CHM 101: General Physical Chemistry

Thermochemistry and simple calculations based on Hess's law. Rate of reaction (Chemical kinetics)

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"Thermochemistry"

Thermochemistry

- **This is a branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.**

- **In 1782 Antoine Lavoisier and Pierre-Simon Laplace laid the foundations of "thermochemistry"**

- **They showed that the heat evolved in a reaction is equal to the heat absorbed in the reverse reaction.**

- **Every substance has a definite amount of energy known as the intrinsic energy or internal energy, E.**

- **The exact value of internal energy cannot be determined but the change in internal energy, ΔE, can be accurately measured experimentally.**

- **When the internal energy of reactants (E_r) is greater than the internal energy of the products (E_p), the difference of internal energy, ΔE, is released as heat energy.**

  $$\Delta E = E_{products} - E_{reactants} \text{ o (or } \Delta E = E_p - E_r)$$
- **Such a reaction is called exothermic reaction.**

- If the internal energy of the products (E_p) is greater than that of the reactants (E_r), heat is absorbed from the surroundings.

- Such a reaction is called endothermic reaction.

- The amount of heat released or absorbed in a chemical reaction is termed the heat of reaction.

- The energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds.

- Thus, thermochemistry provides useful information regarding the bond energies.

Unit of Energy

- **The energy changes are usually expressed as:**
  - **the calorie (cal.),**
  - **kilocalorie (1 kcal = 1000 cal),**
  - **Joule (J) and**
  - **kilojoule (kJ).**
- **It may be noted that 1 cal = 4.18 J and 1 kcal = 4.18 kJ.**

ENTHALPY OF A REACTION

- **Thermochemical measurements are made either at (a) constant volume or (b) constant pressure.**

- **The magnitudes of changes observed under the two conditions are different.**

- **The change in internal energy ($\triangle E$) is the heat change accompanying a chemical reaction at constant volume because no external work is performed.**

- **However at constant pressure not only does the change in internal energy take place but work is also involved because of expansion or contraction.**

- In the laboratory most of the chemical reactions are carried out at constant pressure (atmospheric pressure) rather than at constant volume

- The enthalpy of a system is defined as the sum of the internal energy and the product of its pressure and volume.

$$H = E + PV$$

- Like internal energy, change in enthalpy ($\triangle H$) accompanying a process is what can be measured accurately not absolute H.

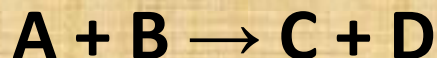$$\triangle H = H_{products} - H_{reactants} = H_p - H_r$$

- Therefore, internal energy is the heat change in a process at constant volume while enthalpy is the heat change in a process at constant pressure.

EXOTHERMIC AND ENDOTHERMIC REACTIONS

- **Consider a general reaction at constant pressure,**

$$A + B \longrightarrow C + D$$

$$\triangle H = H_{products} - H_{reactants} = (H_C + H_D) - (H_A + H_B)$$

- **When $\triangle H$ is zero, the enthalpies of the products and reactants being the same, the heat is evolved or absorbed.**

- **In case $\triangle H$ is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.**

- Such reactions which are accompanied by the evolution of heat energy are called Exothermic reactions.

- When $\triangle H$ is positive, the enthalpy or heat content of the reactants and an equivalent of heat is absorbed by the system from the surroundings.

- Such reactions which are accompanied by absorption of heat are called Endothermic reactions.

- Thus for an exothermic reaction Hp < Hr and $\triangle H = -$ ve, for an endothermic reaction Hp > Hr and $\triangle H = +$ve.
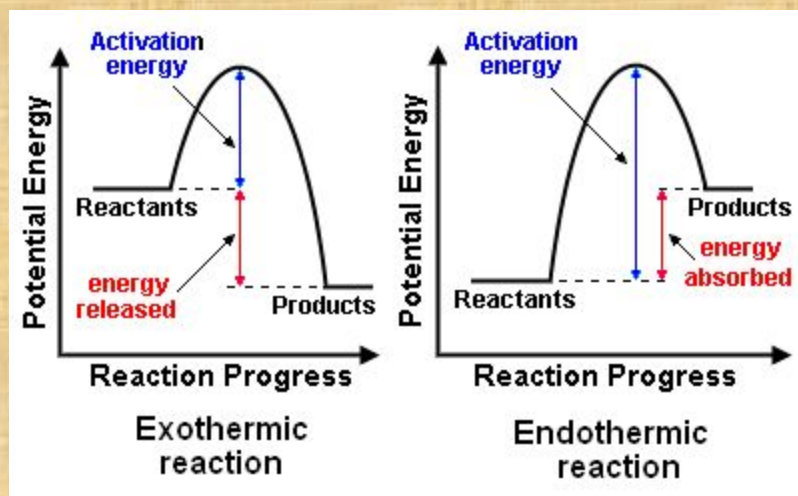
EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC PROCESSES

| Exothermic processes	Endothermic processes
Making ice cubes	Melting ice cubes
Formation of snow in clouds	Conversion of frost to water vapour
Condensation of rain from water vapour	Evaporation of water
Mixing sodium sulfite and bleach	Baking bread
Rusting iron	Cooking an egg
Burning sugar	Producing sugar by photosynthesis
Forming ion pairs	Separating ion pairs
Mixing water and strong acids	Mixing water and ammonium nitrate
Mixing water with an anhydrous salt	Making an anhydrous salt from a hydrate
Crystallizing liquid salts (as in sodium acetate in chemical handwarmers)	Melting solid salts
Nuclear fission	Reaction of barium hydroxide octahydrate crystals with dry ammonium chloride
Mixing water with calcium chloride	Reaction of thionyl chloride ($SOCl_2$) with cobalt(II) sulfate heptahydrate

Example

- **The heat of combustion of ethylene at 17ºC and at constant volume is – 1389.9 kJ. Calculate the heat of combustion at constant pressure considering water to be in liquid state. (R = 8.314 Jmol^{-1}K^{-1})**

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- **Solution**

The chemical equation for the combustion of ethylene is:

$$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}$$
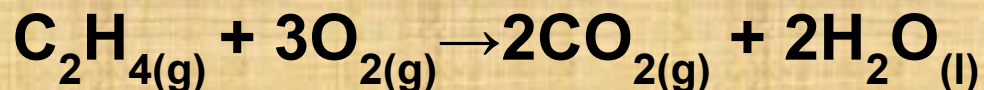
No. of moles of the gaseous products = 2

No. of moles of the gaseous reactants = 4

$$\therefore \Delta n = (2 - 4) = -2$$

We know that $\Delta H = \Delta E + \Delta nRT$ (PV=nRT)

Given that $\Delta E = -1389.9$ kJ

T = 273 + 17 = 290 K

R = 8.314 $\times 10^{-3}$ k Jmol^{-1}K^{-1}

$$\therefore \Delta H = -1389.9 \text{ kJ} + ((8.314 \times 10^{-3} \times -2 \times 290)$$

$$= -1.384.72 \text{ kJ}$$

Assignment

- **The heat of combustion of carbon monoxide at constant volume and at 17°C is − 283.3 kJ. Calculate its heat of combustion at constant pressure (R = 8.314 J degree^{-1} mol^{-1}).**

THERMOCHEMICAL EQUATIONS

- **An equation which indicates the amount of heat change (evolved or absorbed) in the reaction or process is called a Thermochemical equation.**

- **It must essentially :**
  - **be balanced;**
  - **give the value of ΔE or ΔH corresponding to the quantities of substances given by the equation;**
  - **mention the physical states of the reactants and products.**

- **The physical states are represented by the symbols (*s*), (*l*), (*g*) and (*aq*) for solid, liquid, gas and aqueous states respectively.**
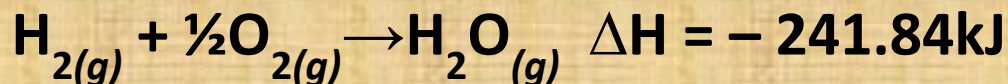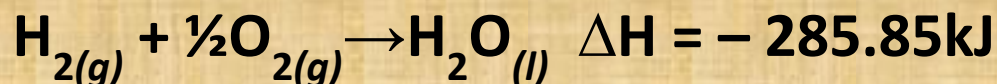
- **The equation :**

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad \triangle H = -285.85 \text{ kJ}$$

1 mole of H_2 with 0.5 mole of O_2, to form 1 mole of water with evolution of 285.85 kJ of at constant pressure.

- **If two moles of hydrogen are burnt, the heat evolved would be (2 × 285.85) kJ**

- **It is not thermochemical equation because it doesn't specify whether H_2O is steam or liquid**

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \triangle H = -285.85\text{kJ}$$
$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \quad \triangle H = -241.84\text{kJ}$$

- **There is difference in the value of $\triangle H$ if water is in the liquid or gaseous state as shown above.**

HEAT OR ENTHALPY OF REACTION

- **Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products.**

$$CO_{(g)} + ½O_{2(g)} \rightarrow CO_{2(g)} \quad \triangle H = -284.5 \text{ kJ}$$
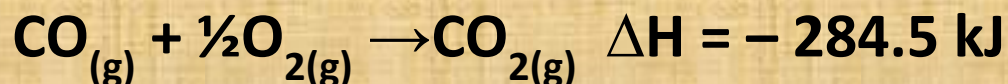
- **The heat of reaction varies with the change in temperature. Thus, the temperature at which the reaction is taking place must be stated.**

- **The temperature of 298 K under pressure of one atmosphere has been fixed as the standard state.**

- **Thus the heat change accompanying a reaction taking place at 298 K and one atmospheric pressure is called the standard heat change or standard enthalpy change. It is denoted by $\triangle H°$.**

VARIATION OF HEAT (OR ENTHALPY) OF REACTION WITH TEMPERATURE

- The variation of heat change of reaction with temperature are represented by *Kirchoff's equations*.

- At constant volume,

$$\Delta E = E_2 - E_1$$

$$\left(\frac{d\Delta E}{dT}\right)_V = \left(\frac{dE_2}{dT}\right)_V - \left(\frac{dE_1}{dT}\right)_V$$

$$\left(\frac{dE}{dT}\right)_V = C_v \qquad \text{\textcolor{red}{\textbf{\textit{C}}}}_{\textcolor{red}{\textbf{\textit{v}}}} \textcolor{red}{\textbf{\textit{ is the constant volume heat capacity.}}}$$

$$\left(\frac{d\Delta E}{dT}\right)_V = (C_v)_2 - (C_v)_1 = \Delta C_v$$

Integrating the above equation between temperatures T_1 and T_2, we have

$$\int_{E_1}^{E_2} d\Delta E = \int_{T_1}^{T_2} \Delta C_v dT = \Delta C_v[T_2 - T_1]$$

Similar process can be used to obtain the enthalpy

$$\int_{E_1}^{E_2} d\Delta H = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p[T_2 - T_1]$$

Exercise

- The heat of reaction $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ at 27 ^{o}C is – 22.1 kcal. Calculate the heat of reaction at 77 ^{o}C. The molar heat capacities at constant pressure at 27ºC for hydrogen, chlorine and HCl are 6.82, 7.70 and 6.80 cal mol^{-1} respectively. (Ans = – 22.123 kcal)

- The heat of reaction $N_2 + 3H_2 \rightarrow 2NH_3$ at 27 ^{o}C was found to be –21.976 kcal. What will be the heat of reaction at 50°C ? The molar heat capacities at constant pressure and at 27ºC for nitrogen, hydrogen and ammonia are 6.8, 6.77 and 8.86 cal mol^{-1} degree^{-1}. (Ans =22.192 kcal)

DIFFERENT TYPES OF HEAT (ENTHALPY) OF REACTION

- **HEAT OF FORMATION: The change in enthalpy that takes place when one mole of the compound is formed from its elements. Denoted as ΔH_f**

- **STANDARD HEAT OF FORMATION OF A COMPOUND: The change in enthalpy that takes place when one mole of a compound is formed from its elements, all substances being in their standard states (298 K and 1 atm pressure).**

- **STANDARD HEAT OF REACTION ($\triangle H^O$) FROM STANDARD HEAT OF FORMATION ($\triangle H^O_f$): The standard heat of reaction is equal to the standard heat of formation of products minus the standard heat of formation of reactants.**

$$\triangle H^o = \triangle H_{products} - \triangle H_{reactants}$$

Excercise

- **Calculate $\triangle H^o$ for the reaction: $CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)}$ given that $\triangle H$ of for $CO_{2(g)}$, $CO_{(g)}$ and $H_2O_{(g)}$ are – 393.5, – 111.31 and – 241.80 kJ mol^{-1} respectively.**

(Ans = 40.4 kJ)

- **The standard heats of formation of $C_2H_5OH_{(l)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ re – 277.0, –393.5 and –285.5 kJ mol^{-1} respectively. Calculate the standard heat change for the reaction**

(Ans = – 1366.5 kJ)

- **HEAT OF COMBUSTION:** the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.
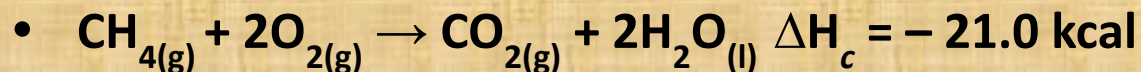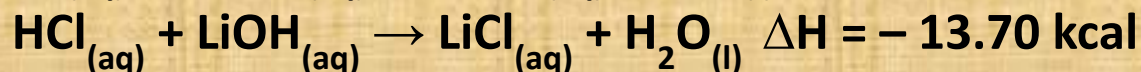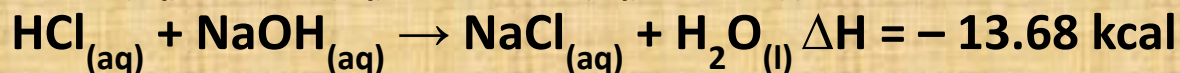
  - $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\triangle H_c = -21.0$ kcal
- **Now consider the chemical equations**

  $$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \triangle H_c = -94.3 \text{ kcal}$$
  $$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \quad \triangle H_c = -26.0 \text{ kcal}$$
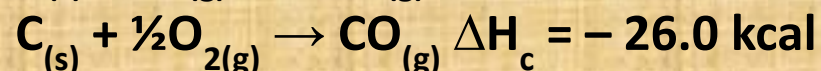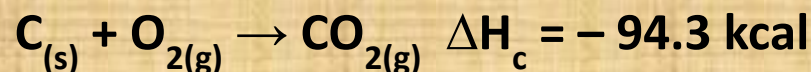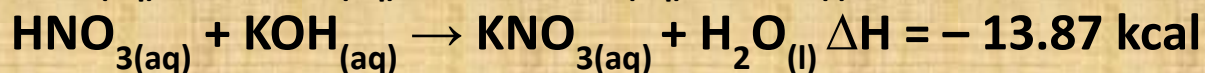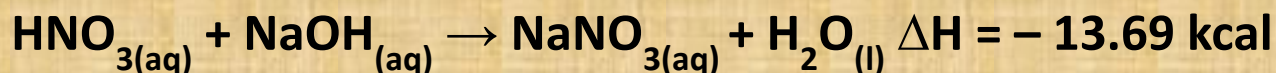
- **The $\triangle H_c$ for C is – 94.3 kcal and not – 26.0 kcal because the combustion is complete only in the first reaction.**

- **The heat of combustion of a substance ($\triangle Hc$) is always negative since heat energy always evolved during the process of combustion.**

- **APPLICATIONS OF THE HEAT OF COMBUSTION**
  - **Calculation of heat of formation**
  - **Determination of calorific value of foods and fuels.**
  - **Deciding constitution**

- **HEAT OF SOLUTION:** the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.

- It is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.

$$KCl_{(s)} + H_2O_{(l)} \rightarrow KCl_{(aq)} \; \triangle H = -4.4 \text{ kcal}$$

- heat of solution of an electrolyte may be due to energy change involved during ionization or some hydrate formation as in case of sulphuric acid.

- **HEAT OF NEUTRALIZATION:** the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralized by one gram equivalent of a base or vice versa in dilute solution.

$$HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O_{(l)} \; \triangle H = -13.69 \text{ kcal}$$
$$HNO_{3(aq)} + KOH_{(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)} \; \triangle H = -13.87 \text{ kcal}$$
$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} \; \triangle H = -13.68 \text{ kcal}$$
$$HCl_{(aq)} + LiOH_{(aq)} \rightarrow LiCl_{(aq)} + H_2O_{(l)} \; \triangle H = -13.70 \text{ kcal}$$

the heat of neutralization of a strong acid and strong base is −13.7 kcal, no matter which acid or base is employed because it is heat of formation of water from hydrogen and hydroxyl ions.

ENERGY CHANGES DURING TRANSITIONS OR PHASE CHANGES

- **HEAT OF FUSION**: *the heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its melting point.*

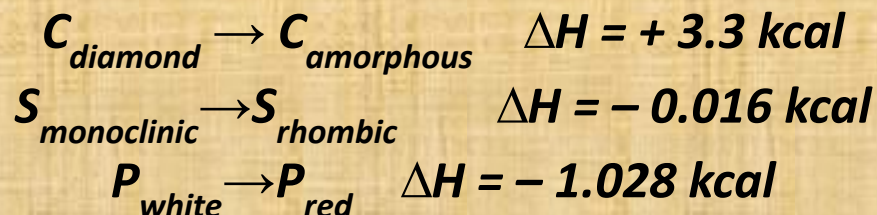$$H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \triangle H = + 1.43 \ kcal$$

- **HEAT OF VAPOURISATION**: *the heat change (or enthalpy change) when one mole of liquid is converted into vapour or gaseous state at its boiling point.*

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \quad \triangle H = + 9.71 \ kcal$$

- **HEAT OF SUBLIMATION**: *the heat change (or enthalpy change) when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.*
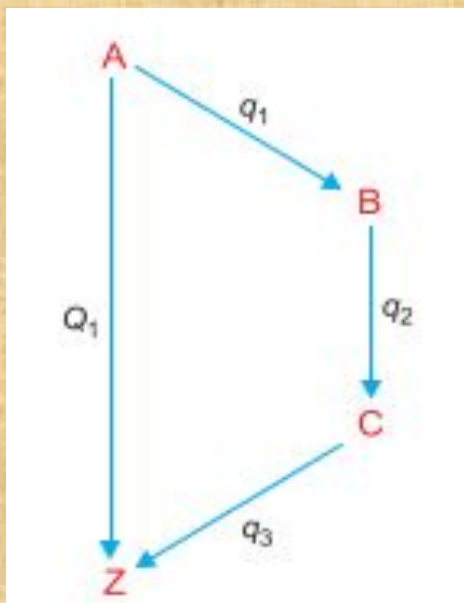
$$I_{2(s)} \rightarrow I_{2(g)} \quad \triangle H = + 14.92 \ kcal$$

- **HEAT OF TRANSITION**: *the change in enthalpy which occurs when one mole of an element changes from one allotropic form to another.*
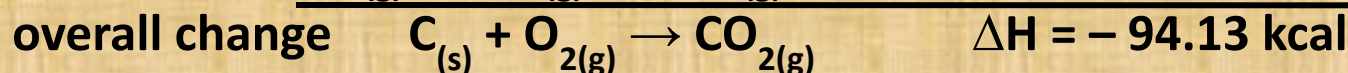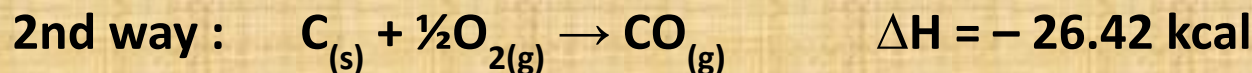
$$C_{diamond} \rightarrow C_{amorphous} \quad \triangle H = + 3.3 \ kcal$$
$$S_{monoclinic} \rightarrow S_{rhombic} \quad \triangle H = - 0.016 \ kcal$$
$$P_{white} \rightarrow P_{red} \quad \triangle H = - 1.028 \ kcal$$

HESS'S LAW OF CONSTANT HEAT SUMMATION

- ΔE and ΔH depend only on the initial state and final state of the system and not the manner or the steps in which the change takes place.

- **Hess's Law states that:** *If a chemical change can be made to take place in two or more different ways whether in one, two or more steps, the amount of total heat change is same no matter by which method the change is brought about.*
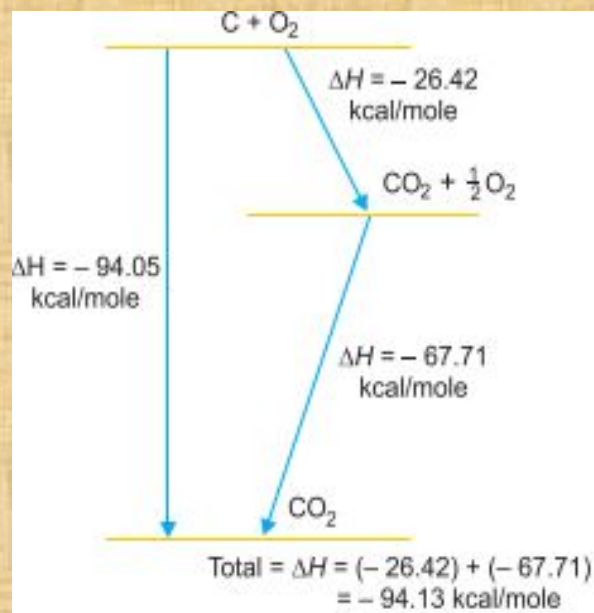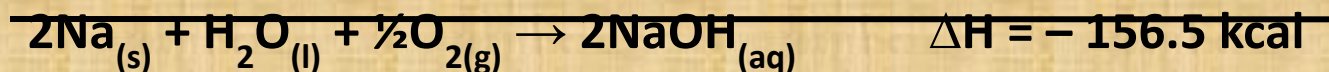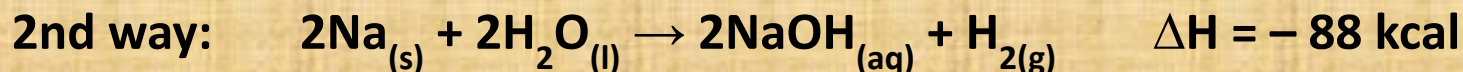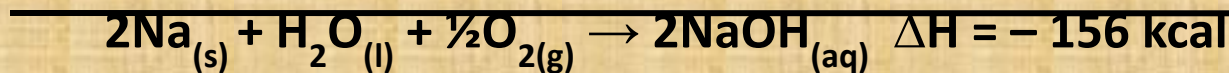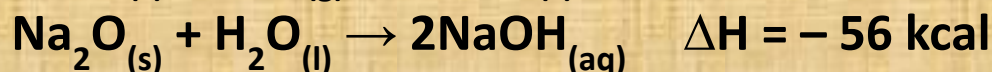
Illustration

- **Burning of carbon to CO_2.**

  1st way : $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\triangle H = -94.05$ kcal

  2nd way : $C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}$ $\triangle H = -26.42$ kcal

                       $CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}$ $\triangle H = -67.71$ kcal

  overall change $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\triangle H = -94.13$ kcal

- **Formation of Sodium hydroxide from Na:**

  1st way: $2Na_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow Na_2O_{(s)}$ $\triangle H = -100$ kcal

                  $Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$ $\triangle H = -56$ kcal

             $2Na_{(s)} + H_2O_{(l)} + \frac{1}{2}O_{2(g)} \longrightarrow 2NaOH_{(aq)}$ $\triangle H = -156$ kcal

  2nd way: $2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$ $\triangle H = -88$ kcal

                $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(g)}$ $\triangle H = -68.5$ kcal

             $2Na_{(s)} + H_2O_{(l)} + \frac{1}{2}O_{2(g)} \longrightarrow 2NaOH_{(aq)}$ $\triangle H = -156.5$ kcal
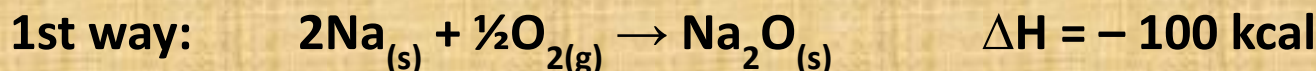
Application of Hess's Law

- **Determination of heat of formation of substances which otherwise cannot be measured experimentally**

- **Determination of Heat of Transition**

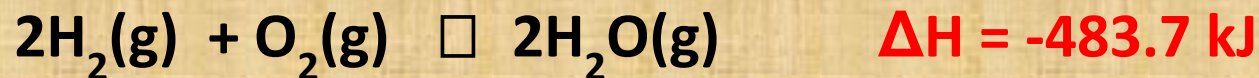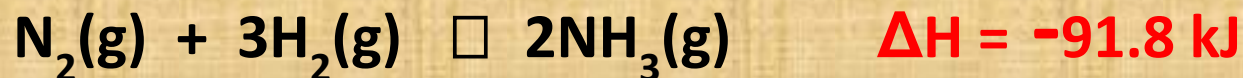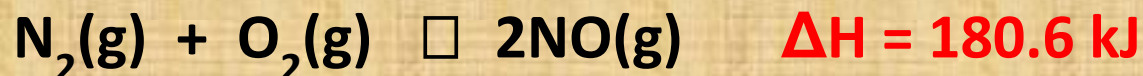- **Determination of heats of various reactions**

FURTHER EXAMPLES ON HESS'S LAW

Determine the heat of reaction for the reaction:

$$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$$

Using the following sets of reactions:

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H = 180.6 \text{ kJ}$$

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H = -91.8 \text{ kJ}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \Delta H = -483.7 \text{ kJ}$$

Hint: The three reactions must be algebraically manipulated to sum up to the desired reaction.

and.. the **ΔH values must be treated accordingly.**

Goal: $4NH_3(g) + 5O_2(g) \; \square \; 4NO(g) + 6H_2O(g)$

Using the following sets of reactions:

$N_2(g) + O_2(g) \; \square \; 2NO(g)$ **ΔH = 180.6 kJ**

$N_2(g) + 3H_2(g) \; \square \; 2NH_3(g)$ **ΔH = −91.8 kJ**

$2H_2(g) + O_2(g) \; \square \; 2H_2O(g)$ **ΔH = -483.7 kJ**

NH$_3$:   **Reverse and x 2** $4NH_3 \; \square \; 2N_2 + 6H_2$ **ΔH = +183.6 kJ**

O$_2$:   **Found in more than one place, SKIP IT (its hard).**

NO: **x2** $2N_2 + 2O_2 \; \square \; 4NO$ **ΔH = 361.2 kJ**

H$_2$O: **x3** $6H_2 + 3O_2 \; \square \; 6H_2O$ **ΔH = -1451.1 kJ**

Goal: $4NH_3(g) + 5O_2(g) \square 4NO(g) + 6H_2O(g)$
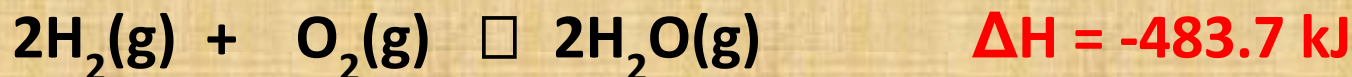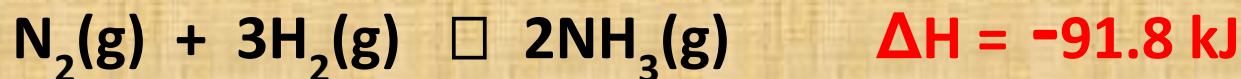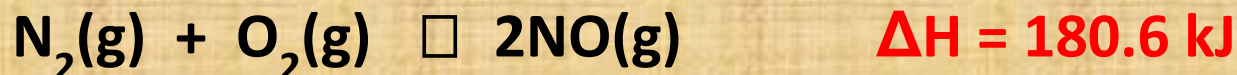
NH_3:   **Reverse and x2** $4NH_3 \square 2N_2 + 6H_2$ $\Delta H = +183.6$ **kJ**

O_2:   **Found in more than one place, SKIP IT.**

NO: **x2** $2N_2 + 2O_2 \square 4NO$ $\Delta H = 361.2$ **kJ**

H_2O: **x3** $6H_2 + 3O_2 \square 6H_2O$ $\Delta H = -1451.1$ **kJ**

Cancel terms and take sum.

$4NH_3 \ +5O_2 \ \square \ 4NO \ +6H_2O$ $\Delta H = -906.3$ **kJ**
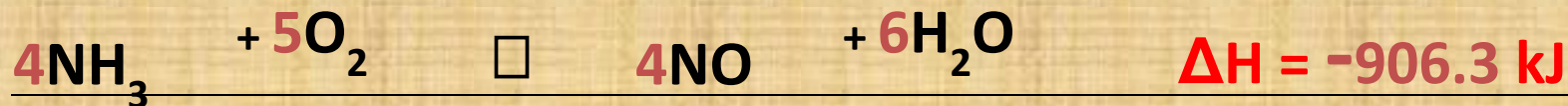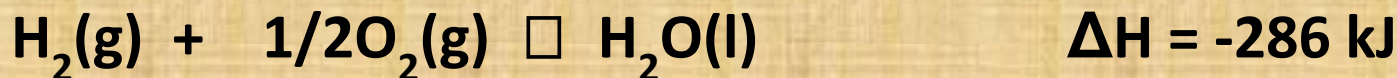

Is the reaction endothermic or exothermic?
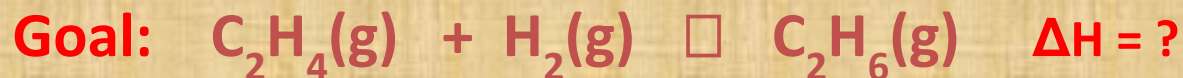
Determine the heat of reaction for the reaction:

$C_2H_4(g)$ + $H_2(g)$ □ $C_2H_6(g)$

Use the following reactions:

$C_2H_4(g)$ + $3O_2(g)$ □ $2CO_2(g)$ + $2H_2O(l)$ $\Delta H = -1401$ kJ

$C_2H_6(g)$ + $7/2O_2(g)$ □ $2CO_2(g)$ + $3H_2O(l)$ $\Delta H = -1550$ kJ

$H_2(g)$ + $1/2O_2(g)$ □ $H_2O(l)$ $\Delta H = -286$ kJ
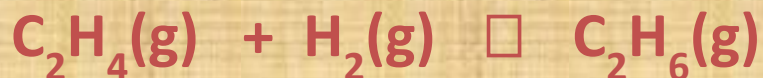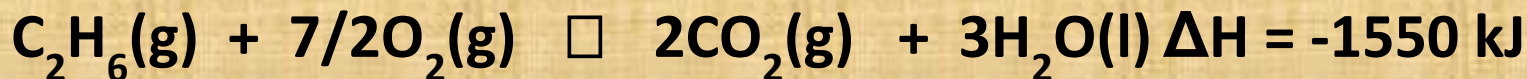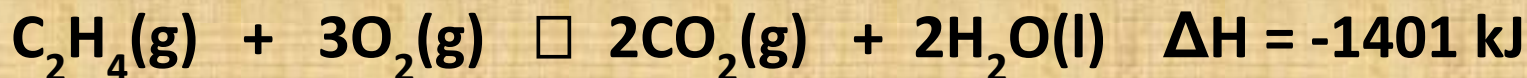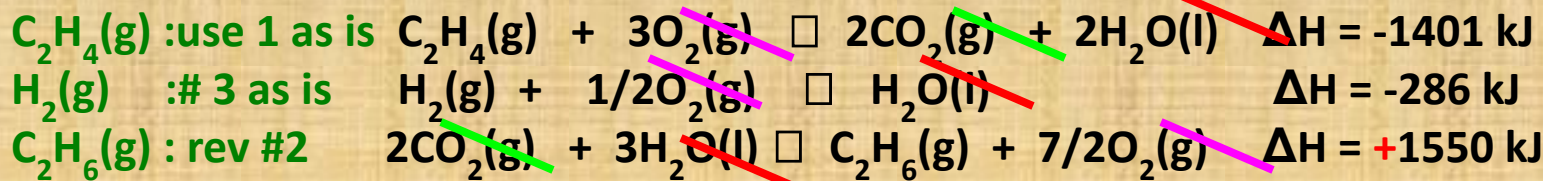
Consult your neighbor if necessary.

Determine the heat of reaction for the reaction:

Goal: $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ **ΔH = ?**

Use the following reactions:

$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$ **ΔH = -1401 kJ**

$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ **ΔH = -1550 kJ**

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ **ΔH = -286 kJ**

$C_2H_4(g)$:use 1 as is $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$ **ΔH = -1401 kJ**
$H_2(g)$:# 3 as is $H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$ **ΔH = -286 kJ**
$C_2H_6(g)$: rev #2 $2CO_2(g) + 3H_2O(l) \rightarrow C_2H_6(g) + 7/2O_2(g)$ **ΔH = +1550 kJ**

_____

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ **ΔH = -137 kJ**
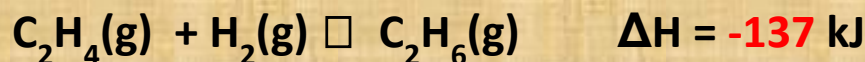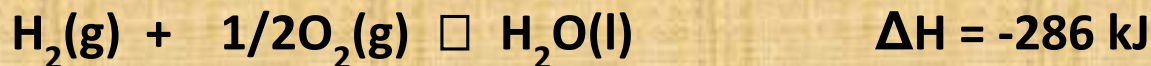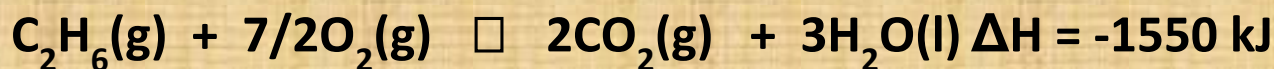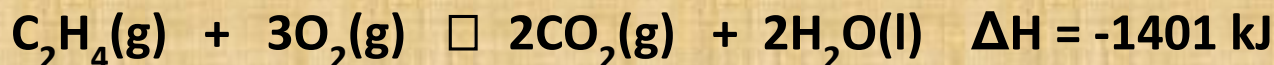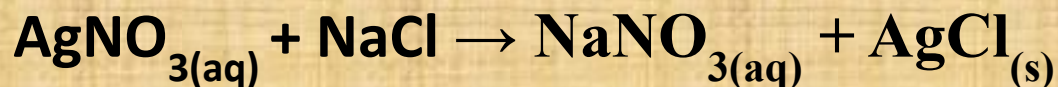
Rates of Reaction /Chemical Kinetics

- **Most chemical reactions are spontaneous reactions. These reactions occur from left to right till all the reactants are converted to products.**

$$A + B \rightarrow Products$$

- **A spontaneous reaction may be slow or it may be fast. For example:**

  – *The reactions between aqueous sodium chloride and silver nitrate is a fast reaction.*

    e.g. the precipitate of AgCl is formed as fast as $AgNO_3$ solution is added to NaCl solution.

$$AgNO_{3(aq)} + NaCl \rightarrow NaNO_{3(aq)} + AgCl_{(s)}$$

 – *On the contrary, the rusting of iron is a slow reaction that occurs over the years.*

- **The branch of Physical chemistry which deals with the rate of reactions is called *Chemical Kinetics***

- **The study of Chemical Kinetics includes :**
  - *The rate of the reactions and rate laws.*
  - *The factors as temperature, pressure, concentration and catalyst, that influence the rate of a reaction.*
  - *The mechanism or the sequence of steps by which a reaction occurs.*

REACTION RATE

- The rate of a reaction tells as to what speed the reaction occurs.
- Consider a simple reaction

$$A \longrightarrow B$$
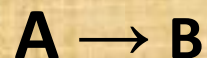
- The concentration of the reactant A decreases and that of B increases as time passes.
- The rate of reactions is defined as the change in concentration of any of reactant or products per unit time.
- For the given reaction, *the rate of reaction* may be equal to the rate of *disappearance of A* which is equal to the rate of *appearance of B.*

$$Rate = -\frac{d[A]}{dt} = \frac{d[B]}{dt}$$

UNITS OF RATE

- **Reactions rate has the units of concentration divided by time.**
  - **$[mol\ dm^{-3}]$ /sec or $mol\ dm^{-3}\ s^{-1}$**
  - **$[mol\ dm^{-3}]$ /min or $moldm^{-3}\ min^{-1}$**
  - **$[mol\ dm^{-3}]$/hour or $mol\ dm^{-3}\ h^{-1}$ and, so on**

Average Rate of Reaction

- **Consider the reaction,**

$$CO_{(g)} + NO_{2(g)} \longrightarrow CO_{2(g)} + NO_{(g)}$$

$$rate = -\frac{\Delta[CO]}{\Delta t} = -\frac{d[CO]}{dt}$$

- **The concentration of CO was found experimentally every 10 seconds.**

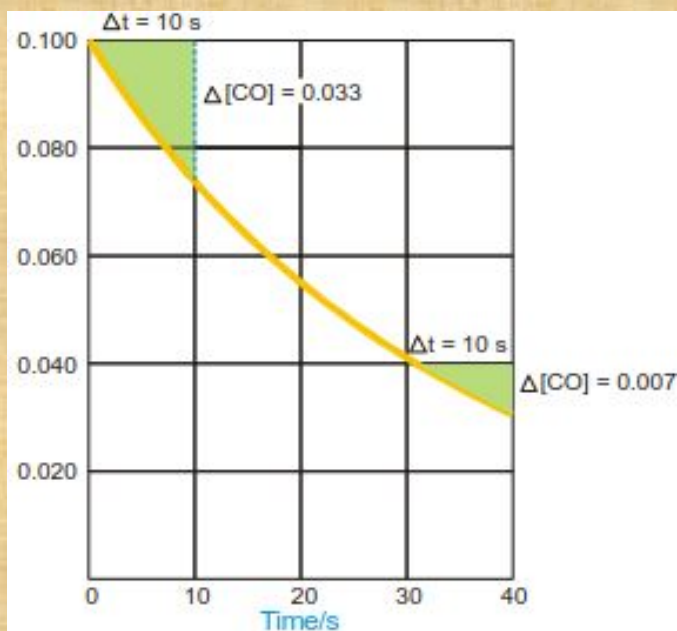| [CO] mol/dm^3	0.1	0.067	0.05	0.04	0.033
Time (s)	0	10	20	30	40

- **Over the first 10 seconds, the average rate is**

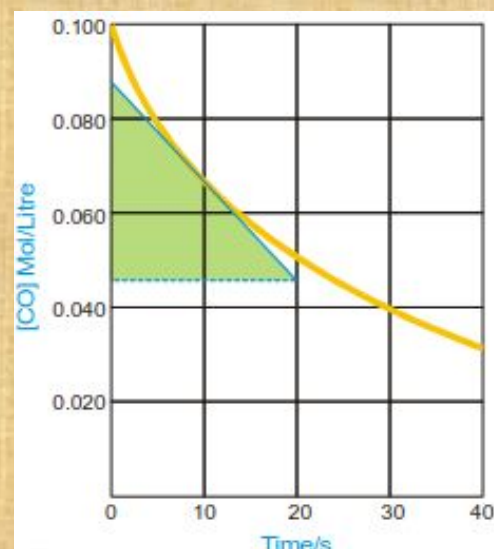$$rate = -\frac{d[CO]}{dt} = \frac{-(0.067 - 0.1)}{10 - 0} = 0.0033 \, mol dm^{-3} s^{-1}$$

- **In the time interval between 30 and 40 seconds, the average rate is much smaller.**

$$rate = -\frac{d[CO]}{dt} = \frac{-(0.033 - 0.04)}{40 - 30} = 0.0007 moldm^{-3}s^{-1}$$

- **So, a better way to estimate the rate of reaction, we need to make the time interval as small as possible.**

The average rate is equal to the slope of the curve.

The slope of tangent at 10 seconds is equal to the instantaneous rate

Instantaneous Rate of Reaction

- The average rates obtained by finding the slope of the curve are not always useful.

- They cover a large time interval during which the rate of reaction changes significantly.

- So, a better way to estimate the rate of a reaction is to make the time interval as small as possible.

- If the interval is infinitesimally small (that is as Δt approaches zero), the rate is referred to as the instantaneous rate

- Thus at any time the instantaneous rate is equal to the slope of a straight line drawn tangent to the curve at that time

$$rate = -\frac{d[\ ]_t}{dt}$$

RATE LAWS

- **The rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.**

$$rate \, \alpha \, [A]^n$$

$$rate = k[A]^n$$

- **For a reaction 2A + B $\rightarrow$ products, the reaction rate with respect to A or B is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as:**

$$rate = k[A]^n[B]^m$$

The power (exponent) of concentration n or m in the rate law is usually a small whole number integer (1, 2, 3) or fractional. The proportionality constant k is called the rate constant for the reaction.

- **An expression which shows how the reaction rate is related to concentrations is called the rate law or rate equation.**

REACTIONS	RATE LAW
(1) $2N_2O_5 \longrightarrow 4NO_2 + O_2$	rate $= k[N_2O_5]$
(2) $H_2 + I_2 \longrightarrow 2HI$	rate $= k[H_2][I_2]$
(3) $2NO_2 \longrightarrow 2NO + O_2$	rate $= k[NO_2]^2$
(4) $2NO + 2H_2 \longrightarrow N_2 + 2H_2O$	rate $= k[H_2][NO]^2$

- **The rate law cannot be written by merely looking at the equation with a background of our knowledge of Law of Mass Action.**
- **The rate law must be determined by experiment, however, for some elementary reactions the powers in the rate law may correspond to coefficients in the chemical equation.**

- **But usually the powers of concentration in the rate law are different from coefficients.**

ORDER OF A REACTION

- **The order of a reaction is defined as the sum of the powers of concentrations in the rate law.**

$$rate = k[A]^n[B]^m$$

Overall order of reaction = m + n

- **The order of a reaction can also be defined with respect to a single reactant.**

- **Thus the reaction order with respect to A is m and with respect to B it is n.**

- **The overall order of reaction may range from 1 to 3 and can be fractional.**

RATE LAW	REACTION ORDER
rate = $k[N_2O_5]$	1
rate = $k[H_2][I_2]$	1 + 1 = 2
rate = $k[NO_2]^2$	2
rate = $k[[H_2][NO]^2$	1 + 2 = 3
rate = $k [CHCl_3][Cl_2]^{1/2}$	1 + ½=1½

- **Based on the rate law above, reactions may be classified according to the order as:**
  - **m + n = 1, it is first order reaction**
  - **m + n = 2, it is second order reaction**
  - **m + n = 3, it is third order reaction**
  - **m + n = 1½ Fractional order**
- **Consider the reaction,**

$$NO_2 + CO \rightarrow NO + CO_2$$

The reaction is zeroth order with respect to CO and second order with respect to $[NO_2]$. The overall reaction order is 2 + 0 = 2
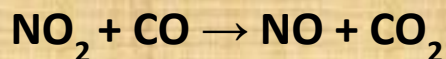
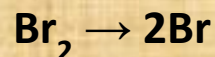- **The rate law for the equation above is given as**

$$Rate = k[NO_2]^2$$

A zero order reaction is one whose rate is independent of concentration.
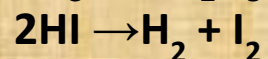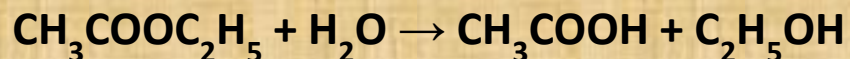
MOLECULARITY OF A REACTION

- **Chemical reactions may be classed into two types:**
  - **Elementary reactions**
  - **Complex reactions**
- **An elementary reaction is a simple reaction which occurs in a single step while complex reaction involved two or more steps.**
- **The molecularity of an elementary reaction is defined as: the number of reactant molecules involved in a reaction.**
- **Unimolecular reactions : (molecularity = 1)**

$$Br_2 \rightarrow 2Br$$

- **Bimolecular reactions : (molecularity = 2)**

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$
$$2HI \rightarrow H_2 + I_2$$

- **Termolecular reactions : (molecularity = 3)**

$$2NO + O_2 \rightarrow 2NO_2$$
$$2NO + Cl_2 \rightarrow 2NOCl$$
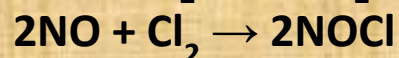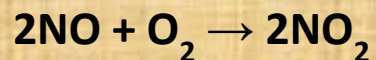
- The term molecularity is often confused with order of a reaction.
- The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the molecularity of reaction.
- The sum of the powers to which the concentrations are raised in the rate law is known as the order of reaction.

Order of a Reaction	Molecularity of a Reaction
• It is the sum of powers of the concentration terms in the rate law expression.	It is number of reacting species undergoing simultaneous collision in the elementary or simple reaction.
• It is an experimentally determined value.	It is a theoretical concept.
• It can have fractional value.	It is always a whole number.
• It can assume zero value.	It can not have zero value.
• Order of a reaction can change with the conditions such as pressure, temperature, concentration.	Molecularity is invariant for a chemical equation

PSEUDO–ORDER REACTIONS

- A reaction in which one of the reactants is present in a large excess shows an order different from the actual order.

- The experimental order which is not the actual one is referred to as the pseudo-order.

- Elementary reactions have similar molecularity and order, thus, pseudo-order reactions is known as pseudo molecular reactions.

- consider a reaction: A + B $\rightarrow$ products

- If B is present in a large excess (i.e. its concentration remains practically constant in the course of reaction).

$$\text{rate} = k\,[A]\,[B]$$
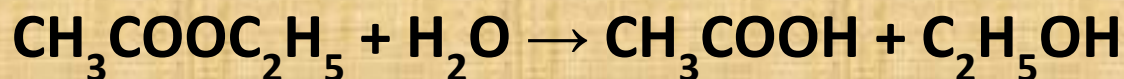
$$\text{rate} = k'\,[A]$$

$$k' = k\,[B].$$

- Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a pseudo-first order.

Examples of Pseudo-order Reactions

- **Hydrolysis of an ester: hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.**

$$CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$$
$$rate = k \, [CH_3COOH][H_2O]$$
$$= k' \, [CH_3COOH]$$

- **Hydrolysis of sucrose: in the presence of a dilute mineral acid hydrolysis of sucrose produces glucose and fructose.**
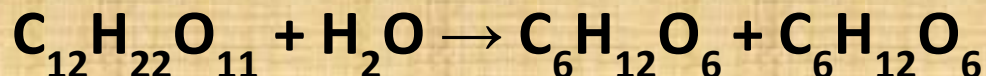
$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$
$$rate = k \, [C_{12}H_{22}O_{11}] \, [H_2O]$$
$$= k' \, [C_{12}H_{22}O_{11}]$$

RATE LAWS

- ## ZERO ORDER REACTIONS

$$A \longrightarrow \textbf{Products}$$

Initial conc.	$[A_0]$	0
Final conc.	$[A_0] - [A_t]$	$[A_t]$

$$-\frac{d[A]}{dt} = k_0[A]^0$$

$$-\frac{d[A]}{dt} = k_0[A]^0 = k_0$$

Upon integration

$$k_0 = \frac{[A]_t}{t}$$

the rate constant is equal to the rate of reaction at all concentrations.

$$[A]_t = k_0 t$$

- **FIRST ORDER REACTIONS**

$$A \rightarrow Products$$

| Initial conc. | $[A_0]$ | 0 |
| Final conc. | $[A_0] - [A_t]$ | $[A_t]$ |

$$-\frac{d[A]}{dt} = k_1[A]^1$$

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[A]}{[A]} = -k_1 dt$$

Upon integration

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]} = -\int_0^t k_1 dt$$

$$\ln[A]_0 - \ln[A] = kt$$

$$\ln\frac{[A]_0}{[A]} = kt$$

- **SECOND ORDER REACTIONS**

$$2A \rightarrow \textbf{Products}$$

Initial conc. $[A_0]$ 0

Final conc. $[A_0] - [A_t]$ $[A_t]$

$$-\frac{d[A]}{dt} = k_2[A]^2$$

$$\frac{d[A]}{dt} = -k_2[A]^2$$

$$\frac{d[A]}{[A]^2} = -k_2\,dt$$

Upon integration

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^2} = -\int_0^t k_2\,dt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_2 t$$

- **THIRD ORDER REACTIONS**

$$3A \rightarrow \textbf{Products}$$

Initial conc. $[A_0]$ 0

Final conc. $[A_0] - [A_t]$ $[A_t]$

$$-\frac{d[A]}{dt} = k_3[A]^3$$

$$\frac{d[A]}{dt} = -k_3[A]^3$$

$$\frac{d[A]}{[A]^3} = -k_3 dt$$

Upon integration

$$\int_{A_0}^{A_t} \frac{d[A]}{[A]^3} = -\int_0^t k_2 dt$$

$$\frac{1}{2[A]_t^2} - \frac{1}{2[A]_0^2} = k_3 t$$

UNITS OF RATE CONSTANT

The units of rate constant for different orders of reactions are different.

- **Units of Zero order Rate constant**

For a zero order reaction, the rate constant k is given by the expression:

$$k_0 = \frac{[A]_t}{t}$$

[A]$_t$ is in mol dm^{-3} while t is in sec, min, hr or years, thus the unit of k$_0$ is in mol dm^{-3} s^{-1}

- **Units of first order Rate constant**

$$k_1 = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}$$

The unit of k$_1$ is in s^{-1} since the $\ln \frac{[A]_0}{[A]_t}$ is unit less

- **Units of second order Rate constant**

$$k_2 = \frac{[A]_0 - [A]_t}{[A]_t[A]_0 t}$$

The unit of k$_2$ is in mol^{-1} dm^3 s^{-1}

- **Units of third order Rate constant**

$$k_3 = \frac{[A]_0^2 - [A]_t^2}{[A]_t^2[A]_0^2 t}$$

The unit of k$_3$ is in mol^{-2} dm^2 s^{-1}

HALF–LIFE OF A REACTION

- **Half-life is the time required for the concentration of a reactant to decrease to half its initial value.**

- **Half-life of Zero order Rate constant**

$$t_{1/2} = \frac{[A]_0}{2k_0}$$ *[A]$_t$ is half of initial concentration*

- **Half-life of first order Rate constant**

$$t_{1/2} = \frac{1}{k_1} \ln \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{1}{k_1} \ln 2 = \frac{0.693}{k_1}$$

- **Half-life of second order Rate constant**

$$t_{1/2} = \frac{\frac{1}{2}[A]_0}{\frac{1}{2}[A]_0[A]_0 k_2} = \frac{1}{[A]_0 k_2}$$

- **Half-life of third order Rate constant**

$$t_{1/2} = \frac{[A]_0^2 - \frac{1}{4}[A]_0^2}{\frac{1}{4}[A]_0^2 [A]_0^2 k_3} = \frac{3}{[A]_0^2 k_3}$$

EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

- As the temperature increases the rate of reaction also increases. As a rule, an increase of temperature by 10°C doubles the reaction rate.

- Arrhenius suggested as simple relationship between the rate constant, *k*, for a reaction and the temperature of the system.

$$k = Ae^{-\frac{E_a}{RT}}$$

This is called the Arrhenius equation in which A is an experimentally determined quantity, Ea is the activation energy, R is the gas constant, and T is Kelvin temperature.

- If k_1 and k_2 are the values of rate constants at temperatures T_1 and T_2 respectively, we can derive

$$\frac{k_1}{k_2} = \frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Exercises

- If 15% of a substance decomposes in first ten minutes in a first order reaction, calculate how much of it would remain undecomposed after one hour?

- A first order reaction is 15% complete in 20 minutes. What is the half-life period of the reaction?

- A second order reaction in which both the reactants have the same concentration is 25% complete in 10 minutes. How long will it take for the reaction to go to 90% completion ?

- The rate constant for a first order reaction is 1.54×10^{-3} sec^{-1}. Calculate its half-life period.

- Calculate the activation energy of a reaction whose reaction rate at 27°C gets doubled for 10° rise in temperature (R = 8.314 J K^{-1} mol^{-1})