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:
- **Selective**
- Ag^+ + Halides (X^-) □ $AgX_{(s)}$
- $Ag^+ + CNS^-$ □ $AgCNS_{(s)}$
- **Specific**
- Dimethylglyoxime (DMG)
- $2\ DMG + Ni^{2+}$ □ $Ni(DMG)_{2(s)} + 2\ H^+$

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

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

- **Peptization**
  - Re-dissolution of coagulated colloids by washing and removing inert electrolyte

Important Factors for Gravimetric Analysis

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

- **Digestion**
  - 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.

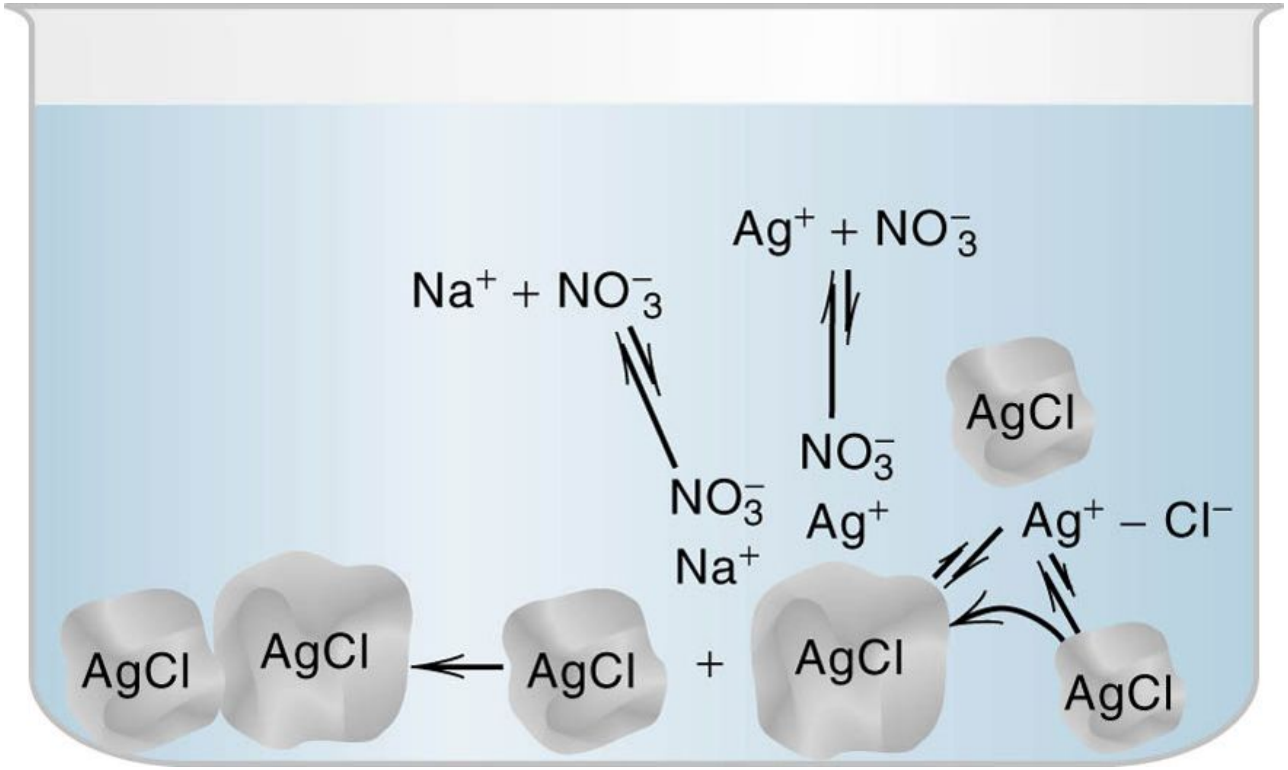

Fig. 10.1. Ostwald ripening.

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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).

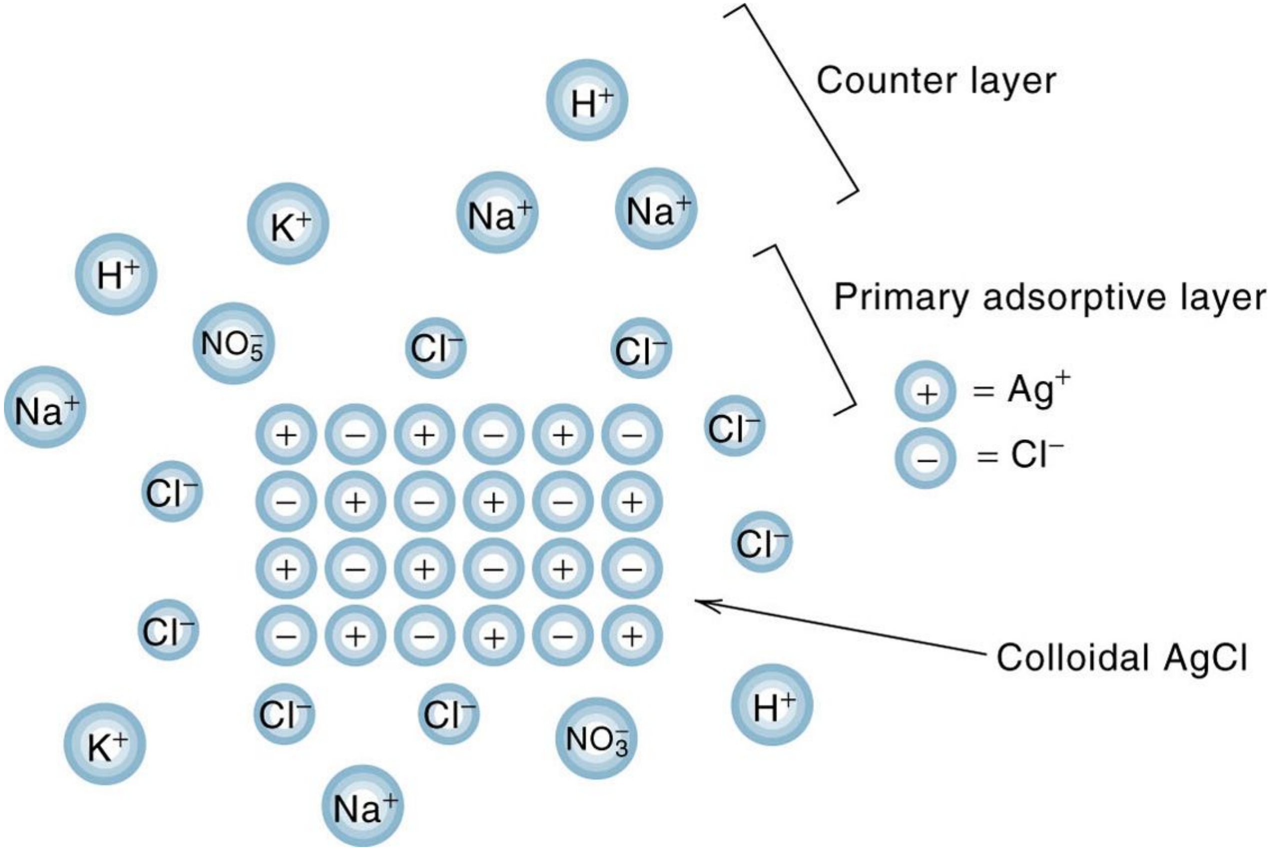

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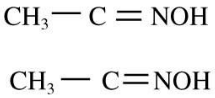
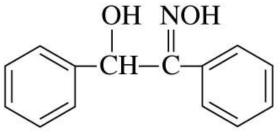
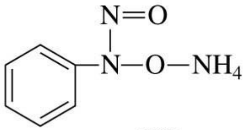
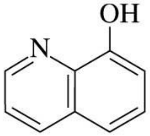
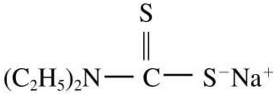
Fig. 10.2. Representation of silver chloride colloidal particle and adsorptive layers when Cl^- is in excess.

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	 $(C_2H_5)_2N—\overset{\overset{S}{\Vert}}{C}—S^-Na^+$	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
- $CaC_2O_{4(s)} \square\ CaO_{(s)} + CO_{(g)} + CO_{2(g)}$
- Volatilization & trapping of component
- $NaHCO_{3(aq)} + H_2SO_{4(aq)} \square\ CO_{2(g)} + H_2O + NaHSO_{4(aq)}$

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 $AgNO_3$
- $Ag^+ + Cl^-$ □ $AgCl$
- $Ag^+ + 2\ Cl^-$ □ $AgCl_2$
- Gravimetric Factor:
- GF = fwt analyte/fwt precipitate x moles analyte/moles precipitate
- Calculation for $Cl^=$ = 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
  - $(NH_2)_2CO$ □ 2 $\underline{OH}^{=}$ + CO_2 + 2 NH_4^+
  - ($S^=$) by thioacetamide decomposition
  - CH_3CSNH_2 □ $\underline{H_2S}$ + CH_3CONH_2
  - (DMG) from biacetyl + hydroxylamine
  - $CH_3C(=0)\text{-}C(=0)CH_3$ + 2 H_2NOH □ $\underline{DMG}$ + 2 H_2O

Precipitation Equilibria: The Solubility Product

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

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}.

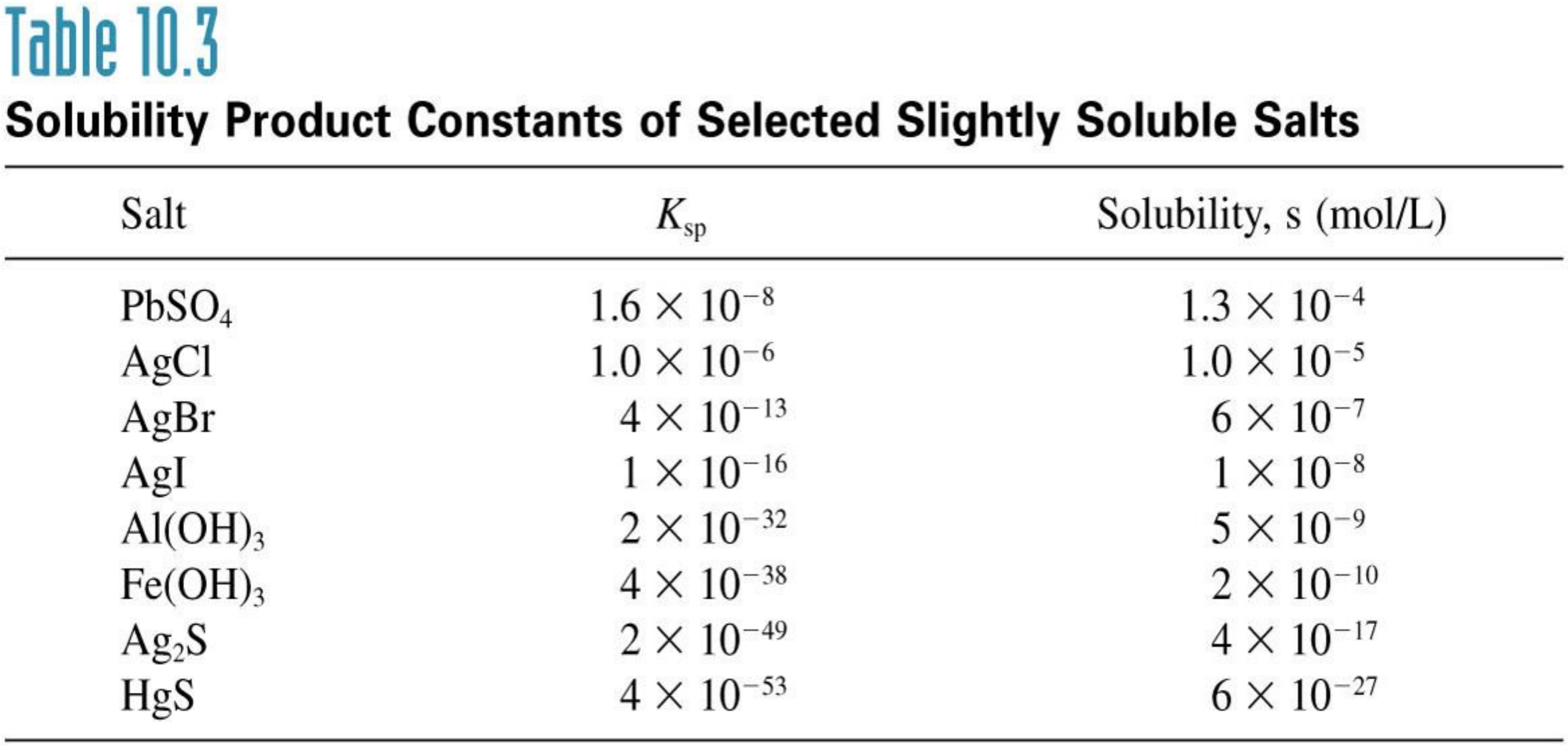

Table 10.3

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.

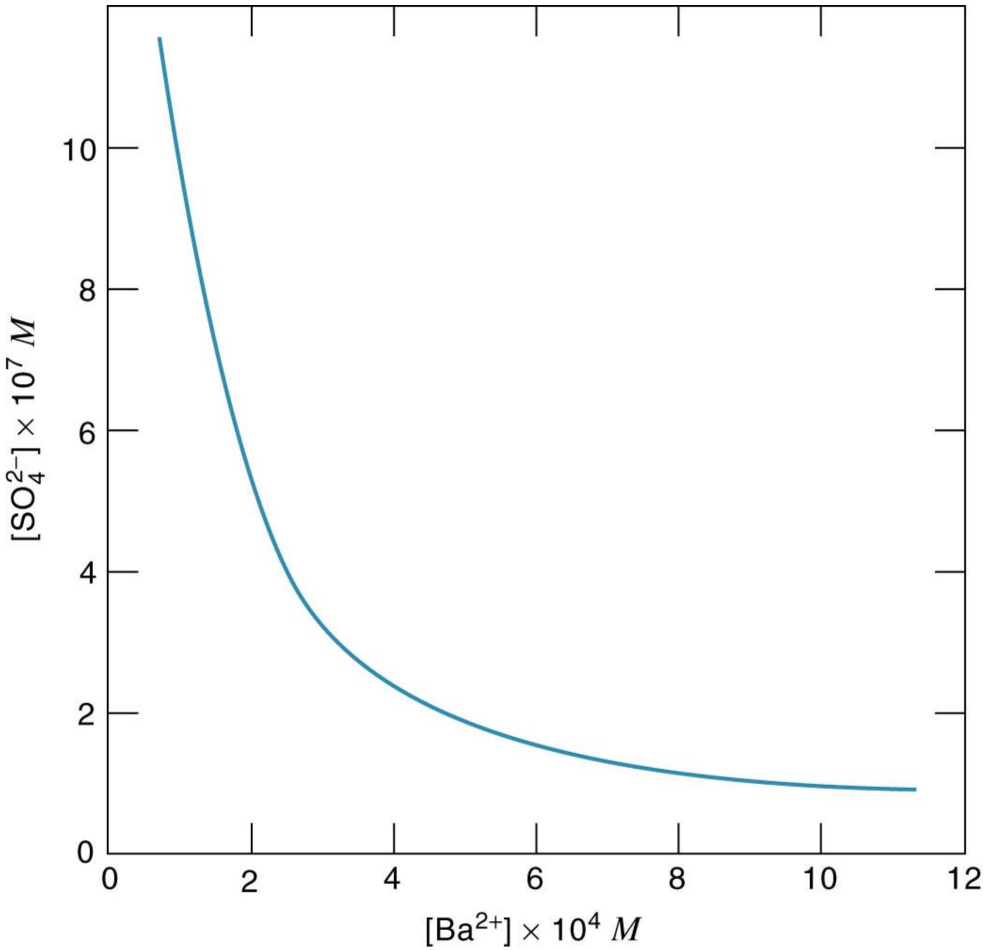

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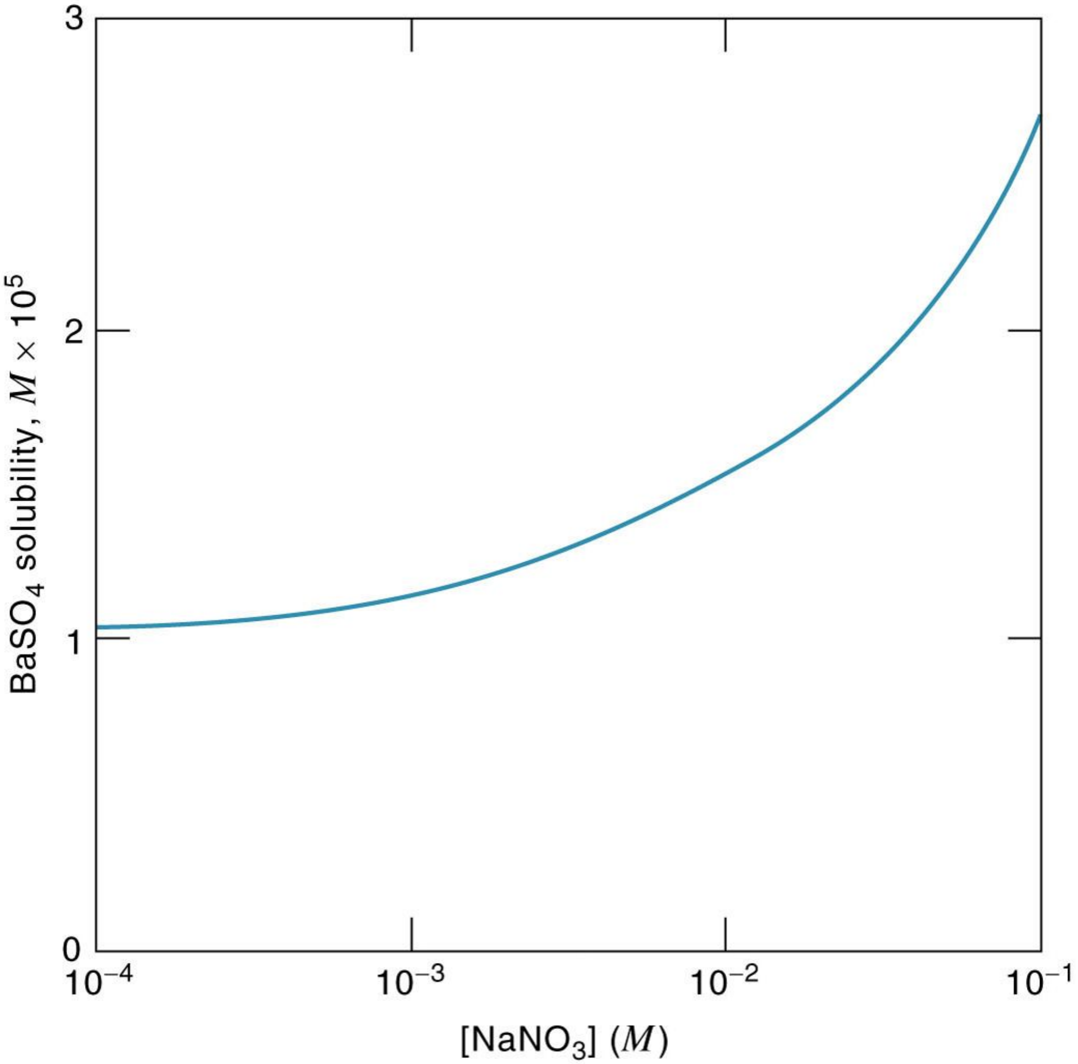
Fig. 10.3. Predicted effect of excess barium ion on solubility of $BaSO_4$.

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
- $AgCl_{(s)}$ □□ $(AgCl)_{(aq)}$ □□ $Ag^{+} + Cl^{-}$
- 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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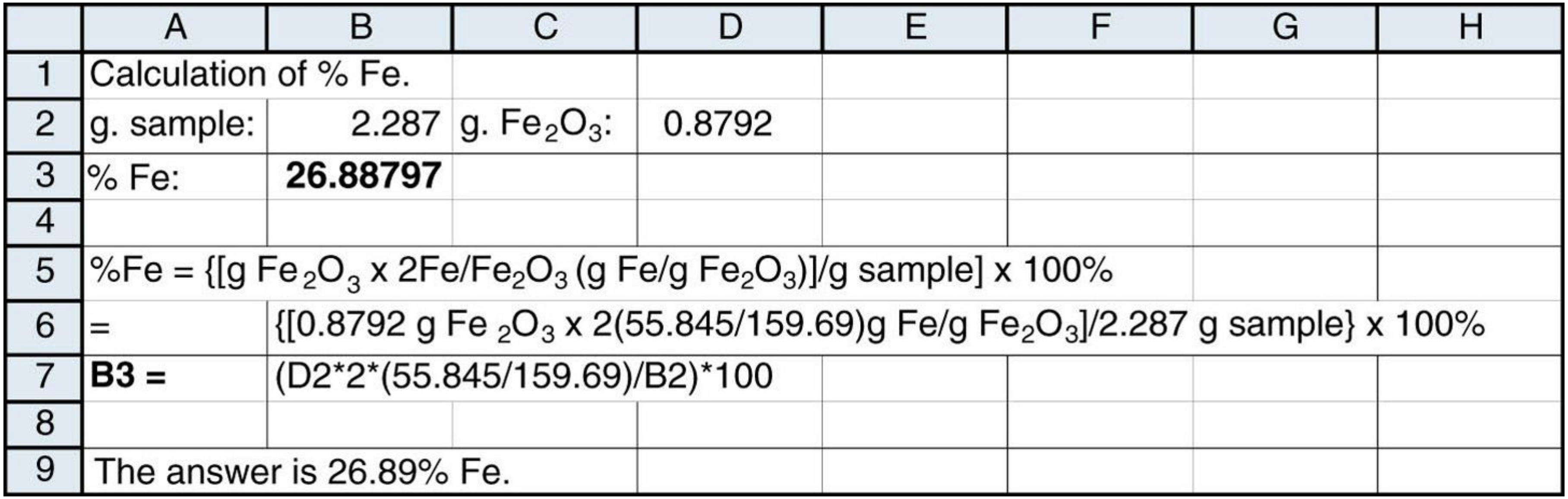
Predicted effect of increased ionic strength on solubility of $BaSO_4$. Solubility at zero ionic strength is 1.0×10^{-5} M.

Gravimetric calculation using spreadsheet.

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

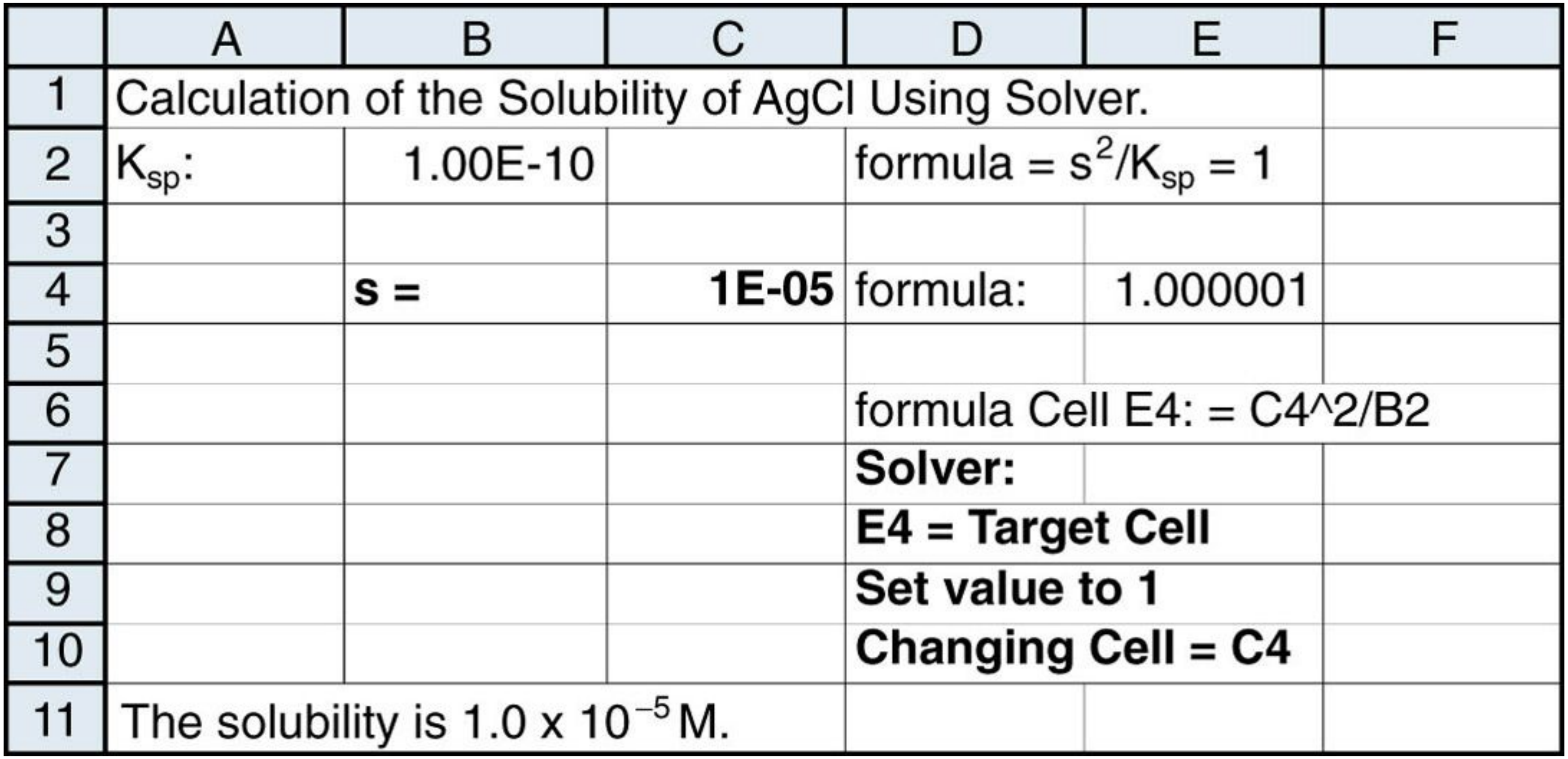


	A	B	C	D	E	F	G	H
1	Calculation of % Fe.							
2	g. sample:	2.287	g. Fe_2O_3:	0.8792				
3	% Fe:	**26.88797**						
4								
5	%Fe = {[g Fe_2O_3 x 2Fe/Fe_2O_3 (g Fe/g Fe_2O_3)]/g sample] x 100%							
6	=	{[0.8792 g Fe_2O_3 x 2(55.845/159.69)g Fe/g Fe_2O_3]/2.287 g sample} x 100%						
7	**B3 =**	(D2*2*(55.845/159.69)/B2)*100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

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.					

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.