Laboratory in Chemistry
2nd semester/Spring 2021

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Reactions and Equilibria of Ions in Aqueous Solutions

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General Information

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❖ Prerequisite: Fundamentals of Chemistry I and II

Reactions of Inorganic Ions and Ionic Equilibria

What topics have you learned last semester that relate to these experiments?

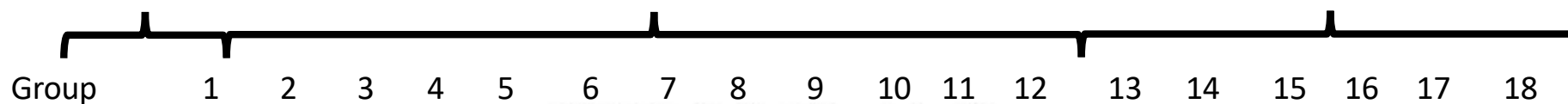**Do You know...have heard about...?**

1. The Periodic Table
2. Atoms, Molecules, Ions...Complex (ion)
3. Mass Relationships in Chemical Reactions...mol, mol weight....
4. Reactions in Aqueous Solutions...reaction equilibrium...
5. Ionic bonds...
6. Liquids and solutions...concentrations....precipitation....

The Periodic System of the Elements

s-block elements   d-block elements   p-block elements

Group   1   2   3   4   5   6   7   8   9   10   11   12   13   14   15   16   17   18

IUPAC Periodic Table of the Elements

Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H hydrogen [1.0078, 1.0082]																	2 He helium 4.0026
3 Li lithium [6.938, 6.997]	4 Be beryllium 9.0122											5 B boron [10.806, 10.821]	6 C carbon [12.009, 12.012]	7 N nitrogen [14.006, 14.008]	8 O oxygen [15.999, 16.000]	9 F fluorine 18.998	10 Ne neon 20.180
11 Na sodium 22.990	12 Mg magnesium [24.304, 24.307]											13 Al aluminium 26.982	14 Si silicon [28.084, 28.086]	15 P phosphorus 30.974	16 S sulfur [32.059, 32.076]	17 Cl chlorine [35.446, 35.457]	18 Ar argon 39.948
19 K potassium 39.098	20 Ca calcium 40.078(4)	21 Sc scandium 44.956	22 Ti titanium 47.867	23 V vanadium 50.942	24 Cr chromium 51.996	25 Mn manganese 54.938	26 Fe iron 55.845(2)	27 Co cobalt 58.933	28 Ni nickel 58.693	29 Cu copper 63.546(3)	30 Zn zinc 65.38(2)	31 Ga gallium 69.723	32 Ge germanium 72.630(8)	33 As arsenic 74.922	34 Se selenium 78.971(8)	35 Br bromine [79.901, 79.907]	36 Kr krypton 83.798(2)
37 Rb rubidium 85.468	38 Sr strontium 87.62	39 Y yttrium 88.906	40 Zr zirconium 91.224(2)	41 Nb niobium 92.906	42 Mo molybdenum 95.95	43 Tc technetium	44 Ru ruthenium 101.07(2)	45 Rh rhodium 102.91	46 Pd palladium 106.42	47 Ag silver 107.87	48 Cd cadmium 112.41	49 In indium 114.82	50 Sn tin 118.71	51 Sb antimony 121.76	52 Te tellurium 127.60(3)	53 I iodine 126.90	54 Xe xenon 131.29
55 Cs caesium 132.91	56 Ba barium 137.33	57-71 lanthanoids	72 Hf hafnium 178.49(2)	73 Ta tantalum 180.95	74 W tungsten 183.84	75 Re rhenium 186.21	76 Os osmium 190.23(3)	77 Ir iridium 192.22	78 Pt platinum 195.08	79 Au gold 196.97	80 Hg mercury 200.59	81 Tl thallium [204.38, 204.39]	82 Pb lead 207.2	83 Bi bismuth 208.98	84 Po polonium	85 At astatine	86 Rn radon
87 Fr francium	88 Ra radium	89-103 actinoids	104 Rf rutherfordium	105 Db dubnium	106 Sg seaborgium	107 Bh bohrium	108 Hs hassium	109 Mt meitnerium	110 Ds darmstadtium	111 Rg roentgenium	112 Cn copernicium	113 Nh nihonium	114 Fl flerovium	115 Mc moscovium	116 Lv livermorium	117 Ts tennessine	118 Og oganesson

| 57 La lanthanum 138.91 | 58 Ce cerium 140.12 | 59 Pr praseodymium 140.91 | 60 Nd neodymium 144.24 | 61 Pm promethium | 62 Sm samarium 150.36(2) | 63 Eu europium 151.96 | 64 Gd gadolinium 157.25(3) | 65 Tb terbium 158.93 | 66 Dy dysprosium 162.50 | 67 Ho holmium 164.93 | 68 Er erbium 167.26 | 69 Tm thulium 168.93 | 70 Yb ytterbium 173.05 | 71 Lu lutetium 174.97 |
| 89 Ac actinium | 90 Th thorium 232.04 | 91 Pa protactinium 231.04 | 92 U uranium 238.03 | 93 Np neptunium | 94 Pu plutonium | 95 Am americium | 96 Cm curium | 97 Bk berkelium | 98 Cf californium | 99 Es einsteinium | 100 Fm fermium | 101 Md mendelevium | 102 No nobelium | 103 Lr lawrencium |

Key:
atomic number
Symbol
name
conventional atomic weight
standard atomic weight

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

For notes and updates to this table, see www.iupac.org. This version is dated 28 November 2016.
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Rows are across and called **Periods. Columns** down are called **Groups**

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The Periodic System of the Elements

s-block elements   d-block elements   p-block elements

IUPAC Periodic Table of the Elements

main groups

transition metals

main groups

lanthanides and actinides

Most **d-block elements**[§] have **several** oxidation states.

d-block elements

+1	+2												-3	-2	-1
+1	+2											+3		-3	-2	-1
+1	+2	+3	+2 +3 +4	+2 +3 +4 +5	+2 +3 +4 +6	+2 +3 +4 +7	+2 +3	+2 +3	+1 +2	+1 +2	+2	+3	+4	-3	-2	-1
+1	+2	+3	+4	+3 +5	+3 +6	+4 +6 +7	+3 +4	+3	+2 +4	+1	+2	+3	+4	+5	-2	-1
+1	+2	+3	+4	+5	+6	+4 +6 +7	+3 +4	+3 +4	+2 +4	+1 +3	+1 +2	+3	+4	+5	+6	-1
+1	+2	+3	+4									+3	+4	+5	+6	

+3 +4	+3	+3	+3	+2 +3	+2 +3	+3	+3	+3	+3	+3	+3	+2 +3	+3
+4	+4 +5	+3 +4 +5 +6	+3 +4 +5 +6	+3 +4 +5 +6	+3 +4 +5 +6	+3 +4	+3 +4	+3 +4	+3	+3	+2 +3	+2 +3	+3

[§] also called "transition metals"

d-block elements have properties, which result from the **partially filled d shell** ⇨ Not observed in s-, p-block (main group) elements

Colours of Various Example Coordination Complexes

	Fe^{II}	Fe^{III}	Co^{II}	Cu^{II}	Al^{III}	Cr^{III}
Hydrated Ion	$[Fe(H_2O)_6]^{2+}$ Pale green Soln	$[Fe(H_2O)_6]^{3+}$ Yellow/brown Soln	$[Co(H_2O)_6]^{2+}$ Pink Soln	$[Cu(H_2O)_6]^{2+}$ Blue Soln	$[Al(H_2O)_6]^{3+}$ Colourless Soln	$[Cr(H_2O)_6]^{3+}$ Green Soln
OH$^-$, dilute	$[Fe(H_2O)_4(OH)_2]$ Dark green Ppt	$[Fe(H_2O)_3(OH)_3]$ Brown Ppt	$[Co(H_2O)_4(OH)_2]$ Blue/green Ppt	$[Cu(H_2O)_4(OH)_2]$ Blue Ppt	$[Al(H_2O)_3(OH)_3]$ White Ppt	$[Cr(H_2O)_3(OH)_3]$ Green Ppt
OH$^-$, concentrated	$[Fe(H_2O)_4(OH)_2]$ Dark green Ppt	$[Fe(H_2O)_3(OH)_3]$ Brown Ppt	$[Co(H_2O)_4(OH)_2]$ Blue/green Ppt	$[Cu(H_2O)_4(OH)_2]$ Blue Ppt	$[Al(OH)_4]^-$ Colourless Soln	$[Cr(OH)_6]^{3-}$ Green Soln
NH$_3$, dilute	$[Fe(H_2O)_4(OH)_2]$ Dark green Ppt	$[Fe(H_2O)_3(OH)_3]$ Brown Ppt	$[Co(H_2O)_4(OH)_2]$ Blue/green Ppt	$[Cu(H_2O)_4(OH)_2]$ Blue Ppt	$[Al(H_2O)_3(OH)_3]$ White Ppt	$[Cr(H_2O)_3(OH)_3]$ Green Ppt
NH$_3$, concentrated	$[Fe(H_2O)_4(OH)_2]$ Dark green Ppt	$[Fe(H_2O)_3(OH)_3]$ Brown Ppt	$[Co(NH_3)_6]^{2+}$ Straw coloured Soln	$[Cu(NH_3)_4(H_2O)_2]^{2+}$ Deep blue Soln	$[Al(H_2O)_3(OH)_3]$ White Ppt	$[Cr(NH_3)_6]^{3+}$ Green Soln
CO$_3^{2-}$	$FeCO_3$ Dark green Ppt	$[Fe(H_2O)_3(OH)_3]$ Brown Ppt + bubbles	$CoCO_3$ Pink Ppt	$CuCO_3$ Blue/green Ppt		

Ppt: precipitate
Soln: solution

Color due to d - d electronic transitions

Characteristic Properties of d-block elements

From left to right, aqueous solutions of:
cobalt(II) nitrate, $Co(NO_3)_2$ (red); potassium dichromate, $K_2Cr_2O_7$ (orange); potassium chromate, K_2CrO_4 (yellow); nickel(II) chloride, $NiCl_2$ (green); copper(II) sulfate, $CuSO_4$ (blue); potassium permanganate, $KMnO_4$ (violet).

Why

↗ **Pd** – Palladium **Pt** – Platinum

↗ **Ag** – Silver (Argentum) **Au** – Gold (Aurum)
Cd – Cadmium **Hg** – Mercury (hydrargyram) "liquid silver"

↗ Most transition metals have **several** oxidation states.

↗ Mn exists in 11 oxidation states -3 up to +7

↗ Transition metals and their compounds are usually **brightly colored**.

Metal complexes are coordination compounds

When metals are dissolved in water they react with water and form hydrated compounds:

$$Na(H_2O)_6^+ \text{ or } Cu(H_2O)_6^+$$

- These are called metal complexes or coordination compounds
- The neutral molecules H_2O, NH_3 or anions CN^-, SCN^-, CH_3COO^- are called **ligands**

$$CuSO_4 + 6\ H_2O \rightarrow Cu(H_2O)_6^{2+} + SO_4^{2-}$$
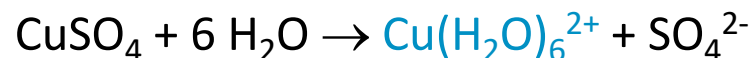
$$Cu(H_2O)_6^{2+} + 4\ NH_3 \rightarrow Cu(NH_3)_2(H_2O)_4^{2+} + 4\ H_2O \qquad \text{Ligand exchange}$$

↬ **Coordination chemistry**

From left to right, aqueous solutions of:
cobalt(II) nitrate, $Co(NO_3)_2$ (red); potassium dichromate, $K_2Cr_2O_7$ (orange); potassium chromate, K_2CrO_4 (yellow); nickel(II) chloride, $NiCl_2$ (green); copper(II) sulfate, $CuSO_4$ (blue); potassium permanganate, $KMnO_4$ (violet).

Alfred Werner: Coordination Chemistry

Alfred Werner and the historical development of the ideas of coordination chemistry

Alfred Werner – in the late 1800's the father of coordination chemistry.

- Studied in Switzerland at the University of Zurich.
- He lectured in both organic and inorganic chemistry.
- He developed the theory of coordination chemistry.
- He prepared and studied coordination compounds and discovered optically active forms of 6-coordinate octahedral complexes.
- His coordination chemistry extended through a whole range of systematic inorganic chemistry and into organic chemistry and he was awarded the **Nobel Prize in Chemistry** in 1913.
- He was the first inorganic chemist to win the Nobel prize, and the only one prior to 1973.

Nobel Lecture
http://nobelprize.org/chemistry/laureates/1913/werner-lecture.html

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Alfred Werner: Coordination Chemistry

Werner's Conclusions:

Coordination complexes are **neutral** and **counter ions** are not bonded to the central metal ion but **balance the charge**.

For example:

$$+3 \quad\quad 0 \quad\quad -3$$

$$[Co(NH_3)_6]Cl_3$$
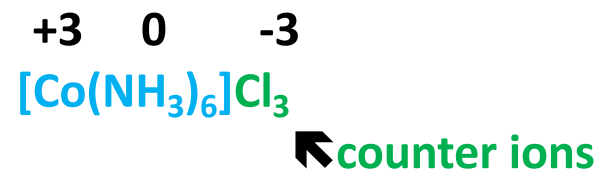
↖counter ions

1. The ligands directly **coordinated to the metal** are contained within the square bracket.
2. Six NH_3 ammine groups are bonded to Co.
3. **3 chloride ions are not bonded to the Co**; these are **counter ions**, they balance the charge (Co^{3+}) they are "free" to react with $AgNO_3$ to give 3 moles of precipating AgCl.

Reactions of Inorganic Ions

2.1 Reactions of inorganic ions (page 24-45 in manual, Experiment 1-3)

Main theme: *"Inorganic compounds are prepared, separated, and purified by relatively simple methods in aqueous solutions". [Chemistry in aqueous solutions]*

You will learn basic procedures in the experiments providing better understanding of
*   **ionic equilibria in aqueous solutions and**
*   **elementary concepts of ion complexes**.

This chapter is divided into **3 parts**:

1. Isolation of a target cation from the sample solution containing metal ions by precipitation of the corresponding salt that forms upon the addition of an appropriate reagent to the sample solution. In this step, the insoluble salt is precipitated by the appropriately chosen combination of a metal cation and an anion species or by adjusting the conditions, such as the pH or temperature of the solution.

2. The resulting precipitate is re-dissolved in water to obtain a solution containing the target metal ion. The solution is then subjected to a reaction in which the target ion forms a precipitate or gives color to the solution due to the formation of a metal-ion complex.

3. Analysis of an unknown sample containing multiple metal ions using the experimental approaches (e.g., reactions to detect specific metal ions and separation of the precipitate) learned in this chapter.

Reactions of Inorganic Ions

2.1.2 Dissolving salts (page 26 in manual)

- Many inorganic compounds are ionic compounds (mainly salts) that are composed of metal-element cations and nonmetal-element anions. (Product of acid-base neutralization)

- The ions in these compounds are attracted to each other by electrostatic forces and form ionic crystals (simple example: rock salt NaCl is $Na^+ Cl^-$)

- When ionic crystals are put in water, the positively charged Cations and negatively charged Anions exposed on its surface interact with water molecules. (dissolution)

- Water molecules are always electrically attracted to dissolved ions and combine with them (hydrate them).

- In general, solubility of salts in water varies, depending on the balance of two forces: the attractive force between the two types of ions in the ionic crystal (lattice energy) and the attractive force between each ion and water molecules (hydration energy).

- Salts can be classified into two categories: those that are soluble in water and those that are insoluble in water.

Reactions of Inorganic Ions

The following salts are **classified as soluble**:
- metal nitrates;
- metal halides (chlorides, bromides, and iodides), **except** silver(I) halides and mercury(I) halides;
- metal sulfates, **except** calcium(II), strontium(II), barium(II), silver(I), mercury(I), and lead(II) salts;
- sodium salts;
- potassium salts;
- ammonium salts.

The following salts are **classified as insoluble**:
- metal hydroxides, except sodium hydroxide, potassium hydroxide, and ammonium hydroxide (although these compounds are not salts (why?), they are included here for your convenience; also, please, note that barium hydroxide is soluble);
- metal carbonates;
- metal phosphates;
- metal sulfides, except salts of calcium(II), strontium(II) and barium(II)}.

However, solubility of these compounds sometimes varies drastically depending on the pH or temperature.
Approximate solubilities of salts in water and acids are listed in Table 2.1. (page 29 in the manual)

Solubility

2.1.3 Water-soluble salts and solubility (page 28 in manual)

"The definition of solubility is the maximum quantity of solute *(the compound to be dissolved)* that can dissolve in a certain quantity of solvent or quantity of solution at a specified temperature or pressure (in the case of gaseous solutes)"

www.chem.fsu.edu/chemlab

Solution   Supernate

Suspension   Precipitate

(Wikipedia)
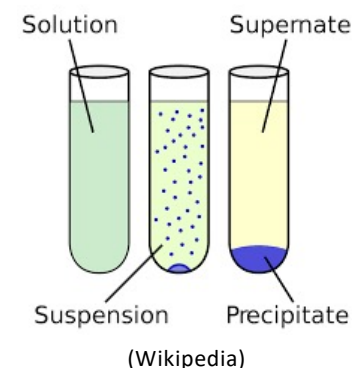
- Solutions of around 10^{-2} M in concentration (0.02 M) are usually used in this class for experiments on inorganic ions (e.g. $AgNO_3$ 0.05 M **(molar concentration, molarity (mol/L)**).
- Substances with solubilities exceeding 10^{-2} M are classified as soluble.
- Sparingly soluble substances have solubilities below 10^{-5} M (< 0.00001 M).
- When the concentration of a specific ion in the supernatant (supernate) decreases to around 10^{-5} M (0.00001 M) after precipitation, the ion remaining in the supernatant cannot be detected in reactions with common reagents.
- Salts with solubilities between 10^{-2} and 10^{-5} M are considered to lie in the intermediate range between soluble and sparingly soluble.
- Water solubility of most salts increases with increasing the temperature.
- Salts with low solubility — for example, those with solubility around 10^{-8} M at room temperature — even if the solubility increases 100-fold upon heating, its dissolution still cannot be visually observed because the solubility remains 10^{-6} M. **15**

Example

- The solubility of $PbCl_2$ is 9.9 g/L at 20°C and 33.4 g/L at 100°C, respectively. In the units of M, the solubility of $PbCl_2$ at 20°C is 3.6×10^{-2} M, since the formula weight (g/mol) of $PbCl_2$ is 278.1, and the solution density can be approximated as 1.0 g/mL. (Can you calculate it?)*

- When precipitate of $PbCl_2$ is formed from a 0.05 M $Pb(NO_3)_2$ solution at 20 °C, the amount of precipitate is estimated as 0.014 mol (3.9 g), as shown below:

$$0.05 \text{ M} - 3.6 \times 10^{-2} \text{ M} = 1.4 \times 10^{-2} \text{ M}$$

(Solubility of $PbCl_2 \Rightarrow 3.6 \times 10^{-2}$ M $\Rightarrow Pb^{2+}$ remains in solution in presence of Cl^-)

- If this suspension is heated from 20 °C to 100 °C, the precipitate dissolves completely because the solubility at 100 °C is 33.4 g/L. This corresponds to a concentration of 0.12 M, which is larger than 0.05 M of the sample. (The solution becomes undersaturated)

You will learn about the relationship between temperature dependency of solubility and solubility product using $PbCl_2$, which is between soluble and sparingly soluble. You will also learn how to analyze inorganic ions by separating Class I metals (Ag^+, Pb^{2+}), which form sparingly soluble chlorides.

$$^* C \left[\frac{mol}{L}\right] = \frac{m[g]}{V[L]} \times \frac{1}{mw\left[\frac{g}{mol}\right]}$$

The Solubility-Product Constant, K_{sp}

- We just mentioned those solubility rules that state a substance is insoluble or soluble. Substances with solubilities exceeding 10^{-2} M are classified as soluble. Substances that have solubilities below 10^{-5} M are insoluble (But actually ….. they are all a bit soluble!)
- Soluble is also sometimes practically defined as "greater than 3 grams dissolving in 100 mL of water". So, there is a lot of wiggle room for solubility up to 3 grams! This type of equilibrium deals with that wiggle room.
- **If you can actually see that a salt is insoluble, then the solution is actually saturated.** Saturated solutions of salts present yet another type of chemical equilibria.

➢ Sparingly soluble salts establish a dynamic equilibrium with the hydrated cations and anions in solution

- When the solid is first added to water, no ions are initially present.
- As dissolution proceeds, the concentration of ions increases until equilibrium is established. This occurs when the solution is saturated.

The equilibrium constant, the K_{sp}, is no more than the product of the ion concentrations at this equilibrium in solution.
(!Remember, solids do not appear in equilibrium expressions!)

Solubility Equilibria

- For a saturated solution of AgCl, the equation would be:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
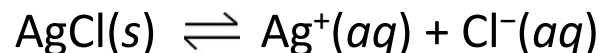
- The solubility product expression would be:

$$K_{sp} = [Ag^+][Cl^-]$$

Conventionally for concentrations and activities, square brackets [ ] are used around the chemical molecular formula: here mol/L

- The AgCl(s) does not appear in the equilibrium expression since solids are left out. Why? The concentration of the solid remains relatively constant.

A table of K_{sp} values is on page 30 in the manual.

In practice, K_{sp} values are determined by careful laboratory measurements using various spectroscopic methods.
Relative solubilities can be deduced by comparing values of $K_{sp.}$. BUT, BE CAREFUL!
These comparisons can only be made for salts having the same ION:ION ratio.
Please don't forget: Solubility changes with temperature! Some substances become less soluble in cold water while other increase in solubility! Aragonite $CaCO_3$ is an example

The Common Ion Effect

Experiments show that the solubility of any salt is always less in the presence of a "common ion" e.g., excess Cl⁻ in the case of AgCl precipitation.

↳ "The solubility products K_{sp}'s are equilibrium constants in heterogeneous equilibria (i.e., between two different phases). If several salts are present in a system, they all ionize in the solution. If the salts contain a common cation or anion, all these salts contribute to the concentration of the common ion. ⇒ **Contributions from all salts must be included in the calculation of concentration of the common ion.**" https://chem.libretexts.org/Core/Physical_and_Theoretical_Chemistry/Equilibria/Solubilty/Common_Ion_Effect

$$NaCl \leftrightharpoons [Na^+]_1 + [Cl^-]_1$$
$$KCl \leftrightharpoons [K^+]_2 + [Cl^-]_2$$

→ $[Cl^-]_{total} = [Cl^-]_1 + [Cl^-]_2$

The common ion concentration is the sum of all concentrations of the common ion

$$Saturated\ solution:\ PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$
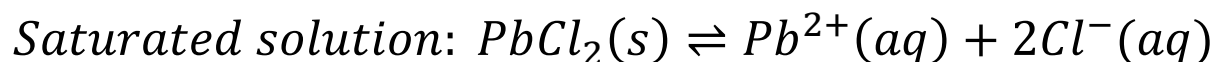
What happens if "extra" chloride is added to the solution? (e.g. by adding KCl)

↳ PbCl₂ will precipitate!

Why? *Le Chatelier's Principle*! According to the law of mass action, the addition of a salt containing the ion common to the precipitate (common ion) shifts the equilibrium of the whole system to the direction of the precipitate (in our case to the left) by increasing solid lead (II) chloride. In fact, the solubility of $PbCl_2$ decreases by adding the common ion!

Le Chatelier Principle

In chemistry, Le Chatelier's principle (1884) can be used to predict the effect of a change in conditions on a chemical equilibrium. The principle is named after Henry Louis Le Chatelier and sometimes Karl Ferdinand Braun who discovered it independently. It can be summarized as:

➢ If a chemical system at equilibrium experiences a change in concentration, temperature, volume, or partial pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.

This principle has a variety of names, depending upon the discipline using it. It is common to take Le Chatelier's principle to be a more general observation, roughly stated:

➢ **Any change in status quo prompts an opposing reaction in the responding system.**

In chemistry, the principle is used to manipulate the outcomes of reversible reactions, often to increase the yield of reactions.

Solubility and Complex Ions

➤ The formation of complex ions can often dissolve otherwise insoluble salts.
➤ Often as the complex ion forms, the solubility equilibrium shifts to the right (away from the solid) and causes the insoluble salt to become more soluble.
➤ Example: If sufficient aqueous ammonia is added to silver chloride, the latter can be dissolved as $[Ag(NH_3)_2]^+$ forms.

$$AgCl\ (s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \qquad K_{sp} = 1.8 \times 10^{-10}$$

$$Ag^+(aq) + 2\ NH_3\ (aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) \qquad K_{formation} = 1.6 \times 10^7$$
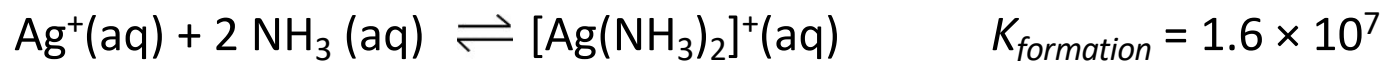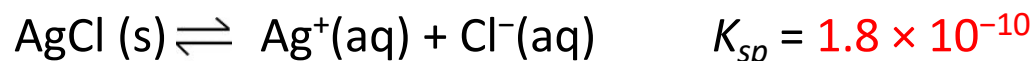
➤ Add these two equations together and determine the new K value.

$$\text{SUM: } AgCl\ (s) + 2\ NH_3\ (aq) \rightleftharpoons Ag(NH_3)_2]^+(aq) + Cl^-\ (aq)$$
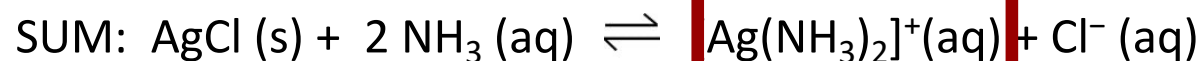
$$K = K_{sp} \times K_{formation} = 2.9 \times 10^{-3} = \frac{\{[Ag(NH_3)_2^+]\}[Cl^-]}{[NH_3]^2}$$

That is a significant improvement regarding the solubility of AgCl(s). The equilibrium constant for dissolving silver chloride in ammonia is not large. If the concentration of ammonia is sufficiently high; the complex ion will form:

↬ $[Ag^+]$ will decrease

↬ AgCl (s) will dissolve (Le Chatelier again!)

Systematic Analysis of Cations

2.2 Systematic analysis of cations (page 34 in manual; Experiment 2)

- By using the information on solubility of salts and properties of complex ions described before, a systematic analysis of cations is possible.

- In this course, metal ions are broadly grouped into four classes (Class I to Class IV) based on solubility (see Table 2.1, page 29).

- Salts that belong to the same class are separated into the respective individual ions through reactions with appropriate reagents.

- The presence of a specific ion can be confirmed by using a **REAGENT THAT SPECIFICALLY REACTS WITH THAT ION**.

- In this section you will learn about conditions under which sulfides and hydroxides of metal ions form and about confirmatory reactions for each ion.

Metal Sulfides

2.2.1 Reactions of metal ions with hydrogen sulfide and the formation and decomposition of sulfides

- Hydrogen sulfide (H_2S) is often used for the precipitation of sulfides.
- In this experiment, hydrogen sulfide is generated by the decomposition of thioacetamide in water because of the high toxicity of hydrogen sulfide (H_2S) gas. Thioacetamide is hydrolyzed to generate hydrogen sulfide (H_2S).

$$CH_3CSNH_2 + 2\ H_2O \rightarrow CH_3COO^-NH_4^+ + H_2S$$

- This reaction is catalyzed by an acid (H+) or a base (OH−) and initiated on heating. Thus, the general method for preparation of metal sulfides, the reaction of a metal ion with hydrogen sulfide, can be substituted by adding an acid or a base to a mixed solution of a metal ion and thioacetamide while heating it.

- **Decomposition of thioacetamide** must be **carried out under a fume hood**, because a part of the hydrogen sulfide generated during the reaction is released from the reaction vessel in the form of gas.

Metal Sulfides

- Because the solubility of sulfides varies with the pH of the solution, sulfides of some metallic ions do not precipitate from an acidic solution. Thus, the catalyst (acid or base) for the decomposition of thioacetamide should be selected carefully.
- The fact that the solubility of sulfides is pH dependent can be explained by the chemical equilibrium that establishes between S^{2-}, and H^+ in solution.

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$
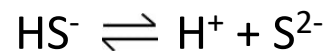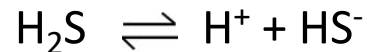
(check details on equilibrium constants in the manual!)

The result is: $\quad\quad$ **$[H^+]^2 [S^{2-}] = 1.2 \times 10^{-23} M^3$** (saturated solution of H_2S (0.1 M at 25 °C))

- According to above Equation, under strongly acidic conditions, when pH = 0 and $[H^+]$ = 1 M, $[S^{2-}]$ is equal to 1.2×10^{-23} M.
- Given that the concentration of a metal ion is 0.05 M, the **product of ion concentrations** in the solution is calculated as $6 \times 10^{-25} M^2$.
- Thus, for example, **Zn^{2+} does not form a precipitate** of ZnS under these conditions because K_{sp}(ZnS) is $1 \times 10^{-23} M^2$ (Table 2.2; page 30), whereas Cu^{2+} does form a precipitate of CuS under the same conditions because K_{sp} (CuS) is $6 \times 10^{-36} M^2$.

$$K_{sp}(ZnS) > K_{ion} \text{ (solution)} > K_{sp}(CuS)$$

- Assuming that pH = 9 ($[H^+]$ = 10^{-9} M) in a basic aqueous solution, $[S^{2-}]$ is estimated as 1.2×10^{-5} M according to the Equation equilibrium of $[H^+]^2 [S^{2-}] = 1.2 \times 10^{-23}$ M³

- As a result, both Zn^{2+} and Ni^{2+} (K_{sp}(NiS) = 3×10^{-19} M²) do form precipitates of ZnS and NiS, respectively. ($[Zn^{2+}]$, $[Ni^{2+}]$ 0.05 M)

$$[Zn^{2+}][S^{2-}] = 6 \times 10^{-7} \text{ M}^2 > K_{sp}(\text{ZnS}) > K_{sp}(\text{NiS})$$

- Because the aqueous solution of sodium sulfide $(Na_2S)_{aq}$ is basic, metal ions that form sparingly soluble salts react with Na_2S to form sulfides on the basis of similar principle.

- Based on the pH dependence of $[S^{2-}]$, metal sulfides that do not form a precipitate in an acidic solution may dissolve upon addition of a strong acid, which generates hydrogen sulfide.

- In actual experiments, dissolution of metal sulfides with an acid is not always consistent with the prediction based on the solubility product. For example, the dense precipitate of NiS that forms when exposed to heat does not dissolve in 1 M HCl or in acids of similar strength. Some sulfides that can precipitate in a strongly acidic solution dissolve in a HNO_3 solution, in which S^{2-} is oxidized.

You will learn about the properties and reactions of sulfides .

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Metal Hydroxides

2.2.2 Metal hydroxides (page 38 in manual; Experiment 2)

- Solubility of hydroxides that form a sparingly soluble precipitate with cations is affected by the **hydrogen ion concentration [H⁺]** in the solution.
- For example, $Fe(OH)_3$ is in equilibrium with the component ions in the solution as shown in Equation below.

$$Fe^{3+} + 3\ OH^- \rightleftharpoons Fe(OH)_3\ (s)$$
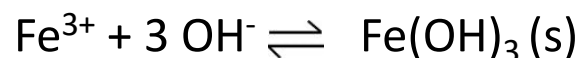
The solubility constant is expressed as

$$K_{sp} = [Fe^{3+}][OH^-]^3 = 1 \times 10^{-38}\ M^4$$

the dissociation constant of water (also called ionic product of water) is expressed as

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}\ M^2$$

↳ The concentration of Fe^{3+} can then be expressed as

$$[Fe^{3+}] = [H^+]^3 \times 10^4 \qquad\qquad [Fe^{3+}] = \frac{1\times10^{-38}M^4}{[OH^-]^3} = \frac{1\times10^{-38}M^4}{\left[\frac{1\times10^{-14}}{[H^+]}\right]^3} = [H^+]^3 \times 10^4$$

Thus, if the pH of a Fe^{3+} solution is 3 ($[H^+] = 1.0 \times 10^{-3}$ M), $[Fe^{3+}]$ can be estimated to be 10^{-5} M. Therefore, almost all (99.98%) of Fe^{3+} precipitates from the 0.05 M Fe^{3+} solution (pH = 1.8) that we use.

Metal Hydroxides

- On the basis of the solubility product of metal hydroxides, Al^{3+} can be precipitated completely under weakly acidic conditions (pH = 6). (cf. calculation for Fe^{3+})
- However, $Ni(OH)_2$ with K_{sp} = 6.5 x 10^{-18} has $[Ni^{2+}]$ equal to 0.07 M (> 0.05 M) at this pH and no precipitate is formed. This indicates that a target metal ion can be separated as a precipitate of metal hydroxide by adjusting the pH of the solution appropriately. To maintain the pH of a solution at a constant level, a buffer may be used.
- It is expected that many metal ions can precipitate as hydroxides in a basic solution, assuming that the concentration of the hydrogen ion and the solubility product are the sole major factors.
- However, when pH increases gradually in a solution of amphoteric metal ions, (e.g. Al^{3+}) the **precipitate formed at the early-stage dissolves to form metal hydroxocomplex ions under strong basic conditions**.
- This peculiar property of amphoteric metal ions can be used to separate specific metal ions from a mixture of metal hydroxides. For example, Fe^{3+} and Al^{3+} can be discriminated (separated) in a mixed solution containing both ions; one forms a hydroxide precipitate while the other forms a metal hydroxocomplex in solution.

You will learn about metal hydroxides and their properties and reactions.

Separation & Confirmation of Mixed Inorganic Ions in Solution

2.3 Separation and confirmation of mixed inorganic ions (analysis of an unknown sample) (page 41 in manual; Experiment 3)

- Sections 2.1 and 2.2 introduced the formation and dissolution of a precipitate as a result of reactions between the metal ion and an anion, the formation of complex ions, and confirmatory reactions of metal ions.
- *This knowledge allows for separating one metal ion from a mixture with another metal ion*, as shown in **Table 2.4. (page 42)**
- An ion can be separated from the mixed solution from another ion (other ions) based on the difference in their properties as described in the corresponding column of Table 2.4.
- Since some precipitates of sulfides and hydroxides and complex metal ions exhibit characteristic color, reactions that form colored substrates are useful in identifying specific metal ions.
- **However,** in order to positively identify a metal ion from the result of a characteristic reaction, it is important to ascertain that the target metal ion is free from contamination by another metal that may form a precipitate of a similar color.
- You should not rely on a single reaction to identify the target metal ions. Rather several different reactions should be used to identify them with certainty.

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- In this section, your understanding of the principles learned in the previous sections of this chapter will be put to test in experiments that aim to identify an individual metal ion in an unknown sample that contains two or three metals selected from the seven metal ions in Table 2.4.

- Table 2.4 suggests that the following precipitation reactions make it possible to separate the target metal ions (see Figure 2.2; page 43):

➤ (i) Ag^+ can be separated as the sole precipitate (R_I) from others in a reaction with the Cl^- ion at high temperature. All the other ions remain in the supernatant (F_I).

➤ (ii) Pb^{2+} and Cu^{2+} can be separated as the next precipitates (R_{II}) in the reaction of the supernatant F_I with H_2S under acidic conditions. Al^{3+}, Fe^{3+}, Zn^{2+}, and Ni^{2+} remain in the supernatant F_{II}.

➤ (iii) Next, Al^{3+} and Fe^{3+} are separated as precipitates R_{III} of the corresponding hydroxide, while Zn^{2+} and Ni^{2+} remain in the supernatant F_{III}, when an excess of NH_3 is added to the supernatant F_{II} that makes it basic.

➤ Thus, according to this protocol, a mixed solution of seven metal ions is separated roughly to the following four groups:

➤ Precipitate of AgCl (R_I), a mixed precipitate of PbS and CuS (R_{II}), a mixture of Al^{3+} and Fe^{3+} (R_{III}), and a supernatant containing Zn^{2+} and Ni^{2+} ions (F_{III}).

Separation & Confirmation of Mixed Inorganic Ions in Solution

- In the next stage, the metal ions are separated from each group (in actual experiments, sometimes one metal ion is the sole component of a specific group). Metal ions should be identified based on confirmatory reactions.

- These processes are summarized as a flow chart in Figure 2.2. In this systematic analysis, **metal ions are divided into four groups**:

- **Class I (Ag^+ and Pb^{2+})**, which form sparingly soluble halides (R_I),

- **Class II (Pb^{2+}, Cu^{2+}, and Sn^{4+})**, whose sulfides precipitate in an acidic aqueous solution (R_{II}),

- **Class III (Fe^{3+}, Al^{3+}, and Cr^{3+})**, whose hydroxides precipitate in a weakly acidic or neutral aqueous solution (R_{III}),

- **Class IV (Zn^{2+}, Ni^{2+}, and Co^{2+})**, whose sulfides precipitate in a basic aqueous solution (R_{IV}).

- Although Pb^{2+} belongs to both Class I and Class II in this classification, the most effective capture of Pb^{2+} is to wash the precipitate R_I with hot water to keep Pb^{2+} in solution F_I and handle it as a Class II metal rather than a Class I metal.

- In addition, Ag^+ in the sample solution should be excluded as precipitate of AgCl from F_I as rigorously as possible. Otherwise, the remaining Ag^+ will result in an incorrect identification of the sample because R_{II} will be contaminated with Ag_2S.

Separation & Confirmation of Mixed Inorganic Ions in Solution

Sample solution

1. Add HCl
2. Centrifuge

R_I

Class I (Insoluble halide)
AgCl↓   PbCl$_2$↓

F_I

1. Adjust to 0.3 M HCl acidic
2. Add thioacetamide
3. Heat
4. Centrifuge

R_{II}

Class II (Insoluble sulfide under acidic conditions)
CuS↓   PbS↓   SnS↓

F_{II}

1. Expel S^{2-}
2. Adjust to pH 6 with NH$_3$–NH$_4$Cl buffered solution
3. Centrifuge

R_{III}

Class III (Insoluble hydroxide at pH 5 –7.5)
Fe(OH)$_3$↓   Al(OH)$_3$↓   Cr(OH)$_3$↓

F_{III}

1. Add thioacetamide under basic conditions with NH$_3$–NH$_4$Cl solution
2. Centrifuge

R_{IV}

F_{IV}

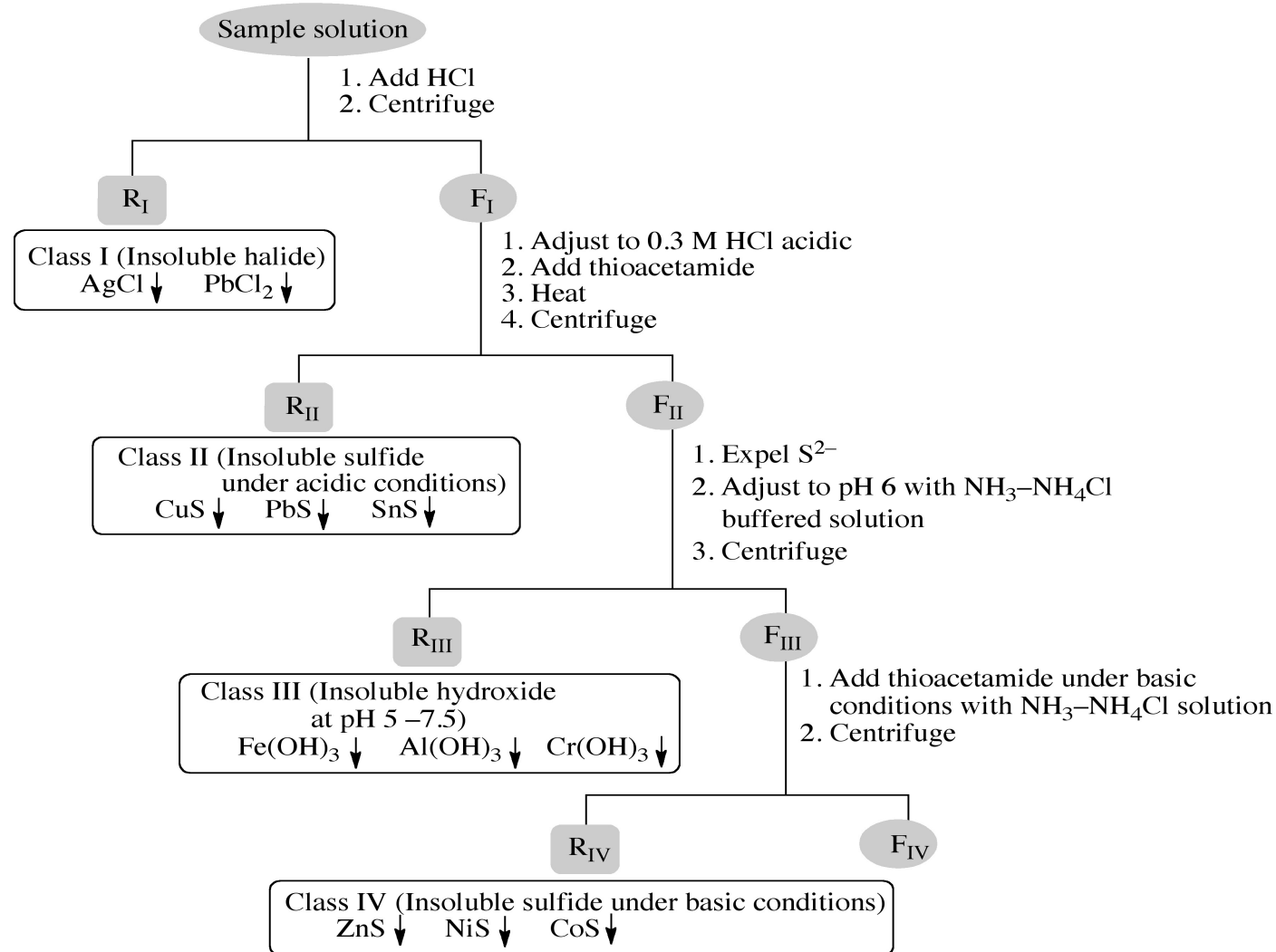Class IV (Insoluble sulfide under basic conditions)
ZnS↓   NiS↓   CoS↓

Figure 2.2 Systematic analyses of cations

Although "R" and "F" stand for the residue and filtrate "Residue" and "Filtrate", respectively, in this figure they mean the precipitate and supernatant in Figure 2.2.

1. Experiment in the Lab

- Bring your prepared laboratory notebook, saftey guide, writing utensils, pocket calculator, and textbook

- Safety glasses ("goggles")!! No sandals/heels!!

- Be in time (13:00) in front of the lab

- Store all of your belongings that are not required for your experiment in the lockers

- No beverages/food inside the lab!