

Chemical Kinetics: ISU Unit №1

Review Sheet 2003-2004

(Distributed by Andrey Zakurdaev – for the good of all IB-2 Chemistry students)

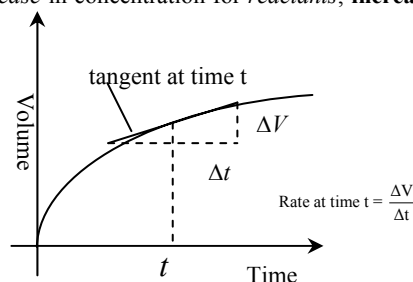
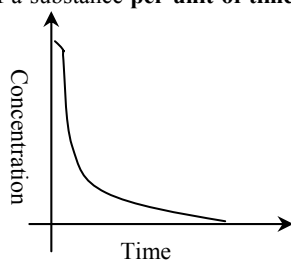
Foreword: This is a detailed summary package which will provide help when studying for the Kinetics unit of chemistry. It will guide you through all the notes, pointing out specific important spots as well as refresh class discussions (also summarized below) in your mind... A variety of different sources were used (such as the famous "Chemistry for the IB diploma" by Geoff Neuss) to compile this information booklet, so reliability is unquestionable. This will save you from making your own review sheet or from digging through the pile of class notes picking out information to be studied. Use this opportunity wisely and save this package for later – to prepare for the awaiting IB exam. Feel free to add extra things to this review sheet. Good Luck ...©

1) Chemical Kinetics (Preface):

- **Chemical Kinetics** – the study of the **factors** that affect the **rate of a chemical reaction** (study of rates of reactions)
- Two parts – [1] Macroscopic (Rates) & [2] Submicroscopic (mechanisms)
- **Rate of reaction** – change in **concentration** of a substance **per unit of time** (*decrease* in concentration for *reactants*; **increase** for *products*)

- Formula & Graph:

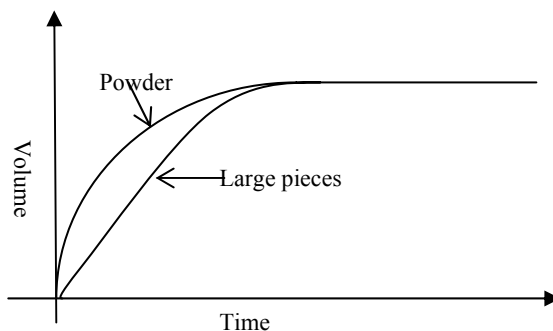
$$\text{Reaction Rate} = \frac{\Delta[\quad]}{\Delta t}$$



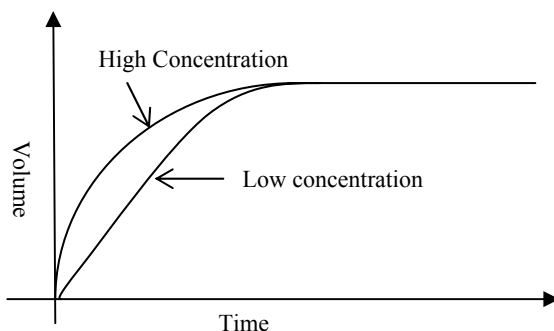
- The **steeper** the curve, the **faster** the rate of the reaction...
- How can the *change in concentration* of a substance **be measured**?
 - **Pressure** (reactions with *gases*) >>> gas syringe measures the **volume of gas formed**
 - **Gravimetric** (weighing the *loss of mass* during reaction)
 - **Color** (spectrometer)
 - **pH** (acidity change)
 - **Electric conductivity** (change in ionic concentrations)
- Rates of reaction usually **decrease with time** as reactants *get used up*
- **Instantaneous rate** – the rate of the reaction **at a particular instant** in time (to determine => **slope of tangent** to that point)
- Instantaneous rate at the **start** of the reaction is – *initial rate*
- In a reaction of $2A + B \longrightarrow 3C + 5D$ the following is the **stoichiometry relation**:

$$\text{Rate} = \boxed{-}\frac{1}{2} \cdot \frac{\Delta[A]}{\Delta t} = \boxed{-}\frac{1}{1} \cdot \frac{\Delta[B]}{\Delta t} = \boxed{+}\frac{1}{3} \cdot \frac{\Delta[C]}{\Delta t} = \boxed{+}\frac{1}{5} \cdot \frac{\Delta[D]}{\Delta t}$$

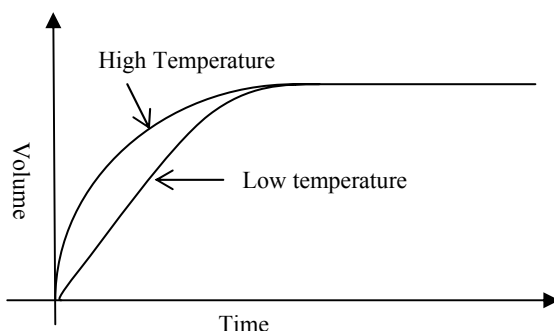
- $\boxed{+}$ for *products* (i.e. formed); $\boxed{-}$ for *reactants* (i.e. consumed)
- **Factors Affecting the Rate of Reaction:**
 - **Nature of Reactants** – the rate depends on the physical states of the reactants
 - *Aqueous ions* reactions are **extremely fast**
 - *Solids* are generally **less reactive** – rate depends on the surface area
 - *Gases* – **most** reactive
 - *Liquids* are **less reactive** than gases
 - **Surface area** – rate is directly proportional to surface area exposed
 - In a solid substance – only particles on *the surface* can *come into contact with surrounding reactant*
 - Powdered = **more** surface area = rate **increases**



- **Concentration**
 - **More** concentrated = **increase** in rate
 - As the reactants *get used up* their concentration *decreases* (approaching zero >>> *graph flattens out...*)



- **Temperature**
 - **Increase** in temperature = **increase** in rate



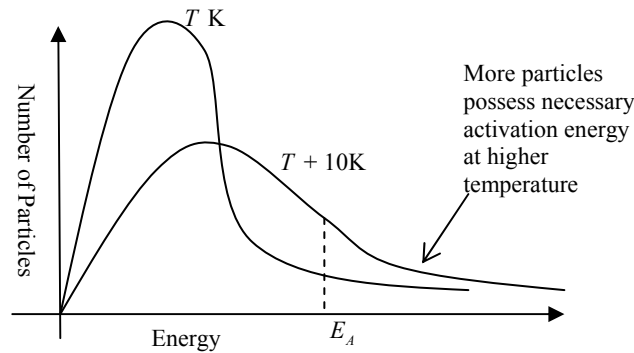
- **Catalysis**
 - Catalysts **increase the rate** of chemical reaction *without themselves being chemically changed* at the end of the reaction

- **Terms to remember:**

1. Catalysts **do not affect** all reactions.
2. **Autocatalysis:** Reaction product is a catalyst.
3. **Promoter:** Species increasing catalyst's power.
4. **Inhibitor:** Species decreasing catalyst's power (Preservatives)
5. **Enzyme:** Catalyst in living things (Enable a substrate that must fit into an active site)
6. **Surface catalyst:** attracts reactants and keeps them close to surface for reaction.
7. **Homogenous Catalyst:** Same state as reactants
8. **Heterogeneous Catalyst:** Different physical state (compared to reactants). Work through adsorption.

2) Collision Theory:

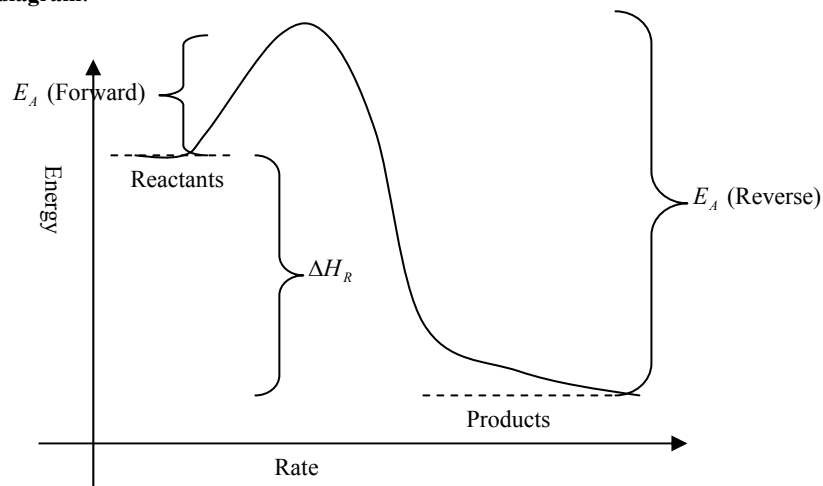
- *Collision theory* – assumes that **molecules must collide** with one another **in order to react** (i.e. rate is proportional to the number of collisions that occur in a given time period)
- For a reaction between two particles to occur *two conditions must be met*:
 1. **Steric Factor** – particles must approach each other in the right **orientation**
 2. **Energy factor** – particles must have a **certain minimum energy**: enough to start breaking bonds
- **Factors explained in terms of Collision theory:**
 - **Nature of Reactants**
 - Which molecule would **give up** electrons **faster** and easily
 - **Surface area**
 - **More** surface area = **more** collisions = rate **increases**
 - **Concentration**
 - The **more** concentrated the reactants the **more collisions** there will *be per second per unit volume*
 - 1/Time vs. Concentration *yields a straight line*
 - **Temperature**
 - As temperature **increases** the particles will **move faster** so there will be **more collisions** per second
 - However *main reason* => more particles *possess the necessary activation energy* (see definition later) resulting in more successful collisions
 - **TEMPERATURE DOES NOT ALTER THE ACTIVATION ENERGY**
 - Generally a **10°C increase** in temperature will **DOUBLE** the rate of a non-instantaneous reaction
 - The distribution curve moves to the right at the higher temperature (**more molecules with higher kinetic energy**)



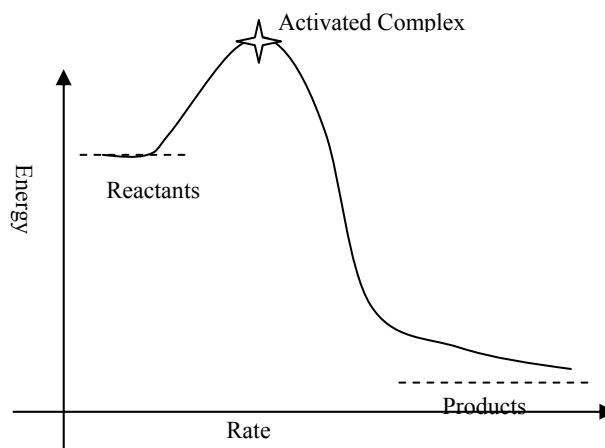
- **Light**
 - Is another form of energy that **will speed up** chemical reactions

3) Energy in Chemical Kinetics:

- *Effect of temperature*
 - **Higher** temperature = **greater** E_K (kinetic energy) = **faster** molecules (mass of molecules does not change) = MORE COLLISIONS = collisions will **have more energy**
- *Activation Energy*
 - **Postulates:**
 - Most molecular collisions are **ineffective**
 - Only **high-energy** collisions are effective
 - At **low** temperature **few** collisions are effective
 - **Higher** temperatures will **increase** the number of effective collisions
 - *Activation energy* – the **minimum** threshold energy needed for the **reaction to happen**
 - Only molecules that have at **least the activation energy** – lead to *effective collisions*
 - **Constant** for a particular reaction (i.e. does not change during the course of the reaction)
 - LOW activation energy = **fast** and easy reaction
 - HIGH activation energy = **slow** and difficult reaction
 - Activation energy will be **different** for forward and reverse reaction
 - **Kinetic energy diagram:**



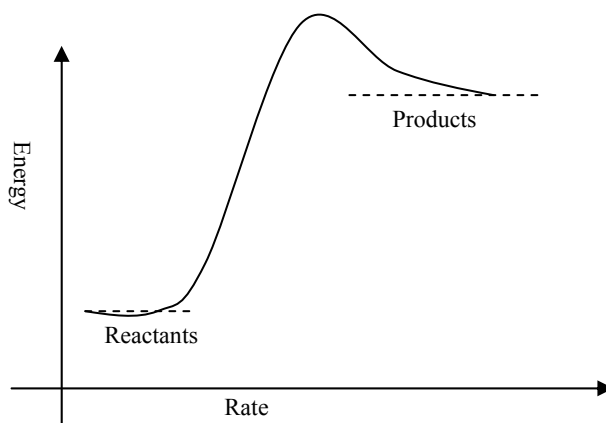
- Energy distribution of a reaction forms a 'bell curve' shaped graph, called the **Maxwell Boltzmann Distribution of Energies**
- *Activated Complex* – the molecules with **energy greater than the activation energy** are most likely to lead to reaction



- Energy necessary to reach the activated complex is the **activation energy**
- Relation between *reverse and forwards* activation energy:

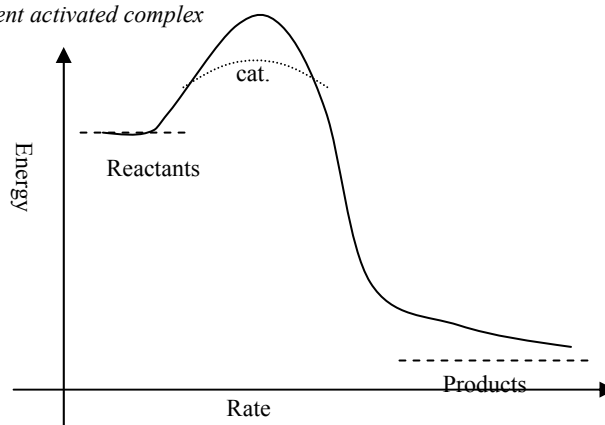
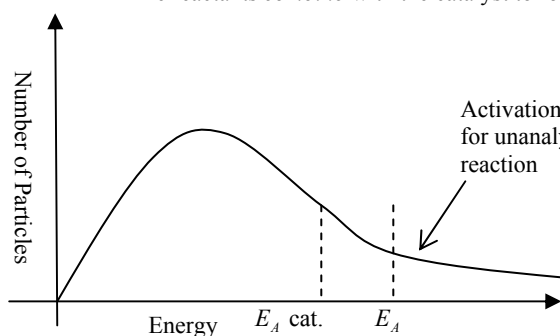
$$E_A(\text{reverse}) - E_A(\text{forward}) = \Delta H_R(\text{enthalpy of reaction})$$

- *Endothermic* reactions always have **high activation energies**:



- *Effect of Catalysts - Catalysis*

- Catalysts **speed up** reactions + **do not appear as products** of the reaction
- *Palladium* and *platinum* are excellent catalysts and are widely used
- Catalysts – **provide a lower energy pathway** from reactants to products
- The reactants *combine* with the catalyst to form a *different activated complex*



- The number of active collisions is **increased** because the **activation energy** E_A (catalyzed) for the catalyzed situation is **lower**

4) Reaction Mechanism:

- *Reaction Mechanism* – the **sequence** of bond-breaking and bond-making **steps** that occurs during the reaction conversion of reactants to products
- Most reactions *occur in a sequence of steps* – each step involving only one or two particles = *reaction mechanism*
- *Elementary step* – **each step** in a mechanism
- *Uni-; Bi-; Tri-Molecular* – number of *molecules* involved (1,2,3)
- All the elementary steps must **add up** to give the balanced equation => overall equation = **sum** of elementary steps
- *Rate determining step* – the **slowest step**, which determines the overall rate of the reaction
- *Intermediate species (a compound)* – the one that **does not appear in the final product** (i.e. a species that are produced in one step and are consumed in another)
- COEFFICIENTS of the reactants in the rate determining step are equal to the **exponents** of the rate law (see definition below)
- The rate equation CANNOT be predicted from its overall stoichiometry
- In general, in the reaction $x\text{A} + y\text{B} \xrightarrow{\text{Slow}} z\text{C}$ the following is the RATE LAW:

$$\text{Rate} = k \cdot [\text{A}]^x \cdot [\text{B}]^y \cdot [\text{C}]^z$$

- The rate constant (k) for a reaction **relates the rate to the concentration of the reactants**

- How to determine easily the order of the reaction for Initial Rate:

- Given a reaction $X + Y \xrightarrow{\text{Slow}} W$ and the following table:

Experiments	[X]	[Y]	Rate of formation [W]
1			
2			

- Express rates with respect to one of the reactants:

$$\text{Rate}_2 = k[\text{conc}_2]^m \quad \text{---} \quad 1 \quad \text{and} \quad \text{Rate}_1 = k[\text{conc}_1]^m$$

- Divide the first equation by the second:

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[\text{conc}_2]^m}{[\text{conc}_1]^m}$$

- Substitute data from table.... And simplify to the following expression:

$$A = B^m$$

- Solve for m... it is the exponent of the concentration of the expressed reactant... do same for the other reactant

5) Half-Life and First-Order Reactions:

- Reaction Half-life ($t_{1/2}$)** – time required for the concentration of a reactant to decrease to **one half** of its initial concentration
- First order reactions have a **CONSTANT HALF-LIFE**
- Half-life has numerous uses such as:
 - Determine the **order** of the reaction
 - Indicates the **stability** of a reactant (the longer the half-life the greater the stability of the reactants)
 - Can determine the **rate constant**:

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

- The shorter the half-life the larger the value of k thus the faster the reaction will occur. Less time required to reach the half-way point
- In summary
 - After one half-life = 50% remains = 0,01M = 50% of the reactant has been consumed
 - After two half-lives = 25% remains = 0,05M = 75% of the reactant has been consumed
 -
- Question – what fraction remaining after ___ seconds? => Use:

$$\ln \left(\frac{[A]_t}{[A]_0} \right) = -kt \quad \text{(solve for } \frac{[A]_t}{[A]_0} \text{)}$$

6) Rate Equations and Temperature: Arrhenius Equation:

- Arrhenius Equation:**

$$k = e^{-\frac{E_A}{RT}}$$

- e – base of all natural logs (2.718...)
- E_A – activation energy of the reaction (J mol^{-1})
- R – molar gas constant ($8,3143 \text{ J K}^{-1} \text{ mol}^{-1}$)
- T – absolute temperature in degrees Kelvin (K)

Taking natural logs of both sides of the equation:

$$\ln(k) = \ln(A) - \frac{E_A}{RT} \quad \Leftrightarrow \quad y = b - mx$$

Graph of $\ln(k)$ against $1/T$ yields a straight line with:

- Slope = $\frac{E_A}{R}$
- y-intercept = $\ln(A)$

Also useful formula:

$$\ln \frac{k_1}{k_2} = \frac{E_A}{R} \left\{ \frac{1}{T_2} - \frac{1}{T_1} \right\}$$

- Reactions with *large values of E_A* have **small k** and therefore are slow
- The equation shows ---- as the **temperature increases**, the value of the **rate constant k also increases** indicating the reaction is **faster** as expected, because **more** molecules can collide

7) Kinetics of Catalysis:

- Catalyst** – substance that **takes part** in a chemical reaction and speeds it up, but itself undergoes **no permanent chemical change**
- Modify** and **speed up** existing pathways or provide **completely new pathways** with a lower activation energy
- Catalysts work in **two** ways:
 - From $k = e^{-\frac{E_A}{RT}}$, if T is constant and E_A is lowered, then k would increase, meaning rate would increase
 - If A is altered then k increases = rate of reaction increases
- Homogeneous catalysis** – catalyst is present in the **same physical state** as the reactants
- The catalyst provides a **new reaction path with a lower activation energy** than the reaction without the catalyst
- Heterogeneous catalysis** – catalyst is present in a **distinct phase (state)** – involve *transition metals*

- Most cases => catalytic action on the **surface of the solid catalyst**
- *Absorption* – collection of one substance on the **surface** of another substance
- The catalyst provides an **ENERGY STORE** – IT PROVIDES ENERGY TO SPLIT BONDS OF REACTANTS ON ITS SURFACE
- Increase in **surface area of the catalyst should increase the rate of the reaction** (i.e. catalysts are more effective when spread over large surfaces)
- *Enzymes* – are **catalysts!** (substance which an enzyme enables to react is called the substrate)
- *Auto-catalysis* – one of the **products** of the reaction acts **as a catalyst for the reaction**
- *Inhibitor* – **increases the activation energy** of a reaction, thus **reducing its rate** (preservatives = slow down the decay of food)
- Types of preservatives:
 - **Antimicrobials** (prevents bacteria, molds, fungi and yeasts)
 - **Antioxidants** (prevents changes in color or flavor because of oxidation)
- Catalytic Converters – **converts pollutants** in vehicle exhaust gases into **harmless products** (converter = transition metal)

8) Rate Graphs:

