CHM 1311E: Principles of Chemistry

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Notes written from Sandro Gambarotta's lectures.

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3 Stoichiometry of Formulas and Equations

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3.3 Writing and Balancing Chemical Equations

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3.5 Fundamentals of Solution Stoichiometry

3.6 The Role of Water as a Solvent

3.7 Writing Equations for Aqueous Ionic Reactions

3.7.1 Redox Reactions

Definition. Redox reactions
Reactions involving the **movement of electrons**.

For **ionic compounds**, this involves **transfer of electrons**.
In **covalent compounds**, this is simply a **shift of electrons**.

Oxidation is the **loss** of electrons and **reduction** is the **gain** of electrons.
The **oxidizing agent** takes electrons and is **reduced**.
The **reducing agent** takes electrons and is **oxidized**.

Definition. Oxidation Number
The number of electrons would have **if** the electrons were transferred completely.

Theorem. General Oxidation Rules

1. **Elemental form** (e.g. Na, O_2, Cl_2), oxidation number = 0.
2. **Monatomic ion**, oxidation number = ion charge.
3. **Compound**, oxidation number = sum of oxidation numbers of atoms = 0.
4. **Polyatomic ion**, oxidation number = ion charge.

Theorem. Specific Oxidation States

1. **Group 1:** +1 in all compounds

2. **Group 2:** +2 in all compounds
3. **Hydrogen:** +1 with nonmetals
   -1 with metals and boron
4. **Fluorine:** -1 in all compounds
5. **Oxygen:** -2 in most cases, unless coupled to a more electronegative centre (e.g. F) or a group 2 or group 2 metal (+2, -1, respectively).
6. **Group 17:** -1 with metals, nonmetals (except O) and other halogens lower in the group.

Definition. Oxidation Number Method

1. Assign oxidation numbers to all atoms.
2. Identify the oxidized and reduced species.
3. Draw tie-lines between the reactant and product species and write the number of electrons lost (oxidation), and electrons gained (reduction) on the line.
4. Multiply the number of electrons by factors so that the number of electrons lost = the number of electrons gained and use the factors as balancing coefficients.
5. Complete the balancing by inspection and add states of matter.

4 Gases and the Kinetic Molecular Theory

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4.1 An Overview of the Physical States of Matter

1. Gas volume changes significantly with pressure.
2. Gas volume changes significantly with temperature.
3. Gases flow very freely.
4. Gases have relatively low densities.
5. Gases form a solution in any proportions.

4.2 Gas Pressure and Its Measurement

$\text{Pressure} = \dfrac{\text{force}}{\text{area}}$

Table 1: Common Units of Pressure

Unit	**Normal Atmospheric Pressure at Sea Level and $0°C$**
pascal (Pa); kilopascal (kPa)	$1.013\,25 \times 10^5$ Pa; 101.325 kPa
atmosphere (atm)	1 atm
millimetres of mercury (mmHg)	760 mmHg
torr (Torr)	760 Torr
bar	1.013 25 bar

4.3 The Gas Laws and Their Experimental Foundations

4.3.1 Boyle's Law

$$V \propto \frac{1}{P}$$
$$P \times V = \text{constant}$$

4.3.2 Charles' Law

$$V \propto T$$
$$\frac{V}{T} = \text{constant}$$

4.3.3 Avogadro's Law

$$V \propto n$$
$$\frac{V}{n} = \text{constant}$$

4.3.4 Standard Conditions

$$STP = 1\,\text{bar}(10 \times 10^5\,\text{Pa}) \text{ and } 0\,°\text{C}(273.15\,\text{K})$$

Definition. Standard molar volume is the *volume* of 1 mol of an ideal gas at STP

$$\text{SMV} = 22.7\,\text{L}$$

4.3.5 Ideal Gas Law

$$PV = nRT$$

Example 4.1. Applying the Volume-Pressure Relationship

$$\begin{aligned} V_1 &= 24.8\,\mathrm{cm}^3 \\ P_1 &= 1.13\,\mathrm{bar} \\ P_2 &= 2.67\,\mathrm{bar} \\ V_2 &= ?\mathrm{bar} \end{aligned}$$

$$\begin{aligned} 24.8\,\mathrm{cm}^3 &= 0.0248\,\mathrm{L} \\ \frac{p_1 \times V_1}{n_1 \times T_1} &= \frac{p_2 \times V_2}{n_2 \times T_2} \\ p_1 \times V_1 &= p_2 \times V_2 \\ V_2 = V_1 \times \frac{p_1}{p_2} &= 0.0248\,\mathrm{L} \times \frac{1.13\,\mathrm{bar}}{2.67\,\mathrm{bar}} = 0.0105\,\mathrm{L} \end{aligned}$$

4.4 Rearrangements of the Ideal Gas Law

$$\begin{aligned} d &\propto M \qquad (i) \\ d &\propto \frac{1}{T} \\ d &= \frac{m}{V} \end{aligned}$$

$$\begin{aligned} n &= \frac{m}{M} \qquad (ii) \\ PV &= \frac{m}{M}RT \\ \frac{m}{V} &= \frac{PM}{RT} \end{aligned}$$

$$d = \frac{PM}{RT} \qquad (iii)$$

4.4.1 Molar Mass from the Ideal Gas Law

$$\begin{aligned} n = \frac{m}{M} &= \frac{pV}{RT} \\ M &= \frac{mRT}{pV} \end{aligned}$$

4.4.2 Mixtures of Gases

Definition. Partial pressure is the pressure exerted by one gas in a mixture.

Definition. Dalton's Law of Partial Pressures is the total p is the sum of **partial pressures**.

The partial pressure of a gas is proportional to its mole fraction:

$$p_A = X_A \times p_{\text{total}}$$
$$X_A = \frac{n_A}{n_{\text{total}}}$$

Example 4.2. Collecting a water-insoluble gaseous product and determining its pressure.

- A water insoluble gaseous product is bubbled through water into a collection vessel.
- The vapor pressure (P_{H_2O}) adds to P_{gas} to give P_{total}.
  - This is because molecules of H_2O enter bubbles of gas.
- In the given example, the water level in the vessel is above the level in the beaker, so $P_{\text{total}} < P_{\text{atm}}$.
- After all the gas has been collected, P_{total} is made equal to P_{atm} by adjusting the height of the collection vessel until the water level in it equals the level in the beaker.

$$\mathbf{P}_{\text{total}} = \mathbf{P}_{\text{gas}} + \mathbf{P}_{\mathbf{H_2O}}$$

4.5 The Kinetic-Molecular Theory: A Model for Gas Behavior

Theorem. Space in between particles
$V_{\text{particle}} \approx 0$

Theorem. Motion of particles
Particles undergo constant, random, straight-line motion, excluding collisions.

Theorem. Elastic collitions
Particles exchange energy on collision but do not lose any due to friction.
$\sum Energy$ remains constant.

Example 4.3. Boyle's Law
Assuming a container for which $P_{\text{gas}} = P_{\text{exterior}}$, then the particles will collide with the walls from an average distance, d_1.
Increasing P_{exterior} but keeping T and n fixed will result in shorter collision distances ($d_2 < d_1$) which results in $P_{\text{gas}} = P_{\text{exterior}}$ again.

Example 4.4. Dalton's Law
Assume two gases in separate containers ($n_A = 0.60\,\mathrm{mol}$ and $n_B = 0.30\,\mathrm{mol}$) with separate pressures ($P_A = 1.0\,\mathrm{bar}$ and $P_B = 0.50\,\mathrm{bar}$).
When the gases are combined, $P_{\text{total}} = P_A + P_B = 1.0\,\mathrm{bar} + 0.50\,\mathrm{bar} = 1.5\,\mathrm{bar}$.

Definition. Charles' Law states that increasing T results in an increase in P.

Theorem. At a given T, all gases in a sample have the same average kinetic energy.

$$E_k = \frac{1}{2}\text{mass} \times \text{speed}^2$$

Kinetic energy dpends on both the mass and the speed of a particle.

4.5.1 Graham's Law of Effusion

Definition. Effusion is the process by which a gas escapes through a small home in its container into an evacuated space.

Definition. Graham's Law of Effusion states that the rate of effusion of a gas is inversely proportional to the square root of its molar mass.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{M}}$$

Example 4.5. Applying Graham's Law of Effusion
A mixture of He and CH_4 is placed in an effusion apparatus. Calculate the ratio of their effusion rates.

$M_{CH_4} = 16.04\,\mathrm{g\,mol^{-1}}$
$M_{He} = 4.003\,\mathrm{g\,mol^{-1}}$

$$\begin{aligned}\frac{rate_{He}}{rate_{CH_4}} &= \sqrt{\frac{16.04}{4.003}}\\ &= 2.002\end{aligned}$$

4.6 Non-Ideal Gases: Deviations from Ideal Behavior

Real gases to not function ideally.

Theorem. Non-ideal gases deviate mostly deviate from ideal behaviour at **low temperature** and **high pressure**.

4.6.1 The van der Waals Equation

Definition. The **van der Waals** equation is an adjustment of the ideal gas law taking into account *real volume of gas particles* and the *effects of interparticle attractions.*

$$(p + \frac{n^2 a}{V^2})(V - nb) = nRT$$

In the above equation, the constant a relates to factors that influence attration between particles.
The constant b relates to particle volume.

5 Thermochemistry

5.1 Forms of Energy and Their Interconversion

Definition. Thermodynamics is the study of energy and its transformations.

Definition. Thermochemistry is a branch of thermodynamics that deals with the heat involved in chemical and physical changes.

Theorem. Transfer of energy produces **work** and **heat**.

Definition. A **system** is a specific region of space being studied.

Definition. Surrondings is everything *outside* the system.

$$\text{System} + \text{Surroundings} = \text{Universe}$$

Definition. Internal Energy (U) is the *sum* of potential and kinetic energies of all particles present.

Theorem. Total energy of the universe remains *constant.*

Theorem. A change in energy is accompanied by an *equal* and *opposite* change in energy of the surroundings.

Theorem. Total change in internal energy is the sum of energy transfered as **heat** (q) and **work** (w).

$$\Delta U = q + w$$

$$\Delta E = E_{final} - E_{initial} = E_{products} - E_{reactants}$$

q	$+$	w	$=$	ΔU
$+$		$+$		$+$
$+$		-		depends on sizes of q and w
-		$+$		depends on sizes of q and w
-		-		-

	q
$+$	**gains** heat
-	**releases** heat

	w
$+$	work done **on** system
-	work done **by** system

5.1.1 The Law of Energy Conservation

Definition. The first law of thermodynamics states that the *total energy of the universe is constant.*

$$\Delta_{universe}U = \Delta_{system}U + \Delta_{surroundings}U = 0$$

5.1.2 Units of Energy

Definition. SI unit of energy is the **joule (J)**.

$$1\,\mathrm{J} = 1\,\mathrm{kg\,m^2\,s^{-2}}$$

Definition. The **calorie (cal)** is the quantity of energy needed to raise the temperature of 1 g of water by 1°C.

$$1\,\mathrm{cal} = 4.184\,\mathrm{J}$$

5.2 Enthalpy: Chemical Change at Constant Pressure

Definition. PV Work is work done when the volume of a system changes in the presence of an external pressure.

Definition. Enthalpy (H) is defined as $U + PV$.

$$\Delta H = \Delta U + \Delta PV$$

If a system remains at constant pressure and semi-constant volume, then $\Delta H \approx \Delta U$.

Theorem. The expansion of a gas pushing back the atmosphere does pV work.

$$w = -P\Delta V$$

5.2.1 ΔU as a measure of ΔH

Definition. ΔH is the change in heat for a system at **constant pressure**.

$$q_p = \Delta U + P\Delta V = \Delta H$$

This means that $\Delta H \approx \Delta U$ for reactions:

- that do not involve gases
- in which the total amount (mol) of gas does not change
- in which q_p is much larger than $P\Delta V$, even if the total mol of gas does change.

5.3 Calorimetry: Measuring the Heat of a Chemical or Physical Change

Definition. The **specific heat capacity (c)** of a substance is the quantity of heat required to change the temperature of **1 gram** of the substance by **1 K**.

$$q = cm\Delta T$$

$$\begin{aligned} q &= \text{heat lost or gained} \\ c &= \text{specific heat capacity} \\ m &= \text{mass in g} \\ \Delta T &= T_{final} - T_{initial} \end{aligned}$$

Definition. The **heat capacity** is the heat required to change the temperature of the substance by **1 K**.

$$q = \text{heat capacity } \times \Delta T$$

5.4 Stoichiometry of Thermochemical Equations

Definition. A **thermochemical equation** is a balanced equation that includes $\Delta_r H$.

Example 5.1.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \qquad\qquad \Delta H = 572\,\text{kJ}$$

Sign of ΔH indicates whether the reaction is *exothermic* or *endothermic.*
Magnitude of $\Delta H \propto$ mol

5.5 Hess's Law: Finding ΔH of Any Reaction

Definition. Hess' Law states that the *enthalpy change* of an overall process is the sum of the enthalpy changes of its individual steps.

$$\Delta_{overall} H = \Delta_1 H + \Delta_2 H + \cdots + \Delta_n H$$

Example 5.2. Calculating ΔH for an overall process

- Identify the target equation (whose ΔH is unknown).
  - Note the amount of each reactant and product.
- Manipulate each equation with known ΔH values so that the target amount of each substance is on the correct side of the equation.
  - Change the sign of ΔH when you reverse an equation.
  - Multiply amount (mol) and ΔH by the same factor.
- Add the manipulated equations and their resulting ΔH values to get the target equation and its ΔH.
  - All substances except those in the target equation must cancel.

5.6 Standard Enthalpies of Reaction ($\Delta_r H^\circ$)

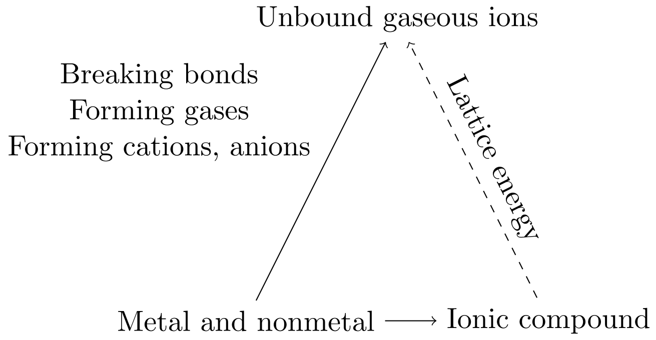
Definition. Standard Enthalpy of Reaction ($\Delta_r H^\circ$) is the enthalpy change of the reaction measured in **standard state**.

- For a gas, standard state is 1 bar and ideal behaviour.
- For aqueous solutions, standard state is 1 M concentration.
- For a pure substance, standard state is the most stable form at 1 bar and the temperature of interest (usually 25 °C)

Definition. Standard Enthalpy of Formation ($\Delta_f H^\circ$) is the enthalpy change associated with the formation of 1 mol of a compound from its elements, in standard state.

$$\Delta_r H^\circ = \Sigma m \Delta_f H^\circ_{products} - \Sigma n \Delta_f H^\circ_{reactants}$$

5.6.1 Born-Haber Cycle



5.7 Bond Energies and $\Delta_r H^\circ$

Theorem. The heat released or absorbed furing a chemical change is due to the differences between the bond energies of reactants and products.

$$\Delta_r H^\circ = \Sigma\Delta_{\text{reactant bonds broken}} H^\circ + \Sigma\Delta_{\text{product bonds formed}} H^\circ$$

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14 Kinetics

← October 2, 2013

14.1 Focusing on Reaction Rate

14.1.1 Factors That Influence Reaction Rate

Theorem. Particles must collide in order to react.

- **Concentration** - more collisions
- **Physical State** - faster mixing
- **Temperature** - more collisions

14.2 Expressing the Reaction Rate

Definition. Reaction rate is measured in terms of the changes in concentrations of reactants or products per unit time.

$$\text{Rate} = \frac{\Delta C_A}{\Delta t} = -\frac{C_{A_2} - C_{A_1}}{t_2 - t_1} = -\frac{\Delta(C_A)}{\Delta t}$$

The general form for an equation is:

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = -\frac{1}{c}\frac{\Delta[C]}{\Delta t} = -\frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

14.3 The Rate Law and Its Components

Theorem. For any general reaction occuring at a fixed temperature

$$aA + bB + \cdots \to cC + dD + \cdots$$
$$Rate = k[A]^m[B]^n$$

k is the **rate constant**, which is specific for a given reaction at a given temperature. m and n are **reaction orders** and are determined by **experiment**.

14.3.1 Reaction Orders

Definition. Individual order is a value specific for a reaction with respect to each reactant.

Example 14.1. Given a reaction $A \to$ products
If the rate doubles when $[A]$ doubles, rate depends on $[A]^1$ and the reaction is **first order** with respect to A.
If the rate quadruples when $[A]$ doubles, rate depends on $[A]^1$ and the reaction is **second order** with respect to A.
If the rate does not change when $[A]$ doubles, rate depends on $[A]^1$ and the reaction is **zero order** with respect to A.

14.3.2 Individual and Overall Reaction Orders

$$\text{order}_{\text{total}} = \Sigma \text{order}_{\text{reactants}}$$

Theorem. Reaction orders must be determined from experimental data and cannot be deduced from the balanced equation.

14.3.3 Determining Reaction Orders

To determine the values of m and n in the rate law, a series of experiements are run where one reactant concentration is kept constant, and the change in the other is measured.

14.4 Integrated Rate Laws: Concentration Changes over Time

An integrated rate law includes **time** as a variable.

First-order rate equation

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A] \qquad ln\frac{[A]_0}{[A]_t} = -kt$$

Second-order rate equation

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A]^2 \qquad \frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Zero-order rate equation

$$rate = -\frac{\Delta[A]}{\Delta t} = k[A]^0 \qquad [A]_t - [A]_0 = -kt$$

Straight-line form first-order rate equations

$$ln[A]_t = -kt + ln[A]_0$$

14.4.1 Reaction Half-life

← October 7, 2013

Definition. Half-life ($t_{1/2}$) is time for concentration to drop to half C_{initial}.

Nota Bene 14.1. In **first-order** reactions, $t_{1/2}$ is not dependant on C_i.

Nota Bene 14.2. For **first-order** reactions, *half-life* is a **constant**.

14.5 Theories of Chemical Kinetics

Definition. Collision theory requires that particles must collide in order to react.

Theorem. The number of collisions depends on the **product** of the numbers of reactant particles, not their sum (in rate law, Cs are multiplied, not added).

14.5.1 Temperature and the Rate Constant

Temperature dramatically affects reaction rate (+10 °C will double or triple the rate).
<u>Arrhenius Equation:</u>

$$\begin{aligned} k &\rightarrow \text{ rate constant} \\ A &\rightarrow \text{ frequency factor} \\ E_a &\rightarrow \text{ activation energy} \\ k &= Ae^{-E_a/RT} \end{aligned}$$

Higher $T \rightarrow$ larger $k \rightarrow$ increased rate

14.5.2 Activation Energy

Theorem. Collisions are only **effective** after a certain energy **threshold**.

Theorem. When particles collide effectively, they enter an **activated state**. The energy difference between the reactants and their *activated state* is the **activation energy** (E_a) for the reaction.

Smaller $E_a \rightarrow$ larger $f \rightarrow$ larger $k \rightarrow$ increased rate

14.5.3 Temperature and Collision Energy

Theorem. An increase in temperature, causes an increase in kinetic energy of the particles.

14.5.4 Calculating Activation Energy

$$\begin{aligned} k &= Ae^{-E_a/RT} \\ \ln k &= \ln A - \frac{E_a}{R}\frac{1}{T} \end{aligned}$$

For two different temperatures:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R}(\frac{1}{T_2} - \frac{1}{T_1})$$

14.5.5 Molecular Structure and Reaction Rate

$$\begin{aligned} k &= Ae^{-E_a/RT} & \qquad p &= \text{ orientation probability factor} \\ A &= pZ & \qquad Z &= \text{ collision frequency} \end{aligned}$$

14.5.6 Transition State Theory

Theorem. An effective collision between particles forms a **transition state** or an **activated complex**.

Theorem. The transition state is an unstable species which contains **partial bonds**.

Transition state exists at $\Sigma E_{P_{\max}}$

14.5.7 Reaction Mechanisms

Definition. The **mechanism** of a reaction is the sequence of single reaction steps that make up the overall equation.

Definition. Individual steps are called **elementary steps**. Each describes **one molecular event**.

Definition. Molecularity of a step = number of particles involved in the reaction.

Theorem. Rate law for a step **can** be deduced from stoichiometry.

14.5.8 The Rate-Determining Step of a Reaction

Definition. The **slowest** step in a reaction is the **rate-determining** or **rate-limiting** step.

Theorem. Rate law for rate-determining step becomes the rate law for the overall reaction.

14.6 Reaction Mechanisms: The Steps from Reactant to Product

Definition. The **mechanism** of a reaction is the sequence of single reaction steps that make up the overall equation.

Definition. Elementary steps in a reaction are individual steps with a **single molecular event**.

Definition. Molecularity is the number of particles (reactants) involved in the reaction.

Theorem. Rate law for an elementary step is determined by *stoichiometry*. Reaction order equals molecularuty for an elementary step only.

Elementary Step	Molecularity	Rate Law
$A \to$ product	Unimolecular	Rate $= [A]$
$2A \to$ product	Bimolecular	Rate $= k[A]^2$
$A + B \to$ product	Bimolecular	Rate $= k[A][B]$
$2A + B \to$ product	Termolecular	Rate $= k[A]^2[B]$

14.6.1 The Rate-Determining Step of a Reaction

Theorem. The **slowest** step in a reaction is the **rate-determining** step.

Theorem. The rate law for the *rate-determining* step becomes the rate law for the *overall reaction.*

14.6.2 Correlating Mechanism with Rate Law

A valid mechanism must meet three criteria:

- Elementary steps must add up to the overall balanced equation.
- Elementary steps must be reasonable.
- The mechanism must correlate with the *observed* rate law.

A mechanism is a *hypothesis*. It cannot be *proven*.
For any mechanism, only reactants involved up to and including the slow (*rate-determining*) step appear in the overall rate law.

14.7 Catalysis: Speeding Up a Reaction

Definition. A **catalyst** increases the reaction rate without participating in the reaction.

A catalyst provides a pathway with a **lower total activation energy**.
It will speed up both the forward and reverse reaction.

15 Equilibrium

← October 23, 2013

15.1 The Equilibrium State

All reactions are **reversible** and under suitable conditions will reach a state of **equilibrium**.

At equilibrium, the concentrations of products and reactants no longer change because the rates of the forward and reverse reactions are equal.

$$\text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

15.1.1 The Equilibrium Constant

Consider the reaction $N_2O_4(g) \leftrightharpoons 2NO_2(g)$

At equilibrium:

$$\begin{aligned}\text{rate}_f &= \text{rate}_r \\ k[N_2O_4]eq &= k[NO_2]^2_{eq} \\ \frac{k_f}{k_r} &= \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}} \\ K = \frac{k_f}{k_r} &= \frac{[NO_2]^2_{eq}}{[N_2O_4]_{eq}}\end{aligned}$$

15.1.2 K and the Extent of Reaction

K reflects a particular ratio of product concentrations to reactant concentrations for a reaction.

K then indicates the **extent** of a reaction, i.e. how far a reaction proceeds towards the products at a given temperature.

$K \propto$ products, meaning **larger** K means more products are produced.

15.2 The Reaction Quotient Q

For the general reaction $aA + bB \leftrightharpoons cC + dD$, the reaction quotient is:

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Q gives the ratio of product concentrations to reactant concentrations *at any point* in a reaction.
At equilibrium: $Q = K$.

Theorem. For a particular system and temperature, the same *equilibrium state* is attained regardless of starting concentrations. The value of Q indicates how close the reaction is to equilibrium, and the direction it must proceed to reach it.

15.2.1 Forms of K and Q

For an overall reaction that is the **sum** of two more individual reactions:

$$\begin{aligned}Q_{\text{overall}} &= Q_1 * Q_2 * Q_3 * \cdots \\ K_{\text{overall}} &= K_1 * K_2 * K_3 * \cdots\end{aligned}$$

The form of Q and K depends on the **direction** in which the balanced equation is written:

$$Q_{c(rev)} = \frac{1}{Q_{c(fwd)}}$$
$$K_{c(rev)} = \frac{1}{K_{c(fwd)}}$$

If the coefficients of a balanced equation are multiplied by a common factor:

$$Q' = Q^n = (\frac{[C]^c[D]^d}{[A]^a[B]^b})^n$$
$$K' = K^n$$

15.2.2 K and Q for Heterogeneous Equilibrium

Definition. A **heterogenous** equilibrium involves reactants and/or products in different phases.

$$CaCO_3(s) \leftrightharpoons CaO(s) + CO_2(g)$$

A pure solid or liquid always has the same *concentration.* Exclude them from Q and K expressions.

For the above reaction, $Q = [CO_2]$

15.3 Expressing Equilibria with Pressure Terms K and K_c

K for a reaction may be expressed using partial pressures of gaseous reactants instead of molarity.

$$P_{\text{partial}} \propto \text{Molarity}$$

$$2NO(g) + O_2(g) \leftrightharpoons 2NO_2(g)$$

$$Q = \frac{P_{NO_2}^2}{P_{NO}^2 P_{O_2}}$$

$$Q_c = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

$$K = K_c(RT)^{\Delta n_{\text{gas}}}$$

If n_{gas} does not change in the reaction, $\Delta n_{\text{gas}} = 0$ and $K = K_c$.

15.4 Determining the Direction of Reaction

- $Q < K$, reactants → products until equilibrium
- $Q > K$, products → reactants until equilibrium
- $Q = K$, at equilibrium

15.5 Solving Equilibrium Problems

If not all equilibrium quantities are given, a **reaction table** is used to find them and get K_c.
A reaction table shows:

- Balanced equation
- *Initial* quantities of reactants and products
- *Changes* in these quantities
- *Equilibrium* quantities

15.5.1 The Simplifying Assumption

We assume that $x([A]_{\text{reacting}})$ can be neglected if:

- K_c is relatively small and/or
- $[A]_i$ is relatively large

If $\dfrac{[A]_i}{K_c} > 400$, the assumption is justified; neglecting x introduces an error $< 5\%$. If $\dfrac{[A]_i}{K_c} < 400$, the assumption is not justified; neglecting x introduces an error $> 5\%$.

15.5.2 Steps in Solving Equilibrium Problems

1. Write the balanced equation.
2. Write the reaction quotient, Q.
3. Convert all amounts into the correct units (M or atm).
4. When reaction direction is not known, compare Q with K.
5. Construct a reaction table.
6. Substitute the quantities into Q.

7. To simplify the math, assume that x is negligible:
   $[A]_i - x = [A]_{eq} \approx [A]_i$
8. Solve for x.
9. Find the equilibrium quantities.

15.6 Le Chatelier's Principle

After a disturbance, a chemical system undergoes a **net reaction** to re-attain equilibrium (*reduces* the disturbance).

15.6.1 The Effect of a Change in Concentration

- If reactant is added, equilibrium position $\rightarrow$
- If product is added, equilibrium position $\leftarrow$
- If reactant is added, equilibrium position $\leftarrow$
- If product is removed, equilibrium position $\rightarrow$

Nota Bene 15.1. Only substances which appear in the expression for Q can have an effect.

Nota Bene 15.2. Change in C does not affect K.

15.6.2 The Effect of a Change in Pressure (Volume)

Nota Bene 15.3. Adding an *inert gas* has *no effect*, assuming constant volume.

Changing the V will cause equilibrium to shift if $\Delta n_{\text{gas}} \neq 0$
Changes in P have *no effect* on K.

15.6.3 The Effect of a Change in Temperature

- An *increase* in temperature *adds* heat, favouring the *endothermic* reaction.
- An *decrease* in temperature *reduces* heat, favouring the *exothermic* reaction.

15.6.4 Temperature and K

T is the only factor which affects K for a system.

- If $\Delta H^\circ_{\text{rxn}} > 0$, $+\Delta T$ means K *increases.*
- If $\Delta H^\circ_{\text{rxn}} < 0$, $+\Delta T$ means K *decreases.*

Represented by the **Van't Hoff Equation**:

$$\ln\frac{K_2}{K_1} = -\frac{\Delta H^\circ_{\text{rxn}}}{R}(\frac{1}{T_2} - \frac{1}{T_1}) \qquad (K_1 \text{ is the equilibrium constant at } T_1)$$

16 Acids and Bases

16.1 Arrhenius Acid-Base Equation

Classifies the behaviour of the substances in *water*.

Definition. An **acid** is a substance with H in its formula that dissociates to yield H_3O^+.

Definition. A **base** is a substance with OH in its formula that dissociates to yield OH^-.

Definition. Reaction of an acid and a base is **neutralization**.

$$H^+(aq) + OH^- \to H_2O(l) \tag{1}$$

16.1.1 Bronsted-Lowry Acid-Base Definition

Definition. An acid is a **proton donor**, any species that donates an H^+ ion.

Definition. A base is a **proton acceptor**, any species that accepts an H^+ ion.

- An acid must have H in its formula.
- A base must have a *lone pair of elections* for an H^+ to bond to.

Definition. An acid-base reaction is a **proton-transfer process**.

16.1.2 Conjugate Acid-Base Pairs

$$H_2S + NH_3 \leftrightharpoons HS^- + NH_4^+ \tag{2}$$

In the **forward** reaction:

- NH_3 *accepts* a H^+ to form NH_4^+
- H_2S *donates* a H^+ to form HS^-

In the **reverse** reaction:

- NH_4^+ *donates* a H^+ to form NH_3

- HS *accepts* a H^+ to form H_2S

Definition. H_2S and HS^- are a **conjugate acid-base pair**.

Definition. HS^- is the **conjugate acid** of the base NH_3.

A Bronsted-Lowry acid-base reaction occurs when an acid and a base react to form their *conjugate base* and *conjugate acid*, respectively.

$$\text{acid}_1 + \text{base}_2 \leftrightharpoons \text{base}_1 + \text{acid}_2 \tag{3}$$

16.1.3 Net Direction of Reaction

The *net* direction of reaction depends on the *relative* strength of the acids and bases involved.

Theorem. A reaction will favour the formation of the *weaker* acid and base.

Theorem. The stronger the acid is, the weaker its conjugate base.

16.1.4 Strong and Weak Acids

Definition. A **strong** acid dissociates *completely* in water.

Definition. A **weak** acid dissociates *slightly* in water.

16.1.5 The Acid Dissociation Constant, K_a

$$HA(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + A^-(aq) \tag{4}$$

$$HA(aq) \leftrightharpoons H^+(aq) + A^-(aq) \tag{5}$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{6}$$

The value of K_a is an indication of acid strength.

$$\text{Stronger acid} \rightarrow \text{higher } [H_3O^+] \rightarrow \text{larger } K_a \tag{7}$$

$$\text{Weaker acid} \rightarrow \text{lower \% dissociation of } HA \rightarrow \text{smaller } K_a \tag{8}$$

16.1.6 Classifying the Relative Strengths of Acids

- **Strong acids** include:
  - Hydrohalic acids ($H+$ halogen)
  - Oxoacids when the number of O atms exceeds the number of ionizable protons by two or more (e.g. HNO_3, H_2SO_4)
- **Weak acids** include:
  - Hydrohalic acid HF
  - Acids in which H is not bonded to O or to a halogen (e.g. HCN)
  - Oxoacids when the number of O atms exceeds the number of ionizable protons by one (e.g. $HClO$)
  - Carboxylic acids, which have the general formula $RCOOH$ (e.g. CH_3COOH)
- **Strong bases** include:
  - Water-soluble compounds containing O^{2-} or OH^- ions.
  - The cations are the most active metals:
    - M_2O or MOH, where M is a group 1 metal.
    - MO or $M(OH)_2$, where M is a group 2 metal.
- **Weak bases** include:
  - Ammonia (NH_3)
  - Amines which have the general formula RNH_2, R_2NH, or R_3N
  - The common structural feature is an N atom with a lone electron pair.

16.2 Autoionization of Water

← November 4, 2013

Definition. Water dissociates very slightly into ions in an equilibrium process known as **autoionization** or **self-ionization**.

$$H_2O \leftrightharpoons H^+(aq) + OH^-(aq) \tag{9}$$

16.2.1 The Ion-Product Constant for Water (K_W)

$$\begin{aligned} H_2O &\leftrightharpoons H^+(aq) + OH^-(aq) \\ K_W &= [H^+][OH^-] = 1.0 \times 10^{-14} \text{ (at } 25\,^\circ\text{C)} \qquad (10) \end{aligned}$$

In pure water:

$$[H^+] = [OH^-] \qquad = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{(at } 25\,^\circ\text{C)} \qquad (11)$$

Both ions are present in all aqueous systems.
A change in $[H_3O^+]$ causes an inverse change in $[OH^-]$, and vice versa.

$$\uparrow [H^+] \rightarrow \downarrow [OH^-] \qquad (12)$$

$$\uparrow [OH^-] \rightarrow \downarrow [H^+] \qquad (13)$$

$$(14)$$

We can define the terms *acidic* and *basic* in terms of the relative concentrations of H_3O^+ and OH^- ions:

In an acidic solution	$[H^+] > [OH^-]$
In an neutral solution	$[H^+] = [OH^-]$
In a basic solution	$[H^+] < [OH^-]$

16.2.2 The pH Scale

$$pH = -\log[H^+] \qquad (15)$$

The pH of a solution indicates its relative acidity:

In an acidic solution	pH < 7.00
In an neutral solution	pH $= 7.00$
In a basic solution	pH > 7.00

The *higher* the pH, the *lower* the $[H^+]$ and the *less acidic* the solution.

$$pK_a = -\log K_a \qquad (16)$$

A *low* pK_a corresponds to a *high* K_a

16.2.3 pH, pOH, and pK_W

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14} \qquad \text{(at } 25\,^\circ\text{C)} \tag{17}$$
$$pH = -\log[H^+] \tag{18}$$
$$pOH = -\log[OH^-] \tag{19}$$
$$\tag{20}$$
$$pK_W = pH + pOH = 14.00 \qquad \text{(at } 25\,^\circ\text{C)} \tag{21}$$

$pH + pOH + pK_W$ for any aqueous solution at any temperature.

Since K_W is a constant, the values of $pH, pOH, [H^+], [OH^-]$ are interrelated:

- If $[H^+]$ increases, $[OH^-]$ decreases (and vice versa).
- If pH increases, pOH decreases (and vice versa).

16.3 Weak Bases

A Bronsted-Lowry base is a species that accepts an H^+. For a weak base that dissolves in water:

$$B(aq) + H_2O(l) \leftrightharpoons BH^+(aq) + OH^-(aq) \tag{22}$$

The **base-dissociation** or **base-ionization constant** is given by:

$$K_b = \frac{[BH^+][OH^-]}{[B]} \tag{23}$$

Note that *no base actually dissociates* in solution, but *ions* are produced when the base reacts with H_2O.

16.3.1 Anions of Weak Acids as Weak Bases

The *anions* of weak acids often function as *weak bases.*

$$A^- + H_2O(l) \leftrightharpoons HA(aq) + OH^-(aq) \tag{24}$$
$$K_b = \frac{[HA][OH^-]}{[A^-]} \tag{25}$$

A solution of HA is *acidic*, while a solution of A^- is *basic.*

$$HF(aq) + H_2O(l) \leftrightharpoons H_3O^+(aq) + F^-(aq) \tag{26}$$

HF is a weak acid, so this equilibrium lies to the left.

$[HF] >> [F^-]$, and $[H_3O^+]_{\text{from } HF} >> [OH^-]_{\text{from } H_2O}$; the solution is therefore *acidic.*

If NaF is dissolved in H_2O, it dissolves completely, and F can act as a weak base:

$$F^-(aq) + H_2O(l) \leftrightharpoons HF(aq) + OH^-(aq) \tag{27}$$

HF is a weak acid, so this equilibrium also lies to the left.
$[F^-] >> [HF]$, and $[OH^-]_{\text{from } F^-} >> [H_3O^+]_{\text{from } H_2O}$; the solution is therefore *basic.*

16.3.2 K_a and K_b for a Conjugate Acid-Base Pair

$$\begin{aligned} \cancel{HA} + H_2O &\leftrightharpoons H_3O^+ + \cancel{A} \qquad &(28)\\ A^- + H_2O &\leftrightharpoons \cancel{HA} + OH^- \qquad &(29)\\ & &(30)\\ 2H_2O &\leftrightharpoons H_3O^+ + OH^- \qquad &(31) \end{aligned}$$

K_c for the overall equation $= K_1 \times K_2$, so:

$$\frac{[H_3O^+]\cancel{[A^-]}}{\cancel{[HA]}} \times \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}} = [H_3O^+][OH^-] \tag{32}$$

$$K_a \times K_b = K_W \tag{33}$$

This relationship is true for any *conjugate acid-base pair.*

16.3.3 Solving Problems Involving Weak-Acid or Weak-Base Equilibria

Problem-solving approach:

1. Write a balanced equation.
2. Write an expression for K_a or K_b.
3. Define x as the change in concentration that occurs during the reaction.
4. Construct a reaction table in terms of x.
5. Make assumptions that simplify the calculation.
6. Substitute values into the K_a or K_b expression and solve for x.
7. Check that the assumptions are justified.

The notation system:

- Molar concentrations are indicated by [].
- A bracketed formula with *no subscript* indicates an *equilibrium concentration.*

The assumptions:

- $[H_3O^+]$ from the autoionization of H_2O is negligible.
- A weak acid has a small K_a and its dissociation is negligible.
  $[HA] \approx [HA]_{\text{init}}$
  Or for weak bases: $[B] \approx [B]_{\text{init}}$

INCOMPLETE

17 Buffers

17.1 Acid-Base Buffers

Definition. An **acid-base buffer** is a solution that lessens the impact of pH from the addition of acid or base.

An acid-base buffer usually consists of a *conjugate acid-base pair* where both species are present in appreciable quanities in solution.
An acid-base buffer is therefore a solution of a *weak acid* and its *conjugate base*, or a *weak base* and its *conjugate acid.*

17.2 Buffers and the Common-ion Effect

Definition. A buffer works through the **common-ion effect**.

Acetic acid in water dissociates slightly to produce some acetate ion:

$$\underbrace{CH_3COOH}_{\text{acetic acid}}(aq) + H_2O(l) \leftrightharpoons \underbrace{CH_3COO^-}_{\text{acetate ion}}(aq) + H_3O^+(aq) \tag{34}$$

If $NaCH_3COO$ is added, it provids a source of CH_3COO^- ion, and the equilibrium shifts to the left.
CH_3COO^- is *common* to both solutions.
The addition of CH_3COO^- reduces the % dissociation of the acid.

17.3 How a Buffer Works

The buffer components (HA and A^-) are able to consume in *small* amounts of added OH^- or H_3O^+ by a *shift in equilibrium position.*

17.4 Relative Concentrations of Buffer Components

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \tag{35}$$

$$[H_3O^+] = K_a * \frac{[CH_3COOH]}{[CH_3COO^-]} \tag{36}$$

K_a is a constant, so $[H_3O^+]$ depends on the **ratio of buffer component concentrations**.

- If the ratio $\frac{[HA]}{[A^-]}$ increases, $[H_3O^+]$ increases.
- If the ratio $\frac{[HA]}{[A^-]}$ decreases, $[H_3O^+]$ decreases.

17.5 The Henderson-Hasselbalch Equation

$$HA(aq) + H_2O(l) \leftrightharpoons A^-(aq) + H_3O^+(aq) \tag{37}$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{38}$$

$$[H_3O^+] = K_a * \frac{[HA]}{[A^-]} \tag{39}$$

$$-\log[H_3O^+] = -\log K_a - \log\frac{[HA]}{[A^-]} \tag{40}$$

$$pH = pK_a + \log(\frac{\text{[base]}}{\text{[acid]}}) \tag{41}$$

$$\tag{42}$$

17.6 Buffer Capacity

Definition. The **buffer capacity** is a measure of the *strength* of the buffer, its ability to maintain the pH followign addition of strong acid or base.

The greater the concentrations of the buffer components, the greater its capacity to resist pH changes.
The closer the component concentrations are to each other, the greater the buffer capacity.

17.7 Buffer Range

Definition. The **buffer range** is the pH range over which the buffer is effective.

The closer $\frac{[HA]}{[A^-]}$ is to 1, the more effective the buffer.

Nota Bene 17.1. Buffers have a usable range within ± pH unit of the pK_a of the acid component.

17.8 Preparing a Buffer

- Choose the conjugate acid-base pair.
  - The pK_a of the weak acid component should be close to the desired pH.
- Calculate the ratio of buffer component concentrations.

$$pH = pK_a + \log(\frac{[\text{base}]}{[\text{acid}]}) \tag{43}$$

- Determine the buffer concentration, and calculate the required volume of stock solutions and/or masses of components.
- Mix the solution and correct the pH.

17.9 Acid-Base Indicators

Definition. An **acid-base indicator** is a weak organic acid (HIn) whose color differs from that of its conjugate base (In^-).

The ratio $\frac{[HIn]}{[In^-]}$ is governed by the $[H_3O^+]$ of the solution.
Indicators can therefore be used to monitor the pH change during an acid-base reaction.
The color of an indicator changes over a *specific, narrow pH range*, a range of about 2 pH units.

17.10 Acid-Base Titrations

← November 11, 2013

Definition. In an **acid-base titration**, the concentration of an acid (or a base) is determined by neutralizing the acid (or base) with a solution of base (or acid) of known concentration.

Definition. The **equivalence point** of the reaction occurs when the number of moles of OH^- *added* is equal to the number of moles of H_3O^+ originally present, or vice versa.

Definition. The **end point** occurs when the indicator changes color.

17.10.1 Calculating the pH during a strong acid-strong base titration

Initial pH:

$$[H_3O^+] = [HA]_{\text{init}} \tag{44}$$

$$pH = -\log[H_3O^+] \tag{45}$$

pH before equivalence point:

$$\text{initial mol } H_3O^+ = V_{\text{acid}} \times M_{\text{acid}} \tag{46}$$

$$\text{mol } OH^- \text{ added } = V_{\text{base}} \times M_{\text{base}} \tag{47}$$

$$n_{H_3O^+_f} = (n_{H_3O^+_i}) - (n_{H_3O^+_{\text{added}}}) \tag{48}$$

$$[H_3O^+] = \frac{n_{H_3O^+_f}}{V_{\text{acid}} - V_{\text{base}}} \tag{49}$$

$$pH = -\log[H_3O^+] \tag{50}$$

pH at the equivalence point:

$$pH = 7.00 \qquad \text{(for a strong acid-strong base titration)} \tag{51}$$

pH beyond the equivalence point:

$$\text{initial mol } H_3O^+ = V_{\text{acid}} \times M_{\text{acid}} \tag{52}$$

$$\text{mol } OH^- \text{ added } = V_{\text{base}} \times M_{\text{base}} \tag{53}$$

$$n_{OH^-_{\text{excess}}} = (n_{OH^-_{\text{added}}}) - (n_{H_3O^+_i}) \tag{54}$$

$$[OH^-] = \frac{n_{OH^-_{\text{excess}}}}{V_{\text{acid}} + V_{\text{base}}} \tag{55}$$

$$pOH = -\log[OH^-] \tag{56}$$

$$pH = 14.00 - pOH \tag{57}$$

17.10.2 Calculating the pH during a weak acid-strong base titration

Initial pH:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{58}$$

$$[H_3O^+] = \sqrt{K_a \times [HA]_i} \tag{59}$$

$$pH = -\log[H_3O^+] \tag{60}$$

pH before equivalence point:

$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]} \tag{61}$$

$$pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]} \tag{62}$$

pH at the equivalence point:

$$A^-(aq) + H_2O(l) \leftrightharpoons HA(aq) + OH^-(aq) \tag{63}$$

$$[OH^-] = \sqrt{K_b \times [A^-]} \quad ([A^-] = \frac{n_{HA_i}}{V_{\text{acid}} + V_{\text{base}}})(K_b = \frac{K_w}{K_a}) \tag{64}$$

$$[H_3O^+] \approx \frac{K_w}{\sqrt{K_b \times [A^-]}} \tag{65}$$

$$pH = -\log[H_3O^+] \tag{66}$$

pH beyond the equivalence point:

$$[OH^-] = \frac{n_OH^-_{\text{excess}}}{V_{\text{acid}} + V_{\text{base}}} \tag{67}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]} \tag{68}$$

$$pH = -\log[H_3O^+] \tag{69}$$

17.11 Equilibria of Slightly Soluble Ionic Compounds

Any *insoluble* ionic compound is actually *slightly* soluble in aqueous solution.
For a slightly soluble ionic compound in water, *equilibrium* exists between *solid solute* and *aqueous ions*.

$$PbF_2(s) \leftrightharpoons Pb^{2+}(aq) + 2F^-(aq) \tag{70}$$

$$Q_{sp} = [Pb^{2+}][F^-]^2 \tag{71}$$

17.11.1 Q_{sp} and K_{sp}

Definition. $\mathbf{Q_{sp}}$ is called the **ion-product expression** for a slightly soluble ionic compound.

For any slightly soluble compound M_pX_q which consists of ions M^{n+} and X^{z-}:

$$Q_{sp} = [M^{n+}]^p[X^{z-}]^q \tag{72}$$

17.11.2 Metal Sulfides

S^{2-} is strongly basic, so metal sulfide dissolution can be considered a two step process.

$$MnS(s) \leftrightharpoons Mn^{2+}(aq) + \cancel{S^{2-}(aq)} \tag{73}$$

$$\cancel{S^{2-}(aq)} + H_2O(l) \rightarrow HS^-(aq) + OH^-(aq) \tag{74}$$

$$MnS(s) + H_2O(l) \leftrightharpoons Mn^{2+}(aq) + HS^-(aq) + OH^-(aq) \tag{75}$$

$$K_{sp} = [Mn^{2+}][HS^-][OH^-] \tag{76}$$

17.11.3 Effect of pH on Solubility

← November 13, 2013

Theorem. Addition of H_3O^+ will *increase* the solubility of a salt that contains the *anion of a weak acid.*

$$CaCO_3(s) \leftrightharpoons Ca^{2+}(aq) + CO_3^{2+}(aq) \tag{77}$$

$$CO_3^{2-}(aq) + H_3O^+(aq) \rightarrow HCO_3(aq) + H_2O(l) \tag{78}$$

$$HCO_3^-(aq) + H_3O^+(aq) \rightarrow [H_2CO_3(aq)] + H_2O(l) \rightarrow CO_2(g) + 2H_2O(l) \tag{79}$$

Adding H_3O^+ to $CaCO_3$ results in the removal of CO_3 ions, which causes an equilibrium shift to the right.
More $CaCO_3$ will dissolve.

17.11.4 Predicting the Formation of a Precipitate

Definition. In a **saturated solution** of a slightly soluble ionic salt:

$$Q_{sp} = K_{sp} \tag{80}$$

When mixing two solutions containing the ions of slightly soluble salts:

- $$Q_{sp} = K_{sp} \tag{81}$$

  Saturated, no change.

- $$Q_{sp} > K_{sp} \tag{82}$$

  Precipitate will form until the remaining solution is saturated.

- $$Q_{sp} \leq K_{sp} \tag{83}$$

  No precipitate will form because the solution is unsaturated.

17.11.5 Selective Precipitation

Selective precipitation is used to separate a solution containing a mixture of ions.

A **precipitating ion** is added to the solution until the Q_{sp} of the **more** soluble compound is almost equal to its K_{sp}.

The **less** soluble compound will precipitate in as large a quantity as possible, leaving behind the ion of the more soluble compound.

18 Appendices

18.1 Solubility Table

Ion	**Solubility**	**Exceptions**
NO_3^-	Yes	
Cl^-	Yes	$AgCl, Hg_2Cl_2, PbCl_2$
SO_4^{2-}	Yes	$BaSO_4, PbSO_4, SrSO_4$
CO_3^{2-}	No	NH_4^+, group 1 cations
OH^-	No	group 1 cations
S^{2-}	No	group 1, 2 cations, NH_4^+