

## KINETICS REVIEW NOTES

### Definition

**Rate of Reaction:** is the change in concentration of reactant or product in a given time.

For the reaction:  $A + B \rightarrow C$

$$\text{Rate} = -d[A]/dt$$

$$= -d[B]/dt$$

$$= +d[C]/dt$$

### Stoichiometry of Equations



$$\text{Rate} = -d[A]/dt = -1/2d[B]/dt = +1/3d[C]/dt$$

### Factors that Affect the Rate of Reaction

- 1) concentration of the reactants (and pressure in gas phase reactions)
- 2) the particle size in heterogeneous reactions
- 3) the temperature of the reacting species (typically the rate doubles for every 10°C rise in temperature; also note that some reactions are affected by light – i.e. photochemical reactions, for example  $\text{CH}_4 + \text{Cl}_2 + \text{UV light}$ )
- 4) the addition of a suitable catalyst

### Measuring the rate of a reaction experimentally

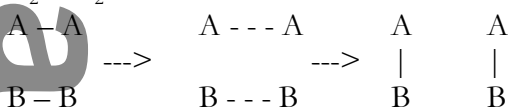
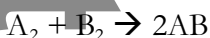
- gas pressure
- gas volume using gas syringe
- gravimetric
- volume changes
- colorimetry – appearance or disappearance of colour
- changes in pH
- thermometric – changes in heat produced
- Initial rate
- Average rate
- Instantaneous rate: Rate at time<sub>t</sub> = ? [ ]/? [ ] (refer to sketch below)

**Activated Complex:** maximum energy  
**Potential Energy Diagram**

**Theory of Kinetics**

For an effective collision (a collision that yields product) to occur:

- 1) particles must collide
- 2) with sufficient energy to break existing bonds – i.e. EA
- 3) and with correct orientation – often called **steric factor**



Not every collision between molecules results in reaction; only every 1 in  $10^{11}$  collisions are 'Effective Collisions'

**Explaining the Factors Which Affect the Rate of Reaction in terms of Collision Theory:**

- 1) **Changes in concentration (or pressure for a gas):** will change the number of particles in a unit volume and hence the number of collisions per unit time in that volume. If the number of collisions changes, the rate will change.
- 2) **Surface area (in heterogeneous reactions):** will change the number of collisions and thus the rate ( i.e. frequency of collisions – probability  $T_3 < T_1$ )
- 3) **Changes in temperature:**
  - a) changes the range of energies
  - b) increases the average kinetic energy
  - c) increases the population of particles with greater energy than the EA

NOTE:  $E_A$  does not change,  $\Delta H$  does not change

The Maxwell Boltzmann Distribution of Energies

**Note:** since the number of molecules is constant, the areas under the curves are all the same

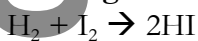
- 4) **Addition of a Catalyst:** can lower the required EA so that a greater number of particles will produce effective collisions.

**Note:**

A catalyst increases the rate of a reaction – without being used up – by providing an alternative reaction pathway with a lower EA by:

- 1) making more collisions have favourable orientation
- 2) increasing concentrations on its surface
- 3) providing a series of single steps rather than one with a very high EA
- 4) increasing the reactivity of the reactive site
- 5) making a group which is a better attacking agent and is later regenerated in the reaction

**Heterogeneous Catalysis:**



- reactive sites on solid surface
- rate is directly proportional to the surface area of the catalyst
- adsorption  $\rightarrow$  desorption (i.e. form weak bonds between the metal atoms  $\rightarrow$  catalyst provides surface to 1) weaken existing bonds, 2) lower energy, EA lowered)
- strength of adsorption on the surface is critical – if too strong, the products will remain on the surface and block further catalysis
- poison of catalyst: when impurities absorb more...
- d-block can use unfilled d-orbitals to form new bonds...reactive intermediates
- Ex: The Haber Process:  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$  -Catalysts used: pea sizes of Fe and  $\text{V}_2\text{O}_5$
- The Contact Process:  $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$

**Homogeneous Catalysis:** *Intermediate Compound Theory*

- the catalyst and reactants are in the same phase; an intermediate is formed in the reaction

**Enzymes:** specific biological catalysts

**Autocatalysis:** one of the products catalyzes the reaction. Thus once some of the reactants have converted to products, the rate of reaction will increase.



**Reaction Mechanism:**

- 1) A complex reaction will occur in a number of **elementary** steps which involve the collision of one of two particles
- 2) The slowest step with the highest EA is the **rate determining step**
- 3) The rate determining step controls the overall rate of reaction – this is expressed in the Rate Law. Ex.  $A + B \rightarrow AB$ , Rate =  $k[A]^m[B]^n$

This leads to the concept of **order** – i.e. what effect will changing the concentration of reactants have on the rate of reaction.

$k$  = constant of proportionality or Rate Constant for a reaction

=  $Ae^{-E_A/RT}$  ( $k$  depends on  $E_A$  and so is affected by catalyst)

= temperature dependent – higher  $k$ , faster reaction

**Order:** The rate of reaction depends on the concentrations, for example, in the rate equation: Rate =  $k[A]^m[B]^n$ , the powers are usually integers but can be fractions, and are characteristic of the reaction. The order is ‘ $m$ ’ with respect to  $[A]$  and ‘ $n$ ’ with respect to  $[B]$ . The overall order of the reaction can be expressed by the sum of the exponents, in this case ( $m + n$ ). The order of a reaction can only be found experimentally and cannot be determined from the stoichiometry of the reaction. Some species may appear in the rate expression and not in the chemical equation, and some may not appear in the rate expression but may appear in the chemical equation.

Zero order: Rate =  $k[A]^0$

First order: Rate =  $k[A]^1$

Second order: Rate =  $k[A]^2$

Ex.  $A + B \rightarrow C$

| Experiment | [A] (mol dm <sup>-3</sup> ) | [B] (mol dm <sup>-3</sup> ) | Rate of rxn [C] (mol dm <sup>-3</sup> s <sup>-1</sup> ) |
|------------|-----------------------------|-----------------------------|---|
| 1          | 0.1                         | 0.1                         | 1.2x10 <sup>-3</sup>                                    |
| 2          | 0.2                         | 0.1                         | 2.4x10 <sup>-3</sup>                                    |
| 3          | 0.1                         | 0.2                         | 4.8x10 <sup>-3</sup>                                    |

-doubling  $[A]$  doubles the rate of reaction, therefore  $[A]^1$

-doubling  $[B]$  quadruples the rate, therefore  $[B]^2$

-Rate =  $k[A]^1[B]^2$

Units of  $k$ :

➤ Zero order: mol dm<sup>-3</sup> s<sup>-1</sup>

➤ First order: s<sup>-1</sup>

➤ Second order: dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>

Information Obtained from Rate Equation

- 1) can be used to determine the mechanism of a reaction
- 2) what species and how many are involved in the rate determining step because only changes in their concentrations will affect the rate of a reaction

Zero Order

First Order

Second Order

**Rate Law: Integrated Form****Zero Order****First Order**

$$\ln[A]_t/[A]_o = -kt$$

$$\ln[A]_t = -kt + \ln[A]_o$$

$$\ln^{1/2}[A]_o/[A]_o = kt_{1/2}$$

$$\ln^{1/2} = kt_{1/2}$$

$$k = 0.693/t_{1/2}$$

**Second Order**

**Half-life:** time taken for the concentration of the reactant to decrease to half of its original value. It is independent of the original concentration for first order.

Constant half-life: 1<sup>st</sup> order reaction

Varying half-life: reaction not 1<sup>st</sup> order

### Arrhenius Equation

3 factors to collision theory and kinetic theory of gases:

- 1) total number of collisions
- 2) fraction of those which have the correct orientation
- 3) fraction which have energy greater than EA

$k = Ae^{-E_A/RT}$  where:  $k$  = rate constant,  $A$  = Arrhenius constant,  $e$  = fraction of molecules with energy greater than  $E_A$ ,  $T$  = temperature in Kelvin, and  $R$  = gas constant

$A = qz$ , where  $q$  = steric factor (the fraction of molecules which collide with the proper orientation), and  $z$  = collision rate: the number of collisions per unit volume per second

Taking the natural log of both sides gives the equation of a line  $y = c - mx$

$$\ln k = \ln A - E_A/RT$$

This form of the equation has two variables,  $k$  and  $T$ , so by plotting  $\ln k$  against  $1/T$ , the slope is defined by  $-E_A/R$  and a y-int. of  $\ln A$ .

Values of  $k$  can be determined at different temperatures; to determine  $E_A$ , plot the data and determine the slope.

$E_A$  and  $A$  can also be calculated using the rate constants from two different temperatures.

$$\ln k_1 - \ln k_2 = -E_A/RT_1 + E_A/RT_2$$

$$\ln (k_1/k_2) = E_A/R (1/T_1 - 1/T_2)$$