

Basic Chemistry Equations

PV = ZnRT; Z = 1.0 for ideal gases

$$u_{mp} : \bar{u} : u_{rms} = 1 : 1.128 : 1.225$$

Average molecular velocities: $\bar{u} = \sqrt{\frac{8RT}{\pi M}} \quad u_{rms} = \sqrt{\frac{3RT}{M}} \quad u_{mp} = \sqrt{\frac{2RT}{M}}$

$$\text{Effusion rate} = \frac{1}{4} \frac{PN_o}{RT} A \sqrt{\frac{8RT}{\pi M}}$$

$$\text{Mean free path: } \lambda = \frac{RT}{\sqrt{2}\pi\sigma^2 N_o P}$$

Heat capacities: monoatomic ideal gases $C_v = \frac{3}{2}R; \quad C_p = \frac{5}{2}R$

diatomic ideal gases $C_v = \frac{5}{2}R; \quad C_p = \frac{7}{2}R$

Henry's law: $P_i = k_i x_i$

Dalton's law: $P_i = y_i P_T$

Clapeyron Equation:

Raoult's law: $P_i = P_i^0 x_i$

Amagat's law: $V_i = y_i V_T$

$$\ln\left(\frac{P_{T2}^0}{P_{T1}^0}\right) = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

freezing point depression $\Delta T_f = -K_f m$

boiling point elevation $\Delta T_b = K_b m$

Colligative properties:

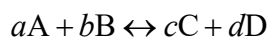
osmotic pressure $\pi = cRT$

vapour pressure drop $\Delta P_i = x_i P_i^0 - P_i^0$

Nernst equation: $\Delta \varepsilon = \Delta \varepsilon^0 - \frac{0.0592}{n} \log Q$ at T = 298 K

$$\Delta \varepsilon = \Delta \varepsilon^0 - \frac{RT}{nF} \ln Q$$

for a reaction of type



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

Arrhenius equation: $k = A_o \exp\left(-\frac{E_a}{RT}\right)$

Nomenclature

A: cross-sectional area of pinhole

A_o: pre-exponential factor

c: molar concentration of solute in solution

C_p: molar heat capacity at constant P

C_v: molar heat capacity at constant V

E_a: activation energy

F: Faraday's constant

K_b: boiling point elevation constant

K_f: freezing point depression constant

k: reaction rate constant

k_i: Henry's law constant

M: atomic or molecular mass

m: molality

n: number of moles

n: number of electrons transferred

N_o: Avogadro's number

P: pressure

P_i: partial pressure of substance i

P_i^o: vapour pressure of pure substance i

P_T: total pressure

Q: reaction quotient

R: gas constant

T: absolute temperature

V: volume

V_i: partial volume of substance i

V_T: total volume

x_i: mole fraction of i in liquid phase

y_i: mole fraction of i in vapour phase

Z: compressibility factor

Δε^o: standard cell potential

Δε: cell potential

λ: mean free path

π: osmotic pressure

σ: molecular diameter

Empirical formula: Gives the relative number of atoms in a molecule. Different substances can have the same empirical formula.

The empirical formula of hexene C_6H_{12} is simply CH_2

Molecular Formula: Shows the actual number of atoms in a molecule.

It can be obtained from the empirical formula if the gas density is known.

At STP (0 °C, 1 atm) 1 mol of most gases have a volume of 22.4 L

Gas density: $\rho = \frac{m}{V} : \left(\frac{g}{L} \right)$

Since at STP: $\frac{22.4 \text{ L}}{\text{mol}}$

Then: $M = \rho \frac{22.4 \text{ L}}{\text{mol}} : \left(\frac{g}{L} \frac{L}{\text{mol}} = \frac{g}{\text{mol}} \right)$

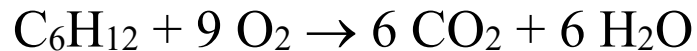
With the empirical formula and the molar mass known, it is easy to calculate the actual number of atoms in a given molecule.

Combustion Problems

Important observations:

- Air (21 mol % O₂ and 79 mol % N₂) is generally the source of O₂ in combustion reactions. Since N₂ is inert, it will be present in the products in the same amount it is present in the reactants.

- Complete combustion of hydrocarbons produces only CO₂ and H₂O



- Presence of CO or C in the products indicates incomplete combustion.

Important Combustion definitions:

- Composition on wet basis: compound mole fractions including water
- Composition on dry basis: compound mole fractions excluding water
Ex: 33.3% CO₂, 33.3% N₂, 33.4% H₂O (wet basis)
50% CO₂, 50% N₂ (dry basis)
- Stack or flue gas: product gas that leaves combustion chamber
- Theoretical oxygen ($n_{O_2 \text{ theor}}$): number of moles of oxygen (O₂) needed for the combustion of all fuel
- Theoretical air ($n_{air \text{ theor}}$): quantity of air that contains the theoretical oxygen

$$n_{air \text{ theor}} = \frac{n_{O_2 \text{ theor}}}{0.21}$$

- Excess air ($n_{air \text{ ex}}$): amount of air fed to the combustion chamber minus theoretical air

$$n_{air \text{ ex}} = n_{air} - n_{air \text{ theor}}$$

- Percent excess air:

$$\frac{n_{air} - n_{air \text{ theor}}}{n_{air \text{ theor}}} \times 100 = \frac{n_{air \text{ ex}}}{n_{air \text{ theor}}} \times 100$$

Ideal Gas Law

The combination of Boyle's and Charles's laws leads to the ideal gas law:

$$\text{Charles law: } V = V_0 \frac{T}{c}$$

$$\text{Boyle's law: } V = \frac{nC_T}{P}$$

$$\text{Solving for } V_0 : V_0 = \frac{nC_{T0}}{P}$$

$$\text{Substituting } V_0 \text{ in Charles's law: } V = \frac{nC_{T0}}{P} \frac{T}{c}$$

$$\text{Rearranging: } PV = n \frac{C_{T0}}{c} T = nRT$$

where $R = C_{T0}/c$.

At SPT it can be proven experimentally that 1 mole of most gases occupy 22.4 L. This can be used to calculate the gas constant, R:

$$R = \frac{PV}{nT} = \frac{(1 \text{ atm})(22.4 \text{ L})}{(1 \text{ mol})(273.15 \text{ K})} = 0.082 \frac{\text{L.atm}}{\text{mol.K}}$$

Therefore, the ideal gas law is expressed as:

$$PV = nRT$$

or

$$PV_m = RT$$

where V_m is the molar volume ($V_m = V/n$).

Sometimes it is more convenient to express the ideal gas law using the last expression, since all variables are intensive, as opposed to the first form where n is an extensive variable.

What is an ideal gas?

→ Idealization that assumes there are no intermolecular forces between gas molecules. It also assumes that gas molecules have no molecular volume. That is why there is no term in the ideal gas law equation to account for differences among gas molecule types

Composition of Solutions

Mole Fraction

$$x_i = \frac{n_i}{n_1 + n_2 + \dots + n_n} = \frac{n_i}{\sum_{j=1}^n n_j}$$

$$x_1 + x_2 + \dots + x_n = \sum_{j=1}^n x_j = 1$$

Molality

$$\text{molality} = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Molarity

$$\text{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Important: molarity varies with temperature

Percentage

25% (v/v) 25 ml of solute in 100 ml of solution

25% (w/v) 25 g of solute in 100 ml of solution

25% (w/w) 25 g of solute in 100 g of solution

Henry's Law

Henry's law is generally applied to gas-liquid solutions. It relates the partial pressure of a gas (solute) to its molar fraction in the liquid (solvent) by the following equation:

$$P_i = k_i x_i$$

where k_i (called Henry's law constant) depends on the solute/solvent pair and on temperature.

Henry's law is an important relationship to calculate the solubility of gases in liquids, since

$$x_i = \frac{P_i}{k_i}$$

Therefore, increasing the pressure of the gas will increase its concentration in the liquid phase at a given temperature. Notice also that increasing k_i will decrease the solubility of the gas in the liquid phase.

Raoult's Law

Raoult's law relates the partial pressure of a gas to its vapour pressure in liquid/liquid and liquid/solid solutions by the simple expression:

$$P_i = x_i P_i^0$$

where P_i^0 is the vapour pressure of pure substance i.

For binary, liquid/liquid solutions:

$$P = P_1 + P_2 = x_1 P_1^0 + x_2 P_2^0 = x_1 P_1^0 + (1-x_1) P_2^0$$

For binary, solid/liquid solutions:

$$P = P_{\text{solid}} + P_{\text{liq}} = x_{\text{solid}} P_{\text{solid}}^0 + x_{\text{liq}} P_{\text{liq}}^0 = x_{\text{liq}} P_{\text{liq}}^0$$

since $P_{\text{liq}}^0 \gg P_{\text{solid}}^0$ in general.

Colligative Properties of Solutions

Consider a solution formed by dissolving a non-volatile solute (such as sugar) in a liquid solvent (such as water). If this solution obeys both Raoult's and Henry's laws it is called an ideal solution. We will study the following four properties of ideal solutions:

Vapour-pressure lowering

Boiling-point elevation

Freezing-point depression

Osmotic pressure

Colligative properties are a consequence of Raoult's law. The equations that will be used apply only for dilute solution, where the assumption of ideality is valid.

The effect of dissociation

If a solute dissociates (as does NaCl when it dissolves in water to form Na⁺ and Cl⁻ ions), then the effective number of solute particles increases.

Because the colligative particles depend on the number of dissolved particles, the equations describing them must be adjusted to take dissociation into account.

The required change is the insertion of an additional factor, the van't Hoff i.

$$\Delta T_b = i K_b m$$

where i equals the number of particles released into solution per formula unit of solute. Its minimum value equals 1 (no dissociation); its maximum value equals the number of particles generated by complete dissociation of a formula unit of solute. For instance, for NaCl, the maximum value i can have is 2. (Because aquated ions of opposite charges associate into ion-pairs as a function of solution concentration, the value of i for NaCl might be less than 2 and must be determined experimentally)

Osmotic Pressure

Osmotic pressure is defined as the pressure exerted by the height of liquid in the column:

$$\pi = h\rho g$$

π is the osmotic pressure (expressed as a 'head' of the fluid)

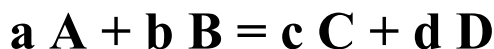
It can be shown that, for ideal solutions,

$$\pi = cRT = \frac{n_2}{V}RT \quad (\text{van't Hoff equation})$$

where c is the molar concentration of solute in solution.

The Empirical Law of Mass Action / **The Equilibrium Constant**

Consider the generic chemical equation:



where A, B, C and D are chemical substances and a , b , c and d their respective stoichiometric coefficients. It can be experimentally demonstrated that at equilibrium, the ratio defined by

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

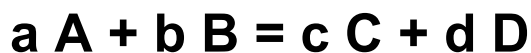
is a constant value (for a given temperature) independent of the initial concentration or reactants and products.

K_c is called equilibrium constant. K_c has units of (concentration)^{d+c-a-b}.

- K_c is an intrinsic property of the chemical reaction
- Large K_c indicates that products are present in higher amount than reactants
- Small K_c indicates that reactants are present in higher amount than products

The Direction of Change and the Reaction Quotient

Consider the generic chemical reaction:



The reaction quotient, Q , for this reaction at any concentration of reactants and products is defined as:

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

Notice that the definition of Q is equivalent to definition for K_c , but Q is defined for any concentration of reactants and products, while K_c is only defined when chemical equilibrium is achieved.

$Q = K_c$	\Rightarrow	chemical equilibrium
$Q < K_c$	\Rightarrow	reactants are in excess
$Q > K_c$	\Rightarrow	products are in excess

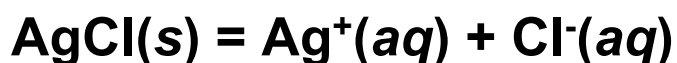
The reaction quotient can also be defined in terms of gas pressures as:

$$Q = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Solubility and Solubility Product Constant

Section 11.1 – 11.3

The equilibrium between solid ionic solute and liquid solvent can be treated in a similar way to the one used to study chemical equilibrium (in fact, several previous examples dealt with dissolution equilibrium):



A solubility product constant is defined in a similar way to the reaction equilibrium constant:

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

Notice that the concentration of the solid species is taken into account implicitly in the definition of K_{sp} , as also done for K_C and K_p .

K_{sp} is related to the solubility of the solute in the solvent, S :

$$S = [\text{Ag}^+] = [\text{Cl}^-]$$

Solubility is simply the maximum amount (in g or mol) of the solute that will dissolve in the solvent at a given temperature.

Therefore, in this case: $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (S)(S) = S^2$

$$S = \sqrt{K_{sp}}$$

ELECTROCHEMISTRY

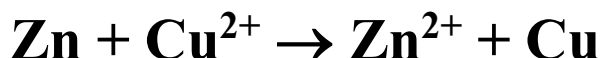
Chapter 12

(Batteries, Fuel Cells , Corrosion, Metal Processing, Plating)

Oxidation States

Useful definitions:

- A chemical substance is oxidized when it loses electrons.
- A chemical substance is reduced when it gains electrons.
- The substance that causes the oxidation of another is called the *oxidizing agent* or *oxidant*.
- The substance that causes the reduction of another is called the reducing agent or reductant.



Zn is oxidized (loses 2 e⁻) → Zn is the reductant

Cu²⁺ is reduced (gains 2 e⁻) → Cu is the oxidant

Oxidation Numbers

(Oxtoby, Section 3.9, pages 80-82)

- The oxidation number of monoatomic species is the net charge on the atom. Ex: the oxidation number of S^{-2} is -2 , of Fe^{3+} is $+3$ and of Cu is 0.
 - For polyatomic species:
 - Zero, for pure elements.
 - $+1$ for alkali metals (Li, Na, K, Rb, Cs, Fr).
 - $+2$ for alkaline earth metals (Be, Mg, Ca, Sr, Ba, Ra).
 - -1 for halogens (F, Cl, Br, I, At), except when combined with oxygen and other halogens. F has always oxidation number of -1 .
 - $+1$ for hydrogen in all compounds, except for those with bonds to metals, in which it is equal to -1 (LiH, for instance).
 - -2 for oxygen in all compounds, except for peroxides (such H_2O_2 and N_2O_2 , where it is -1), or when combined with F (in OF_2 , it is equal to $+2$).
 - All the other oxidation numbers are selected to make the algebraic sum of the oxidation numbers equal to the net charge of the molecule or ion.

Balancing Oxidation-Reduction Reactions

General guidelines for balancing oxidation-reduction equations:

- 1. Write separate half-reactions for oxidation and reduction.**
- 2. Balance all atoms, except H and O.**
- 3. Balance O by adding H_2O .**
- 4. Balance H:**
 - Acidic medium: Add H^+ to the hydrogen-deficient side.**
 - Basic medium: Add H_2O to the hydrogen-deficient side and OH^- to the other side.**
- 5. Balance charges by adding e^- .**
- 6. Add half-reactions to cancel e^- .**

Note: Oxtoby balances the H in acidic medium by adding H_3O^+ to the hydrogen deficient side and an equivalent amount of H_2O to the other side or the chemical equation.

Standard Cell Potentials

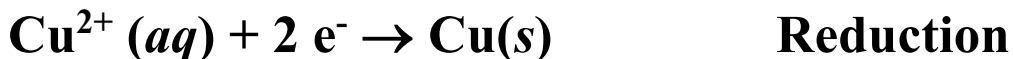
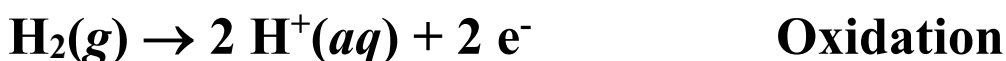
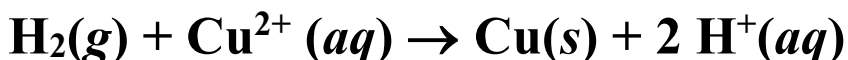
The voltage of galvanic cells depend on:

- reactants used in the two half-cells
- concentrations in the two half-cells
- temperature

In order for one to compare the voltages of different galvanic cells, it is necessary to define a *standard state*:

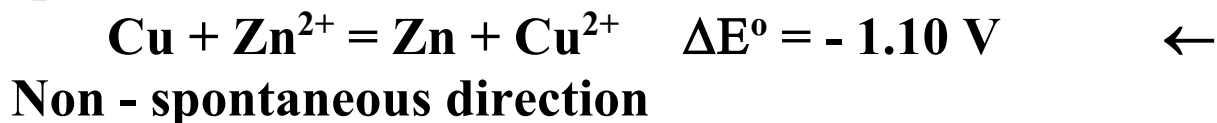
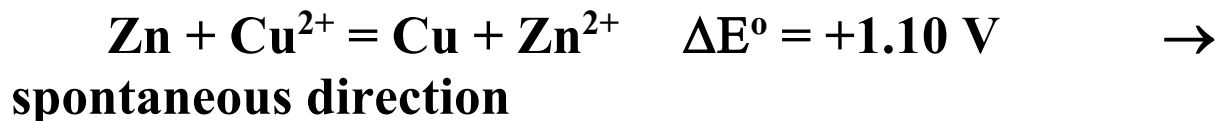
- 1.0 M concentration for dissolved species
- 1 atm pressure for gases
- (Most stable form at 25 °C for solids)

Gas electrodes are used when gases are part of a galvanic cell. The metal surface of these electrodes (made of Pt, for instance), is saturated with gas (H₂ in this case). For this particular case, the redox reaction and the half-cell reactions are:



The *Standard Cell Potential* (ΔE^0) is defined as the voltage measured at the standard state.

Sign convention for E^0 :

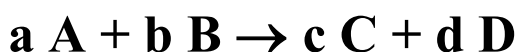


The Nernst Equation

Thus far we have calculated cell voltages at standard conditions (1 M concentration, 1 atm, 25 °C). How can one calculate cell voltages at different conditions?

The Nernst equation quantifies the dependency of cell voltage on the concentration of chemical species and temperature in a galvanic cell.

For a generic cell reaction:



The Nernst equation at 25 °C is:

$$\Delta\varepsilon = \Delta\varepsilon^{\circ} - \frac{0.059}{n} \log_{10} Q$$

where

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

and

ΔE° : standard cell potential

n : number of electrons transferred in the reaction as written

$[A]$: concentration of chemical species A in mol/L

Faraday's law of electrolysis

“The number of moles of material oxidized or reduced at an electrode is related by the stoichiometry of the electrode reaction to the amount of electricity passed through the cell.”

Simply stated:

1 mole e^- → 1 mole Ag^+

→ $\frac{1}{2}$ mole Cu^{2+}

→ $\frac{1}{3}$ mole Al^{3+}

Remember: Charge of 1 mole e^- = 1 F = 96,485 c

$I=Q/t$

**Current (Amperes) Equals Charge passed (Coulombs)
per Unit of Time (Seconds)**

Also Useful:

$\Delta G = -nFE$

Energy Available is ΔG

Power = Current * Voltage

Power * Time = Energy

Differential Rate Laws

Rate laws relate the rate of reaction to the concentration of reactants. Rate laws are generally empirical and cannot be derived from the stoichiometry of reactions, except for some special cases that will be discussed later.

Differential rate laws are generally stated as:

$$r = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n [B]^m$$

where,

n : order of reaction with respect to chemical species A

m: order of reaction with respect to chemical species B

n+m: overall order of reaction

k: reaction rate constant.

Rate constants generally vary significantly with temperature.

Order of Reaction

Important: For a given reaction

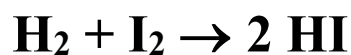


n is not necessarily equal to a

m is not necessarily equal to b

m and n must be determined experimentally

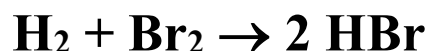
For instance, the rate for the reaction



is determined experimentally to be:

$$r = k[H_2][I_2]$$

but, the rate for the reaction



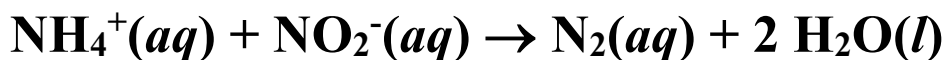
is found to be:

$$r = k[H_2][Br_2]^{1/2}$$

Method of the Initial Rates

In the method of initial rates, the instantaneous rate of reaction is determined at the beginning of the reaction, before reactant concentrations have changed significantly.

Consider the reaction:



The following rate law is proposed:

$$-\frac{d[\text{NH}_4^+]}{dt} = r = k[\text{NH}_4^+]^n [\text{NO}_2^-]^m$$

The following set of experimental data was measured:

	$[\text{NH}_4^+]^0$	$[\text{NO}_2^-]^0$	r^0 (mol/L.s)
1	0.1 M	0.005 M	1.35×10^{-7}
2	0.1 M	0.01 M	2.7×10^{-7}
3	0.2 M	0.01 M	5.4×10^{-7}

where the superscript ⁰ indicates initial conditions.

Therefore for experiments 1 and 2,

$$\frac{r_1}{r_2} = \frac{k[\text{NH}_4^+]_1^n [\text{NO}_2^-]_1^m}{k[\text{NH}_4^+]_2^n [\text{NO}_2^-]_2^m}$$

$$\frac{1.35}{2.7} = \frac{(0.005)^m}{(0.01)^m} = \left(\frac{0.005}{0.01} \right)^m$$

$$0.5 = 0.5^m \Rightarrow m = 1$$

Similarly, for reactions 2 and 3,

$$\frac{r_3}{r_2} = \frac{k[\text{NH}_4^+]_3^n [\text{NO}_2^-]_3^m}{k[\text{NH}_4^+]_2^n [\text{NO}_2^-]_2^m}$$

$$\frac{5.4}{2.7} = \left(\frac{0.2}{0.1} \right)^n$$

$$2 = 2^n \Rightarrow n = 1$$

Therefore, the differential rate law is:

$$r = k[\text{NH}_4^+][\text{NO}_2^-]$$

and an estimate of the rate constant can be calculated by:

$$k = \frac{r}{[\text{NH}_4^+][\text{NO}_2^-]} = \frac{1.35 \times 10^{-7} \text{ mol/L.s}}{(0.1 \text{ mol/L})(0.005 \text{ mol/L})} = 2.7 \times 10^{-4} \frac{\text{L}}{\text{mol s}}$$

Integrated Rate Laws

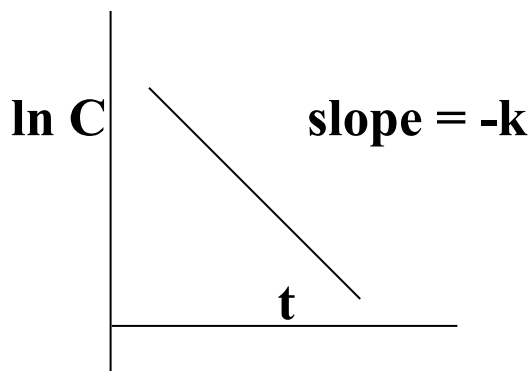
Differential rate laws can be integrated in time to generate integrated rate laws. For instance, given that for the reaction



the differential rate law is

$$-\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

$$-\frac{dC}{dt} = kC$$



The integrated rate law can be calculated as

$$-\frac{dC}{C} = kdt$$

$$-\int_{C_0}^C \frac{dC}{C} = k \int_0^t dt$$

$$-\ln \frac{C}{C_0} = kt$$

$$\ln C = -kt + \ln C_0$$

Therefore, a plot of $\ln C$ versus t is linear, with slope $-k$ and intercept $\ln C_0$ for first order reactions.

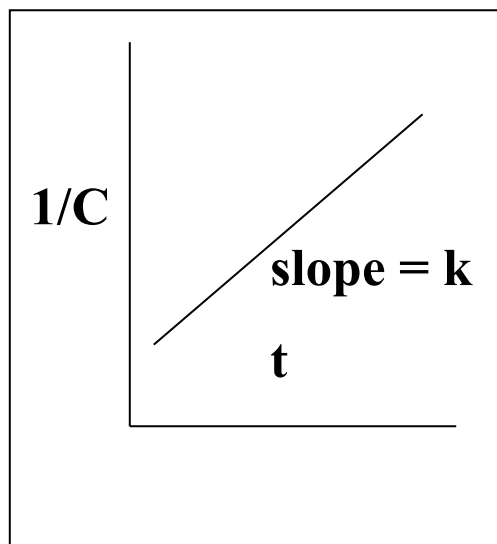
For second order reactions,

$$-\frac{dC}{dt} = kC^2$$

$$-\int_{C_o}^C \frac{dC}{C^2} = k \int_0^t dt$$

$$\frac{1}{C} - \frac{1}{C_o} = kt$$

$$\frac{1}{C} = kt + \frac{1}{C_o}$$



Plot the data of Example 2 as a 1st and as a 2nd order reactions and verify which rate law better represents the data.

Half-Life of Reactions

Half –life ($t_{1/2}$) of a reactant is the time required for its concentration to decrease to $\frac{1}{2}$ of its original value.

1st order reactions

$$-\ln \frac{C}{C_o} = kt$$

$$-\ln \frac{1}{2} = kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k}$$

2nd order reactions

$$\frac{1}{C} - \frac{1}{C_o} = kt$$

$$\frac{2}{C_o} - \frac{1}{C_o} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{kC_o}$$

Note that this concept can be easily extended to other concentrations. One can easily define a $t_{1/3}$, $t_{1/5}$, etc.

