M)= 1
- Ionic Strength, $\mu = \frac{1}{2}\Sigma C_i Z_i^2$
- Z_i = charge on each individual ion.

Activity and Activity Coefficients

- Calculation of Activity Coefficients
- Debye-Huckel Equation:
- $-\log f_i = 0.51 Z_i^2 (\mu)^{1/2} / (1 + 0.33 \alpha_i (\mu)^{1/2})$

□ α_i = ion size parameter in angstrom (Å)

- 1 Å = 100 picometers (pm, 10^{-10} meters)
- Limitations: singly charged ions = 3 Å

$-\log f_i = 0.51 Z_i^2 (\mu)^{1/2} / (1 + (\mu)^{1/2})$

Chemical Equilibria Electrolyte Effects

- Diverse ion (Inert) electrolyte effect
  - For $\mu < 0.1$ M, electrolyte effect depends on μ only, NOT on the type of electrolyte
- **<u>Solute activities:</u>**
- a_x = activity of solute X
- $a_x = [X] f_x$
- f_x = activity coefficient for X
- As $\mu \rightarrow 0$, $f_x \rightarrow 1$, $a_x \rightarrow [X]$

Chemical Equilibria Electrolyte Effects

- **<u>Diverse Ion (Inert Electrolyte) Effect:</u>**
- Add Na_2SO_4 to saturated solution of AgCl
- $K_{sp}^o = a_{Ag^+} \cdot a_{Cl^-} = 1.75 \times 10^{-10}$
- At high concentration of diverse (inert) electrolyte: higher ionic strength, μ
- $a_{Ag^+} < [Ag^+]$; $a_{Cl^-} < [Cl^-]$
- $a_{Ag^+} \cdot a_{Cl^-} < [Ag^+]\,[Cl^-]$
- $K_{sp}^o < [Ag^+]\,[Cl^-]$; $\sqrt{K_{sp}^o} < [Ag^+]$ = solubility
- **Solubility = $[Ag^+] > \sqrt{K_{sp}^o}$**

Chemical Equilibria Electrolyte Effects

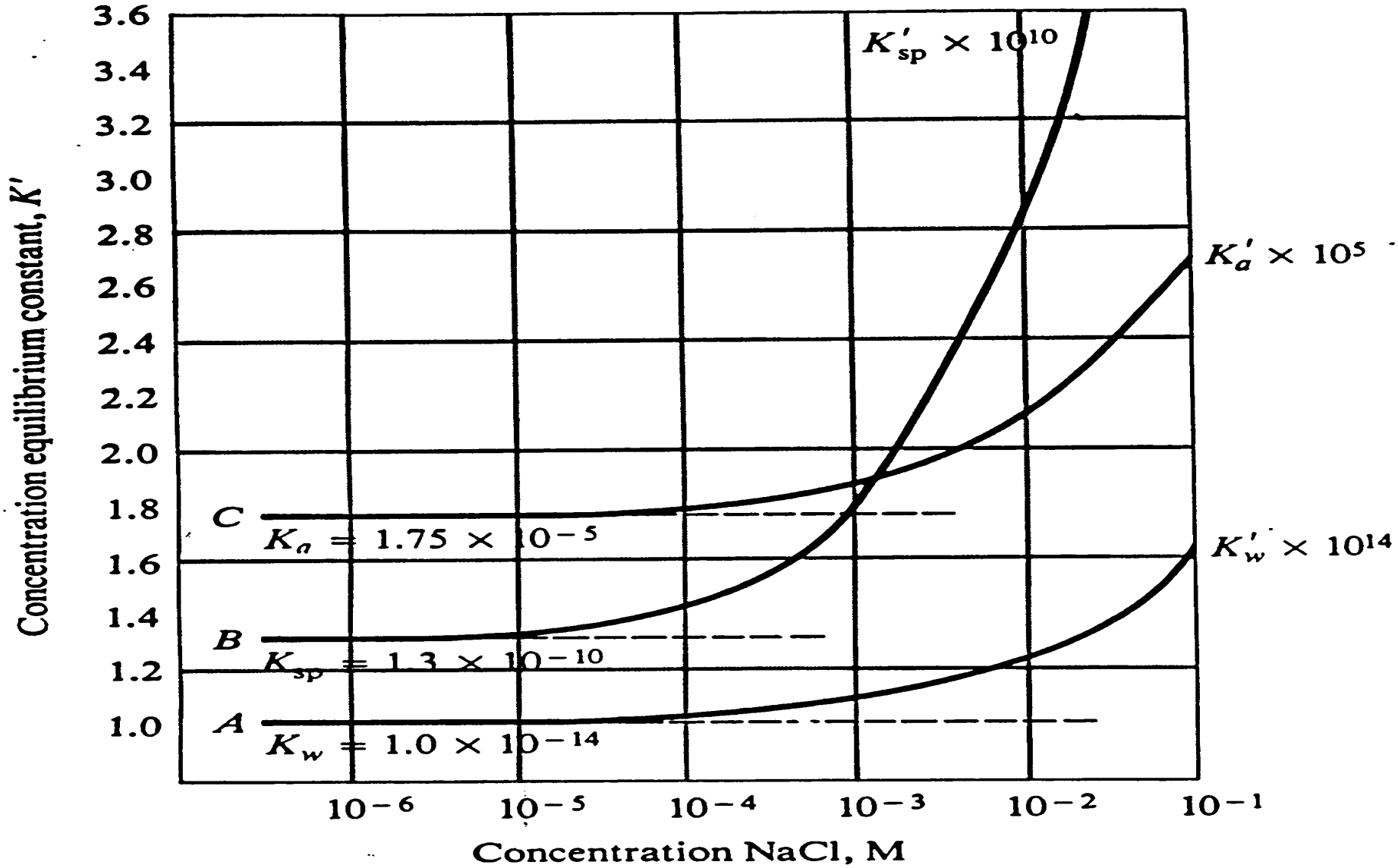
- "Diverse ion (Inert) electrolyte effect"
- Is dependent on parameter called "ionic strength (μ)"
- $\mu = (1/2)\{[A]Z_A^2 + [B]Z_B^2 + \cdots + [Y]Z_y^2\}$
- 0.1 M Na_2SO_4 ; $[Na^+] = 0.2M$ $[SO_4] = 0.1M$
- $\mu = (1/2)\{[A]Z_A^2 + [B]Z_B^2\}$
- $\mu = (1/2)\{[0.2](1+)^2 + [0.1](2-)^2\} =$ **<u>0.3M</u>**

Chemical Equilibria Electrolyte Effects

- **<u>Solute activities:</u>**
- When **μ** is not **<u>zero</u>**, $\mathbf{a_x} = [X]f_x$
- **<u>Equilibrium effects</u>**:
- $mM + xX \leftrightarrow zZ$
- $K^o = (\mathbf{a_z})^{\mathbf{z}}/(\mathbf{a_m})^{\mathbf{m}}(\mathbf{a_x})^{\mathbf{x}}$
- $K^o = ([Z]f_Z)^{\mathbf{z}}/([M]f_M)^{\mathbf{m}}([X]f_x)^{\mathbf{x}}$
- $K^o = \{([Z])^{\mathbf{z}}/([M])^{\mathbf{m}}([X])^{\mathbf{x}}\}\{f_Z{}^z/f_M{}^m f_x{}^x\}$
- $K^o = K\{f_Z{}^z/f_M{}^m f_x{}^x\}$
- $K = K^o\{f_M{}^m f_x{}^x/f_Z{}^z\}$

The Diverse Ion Effect

- The Thermodynamic Equilibrium Constant and Activity Coefficients
  - thermodynamic equilibrium constant, K^o
  - case extrapolated to infinite dilution
  - At infinite dilution, activity coefficient, $f = 1$
- Dissociation $AB \leftrightarrow A^+ + B^-$
- $K^o = a_A\, a_B / a_{AB} = [A^+]\, f_A \cdot [B^-]\, f_B / [AB]\, f_{AB}$
- $K^o = K\, (f_A \cdot f_B / f_{AB})$
- $K = K^o\, (f_{AB} / f_A \cdot f_B)$



Effect of Electrolyte Concentration on Concentration-Based Equil. Constants

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Chemical Equilibria Electrolyte Effects

- **<u>Calculation of Activity Coefficients</u>**
- Debye-Huckel Equation:
- $-\log f_x = 0.51 Z_i^2 (\mu)^{1/2} / (1+0.33\alpha_i(\mu)^{1/2})$
- Where α_x = effective diameter of hydrated ion, X (in angstrom units, 10^{-8}cm), Å
-

Ion	H_3O^+	Li^+	F^-	Ca^{2+}	Al^{3+}	Sn^{4+}
$\boldsymbol{\alpha_x}$, Å	9	6	3.5	6	9	11
f_x @ 0.05 M	.86	.84	.81	.48	.24	.1

Chemical Equilibrium Electrolyte Effects

- **<u>Equilibrium calculations using activities</u>**:
- Solubility of PbI_2 in 0.1M KNO_3
- $\mu = 0.1 = \{0.1(1^+)^2 + 0.1(1^-)^2\}/2$ (ignore Pb^{2+},I^-)
- $f_{Pb} = 0.35$ $f_I = 0.76$
- $\mathbf{K_{sp}^o = (a_{Pb})^1(a_I)^2 = ([Pb^{2+}]f_{Pb})^1([I^-]f_I)^2}$
- $\mathbf{K_{sp}^o} = ([Pb^{2+}]\ [I^-]^2)(f_{Pb}\ f_I^2) = \mathbf{K_{sp}}(f_{Pb}\ f_I^2)$
- $\mathbf{K_{sp} = K_{sp}^o / (f_{Pb}\ f_I)}$
- $\mathbf{K_{sp} = 7.1 \times 10^{-9} /}((0.35)(0.76)^2) = 3.5 \times 10^{-8}$
- $(s)(2s)^2 = \mathbf{K_{sp}}$ $\mathbf{s = (Ksp/4)^{1/3}}$ **<u>s =2.1 x 10^{-3} M</u>**
- **Note: If $s = (K_{sp}^o/4)^{1/3}$ then** **<u>s =1.2 x 10^{-3}M</u>**
- **Solubility calculation difference approx. –43%**

Multiple Chemical Equilibria Compositional Calculations

- **<u>Setting up the problem:</u>**
- Write balanced equations for all equilibria
- Write K_e expressions and find values
- Write mass and charge balance equations
- Write expression for sought for substance
- Determine in No. independent equations (N) at least equals No. of unknowns (U)
  - (if N < U can approximations reduce U?)
- Make approximations to simplify math
- Solve set of equations for all unknowns
- Check validity of assumptions
  - (re-solve with second approximation if needed)

Multiple Chemical Equilibria

- Dissolve $NaHCO_3$ in water:
  - $NaHCO_3 \rightarrow Na^+ + HCO_3^-$
- $HCO_3^- + HOH \leftrightarrow H_2CO_3 + OH^-$ $K_e = Kb = Kw/K_{a1}$
- $HCO_3^- + HOH \leftrightarrow H_3O^+ + CO_3^{2-}$ $K_e = K_{a2}$
- $HOH + HOH \leftrightarrow H_3O^+ + OH^-$ $K_e = K_w$
- 5 chemical species affected by 3 equilibria
- Equilibrium constants do NOT change with chemical additions/ deletions
  - Add Ba^{2+}: $Ba^{2+} + CO_3^{2-} \leftrightarrow BaCO_{3(s)}$ $K_e = K_{sp}$
  - (Now there are 6 species affected by 4 equilibria)
- **Note: For Polyprotic Acids (H_NA): $K_{(step)} = K_{a1}, K_{a2}, \text{--} K_{aN}$**
- $H_2A + HOH \leftrightarrow H_3O^+ + HA^-$ $K_e = K_{a1}$
- $HA^- + HOH \leftrightarrow H_3O^+ + A^{2-}$ $K_e = K_{a2}$

Multiple Chemical Equilibria Compositional Calculations

- **<u>What are concentrations of individual species?</u>**
- For N species, M equilibria
- Need, N independent algebraic expressions:
- Equilibrium expressions ($M < N$)
- Mass balance statements
- Charge Balance statements

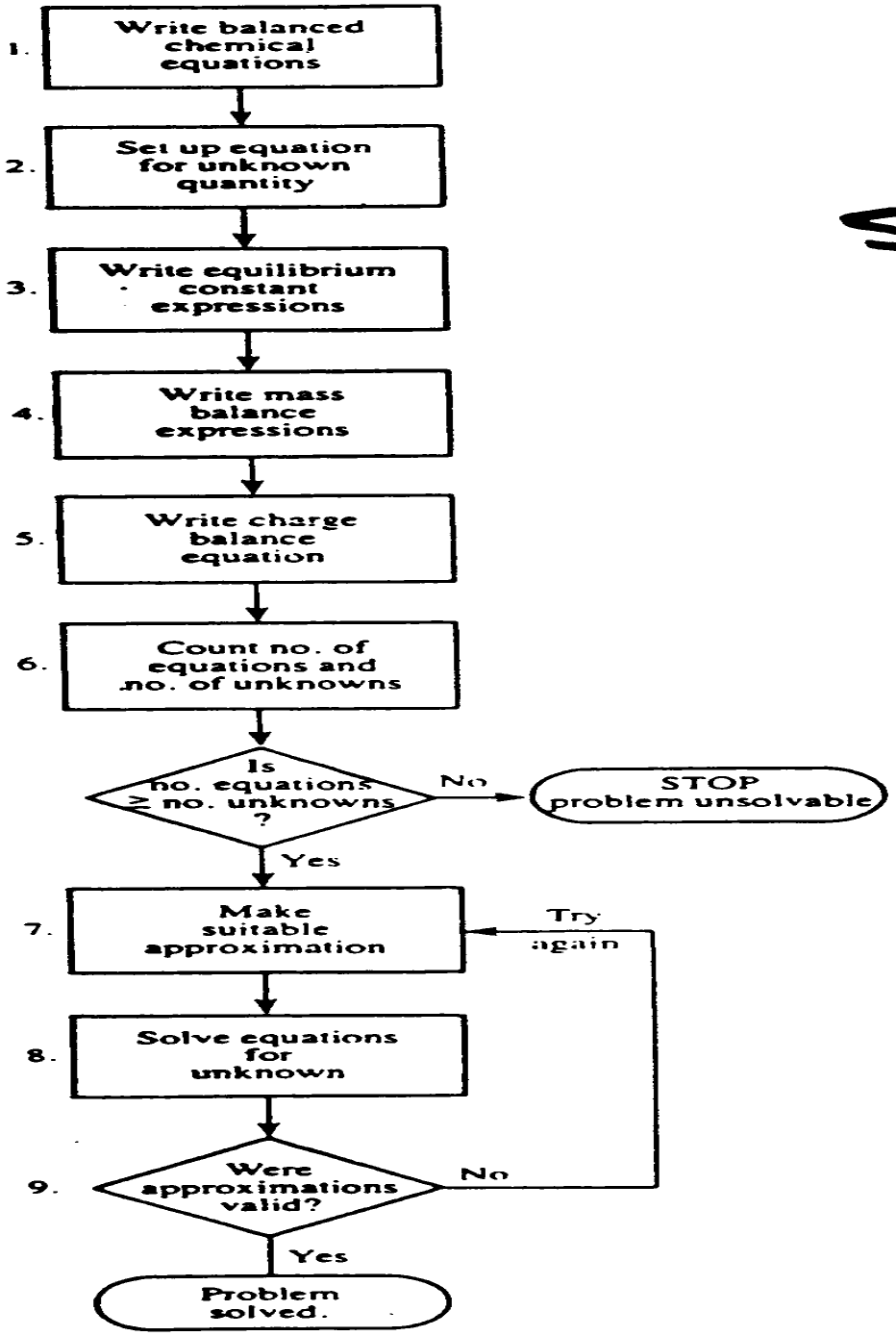
Multiple Chemical Equilibria Compositional Calculations

- **<u>Mass Balance Equations</u>**:
- Relate equilibrium concentrations of species
  - Stoichiometric relationships
  - How the solution was prepared
  - What kinds of equilibria exist
- E.g. 0.1 M HNO_2 (C_{HA} = 0.1 M)
- $HNO_2 + HOH \leftrightarrow H_3O^+ + NO_2^-$ $K_e = K_a$
- C_{HA} (x) (x)
- $HOH + HOH \leftrightarrow H_3O^+ + OH^-$ $K_e = K_w$
- (w) (w)
- $C_{HA} = [HNO_2] + [NO_2^-]$ all forms of "HNO_2"
- $[H_3O^+] = [OH^-] + [NO_2^-] = w + x$ $[H_3O^+]$ from 2 sources

Multiple Chemical Equilibria Compositional Calculations

- **<u>Charge Balance Equations:</u>**
- In any electrolyte solution,
- amt. of <u>positive</u> charge = amt. of <u>negative</u> charge
- solution charge for each species = [conc.][charge/ion]
- E.g. for solution $MgCO_3$
- $MgCO_3$ _→ $Mg^{2+} + CO_3^{2-}$ leads to equilibria:
- $CO_3^{2-} + HOH \leftrightarrow HCO_3^- + OH^-$
- $HCO_3^- + HOH \leftrightarrow H_2CO_3 + OH^-$
- **<u>Charge Balance</u>**:
- $2[Mg^{2+}] + [H_3O^+] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-]$

FLOW CHART FOR SYSTEMATIC APPROACH TO MULTIPLE EQUILIBRIA PROBLEMS



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Systematic Approach to Equilibrium Calculations

- How to Solve Any Equilibrium Problem
- 1. Write balanced chemical reactions
- 2. Write equilibrium constant expressions
- 3. Write all mass balance expressions
- 4. Write the charge balance expression
- 5. Equations >= Chemical Species sol possible
- 6. Make assumptions where possible
- 7. Calculate answer
- 8. Check validity of assumptions

Multiple Chemical Equilibria
Example Problem #1

- **<u>What is pH of $Mg(OH)_2$ solution ?</u>** **(assume a_x= [X])**
- **<u>Equilibria:</u>**
- **$Mg(OH)_{2(s)} \leftrightarrow Mg^{2+} + 2\ OH^-$ $K_{sp} = [Mg^{2+}][OH^-] = 1.8 \times 10^{-11}$**
- $HOH + HOH \leftrightarrow H_3O^+ + OH^-$ $K_e = K_w = 1.0 \times 10^{-14}$
- **<u>Mass Balance:</u>** $[OH^-] = [H_3O^+] + 2\ [Mg^{2+}]$
- **<u>Charge Balance:</u>** $[OH^-] = [H_3O^+] + 2\ [Mg^{2+}]$
- **<u>Expression for unknown :</u>** $[H_3O^+] = K_w / [OH^-]$

Multiple Chemical Equilibria
Example Problem #1

- **<u>What is pH of $Mg(OH)_2$ solution ?</u>** **(assume a_x= [X])**
- **<u>Expression for unknown :</u>** $[H_3O^+] = K_w / [OH^-]$
- **<u>Solution:</u>** Assume $[H_3O^+] << 2\ [Mg^{2+}]$; $[OH^-] = 2\ [Mg^{2+}]$
- Substitute into K_{sp}, $K_{sp} = ([OH^-]/2)([OH^-])^2$
- $[OH^-]^3 = 2\ K_{sp}$; $[OH^-] = (2\ K_{sp})^{1/3} = 3.3 \times 10^{-4}$ M
- $[H_3O^+] = K_w/(3.3 \times 10^{-4}) = 3.0 \times 10^{-11}$ M
- pH = -log $[H_3O^+] = 10.52$ (2 sig figs)
- Note: original approximation was OK!
- i.e. $[H_3O^+] << [OH^-]$ $(3.0 \times 10^{-11} << 3.3 \times 10^{-4})$
- Assumed $[OH^-] = 2\ [Mg^{2+}]$; $[H_3O^+] << 2\ [Mg^{2+}]$
- Assumed $[H_3O^+] << [OH^-]$ ➔ **<u>OK</u>**!

Multiple Chemical Equilibria
Example Problem #2

- **<u>What is pH of 0.1 M Na_3PO_4 solution?</u>** **(C_s = 0.1 M)**
- $Na_3PO_{4(s)} \rightarrow 3Na^+ + PO_4^{3-}$
- **<u>Equilibria:</u>**
- (1) $PO_4^{3-} + HOH \leftrightarrow HPO_4^{2-} + OH^-$ $K_w/K_{a3} = 2.38 \times 10^{-2}$
- (2) $HPO_4^{2-} + HOH \leftrightarrow H_2PO_4^- + OH^-$ $K_w/K_{a2} = 1.6 \times 10^{-9}$
- **(3)** $H_2PO_4^- + HOH \leftrightarrow H_3PO_4 + OH^-$ $K_w/K_{a1} = 1.4 \times 10^{-12}$
- **(4)** $HOH + HOH \leftrightarrow H_3O^+ + OH^-$ $K_w = 1.0 \times 10^{-14}$
- **<u>Mass Balance Equations:</u>**
- (5) $C_s = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$
- (6) $[OH^-] = [H_3O^+] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$
- (*) $K_{a1} = 7.1 \times 10^{-3}$ $K_{a2} = 6.3 \times 10^{-8}$ $K_{a3} = 4.2 \times 10^{-13}$

Multiple Chemical Equilibria
Example Problem #2

- **<u>What is pH of 0.1 M Na_3PO_4 solution?</u>** **(C_s = 0.1 M)**
- **<u>Charge Balance:</u>**
- (7) $[H_3O^+] + [Na^+] = [OH^-] + [H_2PO_4^-] + 2\,[HPO_4^{2-}] + 3\,[PO_4^{3-}]$
- Note: $[Na^+] = 3\,C_s$
- **<u>Is problem solvable?</u>**
- 6 unknowns $[H_3O^+]$,$[OH^-]$,$[H_2PO_4^-]$,$[HPO_4^{2-}]$,$[PO_4^{3-}]$, $[H_3PO_4]$
- 7 equations (see 1-7)
- Thus, the problem should be solvable.

Multiple Chemical Equilibria
Example Problem #2 (solution)

- **<u>What is pH of 0.1 M Na_3PO_4 solution?</u>** **(C_s = 0.1 M)**
- **Assume** $[H_3O^+] + [H_2PO_4^-] + [H_3PO_4] << [HPO_4^{2-}]$
- Then from equation (6): $[OH^-] = [HPO_4^{2-}] = x$
- Also Assume $[HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] << [PO_4^{3-}]$
- Then from equation (5): $[PO_4^{3-}] = C_s = 0.1$ M
- equation (1): $[HPO_4^{2-}][OH^-]/[PO_4^{3-}] = K_w/K_{a3} = 2.38 \times 10^{-2}$
- Thus $x^2/C_s = 2.38 \times 10^{-2}$ $x = [OH^-] = 4.9 \times 10^{-2}$
- $[H_3O^+] = K_w/[OH^-] = 2.0 \times 10^{-13}$M
- **pH = 12.69 (2 sig fig)**
- Note: Check assumptions

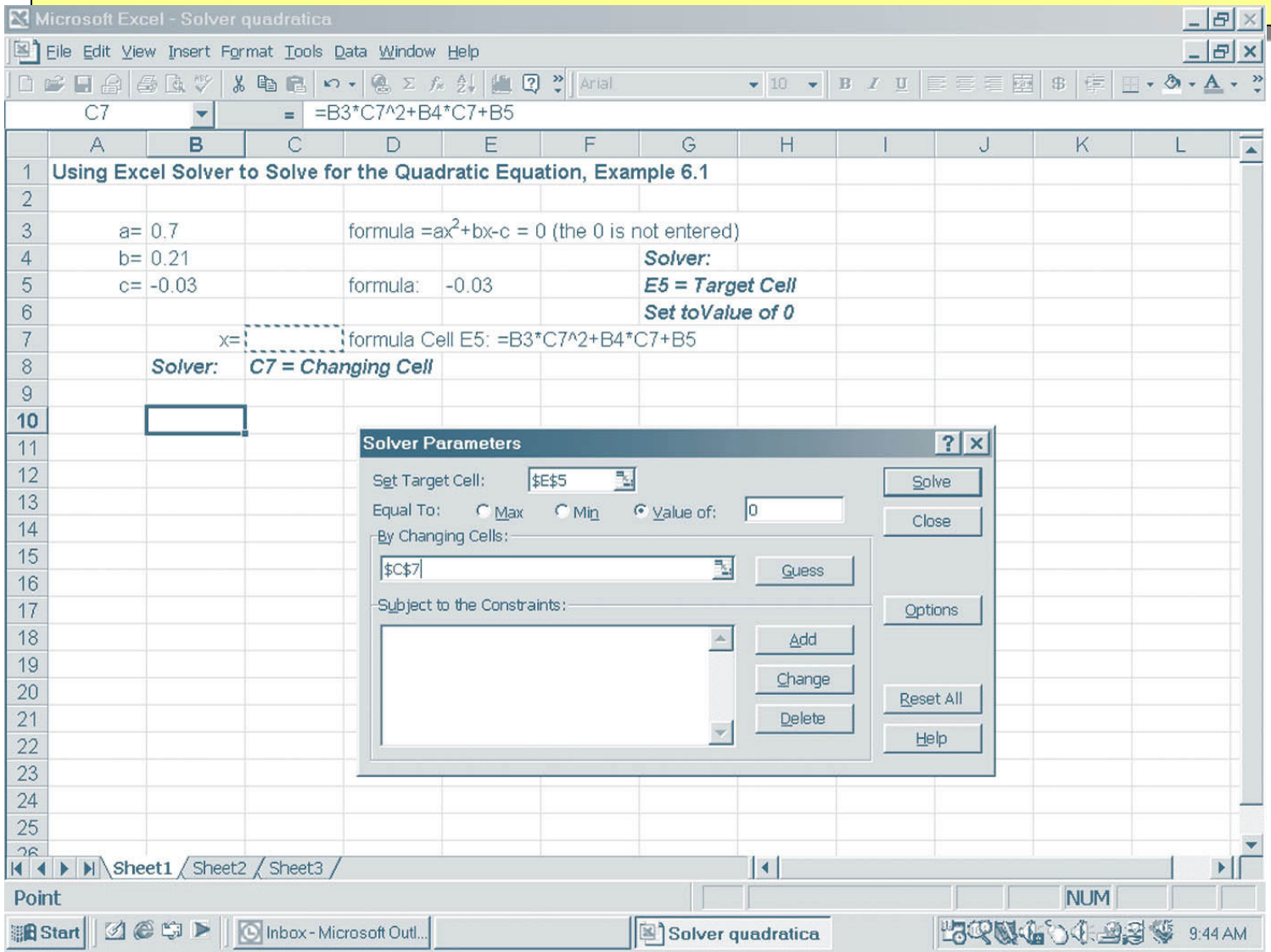
Multiple Chemical Equilibria
Example Problem #2

- Check Assumptions:

Solve $0.70x^2 + 0.21x - 0.30 = 0$. First prepare a spreadsheet containing:

1. **Cells containing the constants a, b, and c to be used in the formula, 0.70, 0.21, -0.30: (B3, B4, B5).**
2. **Cell for the variable, x, to be solved for: ($C$7).**
3. **Cell containing the formula $0.70x^2 + 0.21x - 0.30$ (ES) (do not enter = 0):**

=B3*C7^2+B4*C7+B5 (continued next slide)



Excel Solver to solve the quadratic formula for Example 6.1.

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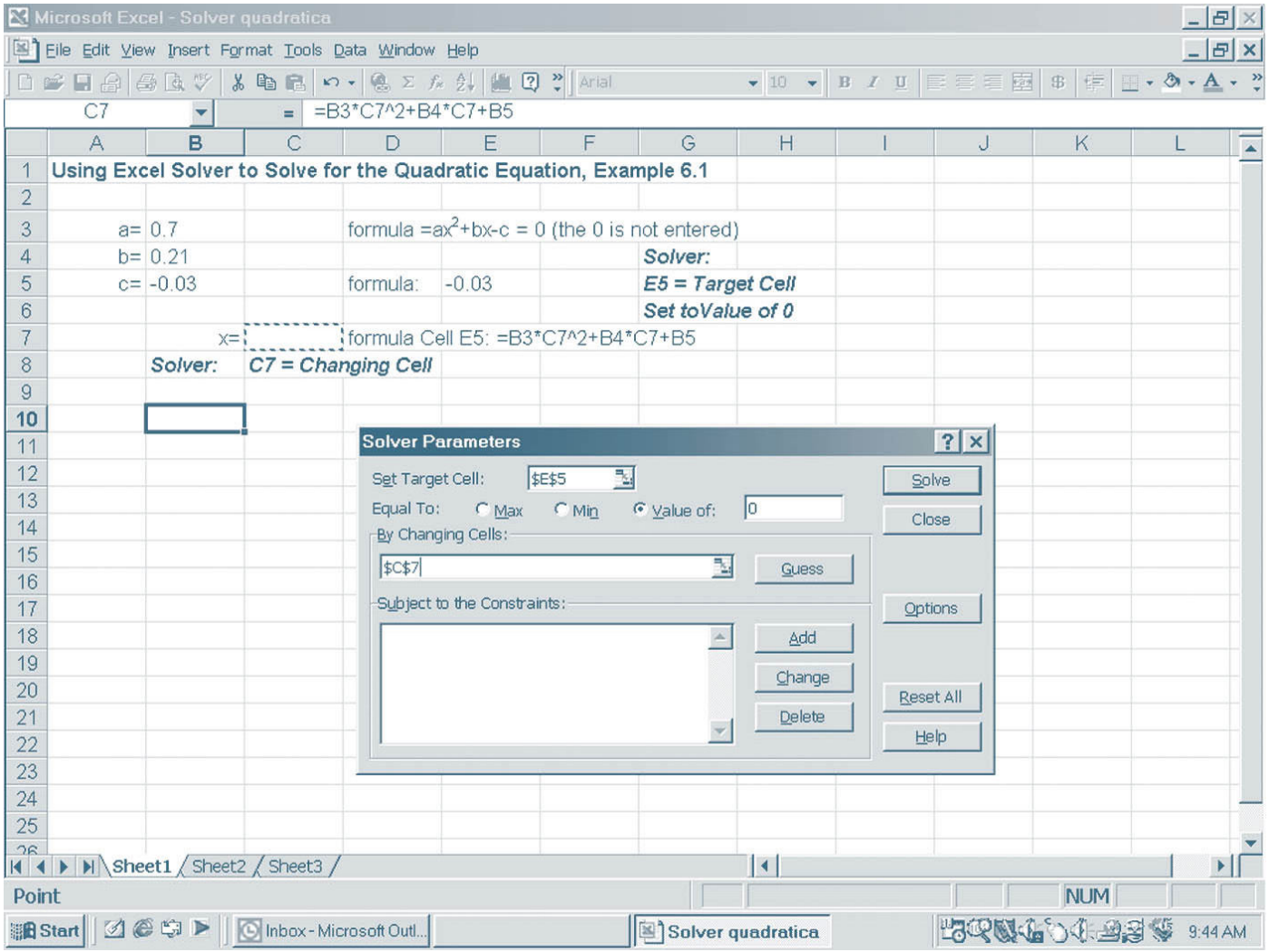
Click on Solver to open the parameters dialogue box. Need to enter 3 parameters:

1. **Set Target Cell: enter the cell containing the formula (E5).**
2. **Equal To: enter the value the equation is set to (0).**
3. **By Changing Cells: enter the cell containing the variable, x (C7).**

Then click Solve. The variable x will be changed by iteration until the equation equals zero. (continued next slide)



Excel Solver to solve the quadratic formula for Example 6.1.

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Click on Solve, and you receive a message that "Solver found a solution."

The answer is x = 0.10565.

The formula after iteration is equal to –8E-08, essentially equal to zero.

	A	B	C	D	E	F	G	H
1	**Using Excel Solver to Solve for the Quadratic Equation, Example 6.1**							
2								
3	a=	0.7		formula =ax^2+bx-c = 0 (the 0 is not entered)				
4	b=	0.21					***Solver:***	
5	c=	-0.03		formula:	-8E-08		***E5 = Target Cell***	
6							***Set toValue of 0***	
7		x=	0.10565	formula Cell E5: =B3*C7^2+B4*C7+B5				
8		***Solver:***	***C7 = Changing Cell***					

The solved quadratic formula.

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Section 07

Acid-Base Equilibria

Acid-Base Titrations

Aqueous Solution Equilibria

- Electrolytes: Substances which form ion in solution
- Strong: Mostly in ionic form in solution
  - HCl, HNO_3, NaOH, KOH
  - $HCl + H_2O \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$
- Weak: Mostly not in ionic form in solution
  - H_2CO_3, acetic acid CH_3COOH, NH_3
  - $NH_3 + H_2O \leftrightarrow NH_4^+{}_{(aq)} + OH^-_{(aq)}$

Aqueous Solution Equilibria

- Acid – Base Theories:
- Arrhenius Theory (Nobel Prize 1894)
- Acid: any substance that ionizes in water to give hydrogen ions (H^+) that associate with the solvent to increase H_3O^+ in solution.
- Base: ionizes in water to give hydroxyl ions (OH^-)

Aqueous Solution Equilibria

- Brønsted – Lowry Theory
- Acid = proton donor
- Base = proton acceptor
  - acid base acid base
  - $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
  - (strong) (weak)

  - $H_2CO_3 + H_2O \quad H_3O^+ + HCO_3^-$
  - (weak) (strong)

Aqueous Solution Equilibria

- Brønsted – Lowry Acid- Base Reactions
  - $HA + H_2O \leftrightarrow H_3O^+ + A^-$
  - $acid_1$ $base_2$ conj. $acid_2$ conj. $base_1$
  - $base_2$ + proton $\leftrightarrow$ conj. $Acid_2$
  - $acid_1 \leftrightarrow$ conj. $base_1$ + proton

  - Note: water can act as an acid or a base.
  - "amphiprotic" solvent.

A Brønsted acid is a proton donor.

A Brønsted base is a proton acceptor.

acid = H^+ + base

These are conjugate pairs.
There must be a proton acceptor before the acid releases its proton.

Table 7.1

Brønsted Acid–Base Reactions

Solvent	$Acid_1$	+	$Base_2$	→	$Acid_2$	+	$Base_1$
NH_3 (liq.)	HOAc		NH_3		NH_4^+		OAc^-
H_2O	HCl		H_2O		H_3O^+		Cl^-
H_2O	NH_4^+		H_2O		H_3O^+		NH_3
H_2O	H_2O		OAc^-		HOAc		OH^-
H_2O	HCO_3^-		OH^-		H_2O		CO_3^{2-}
C_2H_5OH	NH_4^+		$C_2H_5O^-$		C_2H_5OH		NH_3
C_6H_6	H picrate		$C_6H_5NH_2$		$C_6H_5NH_3^+$		$picrate^-$

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A "strong" electrolyte is completely dissociated.

A "weak" electrolyte is partially dissociated.

Table 7.2

Some Strong Electrolytes and Some Weak Electrolytes

Strong	Weak
HCl	$HC_2H_3O_2$ (acetic acid)
$HClO_4$	NH_3
H_2SO_4[a]	C_6H_5OH (phenol)
HNO_3	$HCHO_2$ (formic acid)
$NaOH$	$C_6H_5NH_2$ (aniline)
$NaC_2H_3O_2$	

[a] The first proton is completely ionized in dilute solution, but the second proton is partially ionized ($K_i = 10^{-2}$).

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Aqueous Solution Equilibria

- Other amphiprotic solvents:
- methanol, ethanol, glacial acetic acid
- CH_3OH CH_3CH_2OH CH_3COOH
- Some amphiprotic solutes:
- $HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-}$
- $HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$
- $HPO_4^{2-} + H_2O \leftrightarrow H_3O^+ + PO_4^{3-}$
- $HPO_4^{2-} + H_2O \leftrightarrow H_2PO_4^- + OH^-$

Aqueous Solution Equilibria

- Amphiprotic solvent self-ionization
- Autoprotolysis:
- Generic: $SH + SH \leftrightarrow SH_2^+ + S^-$
- Water: $H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$
- Methanol:
- $CH_3OH + CH_3OH \leftrightarrow CH_3OH_2^+ + CH_3O^-$
- Glacial acid acid:
- $CH_3COOH + CH_3COOH \leftrightarrow CH_3COOH_2^+ + CH_3COO^-$

Acid-Base Equilibria in Water

- Reaction: $HOAc + HOH \leftrightarrow H_3O^+ + OAc^-$
- Thermodynamic Equilibrium Constant
- Thermodynamic acidity constant, K^o_a
- $K^o_a = a_{(H_3O^+)} \cdot a_{(OAc^-)} / a_{(HOAc)} \cdot a_{(H_2O)}$
- **Thermodynamic autoprotolysis or self-ionization constant**
- $\mathbf{H_2O + H_2O \leftrightarrow H_3O^+ + OH^-}$
- $K^o_a = a_{(H_3O^+)} \cdot a_{(OH^-)} / a_{(HOH)} \cdot a_{(HOH)}$
- $K^o_a = a_{(H_3O^+)} \cdot a_{(OH^-)}$

Acid-Base Equilibria in Water

- Reaction: $HOAc + HOH \leftrightarrow H_3O^+ + OAc^-$
- Thermodynamic Equilibrium Constant
- Thermodynamic acidity constant, K^o_a
- $K^o_a = a_{(H_3O^+)} \cdot a_{(OAc^-)} / a_{(HOAc)} \cdot a_{(H_2O)}$
- **Molar equilibrium constants, K_a**
- $K^o_a = K_a \left(f_{(H_3O^+)} f_{(OAc^-)} / f_{(HOAc)} \right)$
- $K_a = [H_3O^+][OAc^-]/[HOAc]$

The pH Scale

- $pH = -\log a_{(H^+)}$ or $pH \cong -\log[H^+]$
- pAnything = - log Anything
- $pK_w = -\log K_w$ at 25°C $pK_w = 14.00$
- $K_w = [H^+][OH^-]$
- $pK_w = pH + pOH = 14$

α Values

Fractions of Dissociating Species at Given pH

- How much of each species?
- Analytical concentration: $C_{(H_3PO_4)}$
- $C_{(H_3PO_4)} = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^{-}] + [H_3PO_4]$

□ $\alpha_0 = [H_3PO_4] / C_{(H_3PO_4)}$, $\alpha_1 = [H_2PO_4^{-}] / C_{(H_3PO_4)}$,

□ $\alpha_2 = [H\,PO_4^{2-}] / C_{(H_3PO_4)}$, $\alpha_3 = [PO_4^{3-}] / C_{(H_3PO_4)}$

□ $\alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 = 1$

□ $\boldsymbol{\alpha_0 = [H^+]^3 / ([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})}$

□ $\boldsymbol{\alpha_1 = K_{a1}[H^+]^2 / ([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})}$

□ $\boldsymbol{\alpha_2 = K_{a1}K_{a2}[H^+] / ([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})}$

□ $\boldsymbol{\alpha_3 = K_{a1}K_{a2}K_{\alpha 3} / ([H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3})}$

The overlapping curves represent buffer regions.

The pH values where α_1 and α_2 are 1 represent the end points in titrating H_3PO_4.

These curves were calculated using a spreadsheet (next slide).

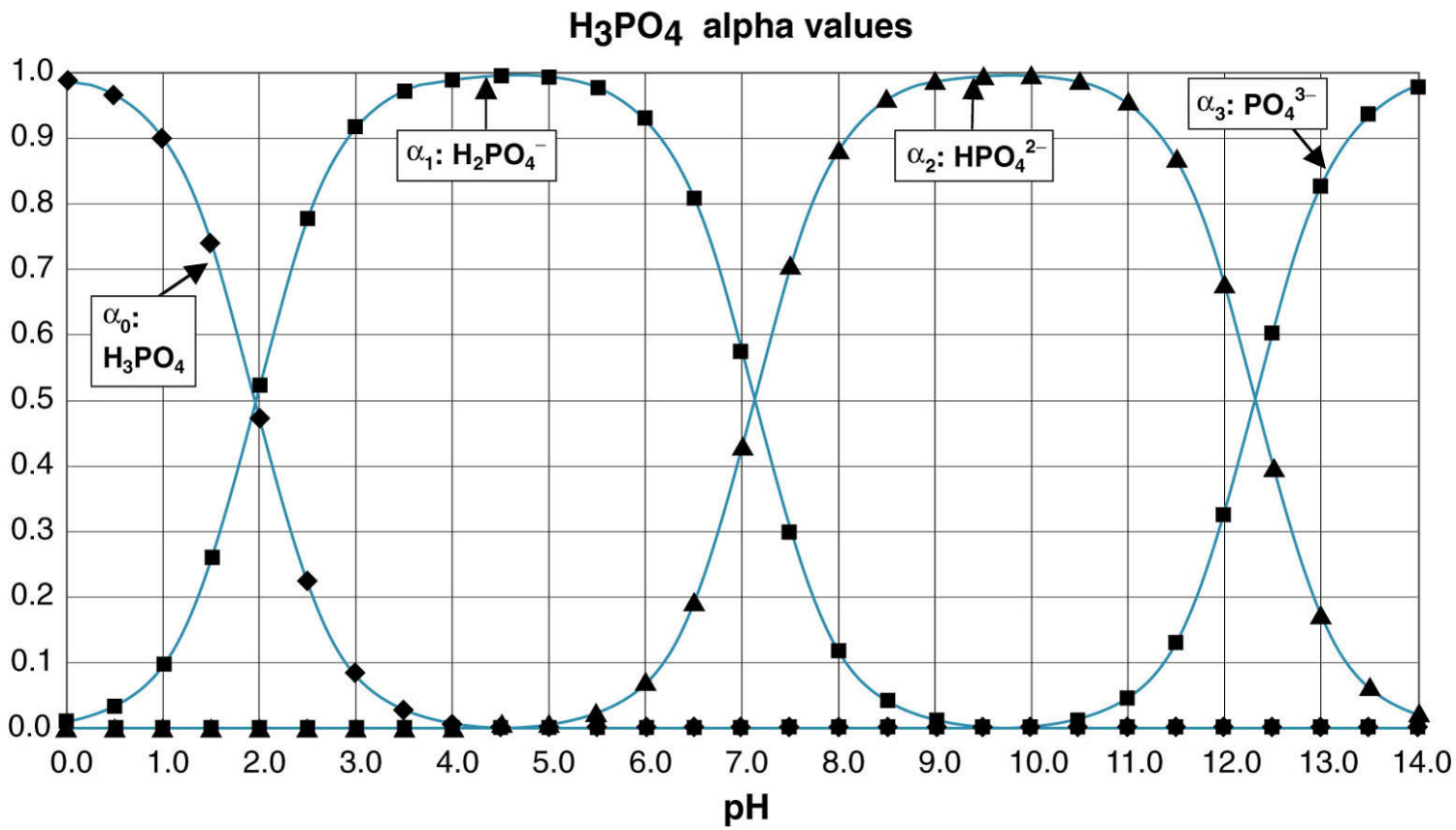

Fig. 7.1. Fractions of H_3PO_4 species as a function of pH.

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The denominator formula (in cell C6) is used for calculating α_0 to α_4 (formulas in cells D6 to G6).

Each formula is copied down in columns D to G for calculations at each pH value.

	A	B	C	D	E	F	G
1	**Calculation of alpha values for H_3PO_4 vs. pH.**						
2	Alpha (a_i) denominator = $[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}$						
3	Numerators: $\alpha_0 = [H^+]^3$; $\alpha_1 = K_{a1}[H^+]^2$; $\alpha_2 = K_{a1}K_{a2}[H^+]$; $\alpha_3 = K_{a1}K_{a2}K_{a3}$						
4	K_{a1}=	1.10E-02	K_{a2}=	7.50E-08	K_{a3}=	4.80E-13	
5	**pH**	**$[H^+]$**	**Denominator**	α_0	α_1	α_2	α_3
6	0.0	**1**	**1.01E+00**	**9.89E-01**	**1.09E-02**	**8.16E-10**	**3.92E-22**
7	0.5	0.316228	3.27E-02	9.66E-01	3.36E-02	7.97E-09	1.21E-20
8	1.0	0.1	1.11E-03	9.01E-01	9.91E-02	7.43E-08	3.57E-19
9	1.5	0.031623	4.26E-05	7.42E-01	2.58E-01	6.12E-07	9.29E-18
10	2.0	0.01	2.10E-06	4.76E-01	5.24E-01	3.93E-06	1.89E-16
11	2.5	0.003162	1.42E-07	2.23E-01	7.77E-01	1.84E-05	2.80E-15
12	3.0	0.001	1.20E-08	8.33E-02	9.17E-01	6.87E-05	3.30E-14
13	3.5	0.000316	1.13E-09	2.79E-02	9.72E-01	2.30E-04	3.50E-13
14	4.0	0.0001	1.11E-10	9.00E-03	9.90E-01	7.43E-04	3.56E-12
15	4.5	3.16E-05	1.11E-11	2.86E-03	9.95E-01	2.36E-03	3.58E-11
16	5.0	0.00001	1.11E-12	9.02E-04	9.92E-01	7.44E-03	3.57E-10
17	5.5	3.16E-06	1.13E-13	2.81E-04	9.77E-01	2.32E-02	3.52E-09
18	6.0	0.000001	1.18E-14	8.46E-05	9.30E-01	6.98E-02	3.35E-08
19	6.5	3.16E-07	1.36E-15	2.32E-05	8.08E-01	1.92E-01	2.91E-07
20	7.0	1E-07	1.93E-16	5.19E-06	5.71E-01	4.29E-01	2.06E-06
21	7.5	3.16E-08	3.71E-17	8.53E-07	2.97E-01	7.03E-01	1.07E-05
22	8.0	1E-08	9.35E-18	1.07E-07	1.18E-01	8.82E-01	4.24E-05
23	8.5	3.16E-09	2.72E-18	1.16E-08	4.05E-02	9.59E-01	1.46E-04
24	9.0	1E-09	8.36E-19	1.20E-09	1.32E-02	9.86E-01	4.73E-04
25	9.5	3.16E-10	2.62E-19	1.21E-10	4.19E-03	9.94E-01	1.51E-03
26	10.0	1E-10	8.30E-20	1.20E-11	1.33E-03	9.94E-01	4.77E-03
27	10.5	3.16E-11	2.65E-20	1.19E-12	4.15E-04	9.85E-01	1.49E-02
28	11.0	1E-11	8.65E-21	1.16E-13	1.27E-04	9.54E-01	4.58E-02
29	11.5	3.16E-12	3.00E-21	1.05E-14	3.66E-05	8.68E-01	1.32E-01
30	12.0	1E-12	1.22E-21	8.19E-16	9.01E-06	6.76E-01	3.24E-01
31	12.5	3.16E-13	6.57E-22	4.81E-17	1.67E-06	3.97E-01	6.03E-01
32	13.0	1E-13	4.79E-22	2.09E-18	2.30E-07	1.72E-01	8.28E-01
33	13.5	3.16E-14	4.22E-22	7.49E-20	2.61E-08	6.18E-02	9.38E-01
34	14.0	1E-14	4.04E-22	2.47E-21	2.72E-09	2.04E-02	9.80E-01
35	Formulas for cells in **boldface**:						
36	**Cell B6** = $[H^+]$ =	10^-A6					
37	**Cell C6**=denom.=	B6^3+$B$4*B6^2+$B$4*$D$4*B6+$B$4*$D$4*$F$4					
38	**Cell D6** = α_0 =	B6^3/C6					
39	**Cell E6** = α_1 =	($B$4*B6^2)/C6					
40	**Cell F6** = α_2 =	($B$4*$D$4*B6)/C6					
41	**Cell G6** = α_3 =	($B$4*$D$4*$F$4)/C6					
42	Copy each formula down through Cell 34						
43	Plot A6:A34 vs. D6:D34, E6:E34, F6:F34, and G6:G34 (series 1, 2, 3, and 4)						

Use of spreadsheet to calculate α-values.

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Logarithmic Concentration Diagrams
How to View Large Concentration Changes

- Write Equilibrium Reactions
- Determine System Point (log[ ], pK_a)
- Write species list
- Zero order species
- Proton condition
- Solve for all species present.

The $[H^+]$ curve has a slope of –1 and passes through the log C point –4 at pH4.

The $[OH^-]$ curve has a slope of +1 and passes through the log C point +4 at pH 10.

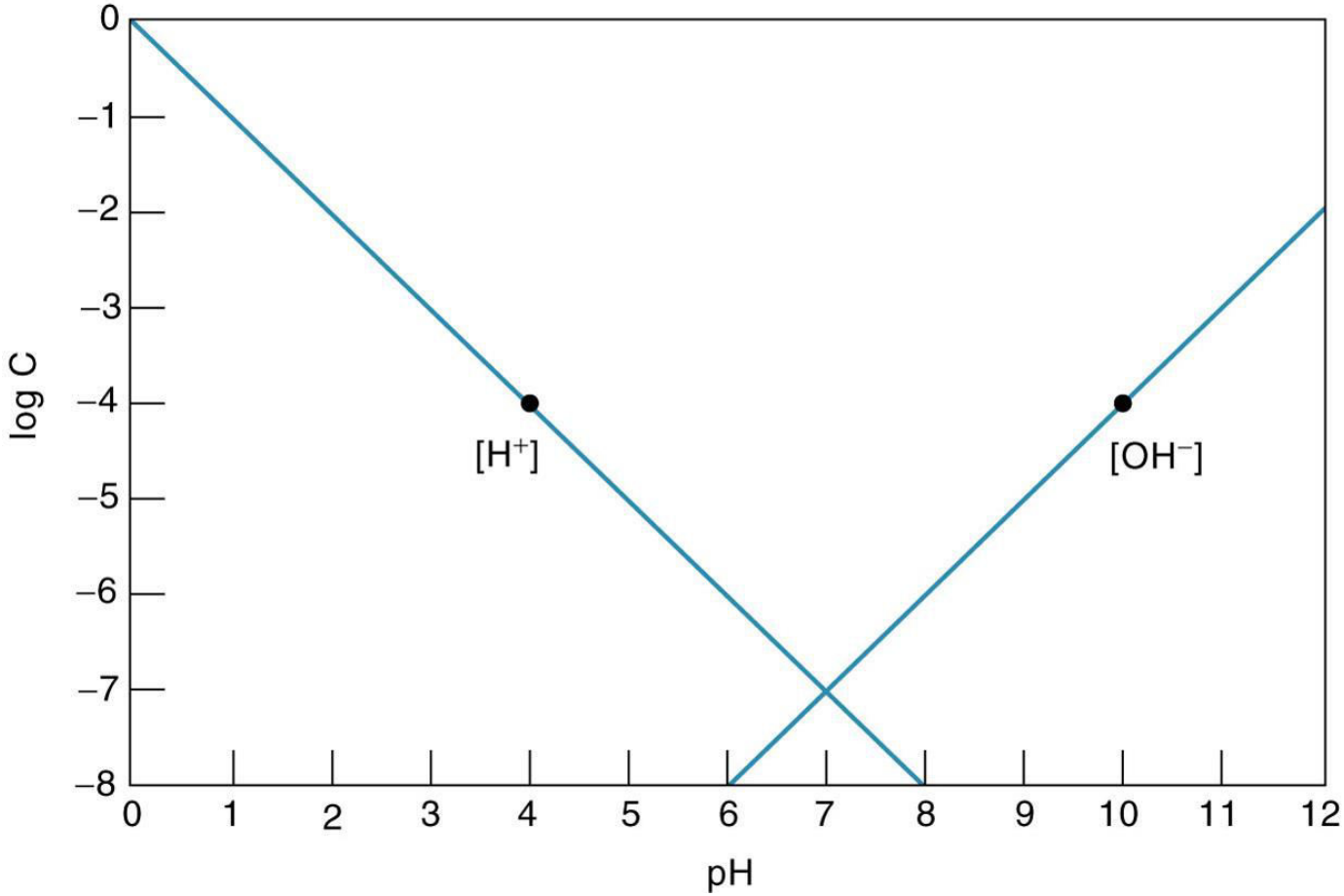

Fig. 7.2. Log concentration diagram for acid-base system. Reference points for H^+ (pH 4, log C = -4) and OH^- (pH 10, log C = -4) are marked by the circled points.

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The HOAc and OAc^- curves cross at pH = pKa, where [HOAc] = [OAc^-].

The system point is where log C = log C_{HOAc} and pH = pK_a, and can serve as a reference point in constructing the linear curves.

Reference points for HOAc (pH 2.76, log C = -4) and OAc^- (pH 6.76, log C = -4) are marked.

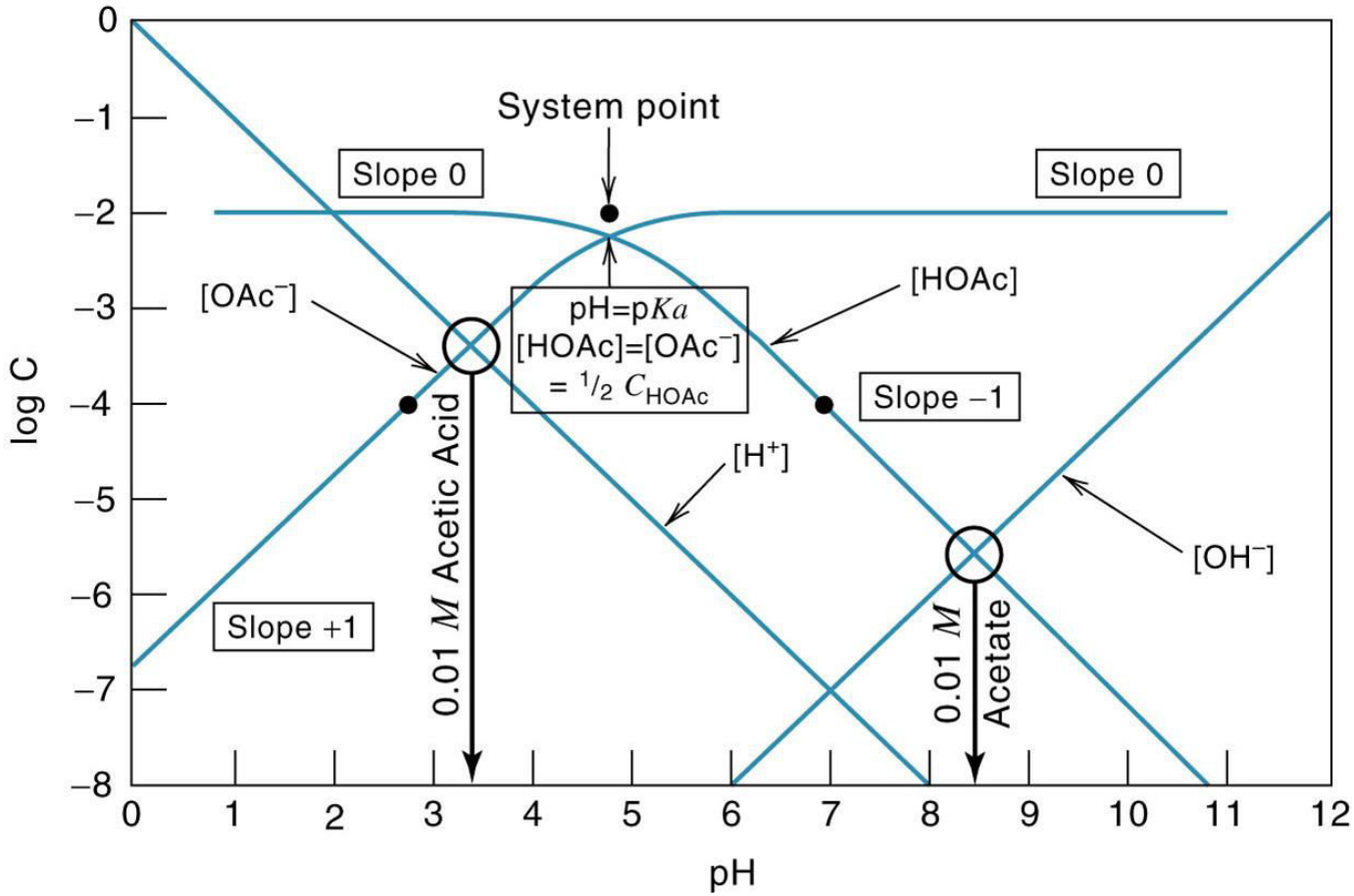

Fig. 7.3. Log concentration diagram for 0.01 M acetic acid system.

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You can prepare the log plots by entering the reference point data in a spreadsheet for given pH values, and the plot the log C values vs. pH.

The effect of concentration can be seen by changing the concentration in Cell C2.

Use of spreadsheet to prepare log curves.

	A	B	C	D	E	F	G	H
1	**Log curves for acetic acid system**							
2		C_{HOAc}=	0.01	K_a=	1.75E-05			
3	**pH**	**[HOAc]**	**log[HOAc]**	**[OAc$^-$]**	**log[OAc$^-$]**	**log[H$^+$]**	**log[OH$^-$]**	
4	0.00	**0.01**	**-2.00**		**-6.76**	**0.00**	**-14.00**	
5	4.00	0.01	-2.00		-2.76	-4.00	-10.00	
6	4.76	**0.005**	-2.30	**0.005**	**-2.30**	-4.76	-9.24	
7	5.50		**-2.74**	**0.01**	-2.00	-5.50	-8.50	
8	12.00		-9.24	0.01	-2.00	-12.00	-2.00	
9	Formulas for cells in **boldface**:							
10	**Cell B4**: [HOAc] = C_{HOac} =			$C$2	(Copy to Cell B5)			
11	**Cell C4**: log[HOAc] =			LOG10(B4)		(Copy to Cell C6)		
12	**Cell E4**: log[OAc$^-$] = log(K_a x C_{HOAc})+ pH =							
13	=	LOG10($E$2*$C$2)+A4			(Copy to Cell E5)			
14	**Cell F4**: log[H$^+$] = -pH =			(-A4)	(Copy to end)			
15	**Cell G4**: log[OH$^-$] = 14 - log[H$^+$] =				(-14-F4)	Copy to end)		
16	**Cell B6**: [HOAc] = C_{HOAc}/2 =			$C$2/2				
17	**Cell D6**: [OAc$^-$] = [HOAc] =			B6				
18	**Cell E6**: log[OAc$^-$] =		LOG10(D6)					
19	**Cell C7**: log[HOAc] = log(C_{HOAc}/K_a) - pH =				LOG10($C$2/$E$2)-A7		(Copy to Cell C8)	
20	**Cell D7**: [OAc$^-$] = C_{HOAc} =			$C$2	Copy to Cell D8)			
21	Plot A4:A8 vs. C4:C8, D4:D8, E4:E8, and F4:F8 (Series 1, 2, 3, and 4)							
22	This spreadsheet can be used for other concentrations of acetic acid just by							
23	changing the value of Cell C2.							

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It's easy to calculate the log curves from α-values at each pH.

The concentration of each species at each pH is $C_{H3PO4}\alpha_i$, so the log C values are simply $\log C_{H3PO4}\alpha_i$, which are plotted vs. pH.

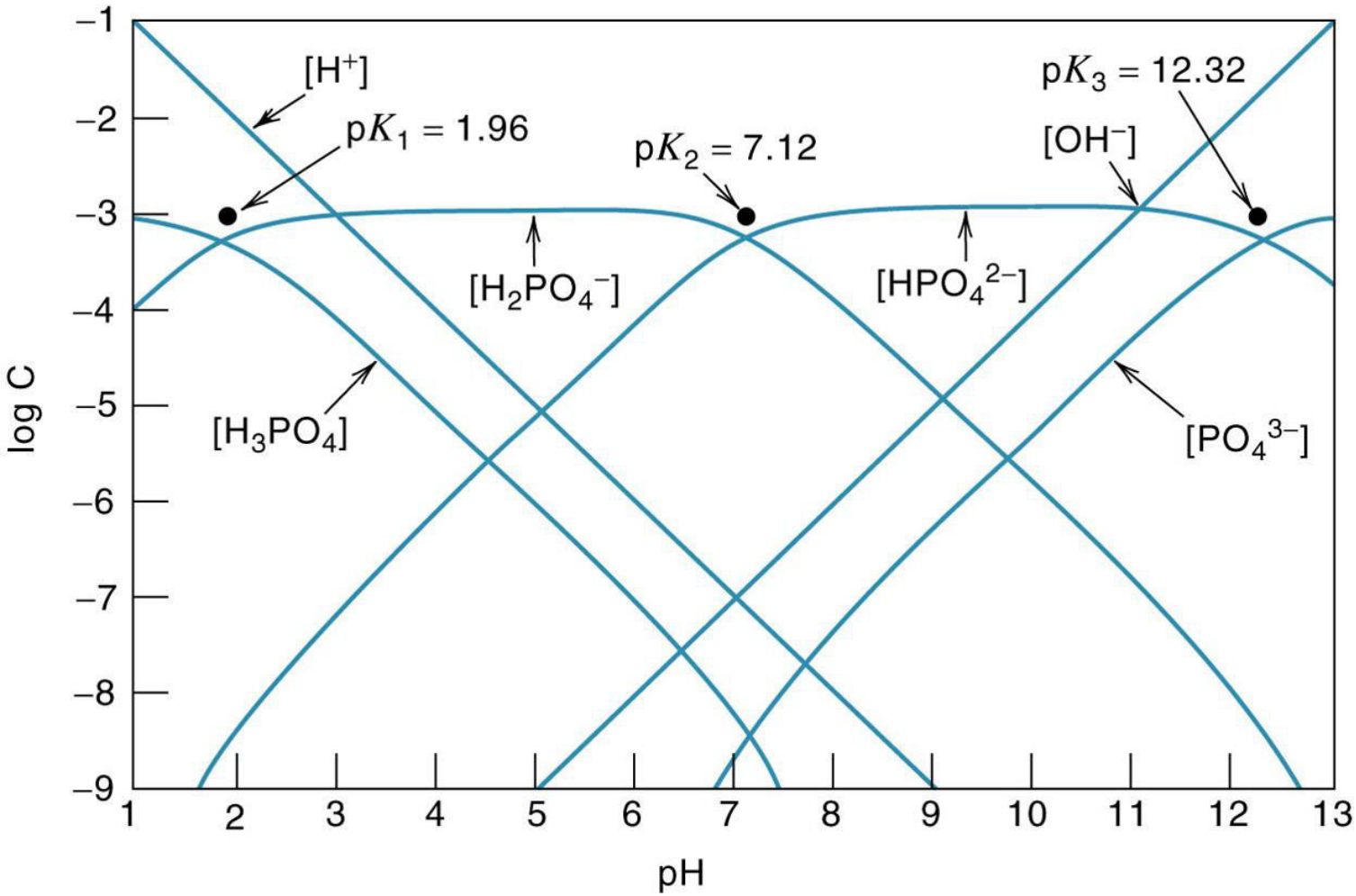

Fig. 7.4. Log concentration diagram for phosphoric acid system, at 0.001 M.

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Titration is a tried-and-true technique, capable of high precision and accuracy.

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Volumetric Analysis
Acid-Base Titrations

- **<u>Titration Curves for Strong Acids and Bases</u>**
- Consider acids & bases completely dissociated in HOH
- (e.g.) HCl, $HClO_4$, NaOH, KOH)
- Consider only one equilibrium, $K_w = [H_3O^+][OH^-]$
- Know the stoichiometry of the acid-base reaction
- (e.g. $HCl + NaOH \rightarrow HOH + Na^+ Cl^-$ S.R. =1:1

Volumetric Analysis
Acid-Base Titrations

- **<u>Titration Curves for Strong Acids & Bases</u>**
- **What is the pH before a titration begins?**
- 100.0 mL of 0.1000M HCl
- $[H_3O^+] = 1.000 \times 10^{-1}M$ $[OH^-] = K_w/[H_3O^+] = 1.000 \times 10^{-13}$
- pH = - Log $[H_3O^+]$ = 1.0000 (4s.f.) pOH = 13.0000 (4s.f.)
- **How do we find the pH of a titration before the equivalence point is reached?**
- When add 1.00 mL of 0.1000M NaOH to 100.0mL of 0.1000M HCl
- $\mathbf{[H_3O^+] = ((C_aV_a - C_bV_b) \times SR)/(V_a + V_b)}$
- $[H_3O^+]$ = (100.0mL x 0.1000M – 1.0mL x 0.1000M)x SR)/(101mL)
- $[H_3O^+] = 0.09802M$ pH = 1.0087 (4s.f.)
- $[OH^-] = K_w/[H_3O^+] = 1.020 \times 10^{-13}M$ pH = 12.9913 (4s.f.)

Volumetric Analysis
Acid-Base Titrations

- **<u>Titration Curves for Strong Acids & Bases</u>**
- **How do we find pH at equivalence point?**
- $HCl + NaOH \rightarrow HOH + Na^+ Cl^-$
- Autodissociation of water governs the pH at equivalence point.
- $HOH + HOH \leftrightarrow H_3O^+ + OH^-$ $K_w = [H_3O^+][OH^-] = 10^{-14}$
- $\mathbf{c = (K_w)^{1/2}} = 1.000 \times 10^{-7}$ pH = 7.0000 (4s.f.)
- **How do we find pH after equivalence point?**
- **Excess base add**
- $\mathbf{[OH^-] = ((C_bV_b - C_aV_a) \times SR)/(V_b + V_a)}$
- $\mathbf{[H_3O^+] = K_w/[OH^-]}$ $\mathbf{pH = -Log\,[H_3O^+]}$
- $\mathbf{pOH = -Log\,[OH^-]}$ **then pH = 14 - pOH**

A strong acid – strong base titration curve has a large end point break.

Phenolphthalein is used as an indicator because the colorless to pink transition is easy to see.

This titration curve was constructed using a spreadsheet (next slide).

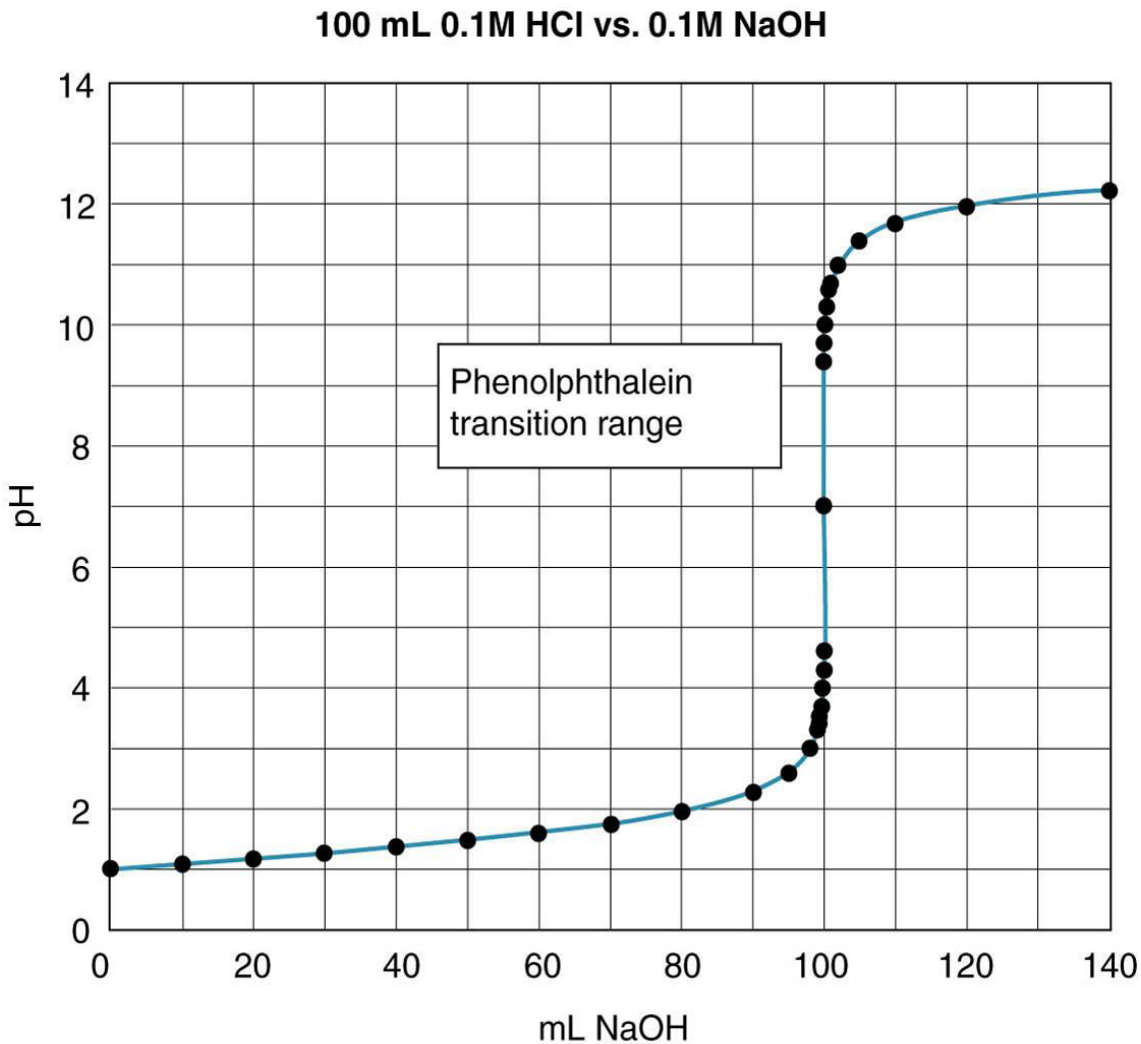

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Fig. 8.1. Titration curve for 100 mL of 0.1 M HCl versus 0.1 M NaOH.

Cell B5 calculates the concentration of unreacted HCl. Cell E5 converts the $[H^+]$ to pH.

Cell C24 is the equivalence point $[H^+]$ ($\sqrt{K_w}$).

Cell C25 calculates the concentration of excess NaOH. Cell D25 converts it to pOH, and Cell E25 to pH.

The cell formulas are copied down.

	A	B	C	D	E	F	G
1	**100.00 mL of 0.1000 M HCl vs. 0.1000 M NaOH**						
2	mL_{HCl}=	100.00	M_{HCl}=	0.1000			
3	M_{NaOH}=	0.1000	K_w=	1.00E-14			
4	**mL_{NaOH}**	**$[H^+]$**	**$[OH^-]$**	**pOH**	**pH**		
5	0.00	**0.1**			**1.00**		
6	10.00	0.0818182			1.09		
7	20.00	0.0666667			1.18		
8	30.00	0.0538462			1.27		
9	40.00	0.0428571			1.37		
10	50.00	0.0333333			1.48		
11	60.00	0.025			1.60		
12	70.00	0.0176471			1.75		
13	80.00	0.0111111			1.95		
14	90.00	0.0052632			2.28		
15	95.00	0.0025641			2.59		
16	98.00	0.0010101			3.00		
17	99.00	0.0005025			3.30		
18	99.20	0.0004016			3.40		
19	99.40	0.0003009			3.52		
20	99.60	0.0002004			3.70		
21	99.80	0.0001001			4.00		
22	99.90	5.003E-05			4.30		
23	99.95	2.501E-05			4.60		
24	100.00	**0.0000001**			7.00		
25	100.05		**2.5E-05**	**4.60**	**9.40**		
26	100.10		5E-05	4.30	9.70		
27	100.20		1E-04	4.00	10.00		
28	100.40		0.0002	3.70	10.30		
29	100.80		0.0004	3.40	10.60		
30	101.00		0.0005	3.30	10.70		
31	102.00		0.00099	3.00	11.00		
32	105.00		0.00244	2.61	11.39		
33	110.00		0.00476	2.32	11.68		
34	120.00		0.00909	2.04	11.96		
35	140.00		0.01667	1.78	12.22		
36	Formulas for cells in **boldface**:						
37	**Cell B5**: $[H^+] = (mL_{HCl} \times M_{HCl} - mL_{NaOH} \times M_{NaOH})/(mL_{HCl} + mL_{NaOH})$						
38	=	($B$2*$D$2-A5*$B$3)/($B$2+A5)			Copy through Cell B23		
39	**Cell E5** = pH =		(-LOG10(B5))		Copy through Cell E24		
40	**Cell B24** = $[H^+] = K_w^{1/2}$ =			SQRT(D3)			
41	**Cell C25** = $[OH^-] = (mL_{NaOH} \times M_{NaOH} - mL_{HCl} \times M_{HCl})/(mL_{HCl} + mL_{NaOH})$						
42	=	(A25*$B$3-$B$2*$D$2)/($B$2+A25)				Copy to end	
43	**Cell D25** = pOH = -log$[OH^-]$ =			(-LOG10(C25))		Copy to end	
44	**Cell E25** = pH = 14 - pH =			14-D25		Copy to end	

Spreadsheet calculation of Fig. 8.1.

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Compare the species and equations for the strong acid with the calculations in the previous spreadsheet.

A strong base-strong acid titration is treated similarly, but we start with excess base, and end with excess acid.

Table 8.1

Equations Governing a Strong-Acid (HX) or Strong-Base (BOH) Titration

Fraction F Titrated	Strong Acid		Strong Base	
	Present	Equation	Present	Equation
$F = 0$	HX	$[H^+] = [HX]$	BOH	$[OH^-] = [BOH]$
$0 < F < 1$	HX/X^-	$[H^+] = [\text{remaining HX}]$	BOH/B^+	$[OH^-] = [\text{remaining BOH}]$
$F = 1$	X^-	$[H^+] = \sqrt{K_w}$ (Eq. 7.13)	B^+	$[H^+] = \sqrt{K_w}$ [Eq. 7.13)
$F > 1$	OH^-/X^-	$[OH^-] = [\text{excess titrant}]$	H^+/B^+	$[H^+] = [\text{excess titrant}]$

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As the concentrations of acid and titrant decrease, the end point break decreases.

So the selection of indicator becomes more critical.

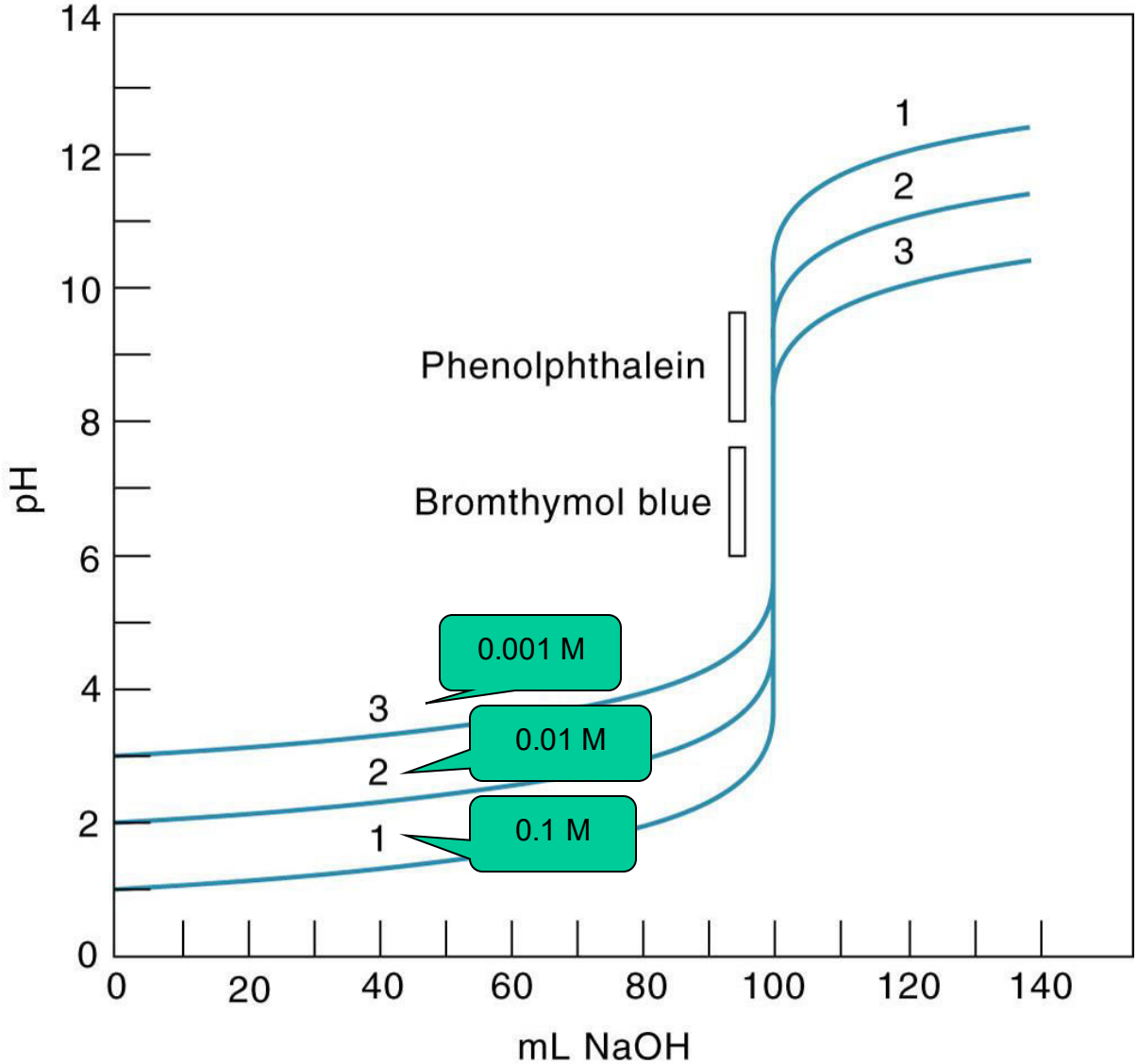

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Fig. 8.2. Dependence of the magnitude of end-point bread on concentration. The concentrations of acid and titrant are the same.

Volumetric Analysis
Acid-Base Titrations

- **<u>Titration Curves for Strong Acids & Bases</u>**
- add standard HCL solution to NaOH solution:
- $HCl + HOH \rightarrow H_3O^+ + Cl^-$ $[H_3O^+] = C_{(HCl} = C_a$
- $NaOH \rightarrow Na^+ + OH^-$ $[OH^-] = C_{(NaOH)} = C_b$
- $HCl + NaOH \rightarrow Na^+ + Cl^- + HOH$
- $H_3O^+ + OH^- \leftrightarrow HOH$ net ionic reaction
- When add 1.00 mL of 0.1000M HCl to 100 mL of 0.1000M NaOH (pH = 13.0000)

Volumetric Analysis
Acid-Base Titrations

- **<u>Titration Curves for Strong Acids & Bases</u>**
- **What is the pH before titration begins?**
- 100.0 mL of 0.1000M NaOH
- $[OH^-] = 1.000 \times 10^{-1}M$ $[H_3O^+] = K_w/[OH^-] = 1.000 \times 10^{-13}$
- pH = - Log $[H_3O^+]$ = 13.0000 (4s.f.)
- **How do we find the pH of a titration before the equivalence point is reached?**
- When add 1.00 mL of 0.1000M HCl to 100.0mL of 0.1000M NaOH
- $[OH^-] = ((C_bV_b - C_aV_a) \times SR)/(V_b + V_a)$
- $[OH^-] = (100.0mL \times 0.1000M - 1.0mL \times 0.1000M) \times SR)/(101mL)$
- $[OH^-] = 0.09802M$
- $[H_3O^+] = K_w/[OH^-] = 1.020 \times 10^{-13}M$ pH = 12.9913 (4s.f.)

Volumetric Analysis
Acid-Base Titrations

- **<u>Titration Curves for Strong Acids & Bases</u>**
- **How do we find pH at equivalence point?**
- $HCl + NaOH \rightarrow HOH + Na^+ Cl^-$
- Autodissociation of water governs the pH at equivalence point.
- $HOH + HOH \leftrightarrow H_3O^+ + OH^-$ $K_w = [H_3O^+][OH^-] = 10^{-14}$
- $\mathbf{c = (K_w)^{1/2}} = 1.000 \times 10^{-7}$ pH = 7.0000 (4s.f.)
- **How do we find pH after equivalence point?**
- **Excess acid added**
- $\mathbf{[H_3O^+] = ((C_aV_a - C_bV_b) \times SR)/(V_a + V_b)}$
- $\mathbf{pH = -Log\,[H_3O^+]}$
- $\mathbf{pOH = 14 - pH}$

This is the mirror image of the HCl titration curve.

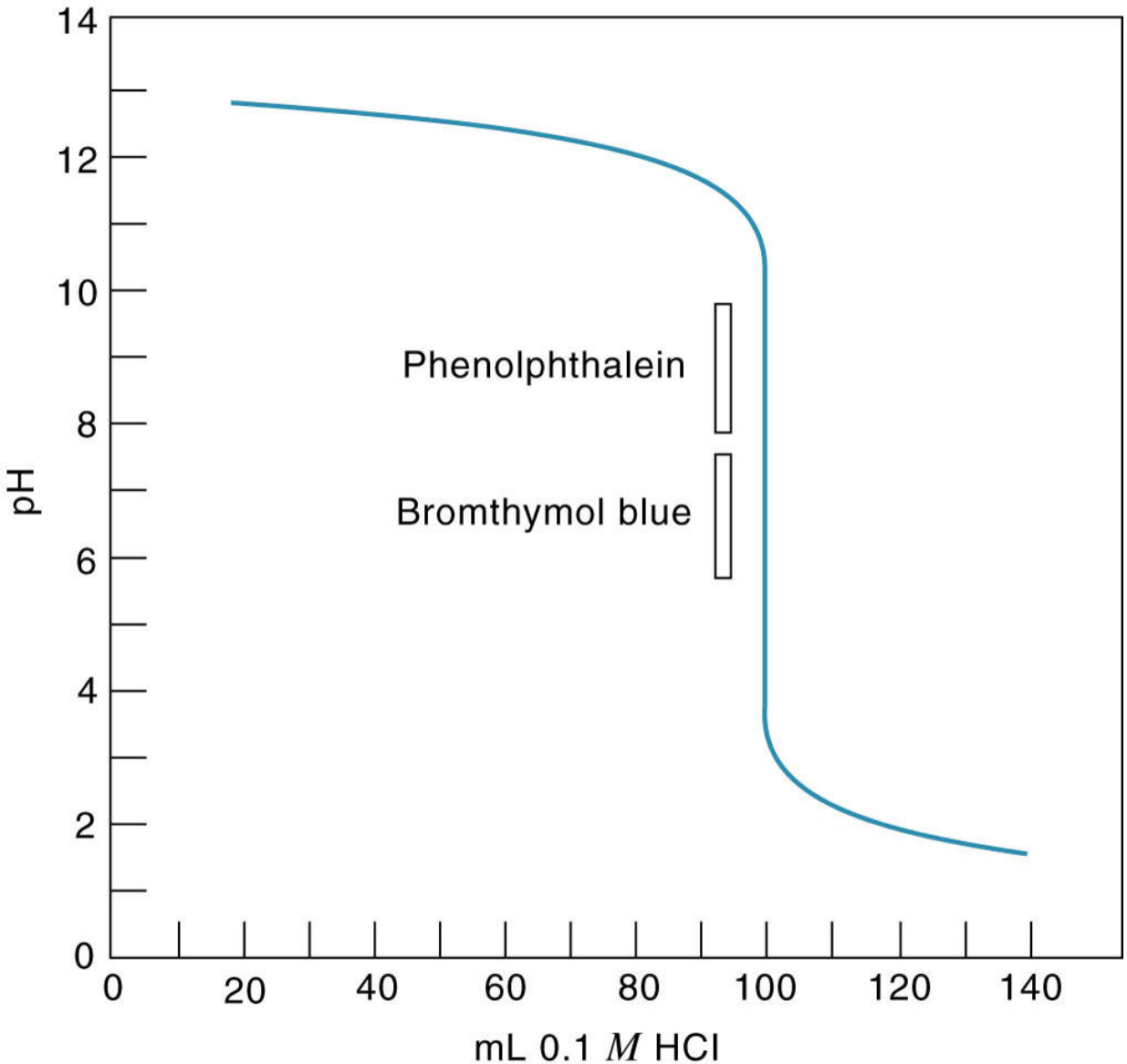

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Fig. 8.3. Titration curve for 100 mL of 0.1 M NaOH versus 0.1 M HCl.

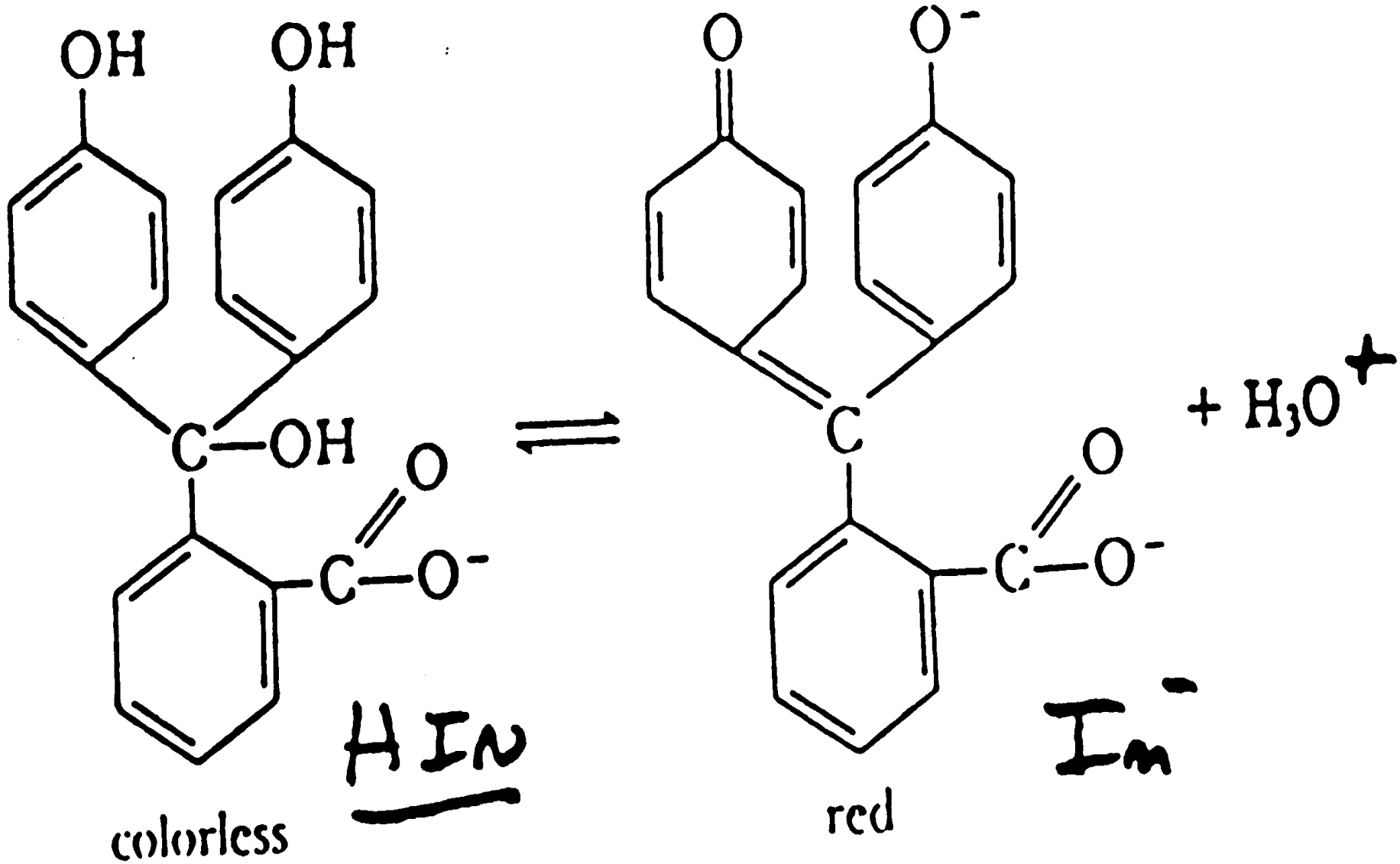
Volumetric Analysis
Acid-Base Titrations

- **Acid-Base Color Indicators**
- Organic weak acids or bases
- Strongly colored acid and/or conjugate base form(*)
- Distinct color change from acid to base form
- **Acid** **conj. Base**
- **HIn** $+ OH^- \leftrightarrow$ **In^-** + HOH
- **Color A** **Color B**

- (*) Only very small amount HIn required to give color ($<< 10^{-3}$ M)
- Assume presence of HIn does not affect pH of acids/bases $> 10^{-3}$ M

Volumetric Analysis
Acid-Base Titrations

- **<u>Acid-Base Color Indicators</u>**
- <u>Color A</u> <u>Color B</u>
- $HIn + HOH \leftrightarrow In^- + H_3O^+$ $K_a = [H_3O^+][In^-]/[HIn]$
- $[H_3O^+] = K_a x\ [HIn]/[In^-]$
- NOTE:
- $[HIn]/[In^-]$ determines solution color
- $[H_3O^+]$ determines $[HIn]/[In^-]$
- High $[HIn]/[In^-]$ (>10:1) gives Color A
- Low $[HIn]/[In^-]$ (<1:10) gives Color B



Phenolphthalein

Volumetric Analysis
Acid-Base Titrations

- **At what pH does an indicator change color?**
- **Color A** **Color B**
- $HIn + HOH \leftrightarrow In^- + H_3O^+$ $K_a = [H_3O^+][In^-]/[HIn]$
- $[H_3O^+] = K_a x\ [HIn]/[In^-]$
- $\mathbf{pH = pK_a + Log([In^-]/[HIn])}$
- Color A, $[In^-]/[HIn] < 1:10$ $pH < pK_a + Log(1/10)$
- Color A, $pH = pK_a - 1$
- Color B, $[In^-]/[HIn] > 10:1$ $pH > pK_a + Log(10/1)$
- Color B, $pH = pK_a + 1$
- **Indicator color change occurs at $pH = pK_a +/- (1)$**

pH transition range = $pK_a \pm 1$.

We select an indicator with a pK_a near the equivalence point pH.

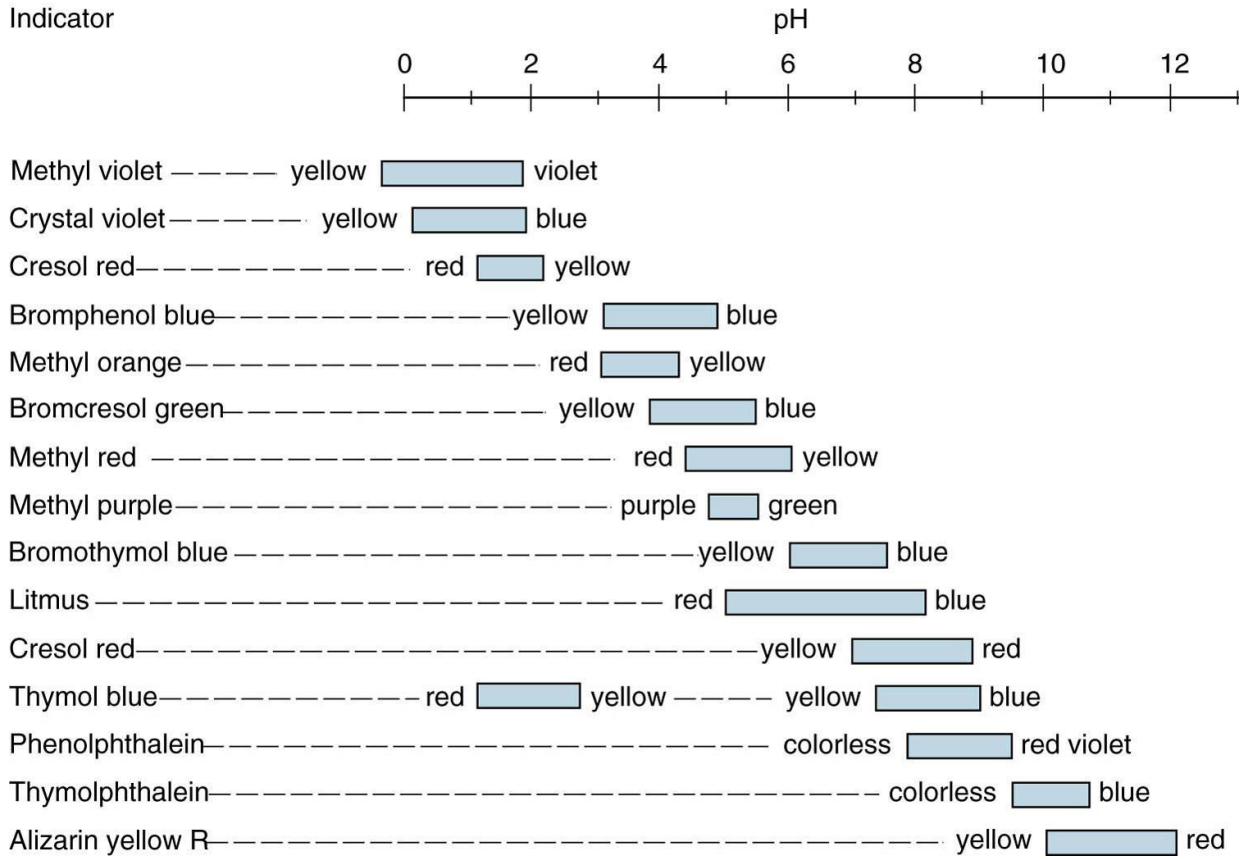


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Fig. 8.4. pH transition ranges and colors of some common indicators.

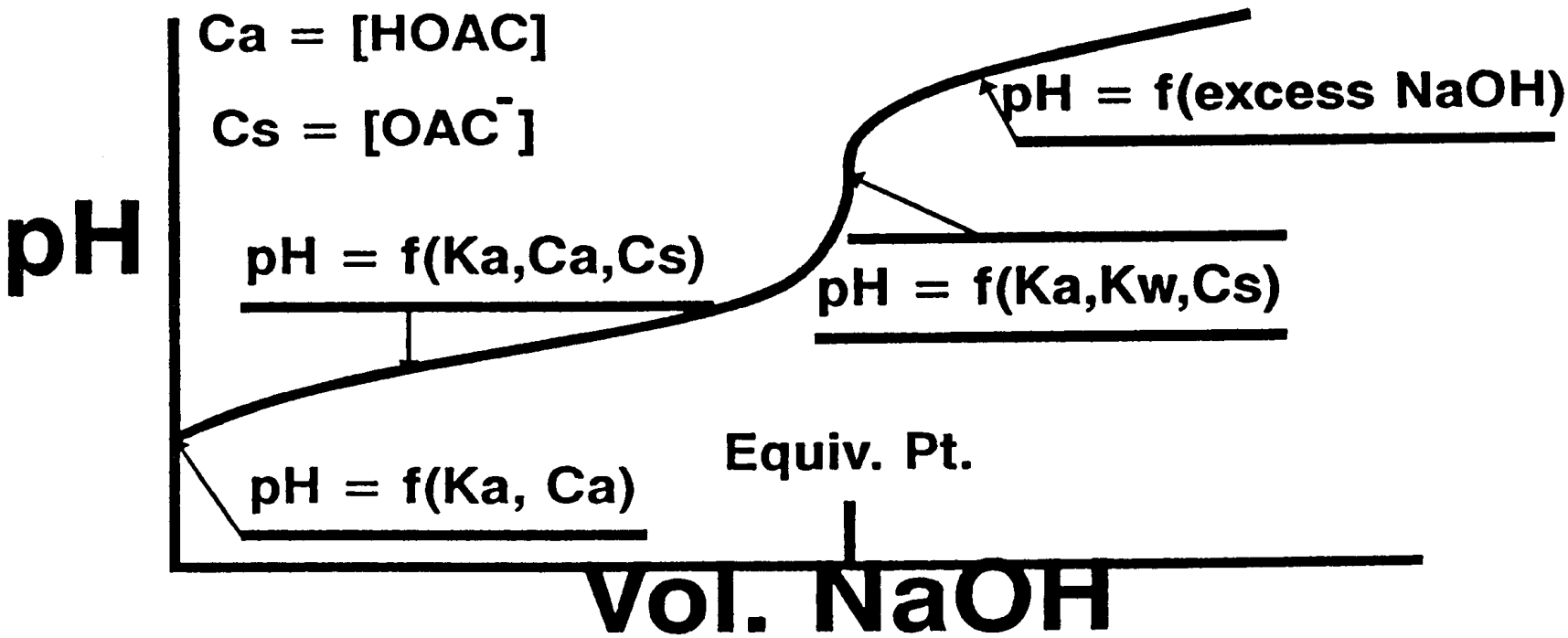
Volumetric Analysis

Acid-Base Titrations

Titration Curves for Weak Acids and Weak Bases

e.g., add standard NaOH solution to acetic acid:

$$HOAC + HOH \rightleftharpoons H_3O^+ + OAC^- \quad Ka = 1.75 \times 10^{-5}$$



Volumetric Analysis
Acid-Base Titrations

- **<u>Titrating 50.0mL 0.1000M HOAc with 0.1000M NaOH:</u>**
- HOAc + NaOH → HOH + OAc^- + Na^+
- Initial Concentration of HOAc = C_{HA} = 0.1000M
- Equilibrium Concentration HOAc = C_a
- Equilibrium Concentration OAc^- = C_s
- (a) **<u>Initial pH:</u>** $[H_3O^+] \cong (K_a \times C_{HA})^{1/2} = (1.75 \times 10^{-5} \times 0.1000)^{1/2}$
- $[H_3O^+] = 1.323 \times 10^{-3}$ M pH = 2.8785 (4 s.f.)
- **(b) <u>Buffer Region:</u>** (e.g. 10.0 mL NaOH added):
- $[OAc^-] = C_s = C_bV_b/(V_a + V_b)$; $C_a = (C_{HA}V_a - C_bV_b)/(V_a + V_b)$
- C_s = (0.1000M x 10.0mL)/(60.0mL) = 0.0167M C_a = 0.0667M
- $[H_3O^+] = K_a[HOAc]/[OAc^-] = K_a C_a/C_s$
- $[H_3O^+] = (1.75 \times 10^{-5})(0.0667/0.0167) = 6.99 \times 10^{-5}$M pH = 4.1556

Volumetric Analysis
Acid-Base Titrations

- **<u>Titrating 50.0mL 0.1000M HOAc with 0.1000M NaOH:</u>**
- $HOAc + NaOH \rightarrow HOH + OAc^- + Na^+$

- (c) **<u>Equivalence Point pH:</u>** $[HOAc] \cong 0 = C_a$
- $\mathbf{[OAc^-] \cong C_b V_b/(V_a+V_b) = C_s} = 0.1000M/2 \cong 0.05000M$
- $OAc^- + HOH \leftrightarrow HOAc + OH^-$ $K_b = K_w/K_a = 5.71 \times 10^{-10}$
- $[HOAc][OH^-] = K_b[OAc^-] = K_b C_s$; $[HOAc] \cong [OH^-]$
- $[OH^-] \cong (K_b C_s)^{1/2} \cong (5.71 \times 10^{-10}(0.05000))^{1/2} = 5.34 \times 10^{-6}M$
- $\mathbf{[H_3O^+] = K_w/[OH^-]} = 1.87 \times 10^{-9}M$; **pH = 8.728 (3 s.f.)**

Volumetric Analysis
Acid-Base Titrations

- **<u>Titrating 50.0mL 0.1000M HOAc with 0.1000M NaOH:</u>**
- $HOAc + NaOH \rightarrow HOH + OAc^- + Na^+$
- (d) **<u>pH After Equivalence Point:</u>**
- Bases present are OAc^- & OH^- (from excess NaOH)
- Excess NaOH is stronger base and determines pH
- Excess $[OH^-] = (C_bV_b - C_{HA}V_a)/(V_a + V_b)$
- **At 0.1 mL past equivalence point. V_b = 50.1 mL**
- $[OH^-] = ((0.1000M)(50.1mL) - (0.1000M)(50.0mL))/(100.1mL)$
- $[OH^-] = 9.99 \times 10^{-5}M$; $[H_3O^+] = K_w/[OH^-] = 1.001 \times 10^{-10}$
- pH = 9.9996 (4 s.f.)

A weak acid gives a smaller end point break.. A stong base titrant is always used.

We start with HOAc. Then we have a buffer mixture of OAc^- and HOAc.

At the equivalence point, we have OAc^-, a weak base.

Beyond the equivalence point, we have excess NaOH (suppresses OAc^- hydrolysis), and the curve follows that for a strong acid titration.

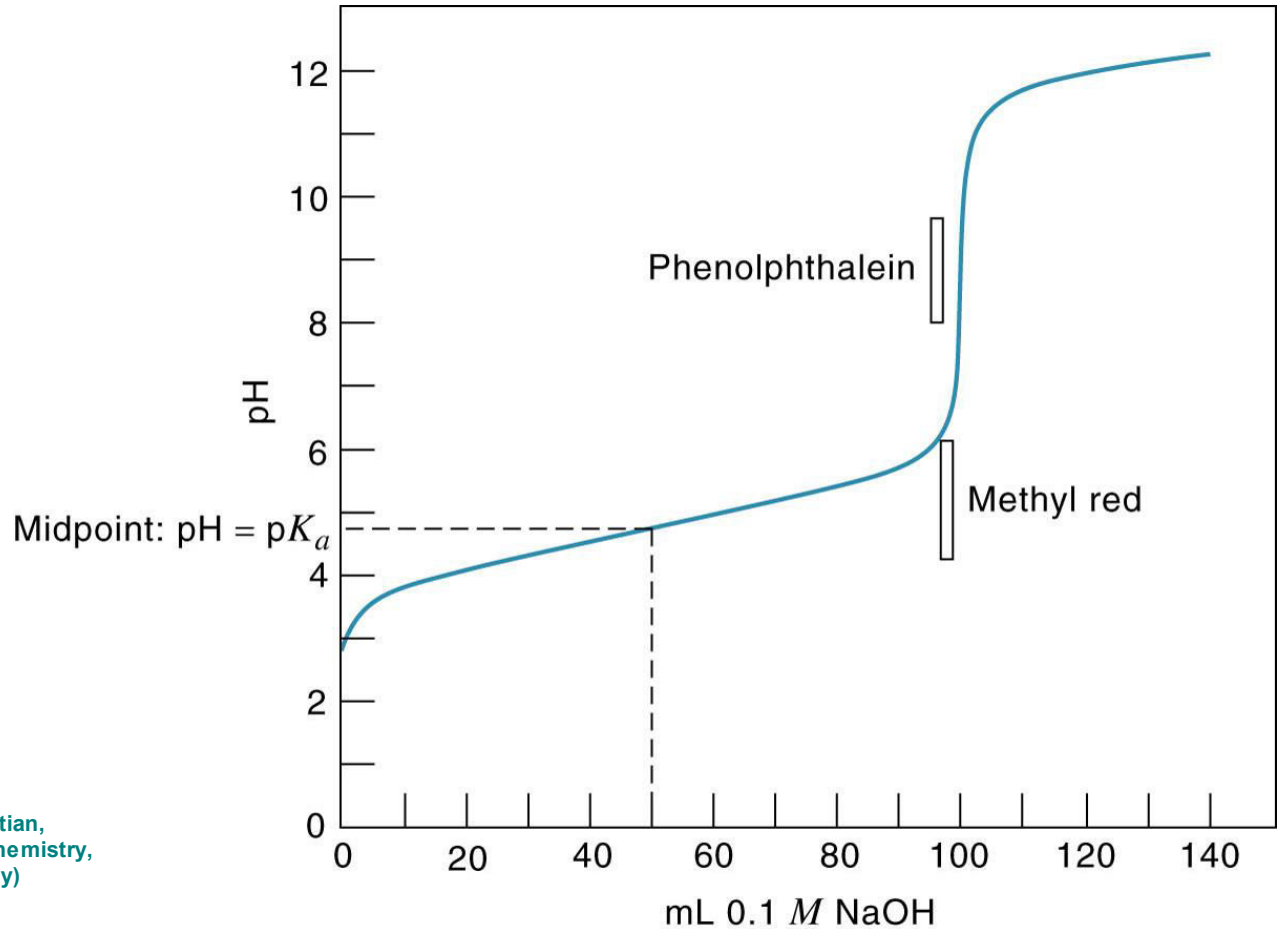


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Fig. 8.5. Titration curve for 100 mL 0.1 M HOAc versus 0.1 M NaOH.

For a weak acid, we start with ionization of HA.

In the buffer region, use the Henderson-Hasselbalch equation.

At the equivalence point, A^- hydrolyzes as a weak base.

Beyond the equivalence point, excess OH^- dominates.

A weak base is treated similarly, but beginning with base and ending with acid.

Table 8.2

Equations Governing a Weak-Acid (HA) or Weak-Base (B) Titration

Fraction F Titrated	Weak Acid		Weak Base	
	Present	Equation	Present	Equation
$F = 0$	HA	$[H^+] = \sqrt{K_a \cdot C_{HA}}$ (Eq. 7.20)	B	$[OH^-] = \sqrt{K_b \cdot C_B}$ (Example 7.8)
$0 < F < 1$	HA/A^-	$pH = pK_a + \log \frac{C_{A^-}}{C_{HA}}$ (Eq. 7.45)	B/BH^+	$pH = (pK_w - pK_b) + \log \frac{C_B}{C_{BH^+}}$ (Eq. 7.56)
$F = 1$	A^-	$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}}$ (Eq. 7.32)	BH^+	$[H^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{BH^+}}$ (Eq. 7.39)
$F > 1$	OH^-/A^-	$[OH^-]$ = [excess titrant]	H^+/BH^+	$[H^+]$ = [excess titrant]

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The buffer regions are about the same for all concentrations.

The equivalence point pH increases with increasing concentration.

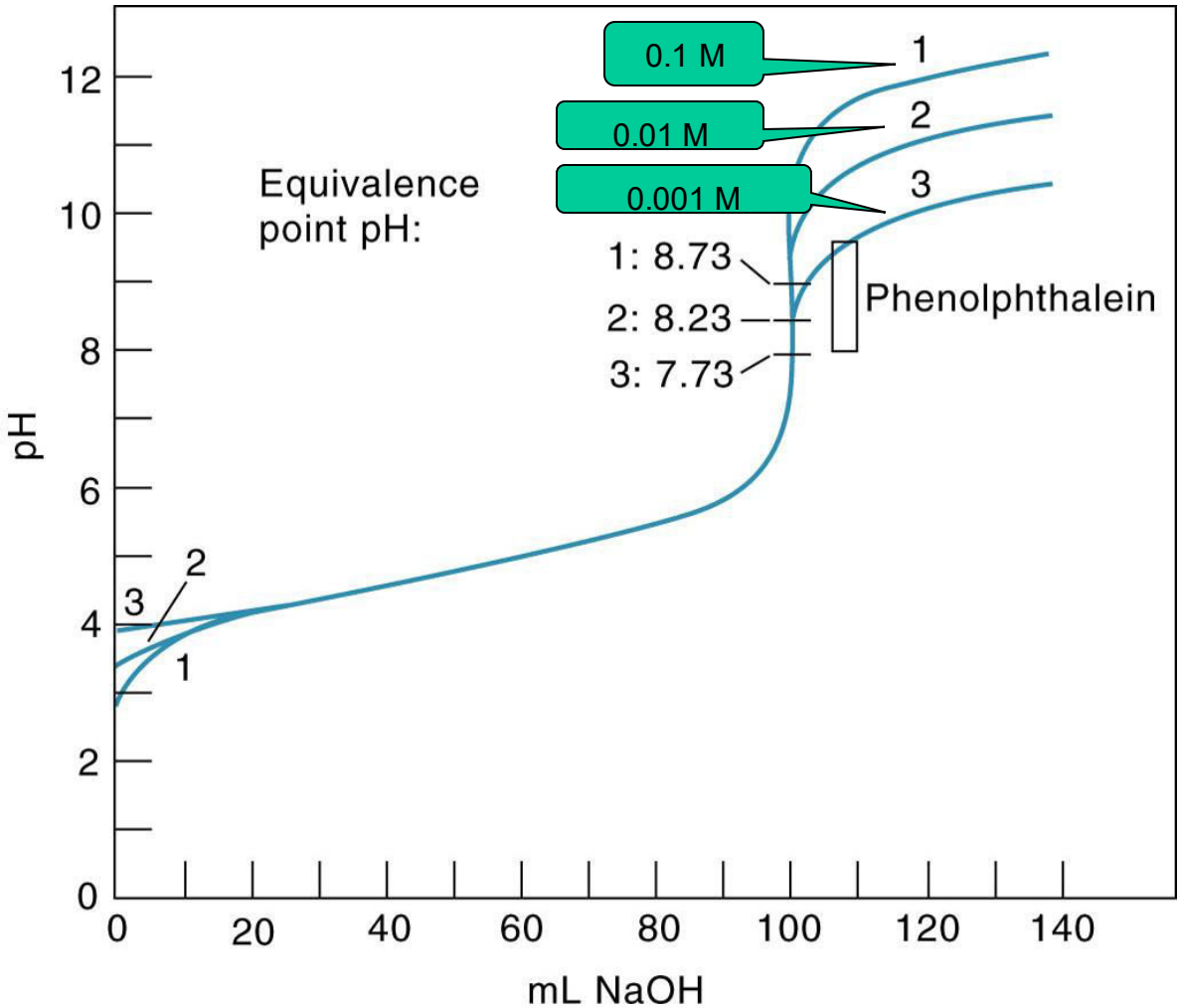

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Fig. 8.6. Dependence of titration curve of 100 mL acetic acid on concentration. NaOH concentration the same as HOAc concentration.

Cell E4 calculates $[H^+]$ from unreacted HOAc.

Cells C5 and D5 calculate the concentrations of HOAc and OAc^- in the buffer region.

Cell F19 calculates the concentration of OAc^- at the equivalence point.

The cell formulas are copied down.

Columns G and H calculate the corresponding pOH and pH.

	A	B	C	D	E	F	G	H
1	50.00 mL 0.05000M HOAc vs. 0.05000M NaOH.						K_w:	1.00E-14
2	mL_{HOAc}:	50.00	M_{HOAc}:	0.05000	M_{NaOH}:	0.05000	K_a:	1.75E-05
3	mL_{NaOH}	Solution	[HOAc]	$[OAc^-]$	$[H^+]$	$[OH^-]$	pOH	pH
4	0.00	HOAc			**0.0009354**			**3.03**
5	2.00	HOAc/OAc^-	**0.046154**	**0.001923**				**3.38**
6	5.00	HOAc/OAc^-	0.040909	0.004545				3.80
7	10.00	HOAc/OAc^-	0.033333	0.008333				4.15
8	15.00	HOAc/OAc^-	0.026923	0.011538				4.39
9	20.00	HOAc/OAc^-	0.021429	0.014286				4.58
10	25.00	HOAc/OAc^-	0.016667	0.016667				4.76
11	30.00	HOAc/OAc^-	0.0125	0.01875				4.93
12	35.00	HOAc/OAc^-	0.008824	0.020588				5.12
13	40.00	HOAc/OAc^-	0.005556	0.022222				5.36
14	45.00	HOAc/OAc^-	0.002632	0.023684				5.71
15	48.00	HOAc/OAc^-	0.00102	0.02449				6.14
16	49.00	HOAc/OAc^-	0.000505	0.024747				6.45
17	49.50	HOAc/OAc^-	0.000251	0.024874				6.75
18	49.95	HOAc/OAc^-	2.5E-05	0.024987				7.76
19	50.00	OAc^-				**3.77964E-06**	**5.42**	**8.58**
20	50.05	OH^-				**2.49875E-05**	4.60	9.40
21	50.50	OH^-				0.000248756	3.60	10.40
22	51.00	OH^-				0.00049505	3.31	10.69
23	52.00	OH^-				0.000980392	3.01	10.99
24	55.00	OH^-				0.002380952	2.62	11.38
25	60.00	OH^-				0.004545455	2.34	11.66
26	65.00	OH^-				0.006521739	2.19	11.81
27	70.00	OH^-				0.008333333	2.08	11.92
28	Formulas for cells in **boldface**:							
29	**Cell E4:**	$[H^+] = (K_a[HOAc])^{1/2} =$		SQRT($H$2*$D$2)				
30	**Cell H4:**	pH = -log$[H^+]$ =		(-LOG10(E4))				
31	**Cell C5:**	[HOAc] = $(mL_{HOAc} \times M_{HOAc} - mL_{NaOH} \times M_{NaOH})/(mL_{HOAc} + mL_{NaOH})$						
32	=	($B$2*$D$2-A5*$F$2)/($B$2+A5)			(Copy through Cell C18)			
33	**Cell D5:**	[OAc-] = $(mL_{NaOH} \times M_{NaOH})/(mL_{HOAc} + mL_{NaOH})$						
34	=	(A5*$F$2)/($B$2+A5)		(Copy through Cell D18)				
35	**Cell H5:**	pH = pKa + log([OAc-]/HOAc])						
36	=	(-LOG10($H$2)+LOG10(D5/C5))			(Copy through Cell H18)			
37	**Cell F19:**	$[OH^-] = (K_w[OAc^-]/K_a)^{1/2}$						
38	=	SQRT($H$1*($D$2/2)/$H$2)						
39	**Cell G19:**	pOH = -log$[OH^-]$ =		(-LOG10(F19))		(Copy to end)		
40	**Cell H19:**	pH = 14 - pOH =		14-G19	(Copy to end)			
41	**Cell F20:**	$[OH^-] = (mL_{NaOH} \times M_{NaOH} - mL_{HOAc} \times M_{HOAc})/(mL_{HOAc} + mL_{NaOH})$						
42	=	(A20*$F$2-$B$2*$D$2)/($B$2+A20)				(Copy to end)		

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Acid-Base Buffers
Buffer Region of Titration Curves

- **<u>Titrating 50.0mL 0.1000M HOAc with 0.1000M NaOH:</u>**
- HOAc + NaOH → HOH + OAc^- + Na^+
- **<u>Buffer Region</u>** (e.g. 25.0mL NaOH added):
- $[OAc^-] = C_s = C_bV_b/(V_a+V_b)$; $C_a = (C_{HA}V_a - C_bV_b)/(V_a+V_b)$
- $C_s = (0.1M)(25.0mL)/(75.0mL) = 0.0333M$; $C_a = 0.0333M$
- $\mathbf{[H_3O^+] = K_a[HOAc]/[OAc^-] = K_aC_a/C_s}$
- $[H_3O^+] = (1.75 \times 10^{-5})(0.0333/0.0333) = 1.75 \times 10^{-5}$ M
- pH = - Log$[H_3O^+]$ = 4.757 (3s.f.)
- **Note: at 50% titration, ½ neutralization point, pH = pK_a**

Acid/Base Buffers
General Relationships

- **<u>Buffer solution from a weak acid & conj. base:</u>**
- $HA + HOH \leftrightarrow H_3O^+ + A^-$
- Prepare solution of HA, NaA at C_{HA}, C_{NaA}
- For $K_a < 10^{-3}$, $[HA] \cong C_{HA}$; $[A^-] \cong c$
- $[H_3O^+] = K_a[HA]/ [A^-] = K_a C_{HA}/ C_{NaA}$

- **Henderson – Hasselbalch Equation**
- $\mathbf{pH = pK_a + Log(C_{NaA}/ C_{HA})}$

Acid/Base Buffers

When the Henderson-Hasslebalch (H-H) Equation fails

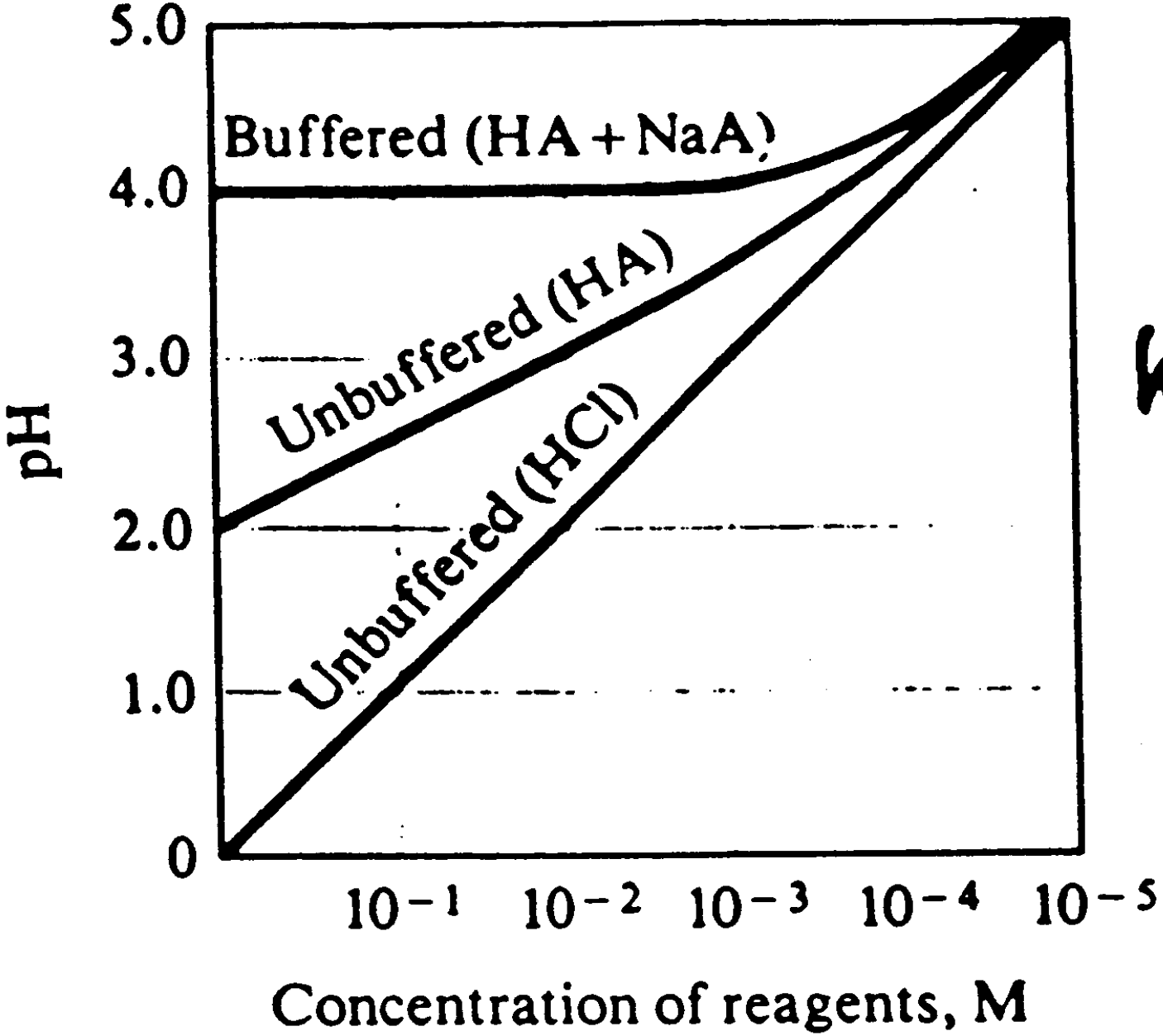
- Calculating buffer pH when $C_{HA} <> [HA]$; $C_{NaA} <> [A^-]$:
- (1) $HA + HOH \leftrightarrow H_3O^+ + A^-$
- (2) $A^- + HOH \leftrightarrow HA + OH^-$
- From Equations (1) and (2):
- (3) $[HA] = C_{HA} + [OH^-] - [H_3O^+]$
- (4) $[A^-] = C_{NaA} - [OH^-] + [H_3O^-]$
- If $[OH^-]$ or $[H_3O^-]$ can be neglected, use the rigorous form of the buffer equation:
- (5) $pH = pK_a + Log([A^-]/[HA])$
- Estimate $[H_3O^-]$ & $[OH^-]$ using H-H Equation, and K_w.
- Substitute into equations (3), (4); then use equation (5)

Acid/Base Buffers
Example Problem

- Add 25.0mL 0.100M NaOH to 50.0mL 0.100M HNO_2
- $K_a = 7.10 \times 10^{-4}$; pKa = 3.149 (3s.f.)
- C_{NaA} = (25.0mL)(0.100M)/(75.0mL) = 0.0333M
- C_{HA} = (50.0mL-25.0mL)(0.100M)/(75.0mL) = 0.0333M
- <u>From H-H Eqn:</u> pH = pK_a + Log ((0.0333)/(0.0333) = **<u>3.149</u>**
- $[H_3O^+] = 7.10 \times 10^{-4}$M ; $[OH^-] = 1.41 \times 10^{-11}$M
- <u>Considering deviations from H-H assumptions:</u>
- $[HA] = C_{HA} + [OH^-] - [H_3O^+] = 0.0325$M
- $[A^-] = C_{NaA} + [H_3O^+] - [OH^-] = 0.0340$M
- pH = pK_a + Log($[A^-]$/ [HA]) = 3.149 + 0.0196 = **<u>3.168</u>**

Acid/Base Buffers
Properties of Buffers

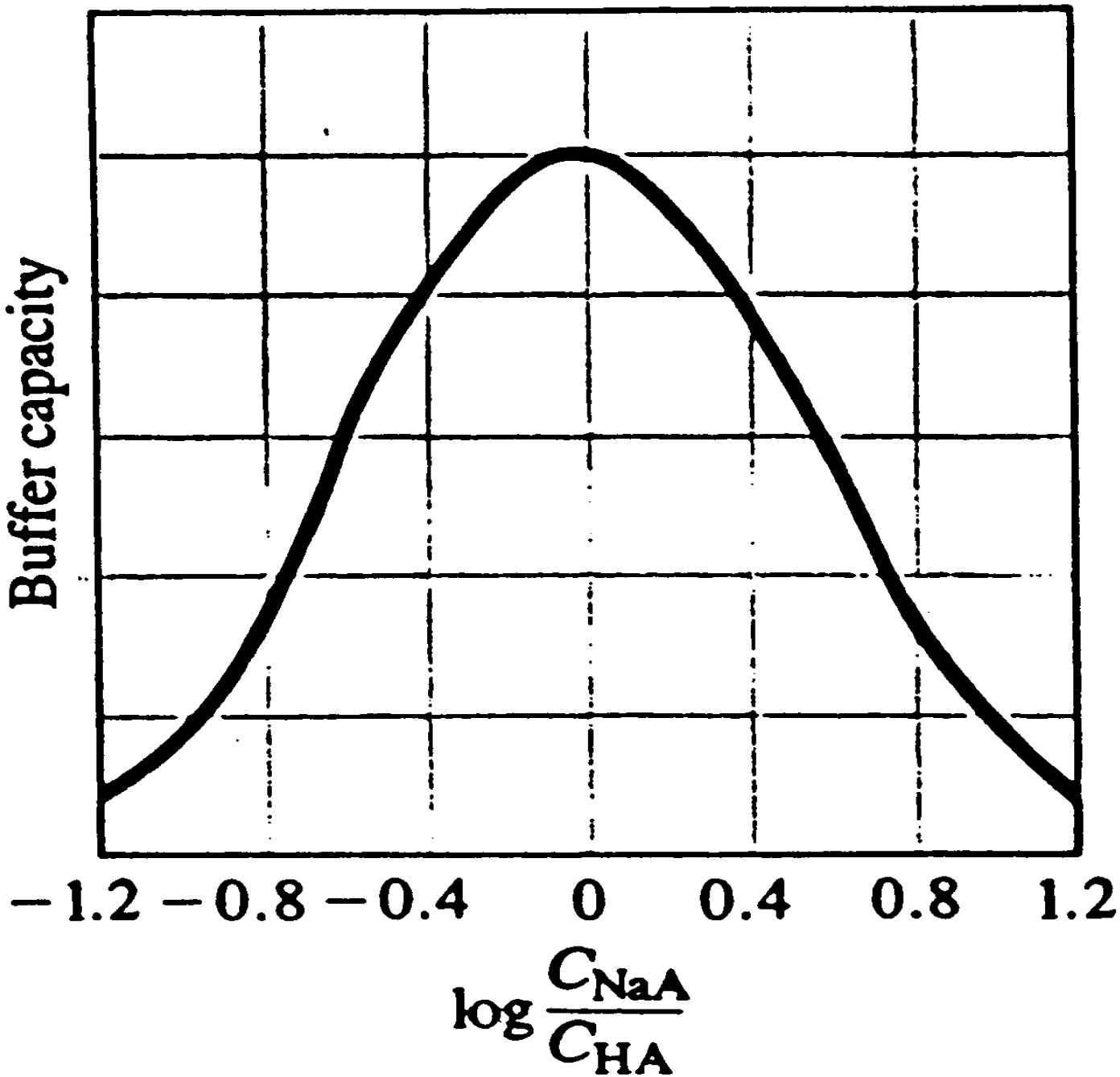
- H-H Equation:
- **$pH = pK_a + Log\ (C_{NaA}/C_{HA})$**
- For $C_{NaA} = C_{HA}$, $pH = pK_a$
- For added H_3O^+ or OH^-, pH changes slowly
- (e.g. $K_a = 10^{-5}$; $C_{NaA} = C_{HA} = 0.1M$; pH = **<u>5.0</u>**
- Add 0.01M NaOH $OH^- + HA \rightarrow HOH + A^-$
- $C_{NaA} = 0.1M + 0.01M = 0.11$; $C_{HA} = 0.10M - 0.01M = 0.09M$
- $pH = pK_a + Log\ ((0.11M)/(0.09M)) = 5.0+0.09 =$ **<u>5.1</u>**



$K_a(HA) = 1 \times 10^{-4}$

Acid/Base Buffers
Properties of Buffers

- **<u>Buffer Capacity</u>** = # moles of strong acid or strong base needed to change pH of 1 L of buffer by 1 pH units
- (e.g., $K_a = 10^{-5}$; $C_{HA} = C_{NaA} = 0.020M$; pH = 5.0
- Add NaOH. $OH^- + \quad HA \rightarrow \quad HOH + \quad A^-$
- $\quad (C-x) \quad (x) \quad (C+x)$
- Log ((0.020 + x)/(0.020 – x)) = new pH – pKa = 1.0
- ((0.020 + x)/(0.020 – x)) = 10;
- x = 0.016 moles/L = buffer cap.
- For initial buffer concentration = 1.0 M, buffer cap. = 0.82


Buffer capacity
−1.2
−0.8
−0.4
0
0.4
0.8
1.2
$\log \frac{C_{NaA}}{C_{HA}}$

Acid/Base Buffers
General Relationships

- **<u>Buffer solution from a weak base & conj. acid:</u>**
- $B + HOH \leftrightarrow BH^+ + OH^-$
- Prepare solution of B, BH^+ at C_b , C_a
- $[OH^-] = K_b \times C_b/C_a$
- $pOH = pK_b + Log\ (C_a/C_b)$
- $pH = 14 - pOH$
- (e.g., 0.10M NH_3 ; 0.20M NH_4Cl ; $K_b = 1.8 \times 10^{-5}$
- **pOH = 4.74 + log((0.20M/(0.10M)) = 5.04; <u>pH = 8.96</u>**

Acid/Base Buffers
Preparation of Buffers

- Use H-H Equation to estimate conditions for desired pH
- Large buffer capacity requires high concentrations
- High ionic strengths
- Activity coefficients less than one
- Use pH meter to determine actual pH
  - (pH electrode measures H_3O^+ activity)
- Make final adjustments with acid or conjugate base to achieve desired pH

The weaker the acid, the smaller the break and the more alkaline the equivalence point.

Visual indicators can be used for K_a of 10^{-6}.

A pH meter provides better precision for weaker acids.

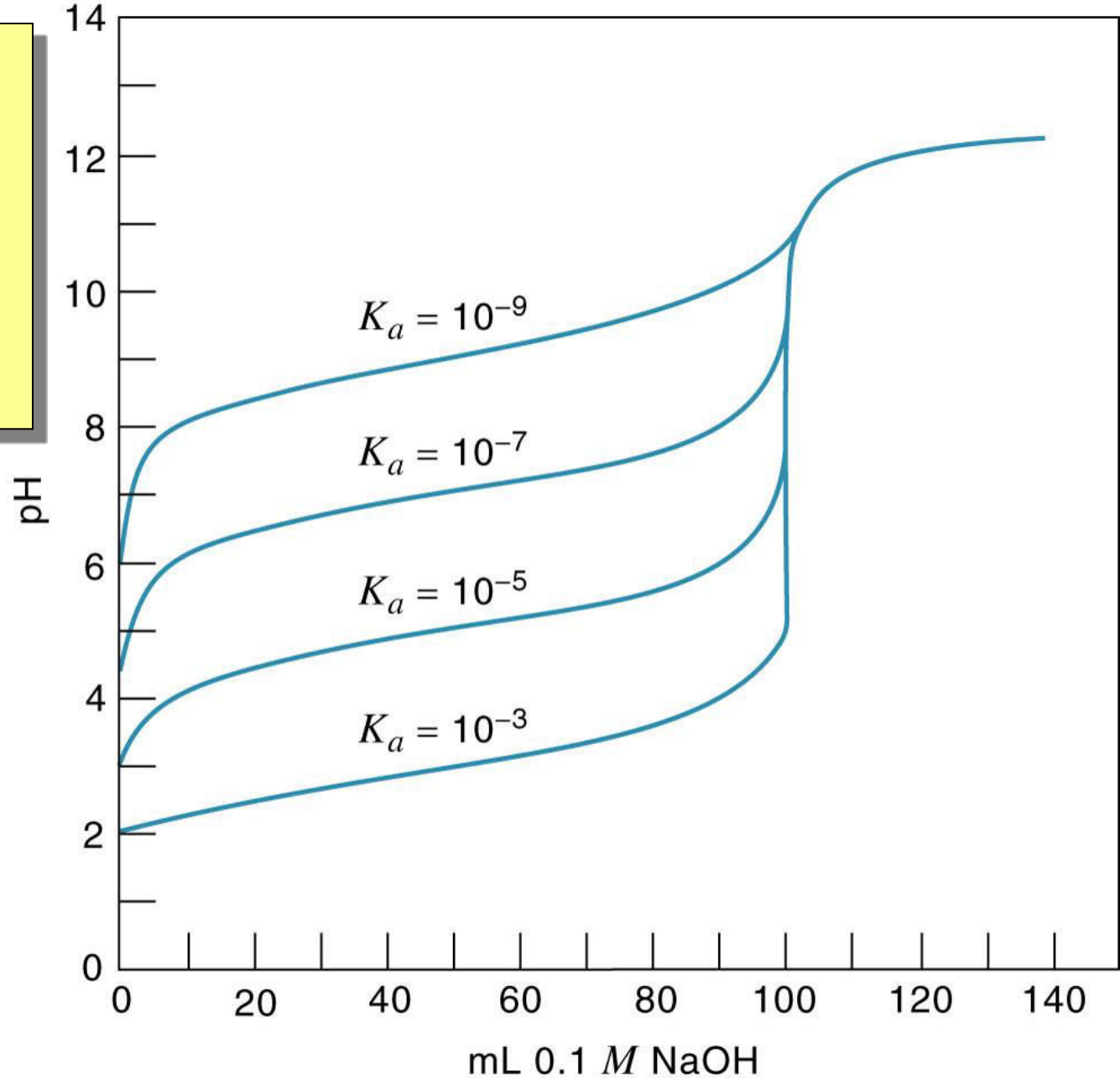


Fig. 8.7. Titration curves for 100 mL 0.1 M weak acids of different K_a values versus 0.1 M NaOH.

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This is the reverse of the HOAc titration curve.

We start with NH_3 weak base. Then we have a buffer mixture of NH_4^+ and NH_3.

At the equivalence point, we have NH_4^+, a weak acid.

Beyond the e.p., we have excess HCl, which suppresses the hydrolysis of NH_4^+, and the curve follows that for a strong base titration.

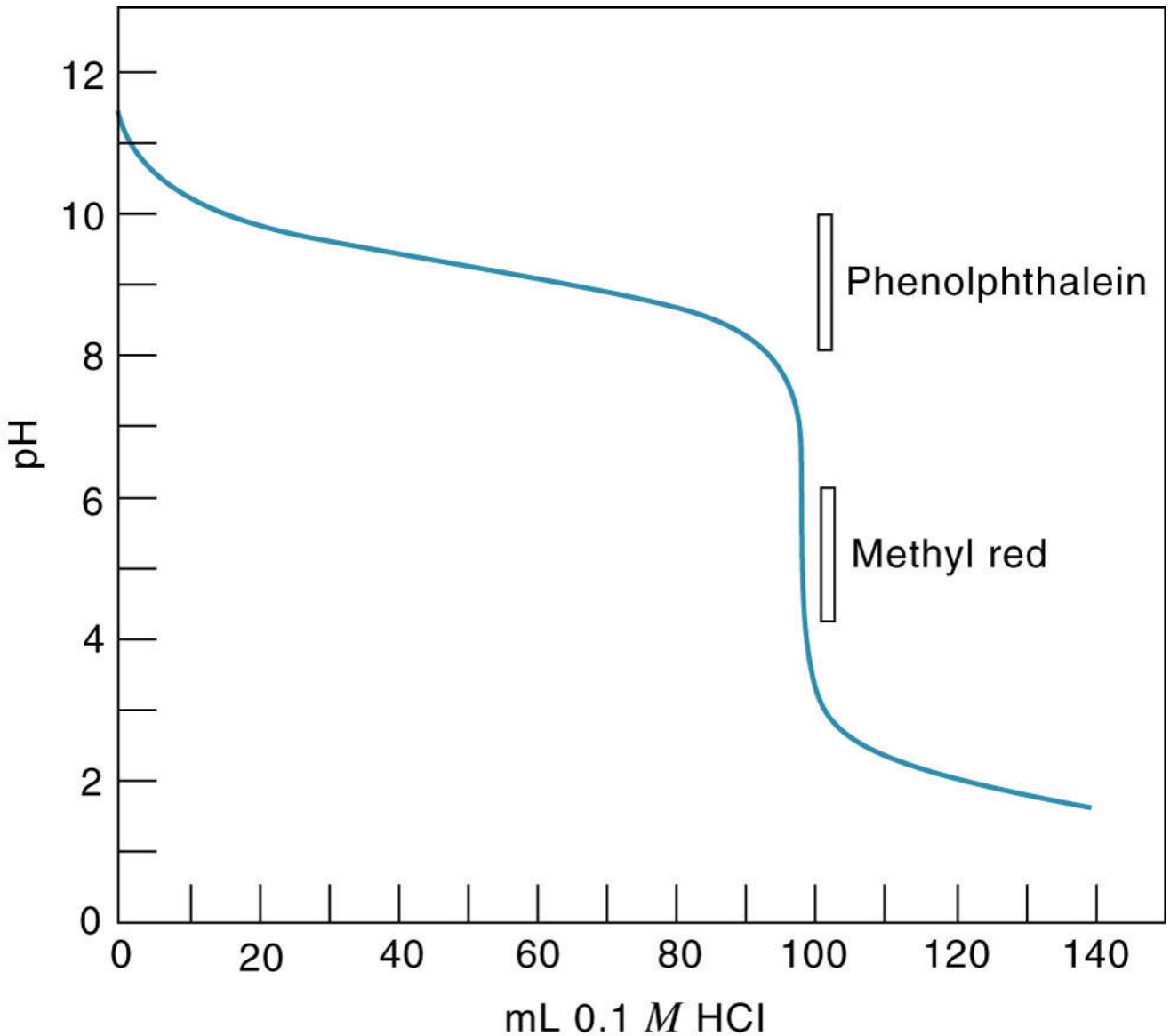

Fig. 8.8. Titration curve for 100 mL 0.1 M NH_3 versus 0.1 M HCl.

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The weaker the base, the smaller the break and more acid the equivalence point.

Visual indicators can be used for K_b of 10^{-6}.

A pH meter provides better precision for weaker bases.

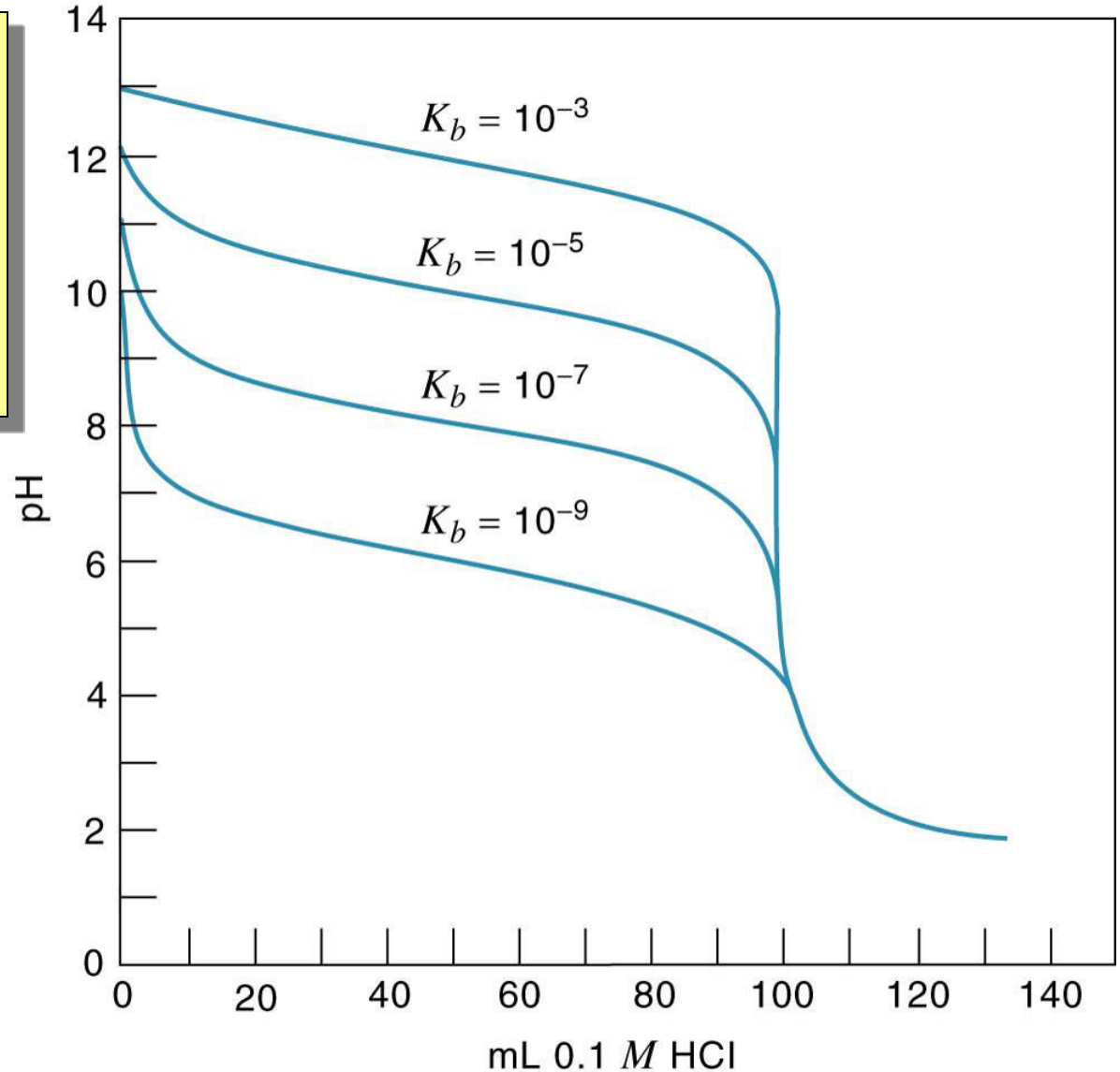

Fig. 8.9. Titration curves for 100 mL 0.1 M weak bases of different K_b values versus 0.1 M HCl.

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Polyfunctional Acids/Bases Equilibria

- **<u>Polyfunctional Acids:</u>**
- H_3PO_4 , H_2CO_3 , H_2SO_4 , H_2SO_3 , $H_2C_2O_4$, H_2S
- $H_2S + HOH \leftrightarrow H_3O^+ + HS^-$ $K_{a1} = 5.7 \times 10^{-8}$
- $HS^- + HOH \leftrightarrow H_3O^+ + S^{2-}$ $K_{a2} = 1.2 \times 10^{-15}$
- **<u>Polyfunctional Bases:</u>**
- ethylenediamine ($NH_2C_2H_4NH_2$), CO_3^{2-}, PO_4^{3-}, HPO_4^{2-}, S^{2-}
- $PO_4^{3-} + HOH \leftrightarrow HPO_4^{2-} + OH^-$ $K_{b1} = K_w/K_{a3} = 2.4 \times 10^{-2}$
- $HPO_4^{2-} + HOH \leftrightarrow H_2PO_4^- + OH^-$ $K_{b2} = K_w/K_{a2} = 1.6 \times 10^{-7}$

Polyfunctional Acids/Bases Titration Curves

- **<u>Polyfunctional acids titrated with strong base:</u>**
- Separate equivalence points observed if ratios of successive dissociation constants > ~10^{-4}

- Equivalence point can be observed for dissociation step where K_a > ~10^{-8}
- e.g. H_3PO_4
- $K_{a1} = 7 \times 10^{-3}$, $K_{a2} = 6 \times 10^{-8}$, $K_{a3} = 4 \times 10^{-13}$
  - **First two end points can be observed**
  - **Third end point is not observed**

Polyfunctional Acids/Bases Titration Curves

- **<u>Polyfunctional acids titrated with strong base:</u>**
- $[H_3O^+]$ in solution of amphiprotic anion (HA^-)
- $OH^- + H_2A \rightarrow HA^- + HOH$
- At first equivalence point, $[HA^-] = C_s \cong$ added OH^-
- $[H_3O^+] = ((K_{a2}C_s + K_w)/(1+ C_s/K_{a1}))^{1/2}$
- **If $C_s/K_{a1} >> 1$; $K_{a2}C_s >> K_w$; then $[H_3O^+] \cong (K_{a1}K_{a2})^{1/2}$**
- **Or $pH = (pK_{a1} + pK_{a2})/2$**

We start with CO_3^{2-}, a quite strong base. Then we have a HCO_3^-/CO_3^{2-} buffer.

At the first equivalence point, we have HCO_3^- ($[H^+] = \sqrt{K_{a1}K_{a2}}$).

Then we have a HCO_3^-/H_2CO_3 buffer, and H_2CO_3 at the second equivalence point.

The first e.p. is used to approximate the second, which is more accurately used.

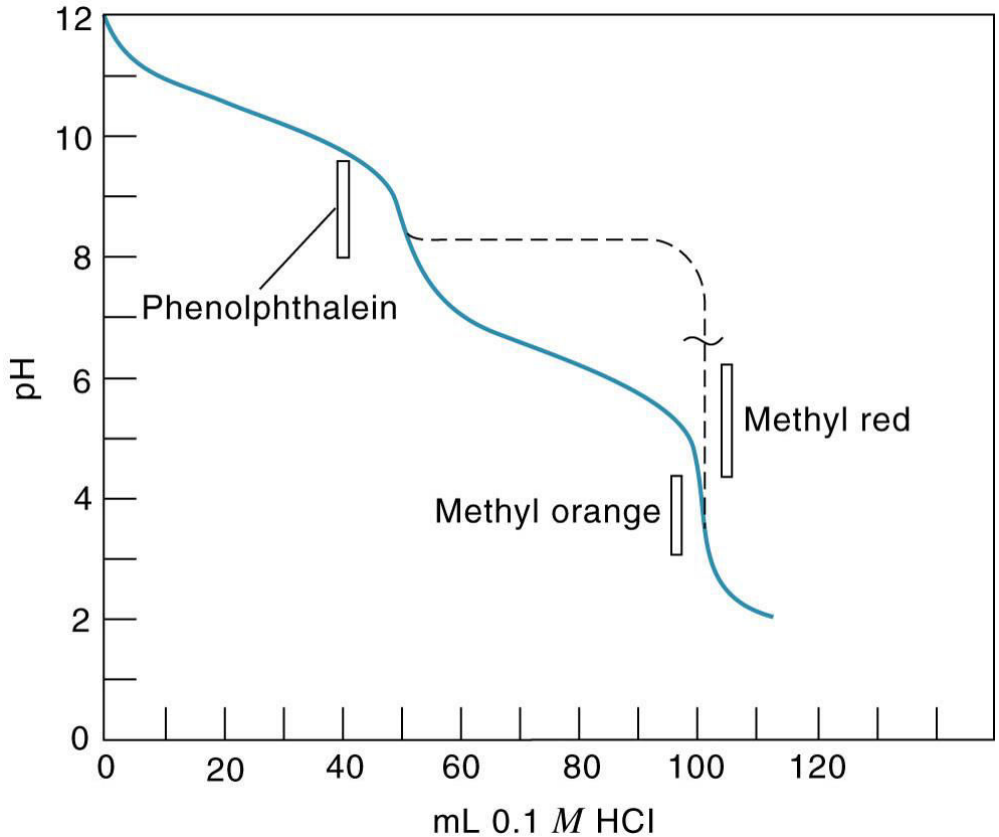

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Fig. 8.10. Titration curve for 50 mL 0.1 M Na_2CO_3 versus 0.1 M HCl. Dashed line represents a boiled solution with CO_2 removed.

Titrate till the methyl red indicator (gradually) changes from yellow through orange to red (occurs just before the equivalence point).

Then boil to remove CO_2 and continue titration for a sharp end point to a pink color.

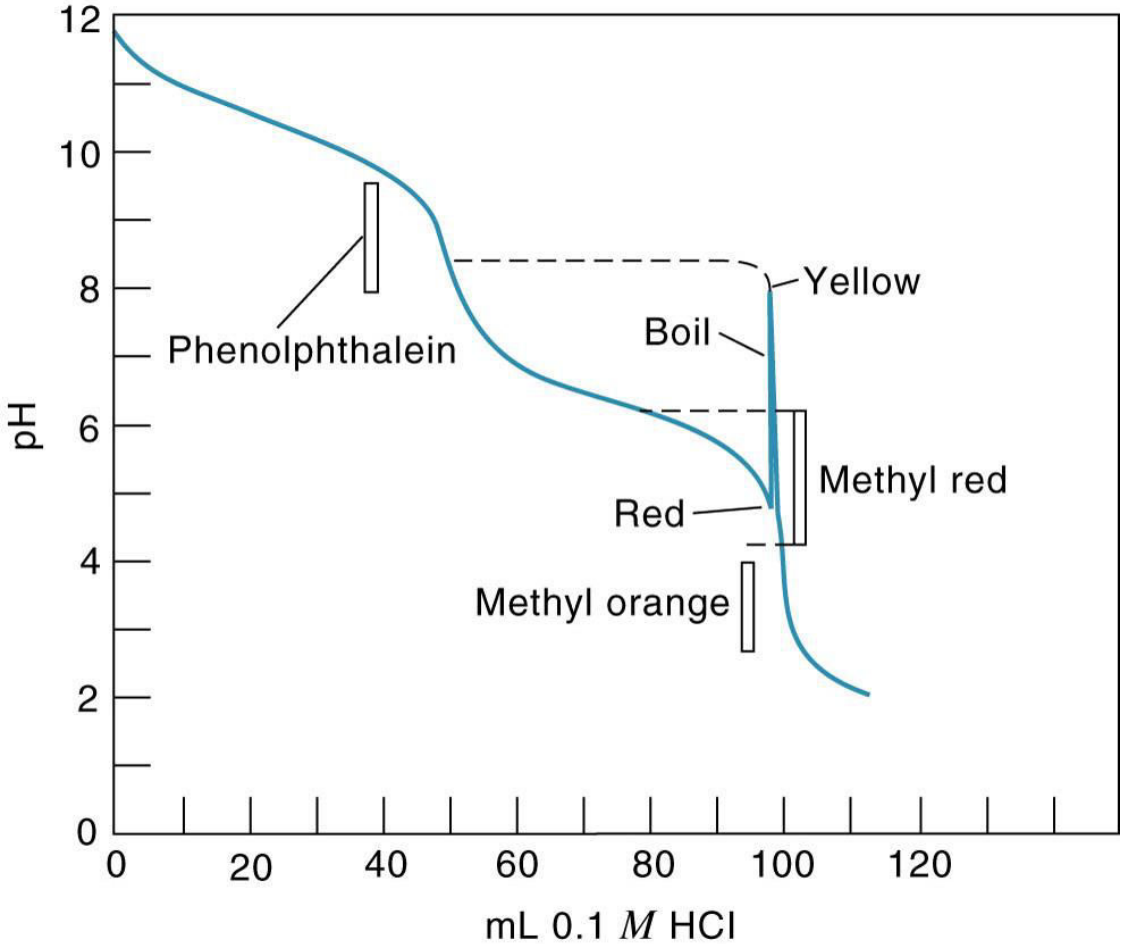

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Fig. 8.11. Titration of 50 mL 0.1 M Na_2CO_3 with 0.1 M HCl using methyl red indicator.

We start with a weak acid, H_2A, followed by a buffer region of HA^- and H_2A.

The first equivalence point is HA^- ($[H^+] \approx$ constant).

Then we have a A^{2-}/HA^- buffer region, and A^{2-} (a fairly strong base) at the second equivalence point, followed by excess titrant.

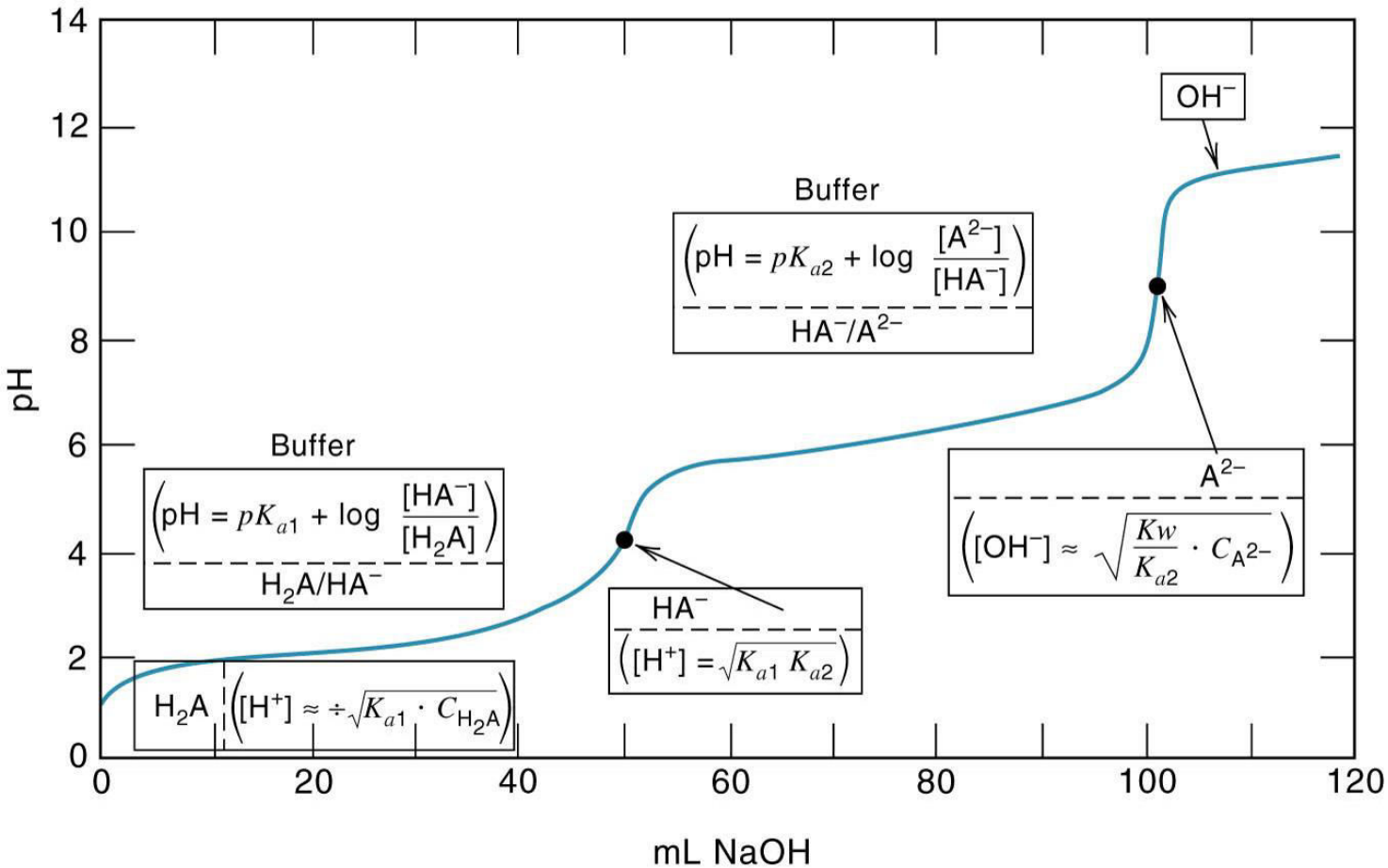

Fig. 8.12. Titration of diprotic acid, H_2A, with sodium hydroxide.

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We start with ionization of H_2A, a weak to moderately strong acid.

In the two buffer regions, use the Henderson-Hasselbalch equation.

At the first equivalence point, HA^- has $[H^+] \approx \sqrt{K_{a1}K_{a2}}$.

At the second equivalence point, A^{2-} hydrolyzes as a fairly strong base.

Then excess OH^- dominates.

Table 8.3

Equations Governing Diprotic Acid (H_2A) Titration

Fraction F Titrated	Present	Equation
$F = 0$ (0%)	H_2A	$[H^+] \approx \sqrt{K_{a1}C_{H_2A}}$ (Example 7.7) (or Eq. 7.20; Ex. 7.17, quadratic, if ~strong acid)
$0 < F < 1$ (>0 to <100%)	H_2A/HA^-	$pH = pK_{a1} + \log \frac{C_{HA^-}}{C_{H_2A}}$ (Eq. 7.45) (or $C_{HA^-} + [H^+]$ and $C_{H_2A^-}[H^+]$ if a strong acid)
$F = 1$ (100%) (1st eq. pt.)	HA^-	$[H^+] \approx \sqrt{K_{a1}K_{a2}}$ (Eq. 7.84) (or Eq. 7.83 if H_2A ~strong acid)
$1 < F < 2$ (>100 to <200%)	HA^-/A^{2-}	$pH = pK_{a2} + \log \frac{C_{A^{2-}}}{C_{HA^-}}$ (Eq. 7.45, Ex. 7.16, 7.22)
$F = 2$ (200%) (2nd eq. pt.)	A^{2-}	$[OH^-] \approx \sqrt{\frac{K_w}{K_{A2}} \cdot C_{A^{2-}}}$ (Eq. 7.32) (or Eq. 7.29, Ex. 7.19, quadratic if A^{2-} ~strong base)
$F > 2$ (>200%)	OH^-/A^{2-}	$[OH^-]$ = [excess titrant]

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Acid/Base Buffers
Examples with Polyfunctional Acids/Bases

- **<u>Example I.</u>** Add HCl to Na_2CO_3 solution.
  - (assume concentration = activity)
- Given: for H_2CO_3 $pK_{a1} = 6.35$; $pK_{a2} = 10.33$
- Start with: $C_{(HCl)} = 0.200M$ and $C_{(CO_3^{2-})} = 0.200M$
- Desired: pH = 11.00; $C_b + C_a = 0.100M$; 1.0 L solution
- Use H-H Equation: $pH = pK_{a2} + \log (C_b/C_a)$
- To get pH = 11; select base = CO_3^{2-}; acid = HCO_3^-
- Because $pK_{a2} = 10.33$ (nearest 11.00)
- $11.00 - 10.33 = 0.67 = \log(C_b/C_a)$
- $C_b/C_a = 4.68$; $C_b + C_a = 0.100M$
- **Thus, $C_a = 0.100M/5.68 = 0.0176M$ HCO_3^- ; $C_b = 0.0824M$ CO_3^{2-}**

Acid/Base Buffers
Examples with Polyfunctional Acids/Bases

- **<u>Example I (cont'd)</u>**
- $CO_3^{2-} + HCl \rightarrow HCO_3^- + Cl^-$
- $C_a = C_{(HCl)} * V_{(HCl)}/1000mL = 0.0176M$
- $V_{(HCl)} = 0.0176M*1000mL/0.200M =$ **<u>88.0mL</u>**
- $C_b = (C_{(CO_3^{2-})} * V_b - C_{(HCl)} * V_{(HCl)})/1000mL = 0.0824M$
- $V_b = (0.0824 *1000 + 0.200*88.0)/0.200=$ **<u>500.0mL</u>**

Acid/Base Buffers
Examples with Polyfunctional Acids/Bases

- **Example II.** Add NaOH (b) to H_3PO_4(a) solution
  - (assume concentration = activity)
- Given: for H_3PO_4, $pK_{a1,2,3}$ = 2.15; 7.20; 12.35
- Start with: C_b = 0.400M and C_a = 0.400M
- Desired: 1L of pH 7.00; use 200.0 mL acid.
- Procedure: Titrate 200.0mL of H_3PO_4 w/ NaOH
- Dilute to 1000. mL
- Use H-H Equation: $pH = pK_a + \log(C_b/C_a)$
- To get pH= 7.00, select base(b) = HPO_4^{2-}; acid(a) = $H_2PO_4^-$
- Because pK_{a2} = 7.20 (nearest 7.00)
- 7.00-7.20 = - 0.20 = $\log(C_b/C_a)$ **C_b/C_a = 0.631**

Acid/Base Buffers
Examples with Polyfunctional Acids/Bases

- **<u>Example II (cont'd)</u>**
- Because total moles of phosphate remain constant:
- $C_b + C_a = V_a * C_a/1000mL$
- $C_b + C_a = (200.0mL)*(0.400M)/1000mL = 0.0800M$
- Thus, $C_b = 0.631C_a$
- $C_a + 0.631C_a = 0.0800M$;
- $C_a = 0.0800M/0.631 =$ **0.0490 M (in 1L)**
- $C_b = 0.631 * C_a =$ **0.0310M (in 1L)**

Acid/Base Buffers
Examples with Polyfunctional Acids/Bases

- **<u>Example II (cont'd)</u>**
- **Titration Reaction (to produce HPO_4^{2-}):**
- $H_3PO_4 + NaOH \rightarrow H_2PO_4^- + HOH + Na^+$ (1)
- $H_2PO_4^- + NaOH \rightarrow HPO_4^{2-} + HOH + Na^+$ (2)
- $V_a * C_a$ = # mmoles $H_2PO_4^-$ produced by Rxn (1)
- 1000mL * C_b = #mmoles HPO_4^{2-} produced by Rxn (2)
- $V_b * C_b = V_a * C_a + C_b * 1000mL$
- V_b = (200.0mL)*(0.400M)+(0.310M)*1000mL/(0.400M)
- **<u>V_b = 277.5 mL NaOH</u>**
- **Add 277.5mL NaOH to 200.0mL H_3PO_4;**
- **dilute to 1000mL**

The strong acid titrates first.
At its equivalence point, we have a mixture of NaCl and HOAc, and the pH is acidic.

This is followed by a buffer region of OAc^- and HOAc, and then the HOAc equivalence point, where we have OAc^-, a weak base.

The weak acid K_a must be no larger than 10^{-5} to give a sharp second end point.

For two weak acids, the K_a's should differ by 10^4 or more.

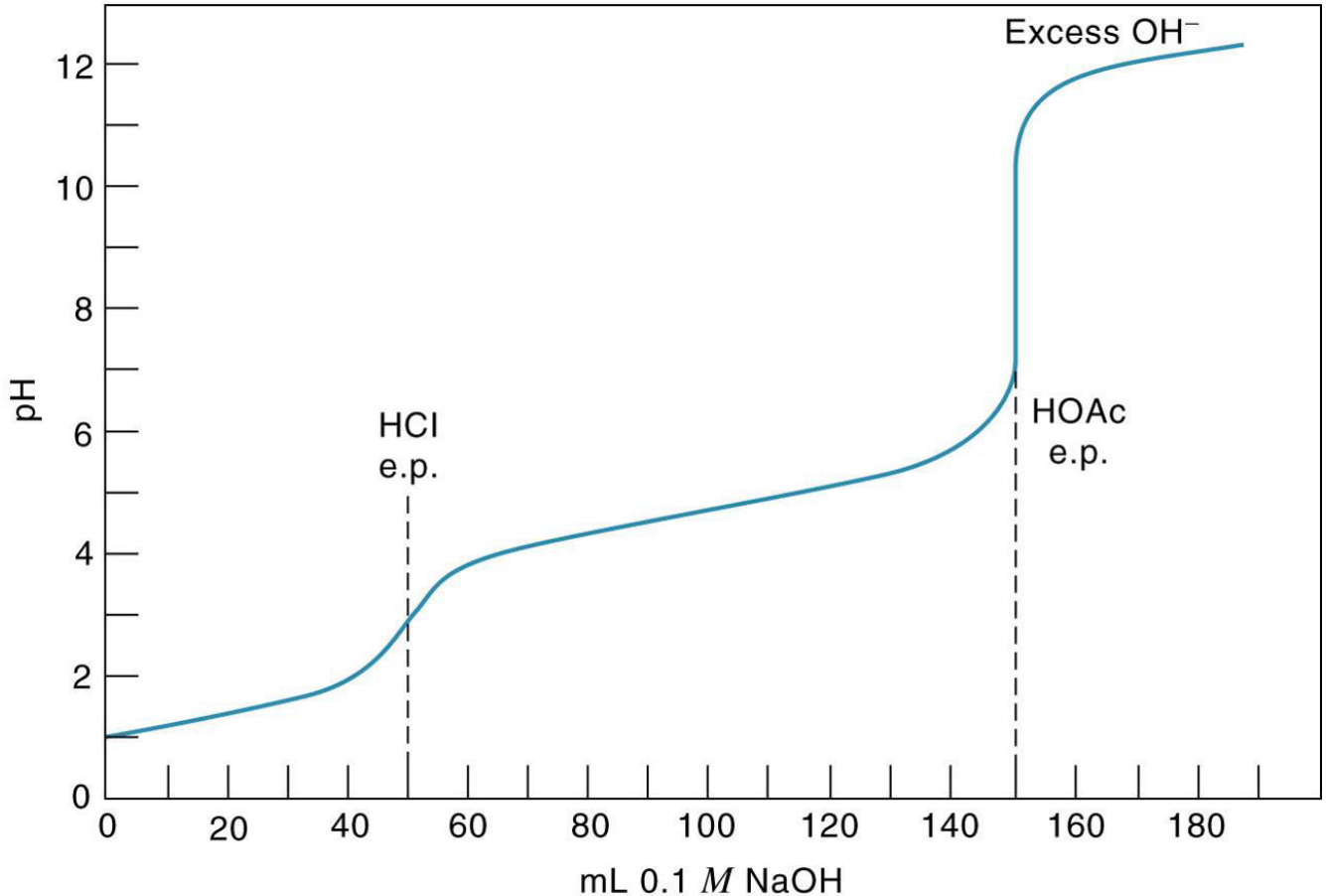

Fig. 8.13. Titration curve for 50 mL of mixture of 0.1 M HCl and 0.2 M HOAc with 0.2 M NaOH.

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Section 8

Complex-Formation Titrations

Complex-Formation Titrations
General Principles

- Most metal ions form coordination compounds with electron-pair donors (ligands)
- $M^{n+} + qL^{m-} \leftrightarrow ML_q^{n-mq}$ $K_f = [ML_q^{n-mq}]/[M^{n+}][L^{m-}]^q$
- The number of covalent bonds formed is called the "coordination number" (e.g. 2,4,6)
- e.g., Cu^{2+} has coordination number of 4
- $Cu^{2+} + 4\ NH_3 \leftrightarrow Cu(NH_3)_4^{2+}$
- $Cu^{2+} + 4\ Cl^- \leftrightarrow Cu(Cl)_4^{2-}$

Complex-Formation Titrations
General Principles

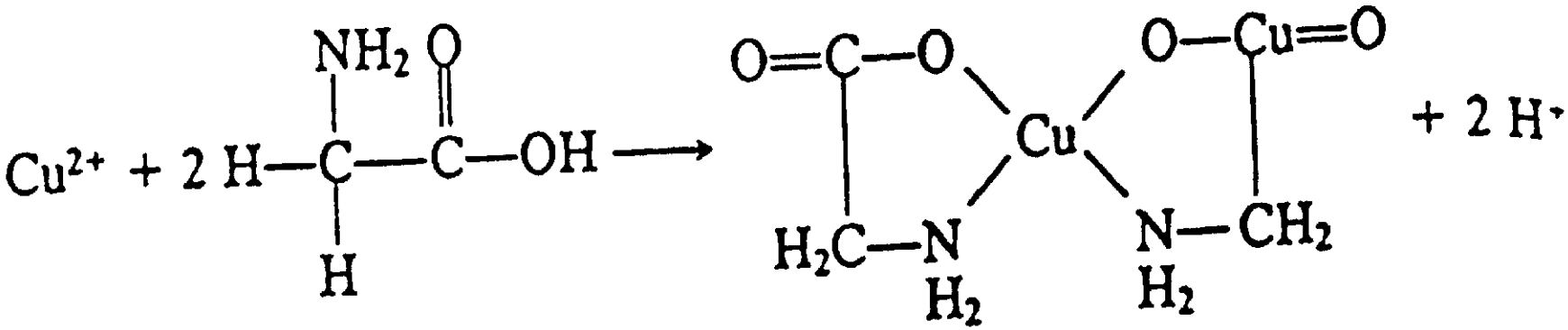
- Typical Inorganic Complex-Formation Titrations

Analyte	Titrant	Remarks
$Hg(NO_3)_2$	**Br^-, Cl^-, SCN^-, CN^-, thiourea**	**Products are neutral mercury(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 AgI; titrate to first tubidity of AgI**
KCN	**Cu^{2+}, Hg^{2+}, Ni^{2+}**	**Products are $Cu(CN)_4^{2-}$, $Hg(CN)_4^{2-}$, $Ni(CN)_4^{2-}$; various indicators used**

Complex-Formation Titrations
General Principles

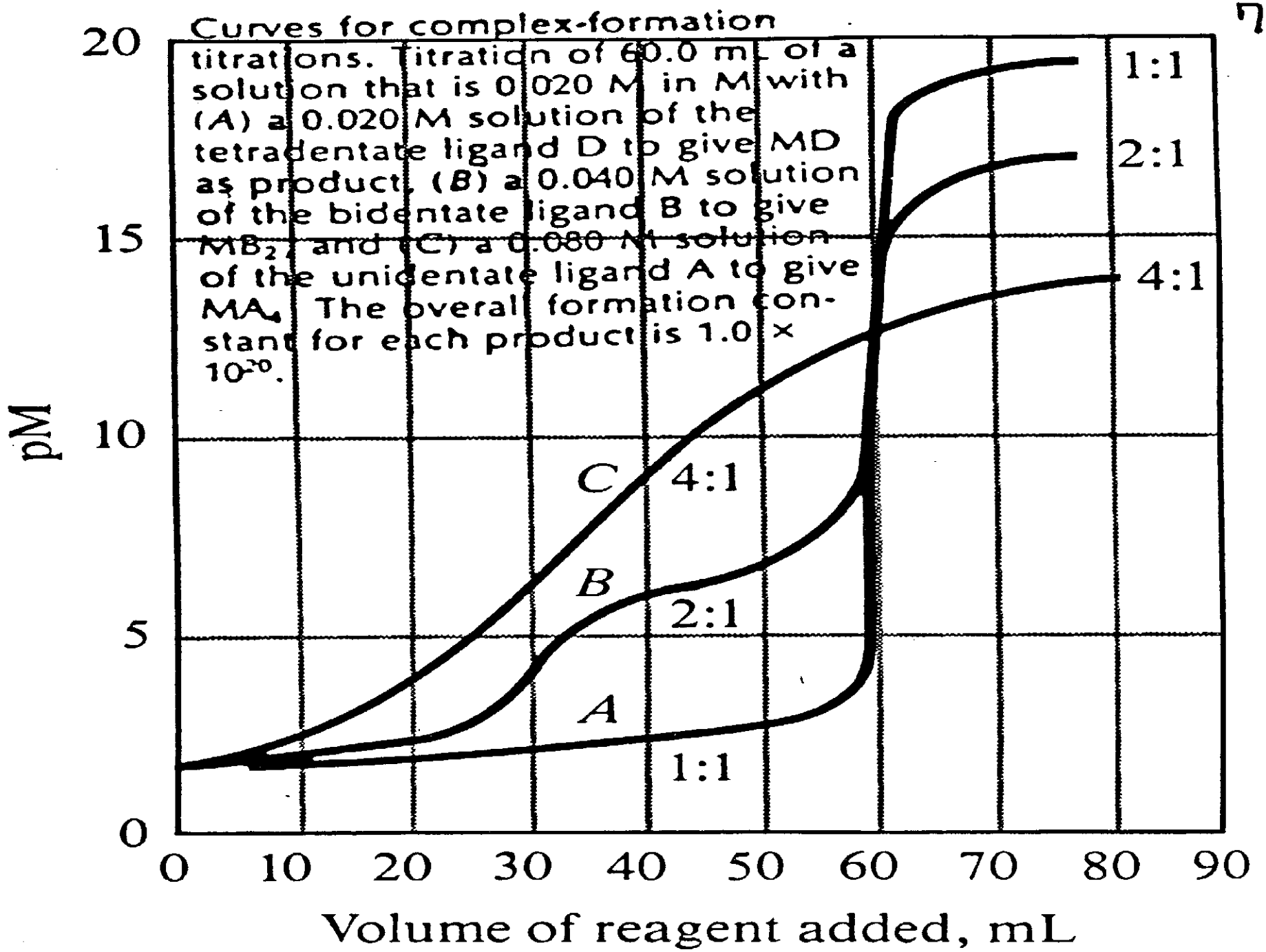
- The most useful complex-formation reactions for titrimetry involve **<u>chelate</u>** formation
- A chelate is formed when a metal ion coordinates with two of more donor groups of a single ligand (forming a 5- or 6- membered heterocyclic ring)

e.g., Cu^{2+} and glycine



Complex-Formation Titrations
General Principles

- Chelate Formation Titrations
- Ligands are classified regarding the number of donor groups available:
- e.g., NH_3 = "unidentate" (one donor group)
- Glycine = "bidentate" (two donor groups)
- (also, there are tridentate, tetradentate, pentadentate, and hexadentate chelating agents)
- Multidentate ligands (especially with 4 and 6 donors) are preferred for titrimetry.
  - **react more completely with metal ion**
  - **usually react in a single step**
  - **provide sharper end-points**



Curves for complex-formation titrations. Titration of 60.0 mL of a solution that is 0.020 M in M with (*A*) a 0.020 M solution of the tetradentate ligand D to give MD as product, (*B*) a 0.040 M solution of the bidentate ligand B to give MB_2, and (*C*) a 0.080 M solution of the unidentate ligand A to give MA_4. The overall formation constant for each product is 1.0×10^{20}.

Complex-Formation Titrations General Principles

- Aminopolycarboxylic acid ligands
- **The most useful reagents for complexometric titrations are aminopolycarboxylic acids**
  - **(tertiary amines with carboxylic acid groups)**
- e.g., ethylenediaminetetraacetic acid (EDTA)

- EDTA is a hexadentate ligand
- EDTA forms stable chelates with most metal ions

Complex-Formation Titrations
Solution Chemistry of EDTA(H_4Y)

- EDTA has four acid dissociation steps
- pK_{a1}= 1.99, pK_{a2}= 2.67, pK_{a3}= 6,16, pK_{a4}= 10.26
- 5 forms of EDTA, (H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, Y^{4-})
- EDTA combines with all metal ions in 1:1 ratio
- $Ag^+ + Y^{4-} \leftrightarrow AgY^{3-}$
- $Fe^{2+} + Y^{4-} \leftrightarrow FeY^{2-}$
- $Al^{3+} + Y^{4-} \leftrightarrow AlY^-$
- $K_{MY} = [MY^{n-4}]/[M^{n+}][Y^{4-}]$

Complex-Formation Titrations

Formation Constants for EDTA Complexes

Cation	K_{MY}	Log K_{MY}	Cation	K_{MY}	Log K_{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}	16.31	V^{3+}	7.9×10^{25}	25.9
Ni^{2+}	4.2×10^{18}	18.62	Th^{4+}	1.6×10^{23}	23.2

Complex-Formation Titrations Equilibrium Calculations with EDTA

- For $M^{n+} + Y^{4-} \leftrightarrow MY^{n-4}$ $K_{MY} = [MY^{n-4}]/[M^{n+}][[Y^{4-}]$
- Need to know $[Y^{4-}]$, which is pH-dependent
- pH dependence of Y^{4-}:
- Define: $\alpha_4 = [Y^{4-}]/C_T$
- $C_T = [Y^{4-}] + [HY^{3-}] + [H_2Y^{2-}] + [H_3Y^{-}] + [H_4Y]$
- Conditional Formation Constant, K_{MY}'
- $[MY^{n-4}]/[M^{n+}][[\alpha_4 C_T] = K_{MY}$
- $K_{MY}' = \alpha_4 K_{MY} = [MY^{n-4}]/[M^{n+}][[C_T]$

Complex-Formation Titrations Equilibrium Calculations with EDTA

- Computing free metal ion concentrations:
- Use conditional formation constants, K_{MY}'

□ α_4 values depend on pH

- Thus, K_{MY}' are valid for specified pH only

□ α_4 values have been tabulated vs pH

□ $\alpha_4 = (K_1K_2K_3K_4) / ([H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4)$

Y^{4-} complexes with metal ions, and so the complexation equilibria are very pH dependent.

Only the strongest complexes form in acid solution, e.g., HgY^{2-}; CaY^{2-} forms in alkaline solution.

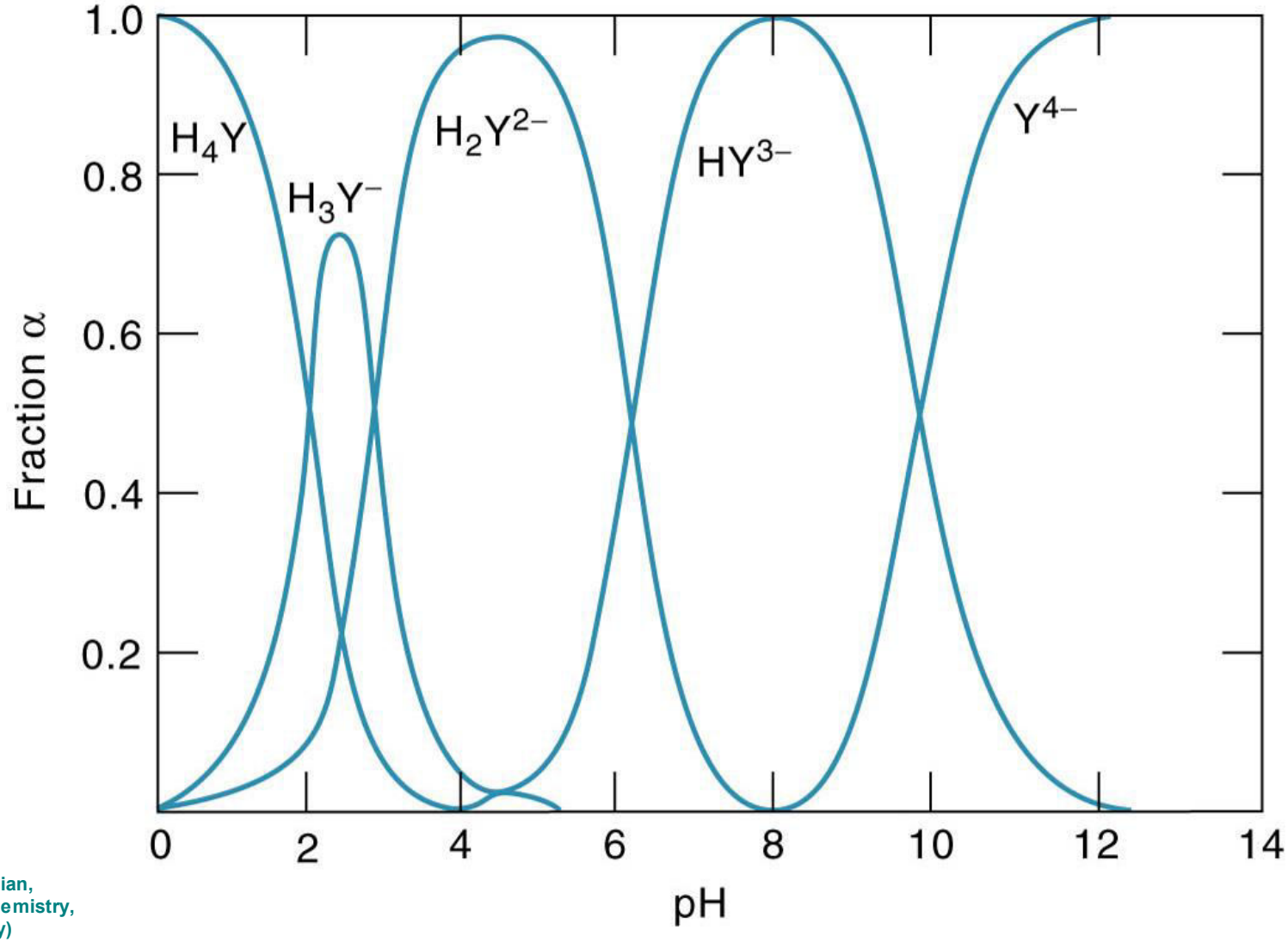


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Fig. 9.1. Fraction of EDTA species as a function of pH.

K_f' = conditional formation constant = $K_f\alpha_4$.

It is used at a fixed pH for equilibrium calculations (but varies with pH since α_4 does).

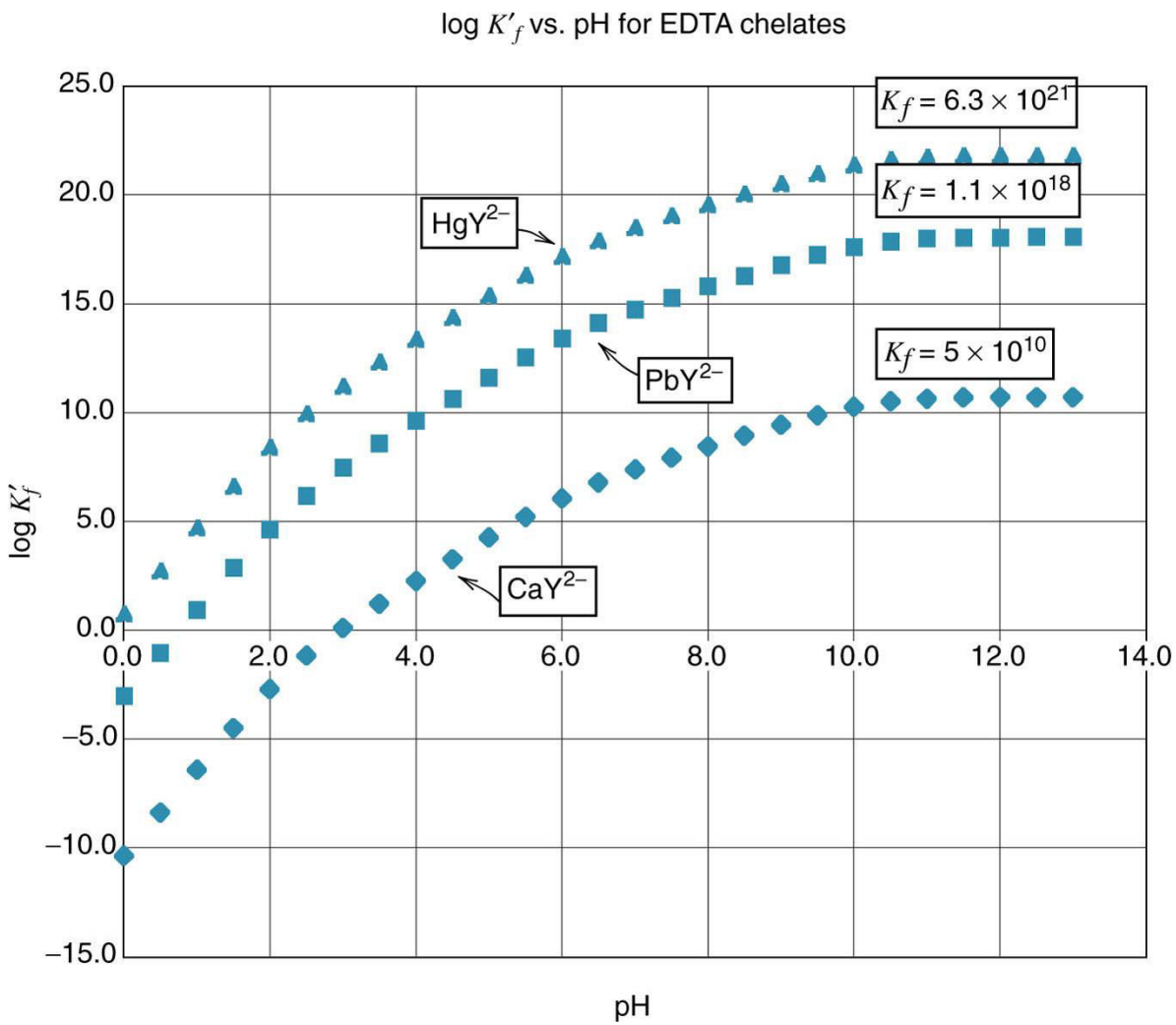

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Fig. 9.2. Effect of pH on K_f' values for EDTA chelates.

Complex-Formation Titrations
Equilibrium Calculations with EDTA

- Example: Add excess EDTA to Ni^{2+} solution at pH 3.0.
- 50.0 mL 0.0500M EDTA added to 50.0 mL 0.030M Ni^{2+}
- Assume very little Ni^{2+} is uncomplexed:
- $C_{(NiY^{2-})} = [NiY^{2-}] = 50.0 \text{ mL} \times 0.030\text{M}/100.0\text{mL} = 0.015\text{M}$
- $C_{(EDTA)} = ((50.0 \times 0.050) - (50.0 \times 0.030))/100.0 = 0.010 \text{ M}$
- $K_{MY}' = \alpha_4 K_{MY} = [NiY^{2-}]/[Ni^{2+}][0.010] = 0.015/[Ni^{2+}][0.010]$
- $K_{MY} = 4.2 \times 10^{18}$; $\alpha_4 = 2.5 \times 10^{-11}$ @ pH = 3.0
- **$[Ni^{2+}] = 1.4 \times 10^{-8}$M**

Complex-Formation Titrations
Metal-EDTA Titration Curves

- **Titration curve is: pM vs EDTA volume**
- Conditional Formation Constant, K_{MY}' for specific pH
- e.g., 50.0mL 0.020M Ca^{2+} with 0.050M EDTA, pH 10.0
- at pH 10.0, $K_{(CaY^{2-})}' = (\alpha_4)(K_{CaY})$ = **$(0.35)(5.0 \times 10^{10}) = 1.75 \times 10^{10}$**
- **(a) pCa values before the equivalence point (10.0mL)**
- **$Ca^{2+} + Y^{4-} \leftrightarrow CaY^{2-}$**
- assume: $[CaY^{2-}]$ = added EDTA – dissociated chelate
- $[Ca^{2+}]$ = unreacted Ca^{2+} + dissociated chelate
- Dissociated chelate = $C_T \ll [Ca^{2+}], [CaY^{2-}]$
- $[Ca^{2+}] = ((50.0 \times 0.020) - (10.0 \times 0.050))/(60.0)$ = **0.0083M**
- **pCa = 2.08 at 10.0mL EDTA**

Complex-Formation Titrations
Metal-EDTA Titration Curves

- Titration curve is: pM vs EDTA volume
- Conditional Formation Constant, K_{MY}' for specific pH
- e.g., 50.0mL 0.020M Ca^{2+} with 0.050M EDTA, pH 10.0
- at pH 10.0, $K_{(CaY^{2-})}' = (\alpha_4)(K_{CaY})$ = **$(0.35)(5.0 \times 10^{10}) = 1.75 \times 10^{10}$**
- **(b) pCa value at the equivalence point (20.0mL)**
- assume: $[CaY^{2-}]$ = added EDTA – dissociated chelate
- $[Ca^{2+}]$ = dissociated chelate = $C_T << [CaY^{2-}]$
- $[CaY^{2-}] = ((20.0mL \times 0.050M)/(70.0mL)) - C_T \cong 0.0142M$
- $K_{(CaY^{2-})}' = [CaY^{2-}] / [Ca^{2+}]\ [C_T] = (0.0142)/[Ca^{2+}]^2$
- **$[Ca^{2+}] = ((0.0142)/(1.75 \times 10^{10}))^{1/2} = 9.0 \times 10^{-7}M$;**
- **<u>pCa = 6.05 at 20.0mL EDTA</u>**
- Note: assumption ($C_T << [CaY^{2-}]$) is OK

Complex-Formation Titrations
Metal-EDTA Titration Curves

- Titration curve is: pM vs EDTA volume
- Conditional Formation Constant, K_{MY}' for specific pH
- e.g., 50.0mL 0.020M Ca^{2+} with 0.050M EDTA, pH 10.0
- at pH 10.0, $K_{(CaY^{2-})}' = (\alpha_4)(K_{CaY})$ = **$(0.35)(5.0 \times 10^{10}) = 1.75 \times 10^{10}$**
- **(c) pCa value after the equivalence point (25.0mL)**
- assume: $[CaY^{2-}]$ = stoichiometric amount – $[Ca^{2+}]$
- C_T = [excess EDTA] + $[Ca^{2+}] \cong$ [excess EDTA]
- $C_T = ((25.0 \times 0.050)-(50.0 \times 0.020))/(75.0) = 0.0033M$
- $[CaY^{2-}] = ((50.0mL \times 0.020M)/(75.0mL))-[Ca^{2+}] \cong 0.0133M$
- $K_{(CaY^{2-})}' = [CaY^{2-}] / [Ca^{2+}]\,[C_T]$; $[Ca^{2+}] = (0.0133)/(0.0033)(K_{(CaY^{2-})}')$
- **$[Ca^{2+}] = 2.30 \times 10^{-10}$**
- **<u>pCa = 9.64 at 25.0mL EDTA</u>**
- Note: assumption ($[Ca^{2+}] << CT << [CaY^{2-}]$) is OK

As the pH increases, the equilibrium shifts to the right.

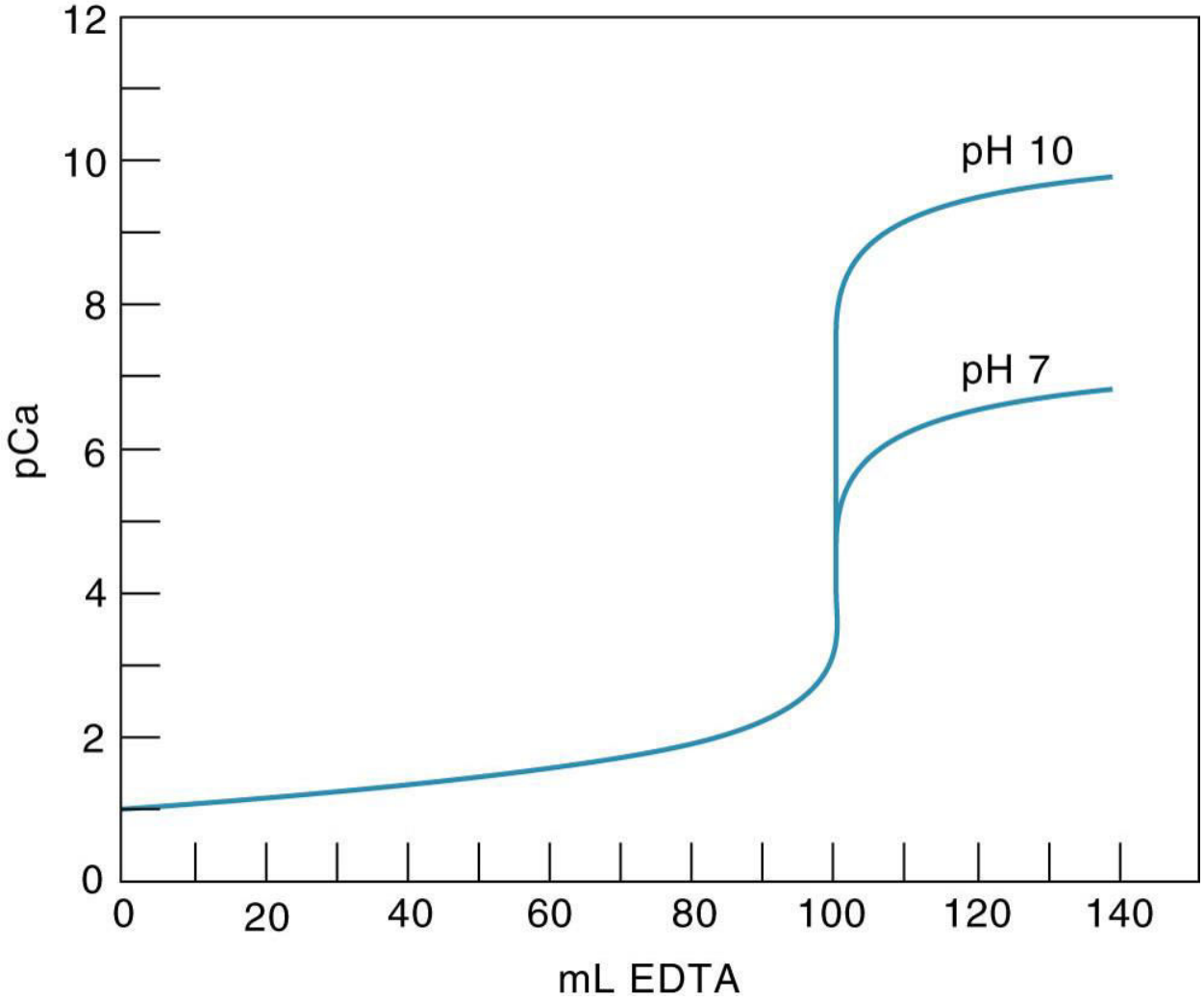

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Fig. 9.3. Titration curves for 100 mL 0.1 M Ca^{2+} versus 0.1 M Na_2EDTA at pH 7 and 10.

The points represent the pH at which the conditional formation constant, K_f', for each metal is 10^6, needed for a sharp end point.

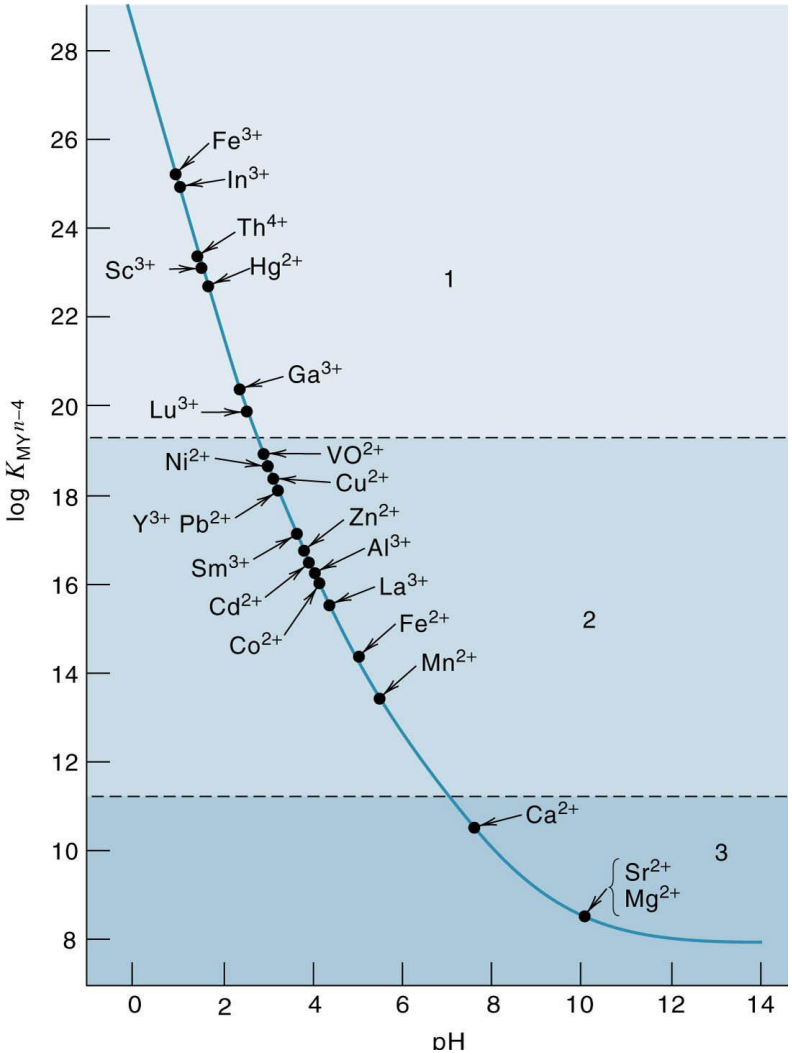

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Fig. 9.4. Minimum pH for effective titrations of various metal ions with EDTA.

Section 09

Gravimetric Analysis and Precipitation Equilibria

How to Perform a Successful Gravimetric Analysis

- **What steps are needed?**

1. Sampled dried, triplicate portions weighed
2. Preparation of the solution
3. Precipitation
4. Digestion
5. Filtration
6. Washing
7. Drying or igniting
8. Weighing
9. Calculation

Gravimetric Analysis

- Gravimetric Analysis – one of the most accurate and precise methods of macro-quantitative analysis.
- Analyte selectively converted to an insoluble form.
- Measurement of mass of material
- Correlate with chemical composition
- Why?
- Simple
- Often required for high precision

Gravimetric Analysis

- How?
- Quantitative collection of material of known composition
  - Precipitation of analyte with selective agent
  - Volitization and collection of analyte
  - w/o loss of material in handling/processing
  - Free from solvent, impurities
- Determination of mass
  - Direct or
  - By difference

Gravimetric Analysis

- Precipitation Techniques
  - Add precipitating reagent to sample solution
  - Reacts with analyte to form insoluble material
  - Precipitate has known composition or can be converted to known composition
- Precipitate handling involves
  - Quantitative collection (no losses)
  - Isolation of pure product
- Measure mass of precipitate
- Calculation of original analyte content (concentration)

Gravimetric Analysis

- Desirable properties of analytical precipitates:
  - Readily filtered and purified
  - Low solubility, preventing losses during filtration and washing
  - Stable final form (unreactive)
  - Known composition after drying or ignition

Gravimetric Analysis

- Precipitating reagents:
- **<u>Selective</u>**
- Ag^+ + Halides (X^-) → $AgX_{(s)}$
- $Ag^+ + CNS^- \rightarrow AgCNS_{(s)}$
- **<u>Specific</u>**
- Dimethylglyoxime (DMG)
- $2\ DMG + Ni^{2+} \rightarrow Ni(DMG)_{2(s)} + 2\ H^+$

Gravimetric Analysis

- Filterability of Precipitates:
- <u>Colloidal suspensions</u>
  - 10^{-7} to 10^{-4} cm diameter
  - Normally remain suspended
  - Very difficult to filter
- <u>Crystalline suspensions</u>
  - > tenths of mm diameter
  - Normally settle out spontaneously
  - Readily filterable

Gravimetric Analysis

- Filterability of Precipitates:
  - Precipitate formation affected by
  - RELATIVE SUPERSATURATION(R.S.)
- R.S. = (Q-S)/S
  - S = Equilibrium Solubilty of Precipitate
  - Q = Instantaneous Concentration
- Larger Q leads to colloidal precipitates.

Important Factors for Gravimetric Analysis

- **Nucleation**
  - Individual ions/atoms/molecules coalesce to form "nuclei"
- **Particle Growth**
  - Condensation of ions/atoms/molecules with existing "nuclei" forming larger particles which settle out
- **Colloidal Suspension**
  - Colloidal particles remain suspended due to adsorbed ions giving a net + or - charge

Important Factors for Gravimetric Analysis

- **<u>Coagulation, agglomeration</u>**
  - Suspended colloidal particles coalesce to form larger filterable particles (inert electrolyte allows closer approach)

- **<u>Peptization</u>**
  - Re-dissolution of coagulated colloids by washing and removing inert electrolyte

Important Factors for Gravimetric Analysis

- **<u>Co-precipitation</u>**
  - Normally soluble compounds carried down with insoluble precipitate (surface adsorption, occlusion, mixed crystals, entrapment)

- **<u>Digestion</u>**
  - Precipitation heated for hour(s) in contact with solution form which it was formed

During digestion at elevated temperature:

Small particles tend to dissolve and reprecipitate on larger ones.

Individual particles agglomerate.

Adsorbed impurities tend to go into solution.

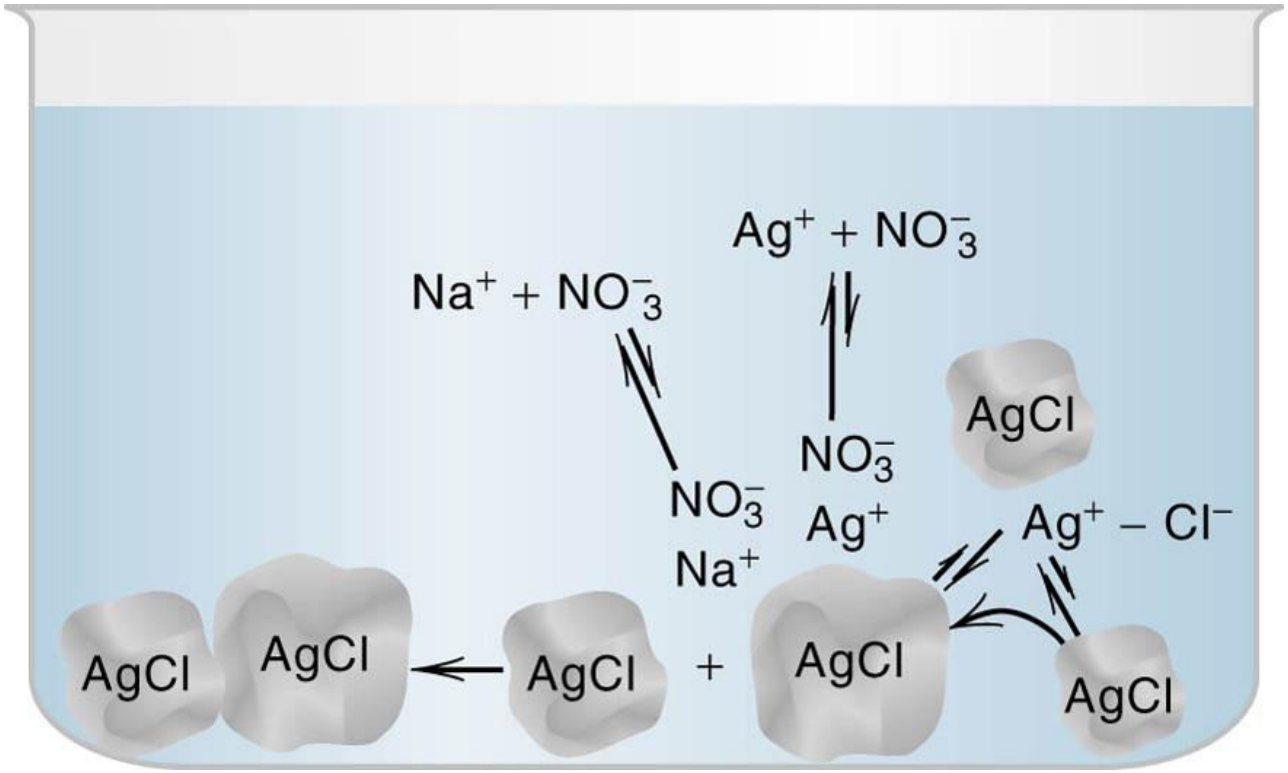

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Fig. 10.1. Ostwald ripening.

Cl^- adsorbs on the particles when in excess (primary layer).

A counter layer of cations forms. The neutral double layer causes the colloidal particles to coagulate.

Washing with water will dilute the counter layer and the primary layer charge causes the particles to revert to the colloidal state (peptization).
So we wash with an electrolyte that can be volatilized on heating (HNO_3).

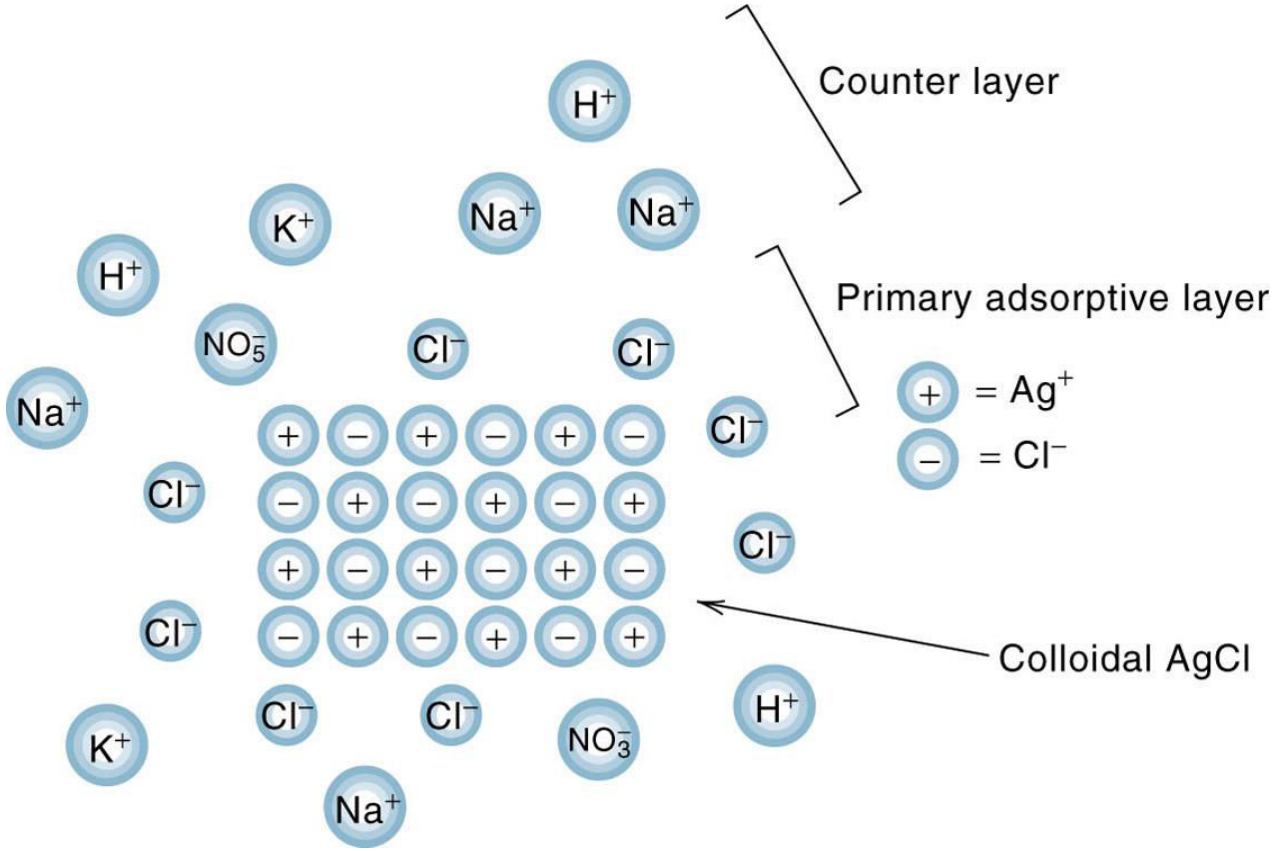

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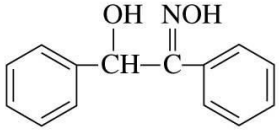
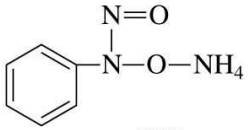
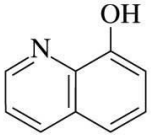
Fig. 10.2. Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.

Organic precipitating agents are chelating agents.

They form insoluble metal chelates.

Table 10.2

Some Organic Precipitating Agents

Reagent	Structure	Metals Precipitated
Dimethylglyoxime	$CH_3-C=NOH$ $CH_3-C=NOH$	Ni(II) in NH_3 or buffered HOAc; Pd(II) in HCl ($M^{2+} + 2HR \rightarrow \underline{MR_2} + 2H^+$)
α-Benzoinozime (cupron)		Cu(II) in NH_3 and tartrate; Mo(VI) and W(VI) in H^+ ($M^{2+} + H_2R \rightarrow \underline{MR} + 2H^+$; $M^{2+} = Cu^{2+}$, MoO_2^+, WO_2^{2+}) Metal oxide weighed
Ammonium nitrosophenylhydroxylamine (cupferron)		Fe(III), V(V), Ti(IV), Zr(IV), Sn(IV), U(IV) ($M^{n+} + nNH_4R \rightarrow \underline{MR_n} + nNH_4^+$) Metal oxide weighed
8-Hydroxyquinoline (oxine)		Many metals. Useful for Al(III) and Mg(II) ($M^{n+} + nHR \rightarrow \underline{MR_n} + nH^+$)
Sodium diethyldithiocarbamate	$(C_2H_5)_2N-C(=S)-S^-Na^+$	Many metals from acid solution ($M^{n+} + nNaR \rightarrow \underline{MRn} + nNa^+$)
Sodium tetraphenylboron	$NaB(C_6H_5)_4$	K^+, Rb^+, Cs^+, Tl^+, Ag^+, Hg(I), Cu(I), NH_4^+, RNH_3^+, $R_2NH_2^+$, R_3NH^+, R_4N^+. Acidic solution ($M^+ + NaR \rightarrow \underline{MR} + Na^+$)
Tetraphenylarsonium chloride	$(C_6H_5)_4AsCl$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-. Acidic solution ($A^{n-} + nRCl \rightarrow R_nA + nCl^-$)

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Gravimetric Analysis

- Calculations of analyte content requires knowledge of :
- Chemistry
- Stoichiometry
- Composition of precipitate

Gravimetry and Solution Equiliria

- Thermal Conversion to Measurable Form
- Removal of volatile reagents & solvent
- Extended heating at 110 to 115 ^{O}C
- Chemical conversion to known stable form
- $CaC_2O_{4(s)} \rightarrow CaO_{(s)} + CO_{(g)} + CO_{2(g)}$
- Volatilization & trapping of component
- $NaHCO_{3(aq)} + H_2SO_{4(aq)} \rightarrow CO_{2(g)} + H_2O + NaHSO_{4(aq)}$

Gravimetric Calculations

- Gravimetric Factor (GF):
- GF = (fwt analyte (g/mol)/fwt precipitate(g/mol))x(a(moles analyte/b(moles precipitate))
- GF = g analyte/g precipitate
- % analyte = (weight analyte (g)/ weight sample (g)) x 100%
- % (w/w) analyte (g) = ((wt ppt (g) x GF)/wt sample) x 100%

Gravimetric Errors

- Unknown Stoichiometry:
- Consider Cl^- determination with $AgNO_3$
- $Ag^+ + Cl^- \rightarrow AgCl$
- $Ag^+ + 2\ Cl^- \rightarrow AgCl_2$
- <u>Gravimetric Factor:</u>
- GF = fwt analyte/fwt precipitate x moles analyte/moles precipitate
- <u>Calculation for Cl^-</u> = wt. Ppt * GF

Gravimetric Errors

Fwt analyte grams	Fwt ppt grams	Moles analyte	Moles ppt	Grav factor	Weigh ppt grams	Weigh analyte grams
35.453	143.32	1	1	.2474	.606	0.149_9 ~0.150
35.453	178.77	2	1	0.3966	.606	0.240_3 ~0.240

Gravimetric Errors

Co-precipitation: (w/AgCl)

Co-precipitant	**Error**	**Rationale**
NaF	Positive	All NaF is excess
NaCl	Negative	Fwt Na<Ag
AgI	Positive	All AgI is excess
$PbCl_2$ (fwt 278.1)	Negative	Gravimetric Factors decreases

Alternative Gravimetry Technique

- Homogeneous Precipitation
- What?
  - Precipitating agent generated slowly by chemical reaction in analyte solution
- Why?
  - Precipitant appears gradually throughout
  - Keeps relative supersaturation low
  - Larger, less-contaminated particles
- How?
  - (OH^-) by urea decomposition
  - $(NH_2)_2CO \rightarrow 2\ \underline{OH^-} + CO_2 + 2\ NH_4^+$
  - ($S^=$) by thioacetamide decomposition
  - $CH_3CSNH_2 \rightarrow \underline{H_2S} + CH_3CONH_2$
  - (DMG) from biacetyl + hydroxylamine
  - $CH_3C(=0)\text{-}C(=0)CH_3 + 2\ H_2NOH \rightarrow \underline{DMG} + 2\ H_2O$

Precipitation Equilibria: The Solubility Product

- Solubility of Slightly Soluble Salts:
- $AgCl_{(s)} \leftrightarrow (AgCl)_{(aq)} \leftrightarrow Ag^+ + Cl^-$
- Solubility Product K_{SP} = ion product
- $K_{SP} = [Ag^+][Cl^-]$
- $Ag_2CrO_{4(s)} \leftrightarrow 2\ Ag^+ + CrO_4^{2-}$
- $K_{SP} = [Ag^+]^2[CrO_4^{2-}]$

The molar solubility depends on the stoichiometry of the salt.

A 1:1 salt is less soluble than a nonsymmetric salt with the same K_{sp}.

Table 10.3

Solubility Product Constants of Selected Slightly Soluble Salts

Salt	K_{sp}	Solubility, s (mol/L)
$PbSO_4$	1.6×10^{-8}	1.3×10^{-4}
AgCl	1.0×10^{-6}	1.0×10^{-5}
AgBr	4×10^{-13}	6×10^{-7}
AgI	1×10^{-16}	1×10^{-8}
$Al(OH)_3$	2×10^{-32}	5×10^{-9}
$Fe(OH)_3$	4×10^{-38}	2×10^{-10}
Ag_2S	2×10^{-49}	4×10^{-17}
HgS	4×10^{-53}	6×10^{-27}

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Precipitation Equilibria: The Common Ion Effect

- Common Ion Effect
- Will decrease the solubility of a slightly soluble salt.

The common ion effect is used to decrease the solubility.

Sulfate concentration is the amount in equilibrium and is equal to the $BaSO_4$ solubility.

In absence of excess barium ion, solubility is 10^{-5} M.

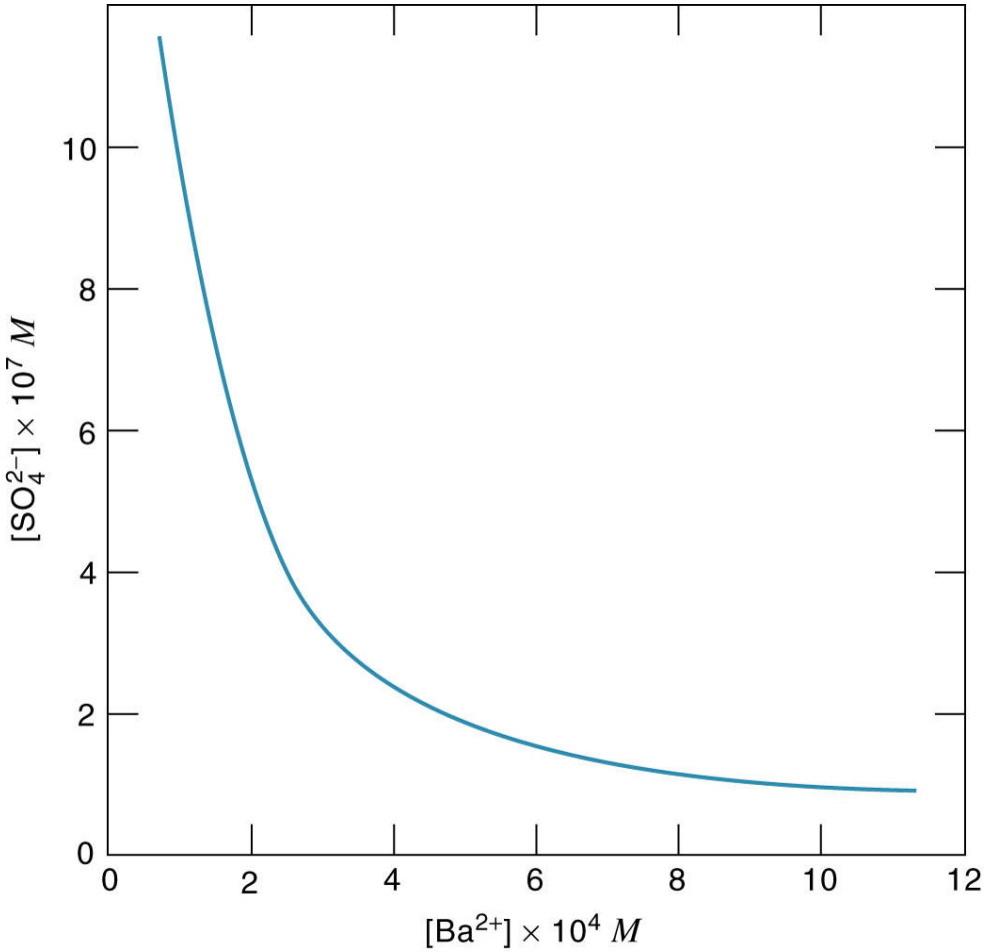

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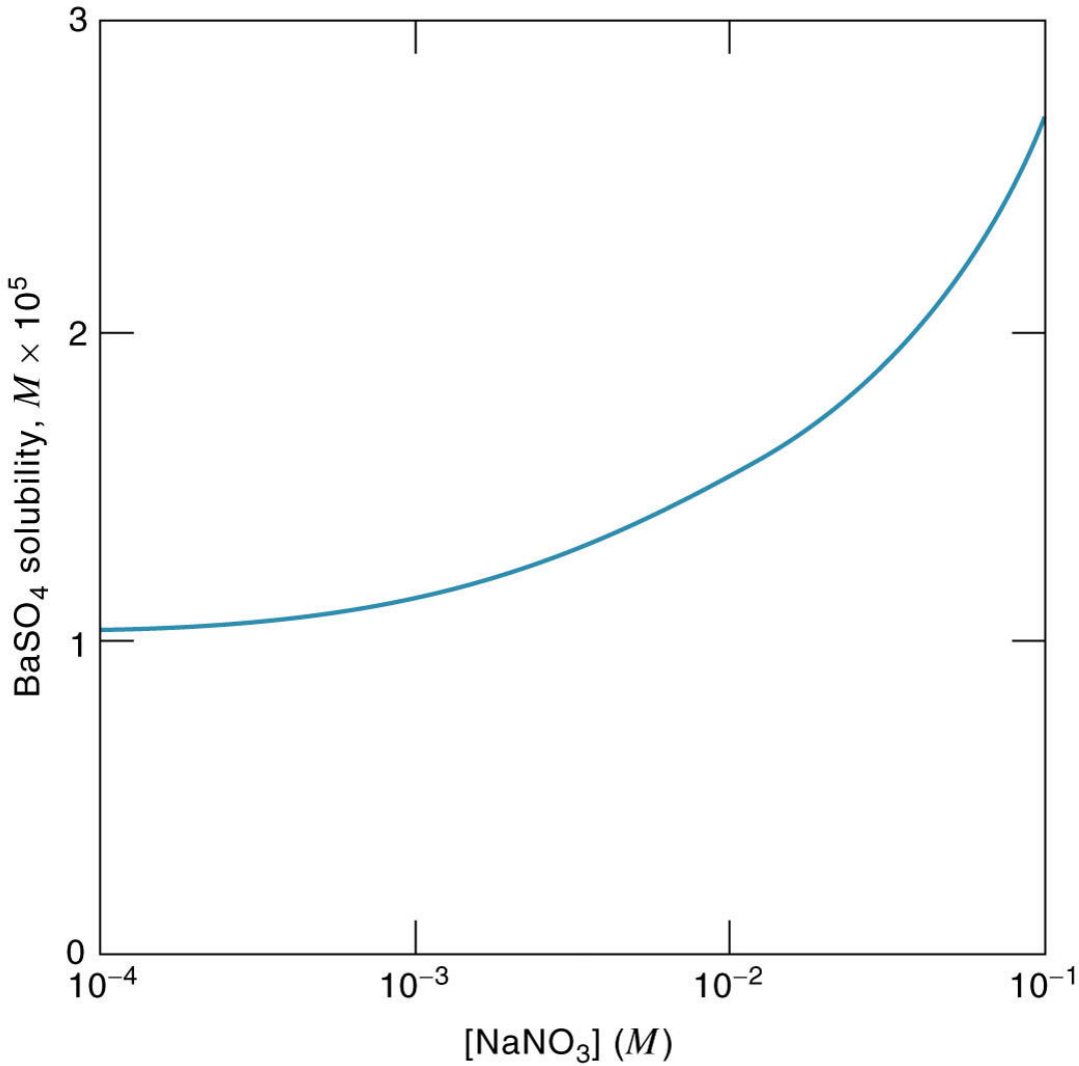
Fig. 10.3. Predicted effect of excess barium ion on solubility of $BaSO_4$.

Diverse Ion Effect on Solubility:

- Presence of diverse ions will increase the solubility of precipitates due to shielding of dissociated ion species.
- K_{SP}^{o} and Activity Coefficients
- $AgCl_{(s)} \leftrightarrow (AgCl)_{(aq)} \leftrightarrow Ag^{+} + Cl^{-}$
- Thermodynamic solubility product K_{SP}^{o}
- $K_{SP}^{o} = a_{Ag+} \cdot a_{Cl-} = [Ag^{+}]f_{Ag+} \cdot [Cl^{-}]f_{Cl-}$
- $K_{SP}^{o} = K_{SP} f_{Ag+} \cdot f_{Cl-}$
- $K_{SP} = K_{SP}^{o}/(f_{Ag+} \cdot f_{Cl})$

$K_{sp} = K_{sp}^0/f_{Ag+}f_{SO42-}$

Solubility increases with increasing ionic strength as activity coefficients decrease.



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Predicted effect of increased ionic strength on solubility of $BaSO_4$. Solubility at zero ionic strength is 1.0×10^{-5} M.

Gravimetric calculation using spreadsheet.

Cell B3 calculates %Fe from g. Fe_2O_3 (Cell D2) and g. sample (Cell B2).

	A	B	C	D	E	F	G	H
1	Calculation of % Fe.							
2	g. sample:	2.287	g. Fe_2O_3:	0.8792				
3	% Fe:	**26.88797**						
4								
5	%Fe = {[g Fe_2O_3 x 2Fe/Fe_2O_3 (g Fe/g Fe_2O_3)]/g sample] x 100%							
6	=	{[0.8792 g Fe_2O_3 x 2(55.845/159.69)g Fe/g Fe_2O_3]/2.287 g sample} x 100%						
7	**B3 =**	(D2*2*(55.845/159.69)/B2)*100						
8								
9	The answer is 26.89% Fe.							

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Using Exel Solver to calculate solubility.

Enter the formula (=s^2/K_{sp}) in Cell E4 (don't enter =1; that goes in Solver).

The value of s (Cell C4) is changed iteratively until the formula equals 1.

	A	B	C	D	E	F
1	Calculation of the Solubility of AgCl Using Solver.					
2	K_{sp}:	1.00E-10		formula = s^2/K_{sp} = 1		
3						
4		**s =**	**1E-05**	formula:	1.000001	
5						
6				formula Cell E4: = C4^2/B2		
7				**Solver:**		
8				**E4 = Target Cell**		
9				**Set value to 1**		
10				**Changing Cell = C4**		
11	The solubility is 1.0 x 10^{-5} M.					

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Calculating Results from Gravimetric Data

- The calcium in a 200.0 mL sample of a 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 26.6002 g. The mass of the crucible plus CaO (fwt 56.077 g/mol) was 26.7134 g. Calculate the concentration of Ca (fwt 40.078 g/mol) in the water in units of grams per 100 mL.

Calculating Results from Gravimetric Data

- An iron ore was analyzed by dissolving a 1.1324 g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide $Fe_2O_3 \cdot xH_2O$ by addition of NH_3. After filtration and washing, the residue was ignited at high temperature to give 0.5394 g pure Fe_2O_3 (fwt 159.69 g/mol). Calculate (a) the % Fe (fwt 55.847 g/mol) and (b) % Fe_3O_4 (fwt 231.54 g/mol) in the sample.

Calculating Results from Gravimetric Data

- A 0.2356 g sample containing only NaCl (fwt 58.44 g/mol) and $BaCl_2$ (fwt 208.23 g/mol) yielded 0.4637 g of dried AgCl (fwt 143.32 g/mol). Calculate the percent of each halogen compound in the sample.

Section 10

Electrochemical Cells and Electrode Potentials

Electrochemistry
Oxidation/Reduction Reactions

- "Redox" reactions involve electron transfer from one species to another
- $Ox_1 + Red_2 \leftrightarrow Red_1 + Ox_2$
- $Ox_1 + ne^- \leftrightarrow Red_1$ (Reduction ½ reaction)
- $Red_2 \leftrightarrow Ox_2 + ne^-$ (Oxidation ½ reaction)
- "Reducing agent" donates electrons (is oxidezed)
- "Oxidizing agent" accepts electrons (is reduced)

Electrochemistry
Oxidation/Reduction Reactions

- **Typical oxidizing agents:** Standard Potentials,V
  - $O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$ +1.229
  - $Ce^{4+} + e^- \leftrightarrow Ce^{3+}$ +1.6 (acid)
  - $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$ +1.51
- **Typical reducing agents:**
  - $Zn^{2+} + 2e^- \leftrightarrow Zn^o$ -0.763
  - $Cr^{3+} + e^- \leftrightarrow Cr^{2+}$ -0.408
  - $Na^+ + e^- \leftrightarrow Na^o$ -2.714

The salt bridge allows charge transfer through the solution and prevents mixing.

The spontaneous cell reaction ($Fe^{2+} + Ce^{4+} = Fe^{3+} + Ce^{4+}$) generates the cell potential.

The cell potential depends on the half-reaction potentials at each electrode.

The Nernst equation describes the concentration dependence.

A battery is a voltaic cell. It goes dead when the reaction is complete ($E_{cell} = 0$).

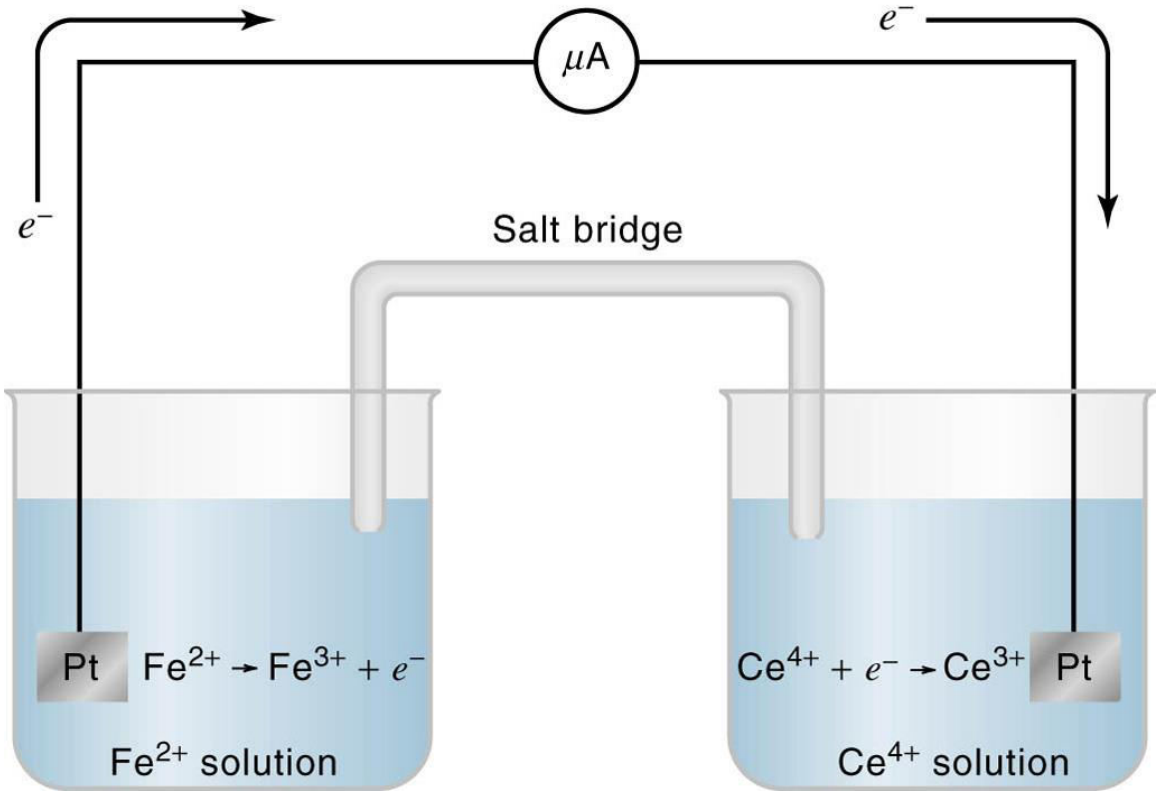

Fig. 12.1. Voltaic cell.

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Electrochemistry
Standard Reduction Potentials

- **<u>Half-Reaction Potentials:</u>**
- They are measured relative to each other
- Reference reduction half-reaction:
- standard hydrogen electrode (SHE)
- normal hydrogen electrode (NHE)
- $2H^{+}_{(\alpha=1.0)} + 2e^{-} \leftrightarrow H_{2(g\ 1atm)}$ 0.0000 volts

The more positive the E°, the better oxidizing agent is the oxidized form (e.g., MnO_4^-).

The more negative the E°, the better reducing agent is the reduced form (e.g., Zn).

Table 12.1

Some Standard Potentials

Half-Reaction	E^0(V)
$H_2O_2 + 2H^+ + 2e^- = 2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e^- = MnO_2 + 2H_2O$	1.695
$Ce^{4+} + e^- = Ce^{3+}$	1.61
$MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$	1.51
$Cr_2O_7^{2-} + 14H^+ + 6e^- = 2Cr^{3+} + 7H_2O$	1.33
$MnO_2 + 4H^+ + 2e^- = Mn^{2+} + 2H_2O$	1.23
$2IO_3^- + 12H^+ + 10e^- = I_2 + 6H_2O$	1.20
$H_2O_2 + 2e^- = 2OH^-$	0.88
$Cu^2 + I^- + e^- = CuI$	0.86
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$O_2 + 2H^+ + 2e^- = H_2O_2$	0.682
$I_2(aq) + 2e^- = 2I^-$	0.6197
$H_3AsO_4 + 2H^+ + 2e^- = H_3AsO_3 + H_2O$	0.559
$I_3^- + 2e^- = 3I^-$	0.5355
$Sn^{4+} + 2e^- = Sn^{2+}$	0.154
$S_4O_6^{2-} + 2e^- = 2S_2O_3^{2-}$	0.08
$2H^+ + 2e^- = H_2$	0.000
$Zn^{2+} + 2e^- = Zn$	−0.763
$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828

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Electrochemistry
Reduction Potentials

- **<u>General Conclusions:</u>**
- 1. The more positive the electrode potential, the stronger an oxidizing agent the oxidized form is and the weaker a reducing agent the reduced form is
- 2. The more negative the reduction potential, the weaker the oxidizing agent is the oxidized formis and the stronger the reducing agent the reduced form is.

Electrochemistry
Oxidation/Reduction Reactions

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  - $Zn^{2+} + 2e^- \leftrightarrow Zn^o$ -0.763
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  - $Na^+ + e^- \leftrightarrow Na^o$ -2.714

Electrochemistry
Oxidation/Reduction Reactions

- **Net Redox Reactions:** Standard Potentials,V
- $MnO_4^- \leftrightarrow Mn^{2+}$
- $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$ +1.51
- $Sn^{4+} + 2e^- \leftrightarrow Sn^{2+}$ +0.154
- **Balanced Net Ionic Reaction:**
- $2MnO_4^- + 16H^+ + 5Sn^{2+} \leftrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H2O$

Electrochemistry
Voltaic Cell

- The spontaneous (Voltaic) cell reaction is the one that gives a positive cell voltage when subtracting one half-reaction from the other.
- $E^o_{cell} = E^o_{right} - E^o_{left} = E^o_{cathode} - E^o_{anode} = E^o_{+} - E^o_{-}$
- Which is the Anode? The Cathode?
- **<u>Convention:</u>**
- The anode is the electrode where oxidation occurs ➔ the more negative half-reaction potential
- The cathode is the electrode where reduction occurs ➔ the more positive half-reaction potential
- anode | solution | cathode

Electrochemistry
Oxidation/Reduction Reactions

- **<u>Net Redox Reactions:</u>** <u>Standard Potentials,V</u>
- $MnO_4^- \leftrightarrow Mn^{2+}$
- $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$ +1.51
- $Sn^{4+} + 2e^- \leftrightarrow Sn^{2+}$ +0.154
- **<u>Balanced Net Ionic Reaction:</u>**
- $2MnO_4^- + 16H^+ + 5Sn^{2+} \leftrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H2O$
- $E^o_{cell} = E^o_{cat} - E^o_{an} = (+1.51 - (+0.154)) = +1.36$ V

Electrochemistry
Nernst Equation

- **<u>Effects of Concentrations on Potentials:</u>**
- $aOx + ne^- \leftrightarrow bRed$
- $E = E^o - (2.3026RT/nF) \log([Red]^b/[Ox]^a$
  - Where E is the reduction at specific conc.,
  - E^o is standard reduction potential, n is number of electrons involved in the half reaction,
  - R is the gas constant (8.3143 V coul $deg^{-1}mol^{-1}$),
  - T is absolute temperature,
  - and F is the Faraday constant (96487 coul eq^{-1}).
- At 25^oC(298.16K) the value of 2.3026RT/F is 0.05916
- Note: Concentrations should be activities

Electrochemistry

- **<u>Calculations:</u>**
- $MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$ $E^o = +1.51$ V
- For $[H^+] = 1.0M$, $[MnO_4^-] = 0.10M$, $[Mn^{2+}] = 0.010M$
- $E = E^o - 0.05916/5 (\log ([Mn^{2+}]/[MnO_4^-][H^+]^8))$
- $E = +1.51 - 0.1183(-1) = +1.63$ V vs NHE
- Note: This is more positive than E^o
- Greater tendency to be reduced compared to standard conditions.

Electrochemistry

- **<u>Calculations:</u>**
- Silver electrode/silver chloride deposit/0.010M NaCl
- $AgCl + 1e^- \leftrightarrow Ag^o + Cl^-$ $E = ?$
- $Ag^+ + 1e^- \leftrightarrow Ag^o$ $E^o = +0.799\ V$
- $AgCl \leftrightarrow Ag^+ + Cl^-$ $K_{sp} = 1.8 \times 10^{-10}$
- $AgCl + e^- \leftrightarrow Ag^o + Cl^-$
- $E = E^o - (0.05916/1)\ Log\ (1/[Ag^+])$
- $[Ag^+] = K_{sp}/[Cl^-] = 1.8 \times 10^{-10}/(0.010) = 1.8 \times 10^{-8}$
- $E = +0.799 - (0.05916)(7.74) =$ **<u>+0.341 V</u>**