### Introduction to Kinetics, Rate equation, Order and Molecularity

Chemists always deal with chemical reactions. Any chemical reaction involves movement of electrons. The movement may be from an atom to another atom, within a molecule or even it may be a movement within the molecular orbitals. The rate at which these electronic movements happens has profound influence in our daily life. Chemical kinetics which is an important branch of Physical Chemistry deals with the speed of these electronic movements or chemical reactions. The field of chemical kinetics evolved during the 17th century and is now a full-fledged branch of Chemistry. Chemical Kinetics deals with the rates of chemical reactions and with how the rates depends on factors such as concentration and temperature. Studies on Chemical kinetics helps an organic chemist to confirm the mechanistic studies, helps a chemical engineer to design an industrial reactor, helps a geologist to understand the flow processes and helps a medicinal chemist to know the drug interactions.

Extent of reaction (Time independent)
Extent of reaction (T. de Donder): For a general reaction

aA + bB → xX + yY
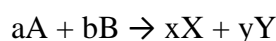
the extent of reaction is defined by

$$\varepsilon = \frac{n - n^0}{\vartheta}$$

Where n^0 is the initial amount of the substance, n is the amount at time t, and v is the stoichiometric coefficient of that species. Thus for the general reaction written above; for each species we could write

$$\varepsilon = \frac{\Delta n_A}{-a} = \frac{\Delta n_B}{-b} = \frac{\Delta n_X}{x} = \frac{\Delta n_Y}{y}$$

Extent of reaction will be same for every reactant and product. For meaningful statement of extent of reaction, the stoichiometry should be time independent.

Problem 1.
A reaction having time independent stoichiometry follows the equation
A + 2B → 2Z
Suppose that initially there are present 0.28 mol of A, 0.39 mol of B and 0.13 mol of Z. a) After a certain time 0.18 mol of A remains. What is the extent of reaction and what are the amounts of B and Z? b) What is the extent of reaction if the process goes to completion?

Rate of reaction (Time dependent)

Kinetic studies involve the study of concentration of reactants and products as a function of time. For a hypothetical reaction A → B; on the course of time concentration of A decreases and concentration of B increases. This can be shown graphically as
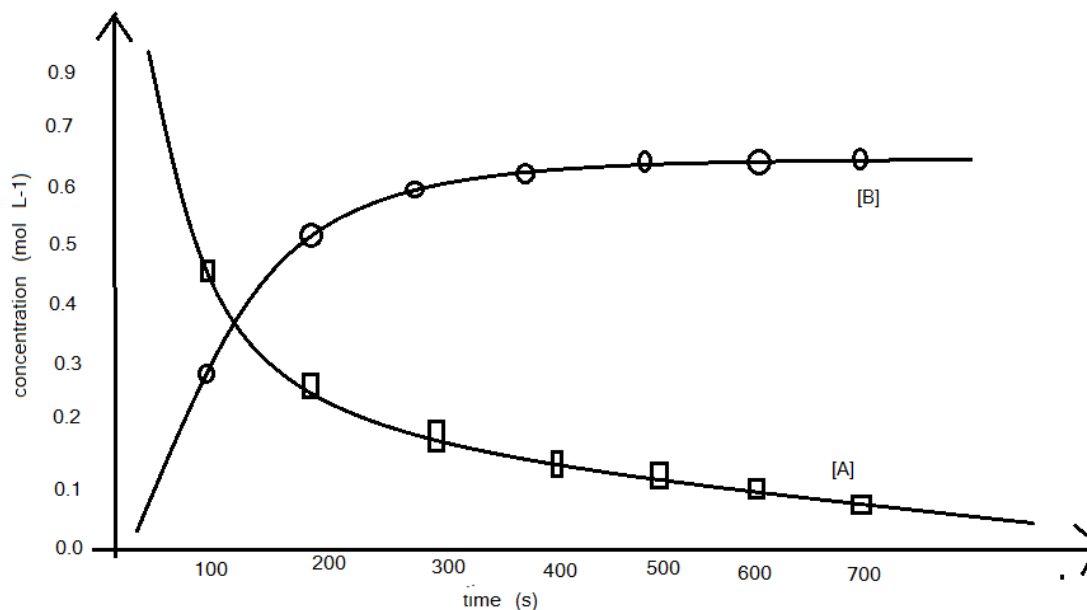
$\Delta A = [A]_2 - [A]_1$
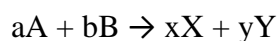
$\Delta B = [B]_2 - [B]_1$

$\Delta t = t_2 - t_1$

The rate of a chemical reaction is defined as the rate of decrease of concentration of a reactant or the rate of increase of concentration of a product.

Thus at a particular time interval;

Average rate of disappearance of A = average rate of appearance of B

Thus $-\dfrac{\Delta A}{\Delta t} = +\dfrac{\Delta B}{\Delta t}$

For a general reaction

aA + bB → xX + yY

average rate of reaction can be given as

$$r_{av} = -\frac{1}{a}\frac{\Delta A}{\Delta t} = -\frac{1}{b}\frac{\Delta B}{\Delta t} = +\frac{1}{x}\frac{\Delta X}{\Delta t} = +\frac{1}{y}\frac{\Delta Y}{\Delta t}$$

The rate of a reaction varies with time. As the graph shows rate is high when the concentration is high at the start of the reaction. To know the rate at a definite time we have choose the instantaneous rate of reaction. The instantaneous rate of reaction for the above general reaction can be expressed as

$$r_{inst} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{x}\frac{d[X]}{dt} = +\frac{1}{y}\frac{d[Y]}{dt}$$

Units: The rate of reaction is usually expressed as *mol L^{-1} s^{-1}* or *mol dm^{-3} s^{-1}*. For gaseous reactions the unit of rate may be *atm s^{-1}, Pa s^{-1}* and *bar s^{-1}*

Problem 2.

For the reaction $N_2 + 3H_2 \rightarrow 2NH_3$, the rate of formation of NH_3, was found to be 2.4 x 10^{-4} mol L^{-1} s^{-1}. i) Calculate the rate of disappearance of nitrogen and ii) rate of disappearance of hydrogen

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Empirical Rate Equations

The kinetic experimentalists of the eighteenth century found that rate depends on the reactant concentration. As reaction proceeds the concentration of reactant decreases and hence the rate also decreases.

For a general reaction

aA + bB products; the rate equation can be given as

rate ∞ $[A]^{\alpha}$ $[B]^{\beta}$

rate (v) = k $[A]^{\alpha}$ $[B]^{\beta}$

where α and β are integers or fractions and k is called as the rate constant of the reaction

Thus, rate of reaction is proportional to some power of molar concentration of each reactant.

Order of a reaction

The exponents α and β in the above equation are called partial orders. Thus the above reaction is α with respect to A and β with respect to B. The overall order of the reaction 'n' is the sum of partial orders. Ie
$\alpha + \beta = n$

Order of a reaction is defined as the sum of powers of the concentration terms in the experimentally determined rate equation for the reaction.

Examples

   a. For a simple reaction A$\rightarrow$ B
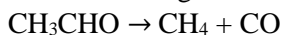
     Rate = v = k[A]; the reaction is first order

b. For reaction 2A → B

Rate = v = k[A]^2

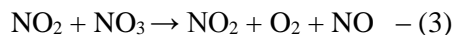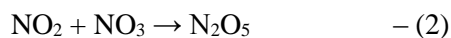c. Often non integral orders are also found. For acetaldehyde decomposition the order is 3/2.
$CH_3CHO \rightarrow CH_4 + CO$
Rate = v = k[CH$_3$CHO]$^{3/2}$

Order of reaction is an experimental quantity and can have any values including zero and non-integral.

Molecularity of a reaction

Any reaction which is a one step process is called an elementary reaction

Thus, for the complex reaction 2N2O5 → 4 NO2 + O2; the elementary reactions are

$N_2O_5 \rightarrow NO_2 + NO_3$ – (1)

$NO_2 + NO_3 \rightarrow N_2O_5$ – (2)

$NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ – (3)

$NO + N_2O_5 \rightarrow 3NO_2$ – (4)

No of molecules taking part in elementary reaction is called the molecularity of the reaction.

In the above elementary reaction's reaction (1) is a unimolecular reaction; while remaining reactions are bimolecular reactions. Molecularity of a reaction is not an experimental value. As elementary reactions happen between molecules; molecularity will have non zero integer values.

Problem 3.
Write the differential rate equations of the following reactions and also considering each of them as elementary reactions write the order and molecularity of them
a) 2A + B →
b) A + 2B + 2C →
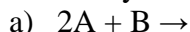
Rate constant (k)

The rate constant k is constant only at a particular temperature. It changes with temperature as per the Arrhenius empirical equation

$$k = A\, e^{-Ea/RT}$$

Where A is called as the pre exponential factor, Ea the activation energy and T the temperature.

Thus, the rate for an elementary reaction A → products reaction can be given as rate = v = k [A]

4

$$rate = v = A \, e^{-Ea/RT}[A][B]$$

Rate is a function of concentration and also of temperature

Unit: For a general nth order reaction

A Products

Rate = k $[A]^n$

$$k = \frac{rate}{[A]^n}$$

Unit of k =

$$\frac{mol \, L^{-1}s^{-1}}{(mol \, L^{-1})^n} \quad or \quad \frac{mol \, dm^{-3}s^{-1}}{(mol \, dm^{-3})^n}$$

$$= (mol \, L^{-1})^{1-n} \, s^{-1} \text{ or } (mol \, dm^{-3})^{1-n} \, s^{-1}$$

Problem 4.

A reaction has the stoichiometry 2A + 2B → Y + 2Z

Some results for the rate of consumption of A are shown below

[A] mol dm^{-3}	[B] mol dm^{-3}	v mol dm^{-3} s^{-1}
1.4 x 10^{-2}	2.3 x 10^{-2}	7.4 x 10^{-9}
2.8 x 10^{-2}	4.6 x 10^{-2}	5.95 x 10^{-8}
2.8 x 10^{-1}	4.6 x 10^{-2}	5.92 x 10^{-6}

Deduce α and β and the rate constants k_A, k_B, k_Y, k_Z and k

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References:

1. Chemical Kinetics: Third Edition; Pearson Education, 1987: **Keith J Laidler**

2. Physical Chemistry: Second Edition; Houghton Mifflin Company, 1995: **Keith J Laidler & John H Meiser**