Atse Yohannes Preparatory School

# Chemistry short notes for Grade 11

## Pactice Questions And answers

On

## Unit 4, 5 and 6

April, 2012 E.C

# UNIT-4

# 1. Chemical Kinetics

## 1.1. INTRODUCTION

This unit is organized into four sections.

1. The first section is concerned with rate ofreaction, with emphasis on how to determine rate of reaction and factors that influencerate of reaction.
2. The second section deals with theories of reaction rates, including collision theory and transition-state theory.
3. The third section deals with rate equation or rate law, which includes order of reaction, rate constant, concentration-time equation and half-life of a reaction.
4. The fourth section deals with reaction mechanism, which includes the molecularity of elementary reactions and the rate-determining step.

**Chemical kinetics**:- Is the area of chemistry concernedwith the speeds, or rates, at which reactions occur. The word "kinetic" suggests movementor change. Chemical kinetics refers to the rate of reaction, which is the change over times in the concentration of a reactant or a product.

Chemical kinetics also the study of rates of chemical processes. This includesinvestigations of how different experimental conditions can influence the speed of achemical reaction. The investigations yield information about the reaction's mechanismand transition states**.** The study of chemical kinetics also uses the construction ofmathematical models that can describe the characteristics of a chemical reaction.

**Rate of reaction** (speed) is not fixed for a particular type of reaction, sinceit depends on several factors. The rate of reaction gets altered when subjected to smallchanges in temperature, concentration, pressure etc.

In 1864, Peter Waage and Cato Guldberg pioneered the development of chemical kinetics by formulating the law of mass action, which states that the speed of a chemical reaction is proportional to the quantity of the reacting substances.

Some chemical reactions proceed quickly,whereas others require days, months or even years to give products. These differencesdepend primarily on the differences in the chemical nature of the reacting substances.The rate of reaction defined for bothreversible and irreversible reactions as well as slow and fast reactions

| Fast reactions | Slow reactions |
|---|---|
| ➢ Combustions of fuel | Rusting of Iron |
| ➢ Reactions of active metal with acids | Oxidations coppers |
| ➢ Precipitation reactions | souring of milk |
| ➢ Firing of gun | Fermentations |
| ➢ Neutralization reactions | Geological reactions |

- Active metal with water

***How do you think that the rate of reaction is measured?***

Rate of reaction is the change in concentration of a reactant or a product over a givenperiod of time.During the course of a reaction, the concentrations of the reactants decrease while those of the products increase.Thus, the rate of a reaction is calculatedby dividing the change in the concentrations of reactants or products by the time takenfor the change to occur.

For a simple reaction,A $\rightarrow$ B

The rate of reaction is expressed in terms of a reactant concentration as

$$r = -\Delta [A]/\Delta t = [A]_f - [A]_i/\Delta t$$

Where $r$ is rate of reaction, A is a reactant, B is a product, $[A]_i$ and $[A]_f$ are initial and final concentration of A respectively, $\Delta [A]$ is change in concentration of A and $\Delta t$ is the change in time.

$[A]_f < [A]_i$. Thus, $\Delta[A] = [A]_f - [A]_i$, is negative. This indicates that the reactant is being consumed. However, the rate of a reaction is a positive quantity.

In terms of product concentration, the rate of a reaction is given by:

$$r = \Delta[B]/\Delta t = [B]_f - [B]_i/\Delta t$$

$[B]_f > [B]_i$. Thus, $\Delta B = [B]_f - [B]_i$ is positive because [B] increases and the rate of a reaction is also positive.

The unit of rate is mol $L^{-}$ $s^{-}$ ($Ms^{-}$) and the unit of concentration is mole per litre (mol/L)

## 1.2 *Reaction Rate and Stoichiometry*

Rate expressions in terms of the disappearanceof the reactants and the appearance of the products:




*A graph of changes inconcentration of a reactant and a product over time where time is written as the x-axisand concentration as the y-axis.*

In general, for the reaction, $aA + bB \rightarrow cC + dD$

$$r = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example

1. Write the rate expressions for the following reactions, in terms of the disappearance of the reactants and the appearance of the products:

a. $3ClO^-(aq) \rightarrow ClO_3^-(aq) + 2Cl^-(aq)$

$$\text{rate of reaction} = -\frac{\Delta[ClO^-]}{3\Delta t} = \frac{\Delta[ClO_3^-]}{\Delta t} = \frac{\Delta[Cl^-]}{2\Delta t}$$

b. $3SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$$\text{rate of reaction} = -\frac{\Delta[SO_2]}{3\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[SO_3]}{2\Delta t}$$

c. $C_2H_4(g) + Br_2(g) \rightarrow C_2H_4Br_2(g)$

$$\text{rate of reaction} = -\frac{\Delta[C_2H_4]}{\Delta t} = -\frac{\Delta[Br_2]}{\Delta t} = \frac{\Delta[C_2H_4Br_2]}{\Delta t}$$

2. Consider the hypothetical reaction.

$X(g) + 2Y(g) \rightarrow XY_2g)$ $\Delta[Y]/\Delta t = -5.0 \times 10^{-2}$mol $L^-$ $sec^-$

What is the rate of formation of $XY_2(g)$

A. $-5.0 \times 10^{-2}$mol $L^-$ sec-
C. $2.5 \times 10^{-2}$mol $L^-$ $sec^-$
B. $5.0 \times 10^{-2}$mol $L^-$ sec
D. $-2.5 \times 10^{-2}$mol $L^-$ sec

C. Answer:- C The formation of the product is half of the rate of the loss of Y. It is correct to change the sign to positive, because we are representing the formation of product, and the negative sign on the reactant to represent loss.

**2.** For the chemical reaction $H_2 + Br_2 \rightarrow 2HBr$, what can besaid of the relative rates of consumption of the reactantswhen compared to the formation of product?

A. HBr will be produced at half the rate that bromine isconsumed.
B. HBr will be produced at the same rate that bromine isconsumed.
C. $Br_2$ and $H_2$ will be consumed at different rates.
D. HBr will be produced at twice the rate that bromine isconsumed
E. It is not possible to tell anything about relative rateswithout the rate law.

Answer: - DThe stoichiometry of the overall reaction will give us answers to the questions about comparative rates of formation of products compared to loss of reactants.

3. For the reaction A + 3B → 2C, how does the rate of disappearance of B compare to the rate of production of C?

A. The rate of disappearance of B is 1/2 the rate of appearance of C
B. The rate of disappearance of B is 3/2 the rate of appearance of C
C. The rate of disappearance of B is 2/3 the rate of appearance of C
D. The rate of disappearance of B is 1/3 the rate of appearance of C

Answer: - BWrite in terms of B

## 1.3 Determination of Rate of Reaction

- The rate of reaction can be determined both quantitatively and qualitatively.

- ✓ Qualitatively: - An idea about the rate of reaction can be obtained by observing either the speed of appearance of the reactants or the speed of appearance (formation) of the products.
- ✓ Quantitatively:- Quantity obtained from formula

EXAMPLE

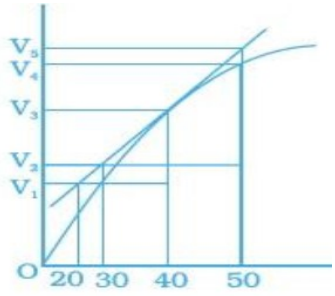
1. A graph of volume of hydrogen released vs time for the reaction between zinc and dil.HCl is given in Fig. On the basis of this mark the correct option is?

(i) Average rate upto 40s is $\frac{V_3 - V_2}{40}$

(ii) Average rate upto 40 seconds is $\frac{V_3 - V_2}{40 - 30}$

(iii) Average rate upto 40 seconds is $\frac{V_3}{40}$

(iv) Average rate upto 40 seconds is $\frac{V_3 - V_1}{40 - 20}$




Answer: - iii because average rate up to 40 means $v_3$- $v_0$/ 40-0 = $v_3$/40

2. Consider the decomposition of $N_2O_5$ to give $NO_2$ and $O_2$:
   $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

| Time (s) | Concentration (M) | | |
|---|---|---|---|
| | $N_2O_5$ | $NO_2$ | $O_2$ |
| 0 | 0.0200 | 0 | 0 |
| 100 | 0.0169 | 0.0063 | 0.0016 |
| 200 | 0.0142 | 0.0115 | 0.0029 |
| 300 | 0.0120 | 0.0160 | 0.0040 |
| 400 | 0.0101 | 0.0197 | 0.0049 |
| 500 | 0.0086 | 0.0229 | 0.0057 |
| 600 | 0.0072 | 0.0256 | 0.0064 |
| 700 | 0.0061 | 0.0278 | 0.0070 |

From the graph looking at t = 300 to 400 s

$$\text{Rate } O_2 = \frac{0.0009M}{100s} = 9 \times 10^{-6} Ms^{-1}$$

$$\text{Rate } NO_2 = \frac{0.0037M}{100s} = 3.7 \times 10^{-5} Ms^{-1}$$

$$\text{Rate } N_2O_5 = \frac{0.0019M}{100s} = 1.9 \times 10^{-5} Ms^{-1}$$

***Why do they differ?***

***Recall***:

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

To compare the rates one must account for the ***stoichiometry.***

$$\text{Rate } O_2 = \frac{1}{1} \times 9 \times 10^{-6} Ms^{-1} = 9 \times 10^{-6} Ms^{-1}$$

$$\text{Rate } NO_2 = \frac{1}{4} \times 3.7 \times 10^{-5} Ms^{-1} = 9.2 \times 10^{-6} Ms^{-1}$$

$$\text{Rate } N_2O_5 = \frac{1}{2} \times 1.9 \times 10^{-5} Ms^{-1} = 9.5 \times 10^{-6} Ms^{-1}$$

***Now they agree!***

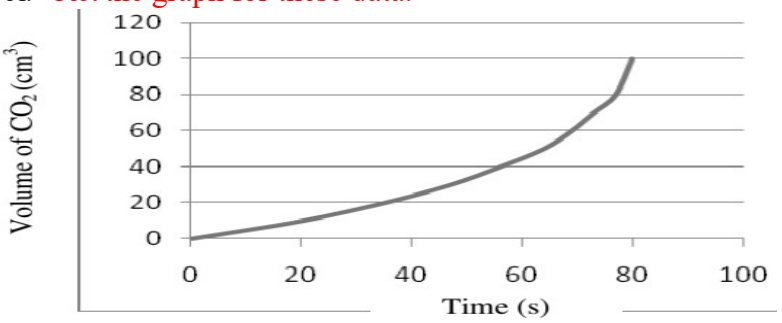
what about with the time interval (t = 100 to 500s )?

3. The results obtained during the reaction between excess of powdered calcium carbonate and hydrochloric acid, are given in the following table:

$CaCO_3(s) + HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

| Volume of $CO_2$/cm³ | 0 | 20 | 35 | 47 | 56 | 64 | 69 | 73 | 77 | 80 |
|---|---|---|---|---|---|---|---|---|---|---|
| Time/s | 0 | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 100 |

A. Plot the graph for these data.




B. What volume of gas has formed after 50seconds?

$$r = \frac{\Delta[CO_2]}{\Delta t} = \frac{(64-0)cm^3}{(50-0)s} = \frac{64}{50} cm^3 s^{-} = 1.28 cm^3 s^{-}$$

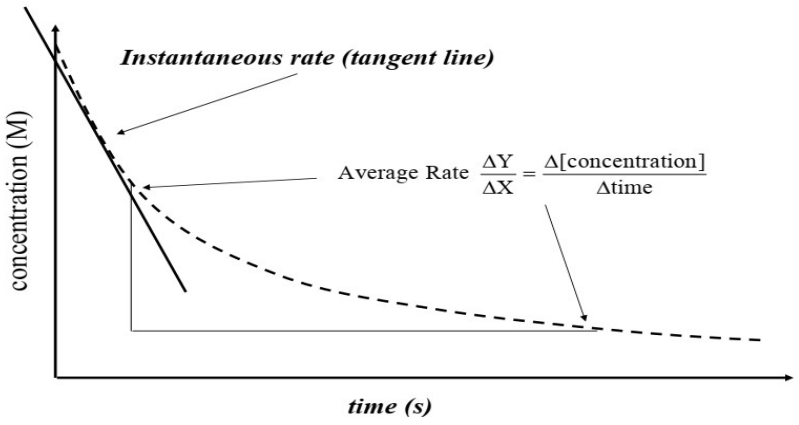
C. What volume of gas has formed after 15 seconds?

$$r = \frac{\Delta[CO_2]}{\Delta t} \quad 1.28\ cm^3 s^{-} = \frac{V_2 - V_1}{(15-0)s} \Rightarrow V_2 - 0 = 19.2\ cm^3 \Rightarrow V_2 = 19.2\ cm^3$$

D. How long did it take for 40 cm3 of carbon dioxide to form?

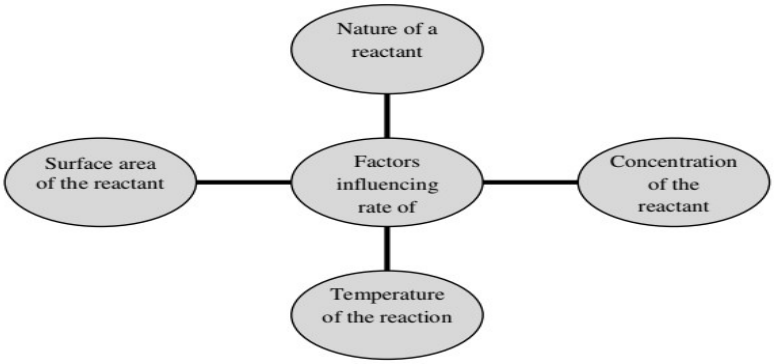
$$r = \frac{\Delta[CO_2]}{\Delta t} \quad 1.28\ cm^3 s^{-1} = \frac{40\ cm^3}{\Delta t} \Rightarrow \Delta t = \frac{40\ cm^3}{1.28\ cm^3 s^{-1}} \Rightarrow \Delta t = 31.25\ s$$

**Instantaneous rate:-** is defined as the rate of a reaction for a given instant oftime and it is obtained from the slope of the tangent to the concentrations curve at that time




## 1.2 Factors Influencing the Reaction Rates

In general, different chemical reactions have different rates. Even a chemical reaction involving the same reactants may have different rates under different conditions.




1. Temperature of reactants:- When temperature increases, rate of reaction increases
   Reason: - When temperature increases overall kinetic energy of all particles of reactantsincreases, so more molecules will have energy greater than activation energy. So,the overall frequency of collisions increases, therefore frequency of effective collisions increases, and thus the reaction rate increases

2. Concentration of reactant:- The concentration of one or more reactants increases, rate of reaction increases.
   Reason: - Increasing the concentration one or more reactants produce more contacts between the reactingparticles, which results in increasing the rate of reaction.

   For gaseous reactants, an increase in pressure increases reactions rate

   Reason: - Increasing pressure means the volume decreases implies contact (concentration) increase as result collision increases and reaction will be fast. However, pressure change hasno effect on the rate of reaction if the reactants are solids or liquids.

3. ***Surface Area of Reactants:-*** ***as surface area increase rate of reaction increases***

   ***Reason:-***When the size of the substance subdivisions decreases, surface area increases. Itmakes the effective collisions increase and therefore the rate of reaction alsoincreases.

4. Nature of reactants:-The rate of a reaction depends on the chemical nature of the substances participatingin the reaction. A more active a substance the reactive

5. ***Effect of Catalyst on Rate of Reaction***A catalyst is a substance that changes reaction rate by providing a different reactionmechanism one with loweractivation energy

   ***Characteristics of catalyst***

   - Speeds up thereaction forward and backward equally
   - May even form temporary chemical bonds with the reactants
   - Recoveredunchanged in original form at the end of the reaction
   - Does not alter the position of equilibrium
   - It provides an alternate mechanism by reducing activation energy
   - Does not consumed itself in the reactions

**EXAMPLE**

1. The rate of a chemical reaction
   A. Is always dependent of the concentration of all reactants.
   B. Is always increased with increasing temperatures.
   C. Is greater with higher activation energies.
   D. Is independent of surface area.

Answer: (B) The collision model indicates that molecular collision is necessary for reaction. Because an increase in temperature raises molecular velocities and the percentage of effective collisions, the reaction rate increases

2. Which of the following statements is correct?
   **A.** The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
   **B.** The rate of a reaction is same at any time during the reaction
   **C.** The rate of a reaction is independent of temperature change.
   **D.** The rate of a reaction decreases with increase in concentration ofreactant(s) Ans A
3. How does a catalyst increase the rate of a chemicalreaction?
   **A.** By changing the magnitude of the enthalpy change.
   **B.** By providing a pathway for the reaction that has lower activation energy.
   **C.** By decreasing the potential energy of the products
   **D.** By increasing the potential energy of the reactants
   **E.** By giving energy to the reactants so more of themhave energies greater than the activation energy Answer B
4. Why do large crystals of sugar burn more slowly than finely ground sugar?
   Answer:- The rate of combustion is proportional to the surface area of sugar exposed to oxygen. Smaller crystals have more surface area and burn faster.
5. How do homogeneous catalysts and heterogeneous catalyst differ?
   A homogeneous catalyst is a catalyst that exists in the same phase (liquid or gas) as the reactants. A
   heterogeneous catalyst, on the other hand, is a catalyst that exists in a different phase form the reactants.

## 1.3 THEORIES OF REACTION RATES

Two important theories help us to explain why different reactions occur at different
rates. These are

- The collision theory and
- The transition-state theory.

These two theories are distinct but in complete agreement, each emphasizing different aspects of reaction processes.

## The collision theory

- *The fundamental concept of the collision theory of rate of reaction is that, in order for a reaction to occur between reacting species (atoms, ions or molecules), they must first collide (come in contact). However, not all collisions between reacting species result in a reaction. This is because collisions between reactants can be either effective or ineffective.*
- *Effective collisions: - are collisions that result in a reaction to form the desired products.*
- *Ineffective collisions: - are collisions that do not result in a reaction to form the desired products.*

Postulates of collision theory are summarized below.

- For a reaction to occur between reactants:

1. *The particles of the reacting substances must collide.*
2. *The particles of the reacting species must have proper orientation.*
3. *The particles of the reactants must collide with energy greater than or equal to the energy of activation*

*Note:- Linear collision is more effective than non linear collision*

### Transition State Theory (Activated Complex and Energy Barrier)

*According to transition-state theory, the collision between two reacting species results in the formation of an activated complex or transition state. An activated complex or transition state is*

- High energy state species that is temporarily formed by the collision of reactant molecules before they form products.
- The species can either fall to back(reactant) or form product
- Short-lived , unstable and barrier
- In the activated complex, the original bonds are lengthened and weakened, and the new bonds are only partially formed

Let us consider the reaction:

$$A_2 + B_2 \rightarrow 2AB$$

*The reactants, $A_2$ and $B_2$, approach each other and collide; they begin climbing up the left side of the potential-energy hill, or barrier.*

*If they have less energy than the energy of activation, Ea, they fail to climb the barrier and, instead, roll back down its left side. In this case, no reaction occurs.*

*The formation of an activated complex in the form of an equation can be shown as,*

$$A_2 + B_2 \rightarrow A_2B_2^{\ddagger} \rightarrow 2AB$$

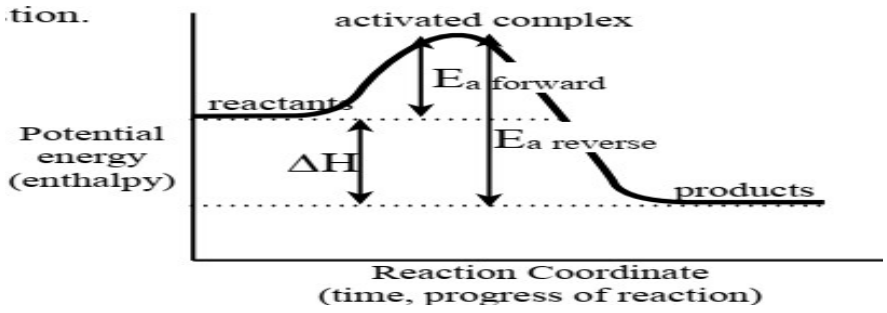
*Where $A_2B_2^{\ddagger}$ is the activated complex or transition state*

Example

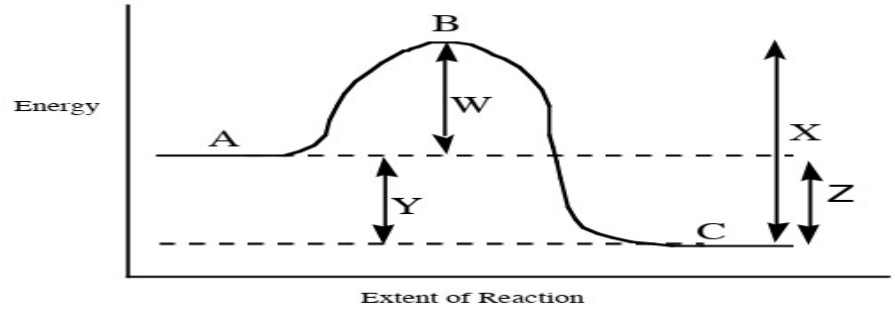
1. Which applies to this reaction as it proceeds at constant temperature?
   I. The rate of the reaction decreases.
   II. The effectiveness of collisions between reactant molecules remains the same.
   III. The frequency of collisions between reactant molecules remains the same.
   A. I only B.II only C. I and II only D. II and III only

   Answer C: - *As the concentrations of the reactants decrease over the course of a reaction, the frequency of collisions will decrease, but the effectiveness of the collisions will remain the same, as that is a function of the molecules themselves, the temperature, and the presence of any catalyst.*
2. Collision theory predicts all of the following EXCEPTthat
   A. A reaction will only occur if the collision geometry iscorrect
   B. A reaction will not occur if the collision occurs withenergy that is less than the activation energy.
   C. A reaction will not occur if the reactants do notcollide
   D. Frequency of collisions will increase with increasingtemperature.
   E. More successful collisions will occur for a reactionwith larger activation energy.

   Answer E: - Higher activation energy is a higher hump, and is harder to get over, making for fewer successful collisions.
3. The values for the change in enthalpy, ΔH, and theactivation energy, Ea, for a given reaction are known. Thevalue of Ea for the reverse reaction equals
   A. Ea for the forward reaction. D. -(Ea) for the forward reaction.
   B. The sum of -(ΔH) and Ea E. The sum of Ea and ΔH
   **C.** The difference between ΔH and Ea ***Answer B,*** **see the fig**




4. For the reaction diagram shown, which of the following statements is true?



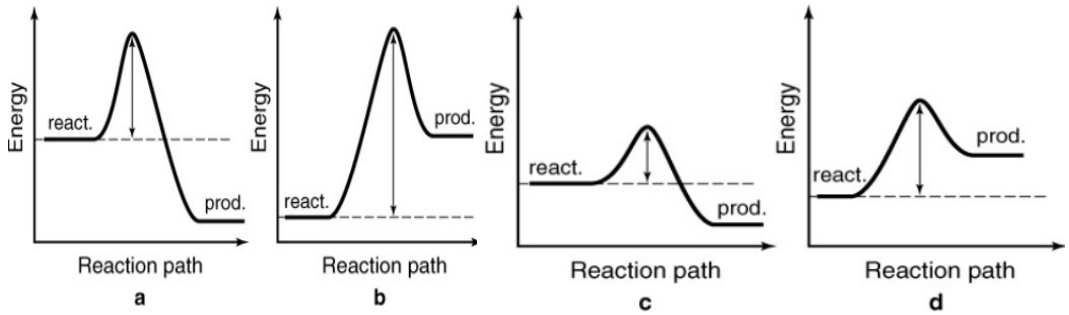
A. Line W represents the ΔH for the forward reaction; point B represents the transition state

B. Line W represents the activation energy for the forward reaction; point B represents the transition state

C. Line Y represents the activation energy for the forward reaction; point C represents the transition state

***D.*** Line X represents the ΔH for the forward reaction; point B represents the transition state. ***Ans. B***

**5.** The energy profiles for four different reactions are shown. Which reaction requires the most energetic collisions to reach the transition state?




*Answer B*

6. Collision theory assumes that the rate of a reaction depends on _____

A. The energy of collisions.

B. The orientation of colliding molecules.

C. The energy of collisions and the orientation of colliding molecules.

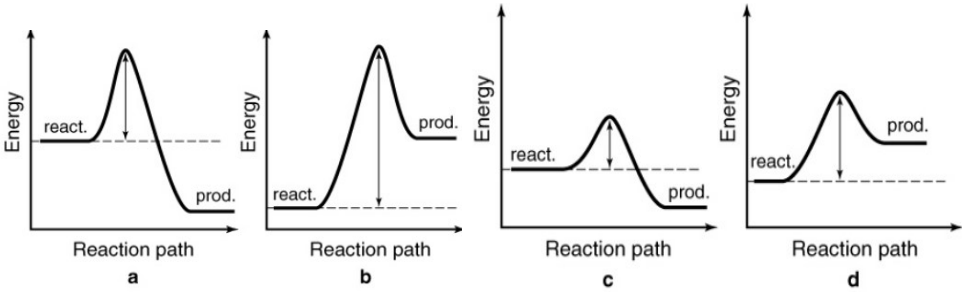
D. The change in energy between the products and the reactants.*Ans. C*

7. The energy needed for a reaction to proceed from reactants to products is called:

A. Collision energy C. Kinetic energy

B. Potential energy D.Activation energy. Ans. D

8. The following energy profiles for four different reactions are shown. Which reaction is the most endothermic?




Ans. B

## 1.4 RATE EQUATION OR RATE LAW

### 1.4.1 Order of Reaction and Rate Constant

- The rate law or rate equation: - for a chemical reaction is an equation which links the reaction rate with the concentrations or pressures of reactants and certain constant parameters (*normally rate coefficients and partial reaction order*). Each concentration is expressed with an order (exponent).

*For the general reaction:* $aA + bB \rightarrow cC + d$

Rate = k $[A]^x[B]^y$ $x$ and $y$ are the reactant orderdetermined from experiment.

$x$and $y$ are **NOT** thestoichiometric coefficients.

Consider a reaction with the rate equation

$r = k[A]^2[B]$, order with respect to A is 2 and 1 with respect to B

2+ 1 = 3 over all order

*If the $[A]^2$is doubled and remain constant the [B] the rate will be increase by factor of 4*

*If the $[A]^2$is tripled and remain constant the [B] the rate will be increase by factor of 9*

Change in initial rate with change in $[A]_o$ for rate = $k$ [A]m

| For a reaction of | If $[A]_0$ is doubled | If $[A]_0$ is tripled |
|---|---|---|
| *Zero-order (m = 0)* | *rate is unchanged* | *rate is unchanged* |
| *First-order (m = 1)* | *rate is doubled* | *rate is tripled* |
| *Second-order (m = 2)* | *rate is quadrupled (x $2^2$)* | *rate is 9 times greater (x $3^2$)* |

## 1.5 Determining Reaction Order: *The Method of Initial Rates*

### *Example*

1. The reaction,$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$was studied at 25°C. The following results were obtained where

   From the following data, *A. determine the order*

   *B. Rate law and*

   *C. Rate constant.*

| $[I^-]_0$ (mol/L) | $[S_2O_8^{2-}]_0$ (mol/L) | Initial Rate (mol/L • s) |
|---|---|---|
| 0.080 | 0.040 | $12.5\times10^{-6}$ |
| 0.040 | 0.040 | $6.25\times10^{-6}$ |
| 0.080 | 0.020 | $6.25\times10^{-6}$ |
| 0.032 | 0.040 | $5.00\times10^{-6}$ |
| 0.060 | 0.030 | $7.00\times10^{-6}$ |

   - The rate law for the reaction is given by: - Rate (M/min) = $k\,[I^-]^x[S_2O_8^{2-}]^y$, but we should have to calculate for the value of X and Y.
     - ✓ To have the value of X keeps constant the value of y and make varies the value of X.
     - ✓ To have the value of y keeps constant the value of X and vary the value of y

   Taking the ratio of the rates of runs 2 and 1 one finds:

   A. Determine the rate law.

$$\text{Rate} = k[I^-]^x[S_2O_8^{2-}]^y$$

Compare experiments 1 and 2.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[I^-]_2^x[S_2O_8^{2-}]_2^y}{k[I^-]_1^x[S_2O_8^{2-}]_1^y}$$

$$\frac{6.25\times10^{-6}}{12.5\times10^{-6}} = \frac{k(0.040)^x(0.040)^y}{k(0.080)^x(0.040)^y},\ 0.5 = 0.5^x,\ x = 1$$

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[I^-]_3^x[S_2O_8^{2-}]_3^y}{k[I^-]_1^x[S_2O_8^{2-}]_1^y}$$

$$\frac{6.25\times10^{-6}}{12.5\times10^{-6}} = \frac{k(0.080)^x(0.020)^y}{k(0.080)^x(0.040)^y},\ 0.5 = 0.5^y,\ y = 1$$

$$\text{Rate} = k[I^-][S_2O_8^{2-}]$$

*SO order with respect to* $[I]$ *is 1 (x = 1) and* $[S_2O_8^{2-}]$ *is 1 ( y = 1)*

B. Calculate a value for the rate constant for each experiment and an average value for the rate constant. Rate constant can be calculated from all or you can choose one the them

$$\text{Experiment 1} = \frac{12.5\times10^{-6}\ \text{mol}}{\text{L}\bullet\text{s}} = k\left(\frac{0.080\ \text{mol}}{\text{L}}\right)\left(\frac{0.040\ \text{mol}}{\text{L}}\right),\ k = 3.9\times10^{-3}\ \frac{\text{L}}{\text{mol}\bullet\text{s}}$$

$$\text{Experiment 2} = \frac{6.25\times10^{-6}\ \text{mol}}{\text{L}\bullet\text{s}} = k\left(\frac{0.040\ \text{mol}}{\text{L}}\right)\left(\frac{0.040\ \text{mol}}{\text{L}}\right),\ k = 3.9\times10^{-3}\ \frac{\text{L}}{\text{mol}\bullet\text{s}}$$

$$\text{Experiment 3} = \frac{6.25\times10^{-6}\ \text{mol}}{\text{L}\bullet\text{s}} = k\left(\frac{0.080\ \text{mol}}{\text{L}}\right)\left(\frac{0.020\ \text{mol}}{\text{L}}\right),\ k = 3.9\times10^{-3}\ \frac{\text{L}}{\text{mol}\bullet\text{s}}$$

$$\text{Experiment 4} = \frac{5.00\times10^{-6}\ \text{mol}}{\text{L}\bullet\text{s}} = k\left(\frac{0.032\ \text{mol}}{\text{L}}\right)\left(\frac{0.040\ \text{mol}}{\text{L}}\right),\ k = 3.9\times10^{-3}\ \frac{\text{L}}{\text{mol}\bullet\text{s}}$$

$$\text{Experiment 5} = \frac{7.00\times10^{-6}\ \text{mol}}{\text{L}\bullet\text{s}} = k\left(\frac{0.060\ \text{mol}}{\text{L}}\right)\left(\frac{0.030\ \text{mol}}{\text{L}}\right),\ k = 3.9\times10^{-3}\ \frac{\text{L}}{\text{mol}\bullet\text{s}}$$

$K_{mean} = 3.9\times10^{-3}$ L/mol•s

C. Rate law = $k[I^-][S_2O_8^{2-}]$

2. The following 2 questions refer to the following equation and table below:

$$2W + 3X + Y \rightarrow Z$$

| Trial | [W]mol $L^{-1}$ | [X]mol $L^-$ | [Y]mol $L^-$ | Rate of Production of Zmol $L^-$ |
|---|---|---|---|---|
| 1 | 0.001 | 0.001 | 0.001 | $2.1\times10^{-4}$ |
| 2 | 0.002 | 0.001 | 0.001 | $2.1\times10^{-4}$ |
| 3 | 0.001 | 0.003 | 0.001 | $6.3\times10^{-4}$ |
| 4 | 0.002 | 0.001 | 0.0005 | $5.25\times10^{-5}$ |

The rate law is:

A. Rate = $k[W]^2[X]^3[Y]$

B. Rate= $k[W]^2[X][Y]$

C. Rate = $k[X]^3[Y]^2$

D. Rate = $k[X][Y]^2$ *Answer D or* $[W]^0 = 1$

3. The reaction X + Y→Z has the rate law, Rate = $k[X]^2[Y]$.If the concentration of X is doubled and the concentrationof Y is tripled, the rate would be increased by a factor of

A. 2 B. 4 C. 5 D.6 E. 12

*ANS E,* $Rate = k[X]^2[Y]$ *thus* $[2]^2[3] = 12$

4. For a reaction 2A + B $\rightarrow$2C, with the rate equation: Rate = k$[A]^2$[B]
   A. The order with respect to A is 1 and the order overall is 1.
   B. The order with respect to A is 2 and the order overall is 2.
   C. The order with respect to A is 2 and the order overall is 3.
   D. The order with respect to B is 2 and the order overall is 2.
   E. The order with respect to B is 2 and the order overall is 3. ANS. C
5. For the rate law, Rate= k$[Q]^2$ $[R]^2$,which statement iscorrect?
   A. The reaction is fourth order overall, and doublingboth the [Q] and [R] while keeping the temperatureconstant will lead to a bigger k and a 16-fold increasein the rate
   B. The reaction is fourth order overall, and doublingboth the [Q] and [R] while keeping the temperatureconstant will lead to a 16-fold increase in the rate
   C. The reaction is fourth order overall, and doublingboth the [Q] and [R] while keeping the temperatureconstant will lead to a bigger k and an 8-fold increasein the rate
   D. The reaction is second order overall, and doublingboth the [Q] and [R] while keeping the temperature constant will lead to a bigger k and a 16-fold increasein the rate
   E. The reaction is second order overall, and doublingboth the [Q] and [R] while keeping the temperatureconstant will lead to a 16-fold increase in the rate
   *ANS. B. Changing concentrations will not affect the rate constant*
6. If tripling the concentration of a single reactant R in amulti-reactant reaction (while leaving all other conditionsunchanged) leads to a nine-fold increase in rate, it can bededuced
   A. That the complete rate law is Rate= k[R]
   B. That the complete rate law is Rate= k[R]
   C. That the complete rate law is Rate= k$[R]^3$
   D. that the complete rate law is Rate= k$[R]^9$
   *E.* Only that the order with respect to [R] is 2 *ANS. E*
7. For the rate law shown below, where the rate is measuredin units of M $s^-$ and the concentrations of X and Y aremeasured in M, which of the following statements is true?
   Rate= k$[X]^2$ [Y]
   I. The units of k = $M^2$ $s^{-1}$
   II. Doubling the concentration of y while keeping allother conditions constant will not affect the rate.
   III. The reaction can be described as third-order.
   A. I onlyB. III onlyC.I and II onlyD. II and III onlyE. I, II, and III
   ✓ ANS.BAdd the individual orders to determine the overall order. For item I, the units would be $M^{-2}s^-$, and doubling Y would double the rate.
8. Consider the reaction: $P_4$ + 6 $H_2$ $\rightarrow$ 4 $PH_3$. A rate study of this reaction was conducted at 298 K. Thedata that were obtained are shown in the table.

| $[P_4]$, mol/L | $[H_2]$, mol/L | Initial Rate, mol/(L · s) |
|---|---|---|
| 0.0110 | 0.0075 | $3.20 \times 10^{-4}$ |
| 0.0110 | 0.0150 | $6.40 \times 10^{-4}$ |
| 0.0220 | 0.0150 | $6.39 \times 10^{-4}$ |

A. What is the order with respect to: $P_4 = 0$, $H_2 = 1$ .
B. Write the rate law for this reaction. $rate = k[H_2]^1[P_4]^0$
C. Determine the value and units of the rate constant, k. plug and check using the rate law & data from experiment 1 andsolving for k, we get k = 0.0427 s

## 1.6 The Arrhenius Equation

- Svante Arrhenius: - Observed that a mathematicalrelationship connects activation energy,temperature, and the rate constant. This relationshipis known as the Arrhenius equation and is written as:

Arrhenius equation

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

$k$ is the rate constant

$E_a$ is the activation energy

$T$ is the temperature in K

$R$ is the ideal-gas constant (8.314 J/Kmol)

$A$ is known the *frequency or pre–exponential factor*

In addition to carrying the units of the rate constant, "A" relates to the frequency of collisions and the orientation of a favorable collision probability

Both $A$ and $E_a$ are *specific to a given reaction*.

- Arrheniusdiscovered that most reaction-rate data obeyed an equationbased on three factors:
  1. The number of collisions per unit time.
  2. The fraction of collisions that occur with the correct orientation.
  3. The fraction of the colliding molecules that have energy greater than or equal to $E_a$.

By combining theequations for the values of $k$ at two different temperatures$T_1$and $T_2$for the samereaction, a relationship is obtained

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

OR $\log k_2/k_1 = Ea/2.303R\ (1/T_1 - 1/T_2)$

### Example

1. Which of the following statements are in accordance with the Arrheniusequation?
   A. Rate of a reaction increases with increase in temperature.
   B. Rate of a reaction increases with decrease in activation energy.
   C. Rate constant decreases exponentially with increase in temperature.
   D. Rate of reaction decreases with decrease in activation energy. ANS:- A & B
2. Consider the Arrhenius equation given below and mark the correct option.

$K = A^{Ea/RT}$

A. Rate constant increases exponentially with increasing activationenergy and decreasing temperature.
B. Rate constant decreases exponentially with increasing activationenergy and decreasing temperature.
C. Rate constant increases exponentially with decreasing activationenergy and decreasing temperature.
D. Rate constant increases exponentially with decreasing activationenergy and increasing temperature.*Ans. D*

3. The activation energy of a first order reaction is 50.2 kJ/mol at 25°C.At what temperature will the rate constant double?

(1) $k_2 = 2k_1$ (2) $\ln\left(\frac{k_2}{k_1}\right) = \ln\left(\frac{2k_1}{k_1}\right) = \ln(2) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

(3) $\frac{E_a}{R} = \frac{50.2\ \text{kJ/mol} \times \frac{10^3\text{J}}{1\text{kJ}}}{8.314\ \frac{\text{J}}{\text{mol}\cdot\text{K}}} = 6.04 \times 10^3\,\text{K}$

(4) $\ln(2) = 0.693 = 6.04 \times 10^3\,\text{K} \times \left(\frac{1}{298\text{K}} - \frac{1}{T_2}\right)$ *A 10°C change of temperature doubles the rate!!*

(5) $\frac{1}{T_2} = 3.24 \times 10^{-3}\,\text{K}^{-1} \longrightarrow$ **$T_2 = 308$ K**

4. Consider the reaction: 2B → C + 3D. In one experiment it was found that at 300 K the rate constant is 0.134L/(mol.s). A second experiment showed that at 450 K, the rate constant was 0.569 L/(mol.s). Determine the activation energy for the reaction.

at 300 K: $k_{300} = Ae^{\frac{-Ea}{RT}}$

at 450 K: $k_{450} = Ae^{\frac{-Ea}{RT}}$

$\ln \frac{k_{450}}{A} = \frac{-E_a}{RT}$

$\ln(k_{450}) - \ln(A) = \frac{-E_a}{RT}$ *where* $\ln(A) = \ln(k_{300}) - \frac{-E_a}{RT}$

*so that*

$\ln(k_{450}) - [\ln(k_{300}) - \frac{-E_a}{RT}] = \frac{-E_a}{RT}$

$\ln(\frac{k_{450}}{k_{300}}) = \frac{E_a}{R}(\frac{1}{T_{300}} - \frac{1}{T_{450}})$

plug and solve for Ea, Ea = 10.8 kJ

5. Given that *E*a for the hydrolysis of sucrose is 108 × $10^3$ kJ / mol, compare therate constant of this reaction at 37°C ($T_1$) with the rate constant of the samereaction at 27°C ($T_2$).

➢ Given that $E_a$for the hydrolysis of sucrose is 108 x $10^3$kJ /mol, compare the rateconstant of this reaction at 37 °C ($T_1$) with the rate constant of the same reaction at27 °C ($T_2$).

$T_1 = 37 + 273 = 310\ K \quad T_2 = 27 + 273 = 300\ K$

$R = 8.31\ J/K.molEa = 108 \times 10^3 = 1.08 \times 10^5\ J/mol \quad A = not\ given$

$$\ln k_1 - \ln k_2 = \left(\ln a - \frac{E_a}{RT_1}\right) - \left(\ln a - \frac{E_a}{RT_2}\right)$$

$$\ln k_1 - \ln k_2 = \ln a - \frac{E_a}{RT_1} - \ln a + \frac{E_a}{RT_2} = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2}$$

$$\ln \frac{k_1}{k_2} = -\frac{E_a}{RT_1} + \frac{E_a}{RT_2} \quad (\text{since } \ln k_1 - \ln k_2 = \ln k_1 / k_2)$$

$$\ln \frac{k_1}{k_2} = -\frac{1.08 \times 10^5}{8.314 \times 310} + \frac{1.08 \times 10^5}{8.314 \times 300} = 1.396$$

$$\frac{k_1}{k_2} = 4.04$$

The reaction at 37 $^{o}$C is about 4 times faster than at 27 $^{o}$C.

## 1.7 Concentration-Time Equation (Integrated Rate Law)

❖ *Rate low tells us how the rate of reaction dependson concentrations of the reactants aa particular moment*

## 1.8 Zero Order Reaction

- Whose rate of reaction does not depend on thereactant concentration
- The rates of these **zero-order reactions** do not vary with increasing nor decreasing reactants concentrations. This means that the rate of the reaction is equal to the rate constant, *k*, of that reaction.

  $A \rightarrow Product \quad Rate = d[A]/dt = k[A]^0 = k = constant$

  $[A]_0 - [A]t = - + kt_o$

  $[A]_t = - kt + [A]_o$Integrated rate equation for $0^{th}$ order reaction

  Where [A] is concentration of A at $t = t$; $[A]_o$is the concentration of A is at $t = 0$.
- This is a linear equation with the form of $y = mx + b$.
- For a zero-order reaction, a plot of [A] versus-time is a straight line, whose slope is $-k$

Example

1. For all zero-order reactions
   A. A plot of time vs. concentration squared is linear.
   B. The rate is independent of time.
   C. The rate constant is zero. .
   D. Ea is very low

   Answer: (B) For zero-order reactions, Rate = k[A]°. Because anything raised to the zero poweris equal to one, Rate = k. This is another way of saying that the rates of zero-order reactions donot change; they do not speed up and they do not slow down, they either take place or they do not

2. The decomposition of the reaction $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$, is a zero order reactions that occurs on a hot platinum surface . The concentrations $N_2O$ reduced from 0.4M to 0.1M in 20s. Then what is rate constant?
   *A.* 0.015 B. 0.15 C. 0.25 D. -0.015 *ANS A*
3. A → C is zero order reaction. If the reaction is 30% complete after 10 min. What is the rate constant for a reaction?If the initial concentration of A was 16M
   *A.* 0.48 B. 48 C. -0.48 D. -48 *ANS A*

✓ *Solution After 10min 30% of A is changed in to C. This means 70% of A remains after 10min. Thus* $[A]_{20min} = {}^{70}/_{100} x16 = 11.2M$

$[A]_{10min} = -Kt + [A]_{20min}$

11.2M = -k x10min +16, Then calculate for k = 0.48

## 1.9 First-Order Reactions

➢ Whose rate of reaction depends on the reactantconcentration raised to the first power

$\ln [A]_t = -kt + \ln [A]_o$ Integrated rate equation for 1st order reaction

Taking the exponent to each side of the equation:

$$\frac{[A]}{[A]_o} = e^{-kt} \qquad \text{or} \qquad [A] = [A]_o e^{-kt}$$

The linear equation $y = mx + b$, in which $m$ is the slope of the line that is the graph of the equation. Thus, a plot of ln[A] versus $t$ gives a straight line with a slope of $k$ (or $m$).

EXAMPLE

1. A certain first-order reaction is 45.0% complete in 65 s. What is the rate constant for this process?

   If $[A]_0$= 100%, then after 65s, 45.0% of A has reacted or $[A]_t$ = 55% For first order reactions:

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

   $\ln[55] - \ln[100] = -k(65\ s)$, $k = 9.2 \times 10^{-3}$ s, use scientific calculator

2. The rate law for the decomposition of phosphine ($PH_3$) is

   $$\text{Rate} = -\frac{\Delta[PH_3]}{\Delta t} = k[PH_3]$$

   It takes 120s for 1.00 M $PH_3$ to decrease to 0.250 M. How much time is required for 2.00 M PH3 to decrease to a concentration of 0.350 M?

$$\ln[PH_3]_t - \ln[PH_3]_0 = -kt$$

$$\ln[0.250]_t - \ln[1.00]_0 = -k(120\ \text{s}) \quad k = 0.0116\ \text{s}^{-1}$$

$$\ln[0.350]_t - \ln[2.00]_0 = -0.0116\ \text{s}^{-1}(t) \quad t = 150.\ \text{s}$$

3. A sealed rigid container holds two first order reactantgases, A and B. If additional moles of gas B are added tothe container while keeping the temperature constant,what can be said of the reaction under these conditions?
   A. The rate of the reaction will increase, as will the rateconstant, k.
   B. The rate of the reaction will remain unchanged as willthe rate constant, k.
   C. The rate of the reaction will increase but the rateconstant, k, will remain unchanged.
   D. The rate of the reaction will remain unchanged but therate constant, k, will increase.
   E. The rate of reaction will decrease as will the rateconstant, k

✓ ANS C. The rate will increase doe to the concentration increase, but the rate constant will remain the same.

4. The value of rate of a pseudo first order reaction
   A. Depends on the concentration of reactants present in small amount.
   B. Depends on the concentration of reactants present in excess.
   C. Is independent of the concentration of reactants.
   *D.* Depend only on one of the reactant E. B & D *ANS E*

5. The first-order reaction A → B, has $k = 5.67\ \text{s}^{-1}$. If [A]0 = 0.500 *M*, how long will it take [A] = 0.124 *M*? A. 0.122s B. 0.244s C. 0.100s D. 0.488s *ANS D*

## 1.10 Second Order Process:

**A → Products** Rate = $k[A]^2$

$$\text{Rate}(\text{Ms}^{-1}) = -\frac{d[A]}{dt} = k[A]^2$$

Integrating as before we find:

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

A plot of 1/[A] versus t is a straight line with slope *k* and intercept $1/[A]_0$

For a second order reaction, a plot of ln[A] vs. *t* is **not linear**.

**Example**

1. The reaction: $2NOBr\ (g) \rightarrow 2\ NO\ (g) + Br_2\ (g)$ is a second order reaction with respect to NOBr. $k = 0.810\ M^{-}\cdot S^{-}$ at 10°C. If $[NOBr]_o = 7.5 \times 10^{-3}$ M, how much NOBr will be left after a reaction time of 10 minutes?

✓ ***SOLUTION:*** One can solve for the amount of NOBr after 10 minutes by substituting the given data into the integrated rate law for a second-order reaction.

$$\frac{1}{[NOBr]_t} = kt + \frac{1}{[NOBr]_0} \qquad (\textit{Second Order})$$

$$\frac{1}{[NOBr]_t} = (0.810\ M^{-1}\cdot s^{-1})\times(600\ s) + \frac{1}{7.5\times10^{-3}\ M}$$

$$\frac{1}{[NOBr]_t} = 6.19\times10^{2}\ M^{-1}$$

$$[NOBr]_t = 1.6\times10^{-3}\ M$$

**2.** What are the units for each of the following if the concentrations are expressed in moles per liter and thetime in seconds?

A. Rate of a chemical reaction — The units for rate are always mol/L•s.

B. Rate constant for a zero-order rate law — Rate = k; k must have units of mol/L•s

C. Rate constant for a first-order rate law — Rate = k[A], k must have units of $s^{-}$

D. Rate constant for a second-order rate law — Rate = $k[A]^2$, k must have units of L/mol•s

3. Which answer choice correctly matches the integrated rate law shown:

$1/[A]t = kt + 1/[A]o$

*A.* A zero order reaction where a plot of $1/[A]t$ versus *t* will be a straight line with slope = k

*B.* A first order reaction where a plot of $1/[A]t$ versus *t* will be a straight line with slope = k

*C.* A first order reaction where a plot of $1/[A]t$ versus *t* will be a straight line with slope = -k

*D.* A second order reaction where a plot of $1/[A]t$ versus *t* will be a straight line with slop = k

*E.* A second order reaction where a plot of $1/[A]t$ versus *t* will be a straight line with slope = -k

*ANS. D*

## 1.11 The Half-life of a Reaction

➢ *Half-life is the time taken for the concentration of a reactant to drop to half its original value*

*This means that half life is the time it takes for the concentrations of A to fall from* $[A]_0$ *to* $\frac{1}{2}[A]_0$

HALF-LIFE FOR FIRST- ORDER

$$[A] = \frac{[A]_o}{2}$$

For a first order process the half life ($t_{½}$) is found mathematically from

(1) $\ln[A] = -kt + \ln[A]_o$

(2) $\ln[A] - \ln[A]_o = -kt$

(3) $\ln\left(\frac{[A]}{[A]_o}\right) = -kt$

(4) $\ln\left(\frac{[A]_o}{[A]}\right) = kt$

(5) $\ln\left(\frac{[A]_o}{[A]_o/2}\right) = kt_{\frac{1}{2}}$

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

**Example**

1. A certain reaction proceeds through first order kinetics.The half-life of the reaction is 180s. What the rate constant?

$$t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{0.693}{k} \qquad k = \frac{\ln 2}{t_{\frac{1}{2}}} = \frac{\ln 2}{180s} = 0.00385s^{-1}$$

2. A reaction is first order in A. If the rate constant of the reaction is $3.45 \times 10^{-3}$ $s^{-}$, what is the half-life ($t_{1/2}$) of the reaction?

   A. $4.98 \times 10^{-3}$ s  B. 100 s  C. 201 s  D. $3.45 \times 10^{-3}$ s  ANS C

3. Iodine -131 has a half life of 8 days. If there are 200g of this sample how much of I-131 will remain after 32days. (the rxn is first order) A. 12.5g  B. 25g  C.6.25g  D. 50g

✓ ***SOLUTION***, One half- life is 8 days total half- life is 32/8 = 4

**200**--8day--**100**---8day---**50**--- 8day **--25** ---8day--12.5 total of 32 days **Ans. A**

4. If a certain first order rxn has a half-life of 30min how much time it required for this reactions to be 35% complete?

   A. 18.7min  B. 36min  C. 70min  D. 40min  ANS A

## Half-life for a second-order reaction

➢ Unlike a first order reaction, the rate constant for a second order process depends on the initial concentration of a reactant.

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_o}$$

at the half–life, $[A]_t = \frac{1}{2} \times [A]_o$

Substituting and solving, $t_{1/2} = \frac{1}{k[A]_o}$

*Example*

1. The reaction 2NOBr (g) → 2 NO (g) + $Br_2$ (g) is a second order reaction with respect to NOBr. k = 0.810 $M^{-}s^{-}$ at 10° C.If $[NOBr]_o = 7.5 \times 10^{-3}$ M, Determine the half-life of this reaction.

✓ *To determine the half-life for this reaction, we substitute the initial concentration of NOBrand the rate constant for the reaction into the equation for the half-life of a second-order reaction.*

$$t_{1/2} = \frac{1}{k[A]_o} \qquad t_{1/2} = \frac{1}{0.810\ M^{-1} \cdot s^{-1} (7.5 \times 10^{-3}\ M)} = 164s$$

2. If the reaction 2HI → $H_2$ + $I_2$ is second order, which of the following will yield a linear plot?

   A. log [HI] vs time  C. [HI] vs time
   B. ln[HI] vs time  D. 1/[HI] vs time  *ANS. D*

3. Nitrosyl chloride, NOCl, decomposes slowly to NO and $Cl_2$ as shown in the equation below.

   2NOC→ 2NO + Cl2  $r = k[NOCl]^2$

   The rate constant, *k* equals 0.020 L/ mol.s at a certain temperature.

If the initial concentration 0.050 M, what will the concentration be after 30 minutes? Assume the reaction is second order

*A.* 0.018M B.0.18M C. 18M D. 1.8M*ANS A*

## 1.12 REACTION MECHANISM

- A *mechanism:*-is a collection of elementary processes (also calledelementary steps or elementary reactions) that explains how the overall reactionproceeds.
- ***Elementarysteps: -*** The individual reactions that make up a reactions mechanism.
- Intermediates:- A substance that is found in elementary steps but not in overall rxns
- Molecularity of a reaction: - The minimum number of reacting particles (molecules, atoms or ions) that come together or collide in a rate determining step to form product or products.

**Example**

| | | |
|---|---|---|
| a | $PCl_5 \rightarrow PCl_3 + Cl_2$ | (Unimolecular) |
| b | $2HI \rightarrow H_2 + I_2$ | (Bimolecular) |
| c | $2SO_2 + O_2 \rightarrow 2SO_3$ | (Termolecular) |
| d | $NO + O_3 \rightarrow NO_2 + O_2$ | (Bimolecular) |
| e | $2CO + O_2 \rightarrow 2CO_2$ | (Termolecular) |
| f | $2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$ | (Termolecular) |

- Rate determining step: - The slowststep in the sequence of steps leading to the formation of products. In other words, the slowest step in the mechanism determines theoverall rate of the reaction.

***NOTE***: - *In elementary steps, the reaction order, Molecularity and Stoichiometric Coefficient are numerically the same also they have different concepts except pseudo order rxns*

Molecularity; - Cannot be zero, negative, fractions and infinite

Example

1. The reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is thought to occur by the following mechanism: the experimentally rate low is Rate = $k[NO_2]^2$

   Step 1: $NO_2(g) + NO_2(g) \rightarrow NO_3(g) + NO(g)$Slow

   Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$Fast

   Check whether the proposed reaction mechanism is acceptable or unacceptable

   1. The sum of these reaction steps must give the overall balanced equation:
   2. Mechanism must be agrees with the experimental rate law

   For the above equation

   The first requirement is full filled because the sum of overall reaction is correct

   The second requirement is full filled because the rate from slowest or rate determining step is agreed with experimentally rate low. So the proposed mechanism is acceptable
3. The proposed steps for a catalyzed reaction between $X^{4+}$ and $Z^{+}$ are represented below.

   step 1: $X^{4+} + Y^{2+} \rightarrow X^{3+} + Y^{3+}$

   step 2: $X^{4+} + Y^{3+} \rightarrow X^{3+} + Y^{4+}$

   step 3: $Y^{4+} + Z^{+} \rightarrow Z^{3+} + Y^{2+}$

   The catalyst in this process is

   A. $X^{4+}$ B. $X^{3+}$ C. $Y^{4+}$ D. $Y^{2+}$

✓ *ANS. D.* A catalyst is a chemical that gets used up during an early step, but returns as a product during a later step

4. From question number 3 which species is intermediate? ANS.$Y^{4+}$, $Y^{3+}$

Because Intermediates are produced in one step and then consumed in a later step

5. The rate equation for the decomposition of nitramide, $H_2NNO_2 \longrightarrow N_2O + H_2O$, is Rate $=k\,[H_2NNO_2][H^+]^{-1}$. Which of the following mechanisms is consistent with this rate equation?

A. $H_2NNO_2 + H^+ \leftrightarrow H_3NNO_2^+$ fast equilibrium
$H_3NNO_2^+ \rightarrow N_2O + H_3O^+$ slow
$H_3O^+ \leftrightarrow H^+ + H_2O$ fast equilibrium

B. $H_2NNO_2 \rightarrow N_2O + H_2O$ slow

C. $H_2NNO \rightarrow OH^- + NH_4^+$ slow
$NH_4^+ \leftrightarrow NH_3 + H^+$ fast equilibrium
$H_2O \leftrightarrow H^+ + OH^-$ fast equilibrium

D. $H_2NNO_2 \leftrightarrow H^+ + HNNO_2^-$ fast equilibrium
$HNNO_2^- \rightarrow N_2O + OH^-$ slow
$H^+ + OH^- \rightarrow H_2O$ fast *ANS. D*

6. The proposed mechanism for a given chemical reaction is shown below.

| | |
|---|---|
| *Step 1*: A + B ⇆ F | *(fast)* |
| *Step 2:* F+ A → C + G | (*slow)* |
| *Step 3*: G + A ⇆ C + D | *(fast)* |

Which is the correct rate law?

A. Rate = k $[A]^2$ [B]
B. Rate = k [A] [B]
C. Rate = k [A] [B] [F] [G]
D. Rate = k $[A]^3$ [B]

✓ *ANS. A* Since the second step is the slow step, cross off the intermediate, and gather all the reactants in the first and second steps.

7. A proposed mechanism for the following reaction, $H_2 + I_2 \rightarrow 2HI$ is

| | |
|---|---|
| $I_2 \leftrightarrow 2I$ | fast, equilibrium |
| $I + H_2 \leftrightarrow H_2I$ | fast, equilibrium |
| $H_2I + I \rightarrow 2HI$ | slow |

A. Show that this mechanism predicts the correct rate law, rate = $k[H_2][I_2]$.

From step 3 (the slow, rate-determining step):

Rate = $k_3[H_2I][I]$

From step 1, Rate1f = Rate1r or $k1r[I_2] = k1r[I]_2$

rearranging, $[I] = \sqrt{\frac{k_{1f}[I_2]}{k_{1r}}}$

From step 2, $Rate_{2f} = Rate_{2r}$ or $k_{2r}[I][H_2] = k_{1r}[IH_2]$

rearranging, $[IH_2] = \frac{k_{2f}[I][H_2]}{k_{2r}}$

Substituting the expression for [I] from step 1 into this latter expression,

$$[IH_2] = \frac{k_{2f}\sqrt{\frac{k_{1f}[I_2]}{k_{1r}}}[H_2]}{k_{2r}}$$

Substituting this expression for [I] and $[IH_2]$ into the rate law deduced from step 1, and the combining terms,

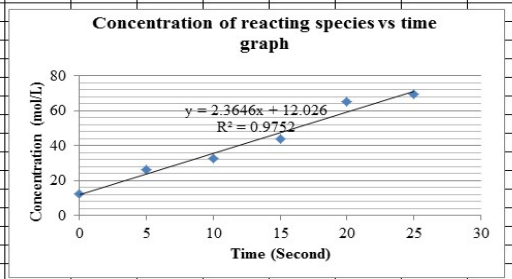
$$Rate = k_3 \times \frac{k_{2f}\sqrt{\frac{k_{1f}[I_2]}{k_{1r}}}[H_2]}{k_{2r}} \times \sqrt{\frac{k_{1f}[I_2]}{k_{1r}}} = \frac{k_3 k_{2f} k_{1f}}{k_{2r} k_{1r}}[H_2][I_2]$$

$Rate = k[H_2][I_2]$

The mechanism **is consistent** with the observed rate law.

8. Each of the choices below gives an elementary reaction. Which one could **not**be true regarding the molecularity of individual step?
   *A. $A + B + C \rightarrow P$ : Trimolecular* *C. $2A \rightarrow P$ : Bimolecular*
   *B. $A \rightarrow P$ :Unimolecular* *D. $A + B \rightarrow P$ :Uimolecular Ans. D*
9. Which of the following statements are applicable to a balanced chemical equation of an elementary reaction?
   A. Order is same as molecularity.
   B. Order is less than the molecularity.
   C. Order is greater than the molecularity.*Ans. A.*
   D. Molecularity can never be positive value
10. The kinetics of the reaction below were studied and it was determined that the reaction rate did not change when the concentration of B was tripled. The reaction is ___ order in B:
    $(A + B \rightarrow P)$
    A. First B. zero C. second D. third Asn. B.
11. **Refer the fig. below.** Which order of the reactionwould represented by this graph, what is the slope and intercept of this graph respectively?

| | |
|---|---|
| 0 | 12.5 |
| 5 | 26 |
| 10 | 32.45 |
| 15 | 44 |
| 20 | 65 |
| 25 | 69.55 |




A. First order, 2.3646 and 0.9752 C. Third order, -2.3646 and -12.026
B. Second order, 2.3646 and 12.026 D. Zero order, 0.9752& 2.3646
Ans. B

12. For the first-order reactions of different substances A and X

$A \rightarrow B$ $t_{1/2} = 30.0$ min

$X \rightarrow Y$ $t_{1/2} = 60.0$ min This means that

A. Doubling the concentration of A will have ½ the effect on half-life that doubling the concentration of B will have on its half-life.
B. A certain number of grams of A will react twice as fast as the same number of grams of X.
C. A certain number of grams of X will react twice as fast as the same number of grams of A.
D. The rate constant for $A \rightarrow B$ is lower than the rate constant of $X \rightarrow Y$.
E. 3 moles of A will react more rapidly than 3 moles of X

✓ Answer: (E) It takes half as much time for A to form B as for X to form Y, as seen by the smaller half-life. Note that option "B" would be incorrect as the grams of A and the grams of X are not the same number of moles.

13. A reaction is first order with respect to [X] and second order with respect to [Y]. When [X] is 0.20 M and [Y] = 0.20 M the rate is $8.00 \times 10^{-3}$ M/min. The value of the rate constant, including correct units, is

A. 1.00 M $min^{-}$ B.1.00 $M^{-2}$ $min^{-}$ C.2.00 $M^{-}$ $min^{-}$ D. 2.00 $M^{-2}$ $min^{-}$

✓ Answer: (B) From these data, it follows that the rate law is Rate = $k[X][Y]^2$. Solving for the rate constant and substituting data for this reaction: $K = Rate/[X][Y]^2$

$= 8.00 \times 10^{-3}$ M/min/(0.200 M)$(0.200\ M)^2$

$= 0.008$ M/min/0.008 $M^3$ $= 1.00\ M^{-2}min$

14. A reaction mechanism

A. Is the sum of all steps in a reaction except the rate determining step.
B. Has a ΔH equal to the ΔH for the most demanding step.
C. Always has a rate determining step.
D. May be absolutely proven from the rate law.
E. Is determined from the balanced expression only.

✓ Answer: (C) In all series of steps (the mechanism for the overall reaction), there must always be aslowest step. The rate determining step is the slowest step.

15. The balanced equation for the reaction of nitrogen dioxide and fluorine is

$2\ NO_2 + F_2 \rightarrow 2\ NO_2F$

The proposed mechanism is

| | |
|---|---|
| step 1: $NO_2 + F_2 \rightarrow NO_2F + F$ | (slow) |
| step 2: $F + NO_2 \rightarrow NO_2F$ | (fast) |

Which of the following are correct?

I. The mechanism supports an experimentally determined rate law of rate = $k[NO_2]^2[F_2]$
II. F is an intermediate
III. The reaction is first order in $F_2$

A. I only B.I and II only C.I and III only D. II and III

✓ ANS. *D* *Since the first step is the slow step, the stoichiometry of that step results in the order of the reaction, thus it s first order for both $NO_2$ and $F_2$. Also, F is an intermediate because it is a product of one step, but gets used up in a subsequent step.*

16. If tripling the concentration of a single reactant R in a multi-reactant reaction (while leaving all other conditionsunchanged) leads to a nine-fold increase in rate, it can be deduced
    A. That the complete rate law is Rate= k[R]
    B. That the complete rate law is Rate= $k[R]^2$
    C. That the complete rate law is Rate= $k[R]^3$
    D. Only that the order with respect to [R] is 2 *ASN. D*

✓ We cannot know the entire rate law, only that the order is second with respect to the reactant

17. The greatest increase in the rate for the reaction between X and Z with rate $r = k[X][Z]^2$ will be caused by:
    A. Doubling the concentration of Z C. Doubling the concentration of X
    B. Tripling the concentration of X D.Lowering the temperature*ASN. A*

18. If a reaction proceeding by the mechanism
    A + B → C + Doccurs at a rate *x*, and if the concentrations of A and B are both doubled, what willbe the new rate of reaction?
    A. X B. 2x C. 4x D. 8x E. 16x *ANS. C*

19. Consider the rate law: rate = $k[Y]^m[Z]^n$. How theexponents*m* and *n are*determined?
    A. By using the balanced chemical equation
    B. By using the subscripts of the chemical formulas
    C. By using the coefficients of the chemical formulas
    D. By educated guess
    *E.* By experiment*ASN. E*

20. For the a reaction the time required for the 20% completion is 40min and 40% completion is 80min what is the order of the reaction?
    A. 1 B. 2 C. 3 D. 0

21. Which of the following statement is true about order and molecularity ?
    A. Order is define for both elementary as well as complex reactions
    B. Molecularity is defined for both elementary as well as complex reactions
    C. Order cannot be zero,negative or fractions
    D. Molecularity can be zero, negative or fractions *ASN. A*

22. Which of the following statement is not true?
    A. Bimolecular, involves the collision of two particles
    B. Termolecular, involves the simultaneous collision of three particles all atone time.
    C. Unimolecular, involves the collision of a single particle
    D. Termolecular collision is easier than bimolecular collision

Ans C. Unimolecular is decomposition or rearrangement of a particles not only collision

# UNIT 5

## Chemical Equilibrium and Phase Equilibrium

**Main topics**

- Chemical Equilibrium
- Phase Equilibrium

### 5.1 Chemical Equilibrium

Having looked at factors that affect the rate of a reaction, we now need to ask some important questions. Does a reaction always proceed in the same direction or can it be reversible? In other words, is it always true that a reaction proceeds from reactants to products, or is it possible that sometimes, the reaction will reverse and the products will be changed back into the reactants? And does a reaction always run its full course so that all the reactants are used up, or can a reaction reach a point where reactants are still present, but there does not seem to be any further change taking place in the reaction?

**Reversible and Irreversible Reactions**

**Reversible reactions**

The reactions in which the products formed during the reaction combine to give back the reactants are called reversible reactions.

It is indicated by writing two half headed arrow marks between the reactants and product (⇌)

$$A + B \rightleftharpoons C + D$$

Question:what do arrow marks indicate?

Answer: the arrow head pointing to the rightrepresents the forward reaction and the arrow head pointing to the left represents the backward reaction.

**Conditions for a reversible reaction:**

i. The reaction should be carried out in a closed vessel.
ii. The products should not be removed from the vessel.
iii. Temperature and pressure should be kept constant.

Examples for reversible reactions

a. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ c. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
b. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

The reactions in which products formed do not combine to give back the reactants are called **irreversible reactions.**

- ✓ The irreversible reactions proceed only in one direction.
- ✓ They are indicated by writing an arrow between reactants and products as:

$A + B \rightarrow C + D$

Question: can irreversible reactions be made reversible ?

Answer: an irreversible reaction can not be made reversibleeven if it is carried out in a closed vessel.

Examples for irreversible reactions:

a. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H\ 2\uparrow$
b. $AgNO_3 + KCl \rightarrow AgCl\downarrow + KNO_3$
c. $Mg + 2HCl \rightarrow MgCl_2 + H_2\uparrow$

**Attainment and characterstics of chemical equilibrium**

**Equilibrium** is a state in which there are no observable changes as time goes by.

Question: what is dynamic chemical equilibrium?

Answer: any reaction will be in dynamic equilibrium if it's reversible and the rates of the forward and reverse reactions are equal**.**

An example of dynamic equilibrium is: $NO_2(g) + CO(g) \rightleftharpoons NO(g) + CO_2(g)$.

Nitrogen dioxide ($NO_2$) reacts with carbon monoxide (CO) to form nitrogen oxide (NO) and carbon dioxide ($CO_2$), and, in the reverse reaction, nitrogen oxide and carbon dioxide react to form nitrogen dioxide and carbon monoxide.

Another example of dynamic equilibrium is, say that you prepare a solution that is saturated with an aqueous solution of NaCl. If you then add solid crystals of NaCl, the NaCl will be simultaneously dissolving and recrystallizing within the solution.

The process, $NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$, will be in dynamic equilibrium when the rate of the dissolution of the NaCl equals the rate of recrystallization.

Below is a table showing the key differences between dynamic and static equilibrium.

| **Dynamic Equilibrium** | **Static Equilibrium** |
|---|---|
| ➢ Reversible | ➢ Irreversible |
| ➢ Reaction is still occurring | ➢ Reaction has stopped |
| ➢ Rate of forward rxn = Rate of reverse rxn | ➢ Both rxn rates are zero |
| ➢ Occurs in a closed system | ➢ Can occur in an open or closed system |

**Chemical equilibrium**

When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time, and there are no visible changes in the system. However,

there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules, it is a dynamic situation.

**Chemical equilibrium** is the state of the reaction when the macroscopic properties like temperature, pressure, volume and concentration of the reaction do not change with time.

### Conditions for attinment of chemical equilibrium

Analogous to the physical systems chemical reactions also attain a state of equilibrium.

- The reactions can occur both in forward and backward directions.
- The rates of the forward and reverse reactions become equal
- The concentrations of the reactants and the products remain constant.
- The equilibrium is dynamic in nature as it consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants

For a better comprehension, let us consider a general case of a reversible reaction,

$$A + B \rightleftharpoons C + D$$

With passage of time, there is accumulation of the products C and D and depletion of the reactants A and B.

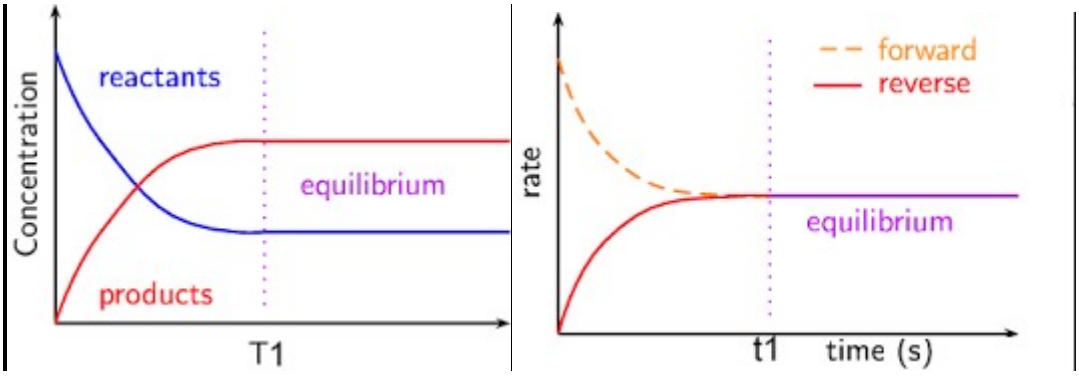



Fig.

This leads to a decrease in the rate of forward reaction and an increase in he rate of the reverse reaction, eventually, the two reactions occur at the samerate and the system reaches a state of equilibrium.We know from "Factors affecting reaction rates" the rate of the forward reaction is directly proportional to the concentration of the reactants. In other words, as the concentration of the reactants increases, so does the rate of the forward reaction. This can be shown using the following equation:

*Rate of forward reaction* $\propto [A][B]$ *or Rate of forward reaction* $= k_1[A][B]$. Similarly,

*Rate of the reverse reaction is directly proportional to the concentration of the products*. This can be shown using the following equation:

*Rate of reverse reaction* $\propto [C][D]$ *or Rate of reverse reaction* $= k_2[C][D]$

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction. This can be shown using the following equation:

$$k_1[A][B] = k_2[C][D] \text{ or}$$

$$\frac{K1}{K2} = \frac{[C][D]}{[A][B]}$$

or, if the constants $k_1$ and $k_2$ are simplifed to a single constant, the equation becomes:

$$Kc = \frac{[C][D]}{[A][B]}$$

A more general form of the equation for a reaction at chemical equilibrium is:

$$aA + bB \rightleftharpoons cC + dD$$

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

It is important to note that if a reactant or a product in a chemical reaction is in either the liquid or solid phase, the concentration stays constant during the reaction. Therefore, these values can be left out of the equation to calculate Kc.

For example, in the following reaction: $C\,(s) + H_2O\,(g) \rightleftharpoons CO\,(g) + H_2\,(g)$

$$Kc = \frac{[CO][H_2]}{[H_2O]}$$

### Characteristics of chemical equilibrium

- Equilibrium is achieved in a closed system. A closed system prevents exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine with each other.
- The rate of the forward reaction is equal to the rate of the backward reaction.
- Equilibrium is dynamic. The reaction hasn't stopped but both forward and backward reactions are still occurring.
- The concentrations of reactants and products remain constant at equilibrium. They are being produced and destroyed at an equal rate.
- At equilibrium there's no change in macroscopic properties.
- Equilibrium can be reached from either direction.
- The free energy change of the reaction is zero at equilibrium

### Equilibrium expression and equilibrium constant

The value of the equilibrium constant expression, Kc, is constant for a given reaction at equilibrium and at a constant temperature.

The equilibrium constant for a general reaction, aA + b B⇌ c C + d Dis expressed as,

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

Where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products. Since pressure is proportional to concentration for gases in a closed system, the equilibrium expression can also be written as, PV = nRT,⇒ P = $\frac{n}{V}$ RT. Here, P is the pressure in Pa, n is the number of moles of the gas, V is the volume in $m^3$ and T is the temperature in Kelvin.Therefore, n/V is concentration expressed in mol/$m^3$. If concentration c, is in mol/L or mol/$dm^3$, and P is in bar then P = cRT.We can also write p = [gas]RT. Here, R= 0.0831 bar litre/mol K. At constant temperature, the pressure of the gas is proportional to its concentration i.e., P∝ [gas].

For a general reaction; aA +bB⇌cC + dD

$$Kp = \frac{P_C^c\, x\, P_D^d}{P_A^a x\, P_B^b}$$

***Example 1:****Write Kp expression for reaction below A + 2B ⇌3C*

*Kp = $P_C^3 / (P_A x\, P_B^2)$*

***Example 2:*** *Consider: $H_2$ (g) + $I_2$ (g) ⇌ 2HI (g)*

$Kp = \frac{(P_{HI})^2}{(P_{H2})\,(P_{I2})}$, $K_P = K_C(RT)^{\Delta n}$,

*Δn = mol gas phase product – mol gas phase reactant*

$K_P = K_C$ *when* $\Delta n = 0$

***Exercise:*** *$CH_4$ reacts with $H_2S$ to form $H_2$ and $CS_2$: $CH_4$ (g) + 2$H_2S$ (g) ⇌ $CS_2$ (g) + 4$H_2$ (g).*Determine the value of $K_P$ for this reaction at 1000 K if the following equilibrium pressures were measured:$P_{CH4}$= 0.20 atm, $P_{H2S}$ = 0.25 atm, $P_{CS2}$ = 0.52 atm and $P_{H2}$ = 0.10 atm. Determine the value of $K_C$ for this reaction at 1000 K.

**Relationship betweenKc and Kp**

From the Ideal Gas Law we know that: PV = nRT and P = (n/V)RT = cRT. Plugging this into the expression for Kp for each substance, the relationship between Kc and Kp becomes:

$Kp = Kc(RT)^{\Delta n}$, where

*Δn = (moles of gaseous product) - (moles of gaseous reactant)*

**Example 1:** The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (g) at $74^0$C are [CO] = 0.012 M, [$Cl_2$] = 0.054 M, and [$COCl_2$] = 0.14 M. Calculate the equilibrium constants Kc and Kp.

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

$$Kc = \frac{[COCl_2]}{[CO][Cl_2]^2} = \frac{0.14}{0.012\ x\ 0.054} = 220,$$

$Kp = Kc(RT)^{\Delta n}$, $\Delta n = 1 - 2 = -1, R = 0.0821, \ T = 273 + 74 = 347\ K$

$Kp = 220\ x\ (0.0821\ x\ 347)^{-1} = 7.7$

**Example 2**: The equilibrium constant Kp for the reaction given below is 158 at 1000K. What is the equilibrium pressure of $O_2$ if the $P_{NO} = 0.400$ atm and $P_{NO2} = 0.270$ atm?

$$2NO_2\ (g) \rightleftharpoons 2NO\ (g) + O_2(g)$$

$$Kp = \frac{(P_{NO})^2(P_{O_2})}{(P_{NO_2})^2}, \text{ this implies } P_{O_2} = Kpx\ \frac{(P_{NO})^2}{(P_{NO_2})^2} = 158\ x\ \frac{(0.400)^2}{(0.270)^2} = 347\ atm$$

**Example3:** For the equilibrium, $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ the value of the equilibrium constant, Kc is $3.75 \times 10^{-6}$ at 1069 K. Calculate the Kp for the reaction at this temperature.

***Solution***

we know that, $Kp = Kc(RT)^{\Delta n}$

For the above reaction, $\Delta n = (2+1) - 2 = 1$, $Kp = 3.75 \times 10^{-6}\ (0.0831 \times 1069)$

$Kp = 0.033$

**Exercise:** The equilibrium constant $K_P$ for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine is found to be 1.05 at 250°C. If the equilibrium partial pressures of $PCl_5$ and $PCl_3$ are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of $Cl_2$ at 250°C?

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

**Homogeneous equilibria:** Occur when all reactants and products are in the same phase.

**Examples:**

a. $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$ b. $CH_4\ (g) + 2H_2S\ (g) \rightleftharpoons CS_2\ (g) + 4H_2\ (g)$

**Heterogeneous equilibria:** Occur when reactant or product in the equilibrium is in a different phase.

Examples;

a. $H_2O\ (l) \rightleftharpoons H_2O\ (g)$ b) $CO_2\ (g) + C\ (s) \rightleftharpoons 2CO\ (g)$

Concentrations of pure solids and liquids are fixed by their density and molar mass (both constants) and do not vary with the amount. The value used for the concentration of a pure substance is always 1.Therefore, the concentrations of solids and liquids do not appear in the equilibrium expression.

- Thus, Omit concentration terms for solids and liquids from Kc and Kp expressions; only include terms for gases (g) and aqueous substances (aq).

**Example 1:** Write the Kc expression for $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. $Kc = [CO_2]$

**Example 2:** $PbCl2\ (s) \rightleftharpoons Pb^{2+}(aq) + 2\ Cl^{-}(aq)$

$$Kc = [Pb^{2+}][Cl^{-}]^2$$

**Example 3:** Write the Kc expression for the following reaction:

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightleftharpoons 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

$$Kc = \frac{[Cu^{2+}]^3[NO]^2}{[NO_3^-]^2\,[H^+]^8}$$

**Modifying Equilibrium Constant Expressions:**

Example: **$2SO_2 + O_2 \rightleftharpoons 2SO_3$, $K_1 = x$**

A. **Changing stochiometric coefficients:**

**$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$, $K_2 = y$**

The equilibrium constant of a reaction that has been multiplied by a number, is the equilibrium constant raised to a power that is equal to that number. Therefore,

**$K_2 = (K_1)^{1/2}$**, $y = (x)^{1/2}$

B. **Reversing the reaction:**

**$2SO_3 \rightleftharpoons 2SO_2 + O_2$, $K_3 = z$**

The equilibrium constant of a reaction in the reverse direction is the reciprocal of the equilibrium constant of the forward reaction. Therefore,

**$K_3 = 1/K_1$**, $z = 1/x$

C. **Adding equations for multiple equilibrium reactions:**

1. **$A + 2B \rightleftharpoons C$, $K_1 = x$**
2. **$A + D \rightleftharpoons B$, $K_2 = y$**
3. **$2A + B + D \rightleftharpoons C$, $K_3 = z$**

The equilibrium constant for a net reaction made up of two or more steps is the product of the equilibrium constants for the individual steps. Therefore,

**$K_3 = K_1 \times K_2 = xy = z$**

**Example 1:** $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$, $Kc = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$ at 100 $^0$C

$2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$, $Kc = \frac{[N_2O_4]}{[NO_2]^2} = 4.72$ at 100 $^0$C

**Example 2:** Consider, $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$; $K_C = 54$ and:

$2\ HI\ (g) \rightleftharpoons H_2\ (g) + I_2\ (g)$; $K_{C1} = ???$

$Kc = \frac{[HI]^2}{[H_2][I_2]} = 54$; $K_{C1} = \frac{[H_2][I_2]}{[HI]^2} = (KC)^{-1} = 0.018$

**Example 3:** $N_2O_4\ (g) \rightleftharpoons 2\ NO_2\ (g)$, $Kc = \frac{[NO_2]^2}{[N_2O_4]} = 0.212$ at 100 $^0C$

$N_2O_4\ (g) \rightleftharpoons 4\ NO_2\ (g)$, $Kc = \frac{[NO_2]^4}{[N_2O_4]^2} = (0.212)^2$ at 100 $^0C$

***Example 4:*** $2NOBr \rightleftharpoons 2\ NO + Br_2$, $K_1 = 0.014$

$Br_2 + Cl_2 \rightleftharpoons 2BrCl$, $K_2 = 7.2$

$NOBr + Cl_2 \rightleftharpoons 2NO + 2BrCl$,

$K_3 = K_1 \times K_2 = 0.014 \times 7.2 = 0.10$

**Example 5:** Consider combining the following equations:

$2P + 3Cl_2 \rightleftharpoons 2PCl_3$; $K_{C3}$

$2PCl_3 + 2\ Cl2 \rightleftharpoons 2\ PCl_5$; $K_{C4}$

---

$2P + 5Cl_2 \rightleftharpoons 2PCl_5$; $K_C$= ???

$K_C = K_{C3} \bullet K_{C4}$; $K_C = \frac{[PCl_5]^2}{[P]^2[Cl_2]^5} = \frac{[PCl_3]^2}{[P]^2[Cl_2]^3} \times \frac{[PCl_5]^2}{[PCl_3]^2[Cl_2]^2}$

**Example 6**: The following equilibrium constants have been determined for carbonic acid at 25°C:

$H_2CO_3\ (aq) \rightleftharpoons HCO_3^-\ (aq) + H^+\ (aq)$, $K_{C1} = 4.2 \times 10^{-7}$

$HCO_3^-\ (aq) \rightleftharpoons CO_3^{2-}\ (aq) + H^+\ (aq)$, $K_{C2} = 4.2 \times 10^{-11}$

The overall reaction is the sum of the two reactions: $H_2CO_3\ (aq) \rightleftharpoons 2H^+\ (aq) + CO_3^{2-}\ (aq)$

**$K_C = K_{C1} \times K_{C2} = (4.2 \times 10^{-7})\ (4.8 \times 10^{-11}) = 2.0 \times 10^{-17}$**

***Exercises:***

a. $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$, $Kc = 1.7 \times 10^{27}$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $Kc = 1.5 \times 10^2$.

Calculate the value of Kc for **$4NH_3\ (g) + 3O_2\ (g) \rightleftharpoons 2N_2\ (g) + 6H_2O\ (g)$**

b. Consider the following reactions at 1200 K.

$CO\ (g) + 3H_2\ (g) \rightleftharpoons CH_4\ (g) + H_2O\ (g)$, $Kc,1 = 3.92$

$CH_4\ (g) + 2H_2S\ (g) \rightleftharpoons CS_2\ (g) + 4\ H_2\ (g)$, $Kc,2 = 3.3 \times 10^4$.

Use the above reactions to determine the equilibrium constant (Kc) for the following reaction at 1200 K.

**$CO\ (g) + 2\ H_2S\ (g) \rightleftharpoons H_2O\ (g) + CS_2\ (g) + H_2\ (g)$.**

Table: Relations between equilibrium constants for a general reaction and its multiples.

| **Chemical equation** | **Equilibrium constant** |
|---|---|
| $aA + bB \rightleftharpoons cC + dD$ | Kc |
| $cC + dD \rightleftharpoons aA + bB$ | $K_{C1} = (1/Kc) = (Kc)^{-1}$ |

| | |
|---|---|
| naA + nbB⇌ncC + ndD | $K_{C2} = (Kc)^n$ |
| sum of 2 reactions with $K_{C3}$& $K_{C4}$ | $K_C = (K_{C3})(K_{C4})$ |

**The relationship between chemical kinetics and chemical equilibrium**

For the reaction: $N_2O_4$ (g) ⇌$2NO_2$ (g)

Rate of forward reaction = Rate of reverse reaction

$$k_f [N_2O_4] = k_r [NO_2]^2$$

**Rearrange;** $K_C = \frac{[NO_2]^2}{[N_2O_4]} = \frac{Kf}{Kr}$

Thus, the equilibrium constant is simply the ratio of the forward and reverse rate constants which are both constant values at a given temperature.

- If $k_f > k_r$, $K_C > 1$, forward reaction is favored equilibrium position lies to the right.
- If $k_f < k_r$, $K_C < 1$ reverse reaction is favored equilibrium position lies to the left

**Application of equilibrium constant**

What does the equilibrium constant tell us?

- ✓ If Kc>>1, the reaction is product-favored; product predominates at equilibrium.
- ✓ If Kc<<1, the reaction is reactant-favored; reactant predominates at equilibrium.

**Predicting the Extent of a Reactions**

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that equilibrium constant does not give any information about the rate at which the equilibrium is reached. The magnitude of Kc or Kp is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa.

**We can make the following generalizations concerning the composition of equilibrium mixtures:**

i. If $Kc > 10^3$, products predominate over reactants, i.e., if Kc is very large, the reaction proceeds nearly to completion.
   Consider the following examples:
   a. The reaction of $H_2$ with $O_2$ at 500 K has a very large equilibrium constant, $Kc = 2.4 \times 10^{47}$.
   b. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ at 300K has $Kc = 4.0 \times 10^{31}$.
   c. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr\ (g)$ at 300 K, $Kc = 5.4 \times 10^{18}$.

ii. If $K\ c < 10^{-3}$, reactants predominate over products, i.e., if Kc is very small, the reaction proceeds rarely.

Consider the following examples:

a. The decomposition of $H_2O$ into $H_2$ and $O_2$ at 500 K has a very small equilibrium constant, $Kc = 4.1 \times 10^{-48}$.

b. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, at 298 K has $Kc = 4.8 \times 10^{-31}$.

**Note:** If Kc is in the range of $10^{-3}$ **to** $10^{3}$, appreciable concentrations of both reactants and products are present. Consider the following examples:

a. For reaction of $H_2$ with $I_2$ to give HI, Kc = 57.0 at 700K.

b. Also, gas phase decomposition of $N_2O_4$ to $NO_2$ is another reaction with a value of Kc = $4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large.

Hence, equilibrium mixtures contain appreciable concentrations of both $N_2O_4$ and $NO_2$.

**Predicting the direction of reaction:**

Equilibrium constant can be used to predict the direction of net reaction. For a reaction of known Kc value, the direction of net reaction can be predicted by calculating the reaction quotient, Qc.

Qc is called the reaction quotient, where for a reaction such as:aA + bB⇌cC + dD

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

Qc has the same expression as Kc, but it is calculated using concentrations that are not necessarily at equilibrium.

i. If Qc<Kc, the reaction will go to the right.

The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.

ii. If Qc = Kc, the reaction mixture is already at equilibrium, so no shift occurs.

**Exasmple1:** At 448°C, K = 51 for the reaction: $H_2$ (g) + $I_2$ (g) ⇌2HI (g). Predict the direction the reaction will proceed, if at 448°C the pressures of HI, $H_2$, and $I_2$ are 1.3, 2.1 and 1.7 atm., respectively.

Solution: $Q = \frac{[P_{HI}]^2}{[P_{H_2}]\,[P_{I_2}]} = \frac{(1.3)^2}{(2.1)(1.7)} = 0.47$

0.47 < 51, imply system are not at equilibrium.Numerator (products) must increase and denominator (reactants) must decrease. Consequently reaction must shift to the right.

**Example2:** Consider the gaseous reaction of $H_2$ with $I_2$, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; Kc = 57.0 at 700 K. Suppose we have molar concentrations $[H_2]_t$=0.10M, $[I_2]_t$ = 0.20 M and $[HI]_t$ = 0.40 M. (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium).

Solution: Thus, the reaction quotient, Qc at this stage of the reaction is given by:

$Qc = [HI]_t^2 / [H_2]_t\,[I_2]_t = (0.40)^2/(0.10)\times(0.20) = 8.0$

Now, in this case, Qc (8.0) does not equal Kc (57.0), so the mixture of $H_2(g)$, $I_2(g)$ and HI(g) is not at equilibrium; that is, more $H_2(g)$ and $I_2(g)$ will react to form more HI(g) and their concentrations will decrease till Qc = Kc

**Example 3:** The value of Kc for the reaction $2A \rightleftharpoons B + C$ is $2 \times 10^{-3}$. At a given time, the composition of reaction mixture is [A] = [B] = [C] = $3 \times 10^{-4}$ M. In which direction the reaction will proceed?

**Solution:** For the reaction, the reaction quotient Qc is given by, $Qc = [B][C]/[A]^2$ as [A] = [B] = [C] = $3 \times 10^{-4}$M, $Q_c = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$ as Qc >Kc so the reaction will proceed in the reverse direction.

**Exercises:** For the reaction, $B \rightleftharpoons 2A$, Kc = 2.

Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask.

a. In which direction will the reaction proceed to attain equilibrium?

b. Will the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?

**Calculating Equilibrium Concentrations**

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

**Step1.** Write the balanced equation for the reaction.

**Step2.** Under the balanced equation, make a table that lists for each substance involved in the reaction:

a. the initial concentration,

b. the change in concentration on going to equilibrium, and

c. the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

**Step3**. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

**Step4**. Calculate the equilibrium concentrations from the calculated value of x.

**Step5.** Check your results by substituting them into the equilibrium equation.

**Example1.** Use K to find conc. of reactants and products at equilibrium.

Given K= $2.7 \times 10^{-7}$ and initial amounts of [A]=1.0 [B]=0 and [C]=0 then find concentrations at equilibrium for reaction $2A \rightleftharpoons B + 3C$

a. Make table of initial, change, and final in symbolic form

| | 2A | ⇌ | B | + | 3C |
|---|---|---|---|---|---|
| Initial | 1.00 | | 0 | | 0 |
| Change | -2x | | +x | | +3x |
| Equilibrium | 1.00-2x | | x | | 3x |

b. Write Equilibrium expression and substitute in symbols

$Kc = [B][C]^3/[A]^2 = [x][3x]^3/[1-2x]^2$

c. Substitute in for K and solve math exactly or simplify to approximate

$2.7x10^{-7} = (27)(x^4) / [1-2x]^2$

Since Kc is small then x is small so approximate 1-2x ~ 1

$2.7x10^{-7} = (27)(x^4) / [1-2x]^2$, $1.0\ x10^{-8} = x^4$, $(1.0\ x10^{-8})^{1/4} = (x^4)^{1/4}$, **$1.0\ x\ 10^{-2} = x$**

**Example2:** $SO_2\,(g) + NO_2\,(g) \rightleftarrows SO_3\,(g) + NO\,(g)$; $K_C = 3.75$

1.24 mol $SO_2$ (g) and 0.750 mol $NO_2$ (g) are combined in a 2.50 L flask, and the reaction is allowed to reach equilibrium. Determine the concentration of each species present at equilibrium.

| | $SO_2$ (g) + | $NO_2$ (g) ⇄ | NO (g) + | $SO_3$ (g) |
|---|---|---|---|---|
| initial [ ] | 0.496 M | 0.300 M | 0 M | 0 M |
| Δ [ ] | – x | – x | + x | +x |
| equil [ ] | (0.496 – x) M | (0.300 – x) M | x M | x M |

$$K_C = \frac{[NO][SO3]}{[SO2][NO2]} = \frac{(x)(x)}{(0.496-x)(0.3-x)} = \frac{x^2}{0.149 - 0.796\,x + x2}$$

Using the quadratic formula: x = 0.847 (extraneous) or 0.240

So at equilibrium:$[SO_2] = 0.496 – x = 0.256$ M

$[NO_2] = 0.300 – x = 0.060$ M

$[SO_3] = [NO] = x = 0.240$ M

**Example 3:** The value of Kc = 4.24 at 800K for the reaction, CO (g) + $H_2O$ (g) ⇌ $CO_2$ (g) + $H_2$ (g) Calculate equilibrium concentrations of $CO_2$, $H_2$, CO and $H_2O$ at 800 K, if only CO and $H_2O$ are present initially at concentrations of 0.10M each.

**Solution:**

| | CO (g) + | $H_2O$ (g) ⇌ | $CO_2$ (g) + | $H_2$ (g) |
|---|---|---|---|---|
| initial [ ] | 0.1M | 0.1M | 0 | 0 |
| Δ [ ] | – x | – x | + x | +x |
| equil [ ] | (0.1-x) M | (0.1-x) M | x M | x M |

Hence, equilibrium constant can be written as, $K_c = x^2/(0.1-x)^2 = 4.24$

$3.24x^2 – 0.848x + 0.0424 = 0$

Using the quadratic formula; x = 0.067 or 0.194.The value 0.194 should be neglected because it will give concentration of the reactant which is more than initial concentration.Hence the equilibrium concentrations are, $[CO_2] = [H_2] = x = 0.067$ M

$[CO] = [H_2O] = 0.1 – 0.067 = 0.033$ M

**Example4:** 13.8g of $N_2O_4$ was placed in a 1L reaction vessel at 400K and allowed to attain equilibrium. $N_2O_4\,(g) \rightleftharpoons 2NO_2(g)$.The total pressure at equilibrium was found to be 9.15 bar. Calculate Kc, Kp and partial pressure at equilibrium.

**Solution:**

we know pV = nRT, total volume (V ) = 1 L, molecular mass of $N_2O_4$ = 92 g, number of moles = 13.8g/92 g = 0.15 of the gas (n), Gas constant (R) = 0.083 bar L $mol^{-1}K^{-1}$, Temperature (T ) = 400 K.

pV = nRT = p × 1L = 0.15 mol × 0.083 bar L $mol^{-1}K^{-1}$ × 400 K

p = 4.98 bar

| | $N_2O_4$ ⇌ | $2NO_2$ |
|---|---|---|
| Initial pressure: | 4.98 bar | 0 |
| At equilibrium: | (4.98 – x) bar | 2x bar |

Hence, $P_{total}$ at equilibrium = $P_{N2O4}$+ $P_{NO2}$

9.15 = (4.98 – x) + 2x

9.15 = 4.98 +x

x = 4.17 bar

Partial pressures at equilibrium are;

$P_{N2\,O4}$ = 4.98 – 4.17 = 0.81bar, $P_{NO2}$ = 2x = 2 × 4.17 = 8.34 bar

$Kp = \frac{[P_{NO_2}]^2}{[P_{N_2O_4}]}$ = = $(8.34)^2/0.81 = 85.87$

$Kp = Kc(RT)^{\Delta n}$

$85.87 = Kc(0.083 \times 400)^1$

Kc = 2.586 = 2.6

**Example 5:** 3.00 mol of $PCl_5$ kept in 1L closed reaction vessel was allowed to attain equilibrium at 380K. Calculate composition of the mixture at equilibrium. Kc= 1.80

**Solution:**

| | $PCl_5$ ⇌ | $PCl_3$ + | $Cl_2$ |
|---|---|---|---|
| Initial concentration: | 3.0 | 0 | 0 |
| At equilibrium: | (3-x) | x | x |

$Kc = [PCl_3][Cl_2]/[PCl_5]$

$1.8 = x^2/(3 - x)$

$x^2 + 1.8x - 5.4 = 0$

Using quadratic formula, x = 1.59

$[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41$ M, $[PCl_3] = [Cl_2] = x = 1.59$ M

**Changing equilibrium conditions-Le Chatelier's principle**

**Factors affecting equilibria**

Equilibrium constant, Kc is independent of initial concentrations. But if a system at equilibrium is subjected to a change in the concentration of one or more of the reacting substances, then the system is no longer at equilibrium; and net reaction takes place in some

direction until the system returns to equilibrium once again. Similarly, a change in temperature or pressure of the system may also alter the equilibrium. In order to decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use:

**Le Chatelier's principle:States, when a stress is applied to a system at equilibrium, the equilibrium position will shift in the direction that relieves the applied stress.**

**Stresses include:**

- Changes in concentration or pressure of reactants or products by the addition or removal
- Changes in pressure as a result of changes in volume of container
- Changes in temperature (value of K will change)
- Addition of a catalyst

## A. Effect of Changes in Concentration on Equilibrium Position

In general, when equilibrium is disturbed by the addition/removal of any reactant/ products, Le Chatelier's principle predicts that:

- ❖ The concentration stress of an added reactant/product is relieved by net reaction in the direction that consumes the added substance
- ❖ The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance.

Example: $N_2$ (g) + $3H_2$(g) ⇌ $2NH_3$(g)

0.683 M 8.80 M 1.05 M

Increase the concentration of $NH_3$ to 3.65M, the position of equilibrium shifts to the left

$$Q_C = \frac{[NH3]^2}{[N_2]\,[H2]^3} = \frac{(3.65)^2}{(0.683)(8.80)^3} = 0.0286$$

$$\text{But } K_C = \frac{[NH3]^2}{[N_2]\,[H2]^3} = \frac{(1.05)^2}{(0.683)(8.80)^3} = 0.02$$

QC >Kc, a net reverse reaction (equilibrium shifted to the left)

## B. Effect of Changing Pressure on Equilibrium Position

- A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction where the total number of moles of gaseous reactants and total number of moles of gaseous products are different.
- In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.

**Example 1:** How does the position of equilibrium change as the pressure is increased?

2PbS (s) + $3O_2$ (g) ⇌ 2PbO (s) + $2SO_2$(g)

three moles of gaseous reactant two moles of gaseous product

An increase in pressure causes an increase in products.

**Example 2:** Consider the reaction, $CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$

Here, 4 mol of gaseous reactants ($CO + 3H_2$) become 2 mol of gaseous products ($CH_4+H_2O$).

Suppose equilibrium mixture (for above reaction) kept in a cylinder fitted with a piston at constant temperature is compressed to one half of its original volume.Then, total pressure will be doubled (according to PV = constant).

The partial pressure and therefore, concentration of reactants and products have changed and the mixture is no longer at equilibrium.

The direction in which the reaction goes to re-establish equilibrium can be predicted by applying the Le Chatelier's principle.

Since pressure has doubled, the equilibrium now shifts in the forward direction, a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas).

This can also be understood by using reaction quotient, Qc.

Let [CO], [$H_2$], [$CH_4$] and [$H_2O$] be the molar concentrations at equilibriumfor methanation reaction.

When volume of the reaction mixture is halved, the partial pressure and the concentration are doubled.

We obtain the reaction quotient by replacing each equilibrium concentration by double its value.As Qc <Kc , the reaction proceeds in the forward direction

**Example 3**: In reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, when pressure is increased, the reaction goes in the reverse direction because the number of moles of gas increases in the forward direction.

### C. Effect of Inert Gas Addition

If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

### D. Effect of Temperature Change

Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Qc no longer equals the equilibrium constant, Kc. However, when a change in temperature occurs, the value of equilibrium constant, Kc is changed.

In general, the temperature dependence of the equilibrium constant depends on the sign of $\Delta H$ for the reaction.

- ✓ The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases
- ✓ The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Note: temperature changes affect the equilibrium constant and rates of reactions.

**Example:** $N_2O_4\,(g) + 58\ KJ \rightleftharpoons 2NO_2\,(g)$.Endothermic reaction

Increase temperature: Favours forward reaction

**Example:** Production of ammonia according to the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\ ;\ \Delta H = -92.38\ kJ\ mol^{-1}$$

According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used

### E. Effect of a Catalyst

- A catalyst enhances the rate of a reaction by lowering the reaction's activation energy.
- A catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent. We can therefore conclude that:
- The presence of a catalyst does not alter the equilibrium constant, nor does it shift the position of an equilibrium system.
- Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium sooner.
- The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen.

**Note: catalyst lower the activation energy of reactions and make the reaction faster but does not change the equilibrium constant (Keq).**

**Example:** Let us consider the formation of $NH_3$ from dinitrogen and dihydrogen which is highly exothermic reaction and proceeds with decrease in total number of moles formed as compared to the reactants. Equilibrium constant decreases with increase in temperature.

**Chemical equilbrium and industry**

**A. Haber process for the manufacture of ammonia**

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)\ ;\Delta H = -92\ KJ/mol$$

For reaction above equilibrum constants are shown below

| T | K |
|---|---|
| 398K | 57 |
| 298K | 812 |
| 198K | $1.6x10^5$ |

Equilibrium favors products at high pressure and low temperature. However, speed of reaction favored at high temperature.At low temperature rate decreases and it takes long time to reach at equilibrium, whereas high temperatures give satisfactory rates but poor yields.
German chemist, Fritz Haber discovered that a catalyst consisting of iron catalyse the reaction to occur at a satisfactory rate at temperatures, where the equilibrium concentration of $NH_3$ is reasonably favourable. Since the number of moles formed in the reaction is less than those of reactants, the yield of $NH_3$ can be improved by increasing the pressure. Optimum conditions of temperature and pressure for the synthesis of $NH_3$ using catalyst are around 380 – 450 $^0$C and 200 atm.

| $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ; $\Delta H = -92$ KJ/mol | | |
|---|---|---|
| Typical conditions | Pressure | 20000 Kpa (200 atm) |
| | Temperature | 380 – 450 $^0$C |
| | Catalyst | Iron |
| Equilibrium theory Favors | Low temperature | Exothermic reaction-higher yield at low T |
| | High pressure | Decrease in number of gaseous molecules |
| Kinetic theory favors | High temperature | Greater average energy + more frequent collision |
| | High pressure | More frequent collisions for gaseous molecules |
| | Catalyst | Lower activation energy |
| Compromise conditions | Which is better? | A low yield in a shorten time **or** A high yield over a longer period |

**B. Contact process for the manufacture of sulphuric acid**

Most of the sulfuric acid manufactured is produced using the Contact Process, a process involving the catalytic oxidation of sulphur dioxide, $SO_2$, to sulphur trioxide, $SO_3$.This process is called the Contact Process (because the $SO_2$ and $O_2$ gases must come into contact with a catalyst.

1. Liquid sulphur is sprayed with excess dry air at atmospheric pressure.
   $$S(l) + O_2(g) \rightarrow SO_2(g)$$
2. The oxidation of $SO_2$ to $SO_3$ is the most difficult part of making sulfuric acid. The reaction is as follows:
   $$SO_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons SO_3(g), \quad \Delta H = -99 kJ/mol.$$

This reaction is an exothermic reaction (energy is released), so by Le Chatelier's Principle, higher temperatures will force the equilibrium position to shift to the left of the equation favouring the production of sulphur dioxide. Lower temperatures would favour the production of the product sulphur trioxide and result in a higher yield. However, the rate of reaching equilibrium at the lower temperatures is extremely low. Higher temperature means equilibrium is established more rapidly but the yield of sulphur trioxide is lower. A temperature of 450$^0$C is a compromise whereby a faster reaction rate results in a slightly lower yield.

Similarly, at higher pressures, the equilibrium position shifts to the side of the equation in which there are the least numbers of gaseous molecules. On the left hand side of the reaction there are 3 moles of gaseous reactants, and the right hand side there are 2 moles of gaseous products, so higher pressure favours the right hand side, by Le Chatelier's Principle. Higher-pressure results in a higher yield of sulphur trioxide. A vanadium catalyst is also used in this reaction in order to speed up the rate of the reaction.

In summary, the conditions used to convert $SO_2$ to $SO_3$ is pressure a little above atmospheric, small excess of oxygen, a catalyst of vanadium oxide supported on silica and temperatures of catalyst beds of 550 $^0$C (for high rate) and 400 $^0$C (for high conversion).

3. Any unreacted gases from the above reaction are recycled back into the above reaction.
4. Sulphur trioxide, $SO_3$ (g) is dissolved in 98% (18M) sulfuric acid, $H_2SO_4$, to produce disulfuric acid or persulfuric acid, also known as fuming sulfuric acid or oleum, $H_2S_2O_7$.
   $SO_3$ (g) + $H_2SO_4$ → $H_2S_2O_7$

This is done because when water is added directly to sulphur trioxide to produce sulfuric acid the reaction is slow and tends to form a mist of sulfuric acid droplets in residual gasses ($N_2$ with some $O_2$) in which the particles refuse to coalesce.

$$SO_3 (g) + H_2O (l) \rightarrow H_2SO_4 (l)$$

5. Water is added to the disulfuric acid, $H_2S_2O_7$, to produce sulfuric acid, $H_2SO_4$
   $H_2S_2O_7$ (l) + $H_2O$ (l) → $2H_2SO_4$(l)

**5.2 Phase equilibrium**

**Common terms: phase, components and degree of freedom**

**Phase:**" The physically distinct, homogenous and mechanically separable part of a system are called phases".

**Examples**

i. A gaseous mixture constitutes a single phase since gases are completely miscible. Air is a mixture of $N_2$ , $O_2$ , $CO_2$ , water vapour etc. Which constitute a single phase.
ii. Two or more liquids which are miscible with one another constitute a single phase as there is no bounding surfaces separating the different liquids. e.g., water and alcohol, benzene & chloroform constitute one phase system.
iii. A system consisting of a liquid in equilibrium with its vapour constitute a two phase system

**Component :** The number of component of a system at equilibrium is defined as the minimum number of independently variable constituents which are required to express the composition of each phase in the system. In a chemically reactive system, the number of components is given by

$$C = N - E$$

where C = components, N = Number of chemical species, E = Number of independent equations relating the concentrations of the N species. Each independent chemical equilibrium involving the constituents counts as one equation.The condition that a solution be electrically neutral also counts as one equation if ions are considered as constituents.

**Examples**

i. **Sulphur system:** Consists of four phases namely monoclinic sulphur, rhombic sulphur, liquid sulphur and sulphurvapour. The composition of each phase of the system can be expressed in terms of sulphur only, so, it is a one component system.

ii. **Water system**: It is a one component system because the composition of each of the three phases present can be expressed as $H_20$.

iii. **$Na_2SO_4$ + water system**: Certain salts are capable of existing as hydrates with different number of water molecules of crystallization. These hydrates correspond to different solids and hence two different phases. The system is a two component , because the composition of each phase of the hydrates is completely described in terms of the anhydrous salt and water alone. e.g., $Na_2SO_4$ + water

**Degrees of Freedom :** The degree of freedom or variance of a system is defined as the minimum number of variable factors such as temperature, pressure and concentration which should be arbitrarily fixed in order to define the system completely.

**Examples**

i. For a given sample of any gas PV = nRT. Any two of the three variables P, V, T define the system completely. Hence the system is bivariant or it has two degrees of freedom.

ii. A gaseous mixture say $N_2$ and $O_2$ gases (mixed 50% each), is completely defined when three variables temperature, pressure and concentration are specified. Thus, the degrees of freedom is three or the system is trivariant.

**Note:**

- The greater the number of components in a system, the greater is the degree of freedom for a given number of phases.
- The greater the number of phases, the smaller is the number of degrees of freedom.
- The number of phases is maximum when the number of degrees of freedom = Zero, for a given number of components.

**Phase Rule**

The phase rule, also known as the Gibbs phase rule, relates the number of components and the number of degrees of freedom in a system at equilibrium by the formula:

$$F = C - P + 2$$

Where: F equals the number of degrees of freedom or the number of independent variables,

C equals the number of components in a system in equilibrium and

P equals the number of phases

The digit 2 stands for the two variables, temperature and pressure.

**Example**: In the reaction involving the decomposition of calcium carbonate on heating, there are three phases – two solid phases and one gaseous phase.

$CaCO_3$ (s) ⇌CaO (s) + CO2 (g).

There are also three different chemical constituents, but the number of components is only two because **any two constituents completely define the system in equilibrium.** Any third constituent may be determined if the concentration of the other two is known.

Substituting into the phase rule we can see that the system is univariant, since:

**F = C – P + 2 = 2 – 3 + 2 = 1.**

Therefore only one variable, either temperature or pressure, can be changed independently. (The number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium.)

**Application of Gibbs Phase Rule to One Component System:**

From the mathematical expression, **F = C – P + 2**

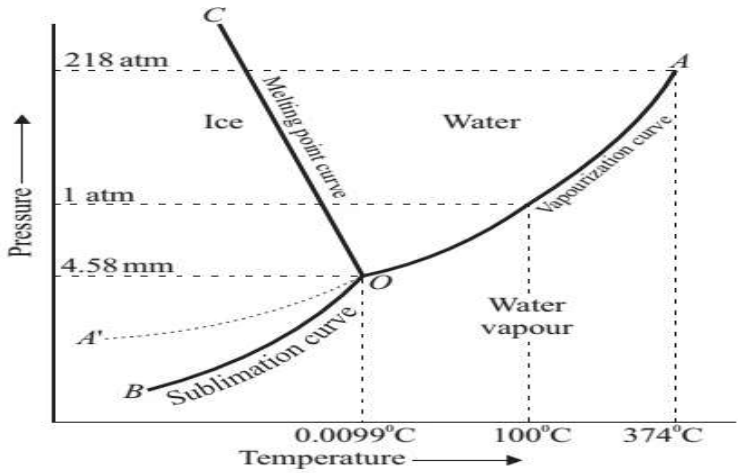
When C = 1, P = 1, F = 1-1+2 = 2

Hence, all one component systems can be completely described graphically by stating only two variables, pressure and temperature on appropriate axis.

**The Water System** : It is a one component system. Water exists in three possible phases viz. ice (solid) , water (liquid), and vapour (gas). These three single phases may form four possible equilibria.

i. Solid⇌ Liquid
ii. Liquid ⇌Vapour
iii. Solid ⇌Vapour
iv. Solid ⇌Liquid ⇌Vapour

**Phase Diagram of water system**



**The phase diagram consists of :**

i. Stable curves: three OB, OA and OC
ii. Metastable curve: one OA'
iii. Areas: three AOB, COB and AOC
iv. Triple point: One O

**Stable curves**

**OA :**It is known as vapour pressure curve of water.

- ❖ The curve OA starts from point O i.e., freezing point of water, 0.0098°C under 4.579 mm of Hg pressure and ends at A, the critical temperature ($374^0$C at 218 atm.).
- ❖ Above critical temp. on the vapour phase exists whatever may be the value of pressure
- ❖ The vapour pressure of water increases with increase in temperature.
- ❖ The rate of increase of its vapour pressure with temperature is relatively higher at higher temperatures and therefore the curve OA slants upwards and slopes away from the temperature axis.
- ❖ From phase rule, F = C – P + 2 = 1- 2 + 2 = 1
- ❖ The water vapour system is univariant

**OB :**It is the sublimation curve of ice.

- ✓ Along this curve, solid ice is in equilibrium with its vapour.
- ✓ This curve is not the prolngation of curve A but falls of more steeply.
- ✓ Curve OB starts From the temperature 0.0098°C above which solid water i.e., ice cannot exist.
- ✓ The curve terminates at B i.e., absolute zero (- 273°C). At this temperature, no vapour can exist and, therefore, only ice is left. But on other points of the curve OB, ice is in equilibrium with vapour.

Hence, there are two phases.

- ✓ According to phase rule, F = C – P + 2 = 1 – 2 + 2 =1.
- ✓ Thus, the system is univariant. This means that for each temperature; there may be one pressure and for each pressure there may be one temperature.

**OC :**This curve is the melting point curve or fusion curve of ice.

- ➢ Along this curve two phases, ice and water are in equilibrium.
- ➢ The inclination of OC line towards the pressure axis indicates that the melting point of ice is slightly lowered by increase of pressure.
- ➢ (According to Le Chatelier's principle the increase in pressure causes the water - ice equilibrium to shift in such a direction that there is a decrease in volume.).
- ➢ As the melting point of ice is accompanied by decrease in volume, it should be lowered by the increase of pressure.
- ➢ The curve OC starts from point O but there is no limit for this curve. It goes upto a point corresponding to 2000 atm. and - 20°C.
- ➢ According to phase rule, F = C – P + 2 =1-2+2 = 1.

- Thus, the system is univariant. This means that for any given pressure, melting point must have one fixed value.

**Metastable Curve**

**OA' :**It is a metastable curve shown in continuation of AO.

- When water is cooled below its freezing point (when it is not vigorously stirred) without separation of ice, the water is said to be super cooled.
- The vapour pressure curve of liquid water AO extends below O as shown by the dotted curve OA'.
- Along curve OA' liquid water coexists with vapour and vapour pressures are different than over the solid.
- This equilibrium is called metastable equilibrium as slight disturbance brings it to the stable region OB of the phase diagram.

**Areas**

- The areas give the conditions of temperature and pressure under which single phase - ice (solid), water (liquid) and vapour (gas) can exist.
- It is necessary to specify both temperature and pressure to define a system within this area.
- In the area BOC, AOC and AOB exists, ice (solid), water (liquid) and vapour (gas) respectively.
- In these areas, the degrees of freedom for the system is**two** or they are **bivariant.**

**The Triple point O**

- The point O at which the curves AO, BO and CO meet is called the triple point.
- At this point all the three phases viz , ice, water and vapour co-exist.
- Thus, P =3.
- According to phase rule, at triple point O,F = C –P + 2 =1-3+2 = 0
- Thus, the degree of freedom at triple point is zero, which indicates that there is only one set of variables P, T at which all the three phases coexist.
- If any of the variables is changed, then the number of phases decreases.

For example, if the temperature is raised, heat causes more and more of the solid (ice) to melt but no change in temperature or pressure of the system occurs till the whole of the solid has completely changed into liquid (water) and the system becomes a two phase system.

On applying the pressure to the system, vapours start condensing to liquid or solid phase. As long as there are three phases, temperature and pressure remains same.

The triple point O is a self defined point corresponding to 0.0075°C temperature and 4.579 mm of Hg pressure (difference from the ordinary freezing point,($0.000^0$C at 760mm pressure) because freezing temperature is lower than triple point temperature due to effect of high pressure and dissolved air).

## Review Exercise

Choose the Correct answer for the following questions.

1. Consider the following equilibrium:
   $2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$ + energy
   The equilibrium will shift to the left as a result of
   A. Adding a catalyst. C. Increasing the volume.
   B. Removing some $N_2O_4$. D. Decreasing the temperature.
2. Ethene, $C_2H_4$, can be produced in the following industrial system:
   $C_2H_6\ (g)$ + energy$\rightleftharpoons C_2H_4\ (g) + H_2\ (g)$
   The conditions that are necessary to maximize the equilibrium yield of $C_2H_4$ are:
   A. Low temperature and low pressure. C. Low temperature and high pressure
   B. High temperature and low pressure. D. High temperature and high pressure.
3. Consider the following equilibrium: $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$.
   The volume of the equilibrium system is increased and a new equilibrium is established. Compared to the rates in the original equilibrium, which of the following describes the rates of the forward and reverse reactions as a new equilibrium is being established?

| | FORWARD RATE | REVERSE RATE |
|---|---|---|
| A. | decreased | decreased |
| B. | increased | increased |
| C. | decreased | increased |
| D. | remained constant | remained constant |

4. Consider the following equilibrium:
   $CO_2(g) + 2H_2O(g) \rightleftarrows CH_4(g) + 2O_2(g)$
   Which of the options below indicates that the reactants are favored?
   A. Keq is zero. C. Keq is very small
   B. Keq is slightly less than 1 D. Keq is slightly greater than 1.
5. The value of Keq changes when:
   A. A catalyst is added C. The temperature changes
   B. The surface area changes. D. The concentration of reactants changes
6. Which of the following is true for a chemical reaction at equilibrium?
   A. Only the forward reaction stops
   B. Only the reverse reaction stops
   C. Both the forward and reverse reactions stop
   D. The rate constants for the forward and reverse reactions are equal
   E. The rates of the forward and reverse reactions are equal
7. Which of the following is true regarding the concentration of products, for a chemical reaction that is already at equilibrium, assuming no disruptions to the equilibrium?
   A. The concentrations of products will not change because there are no more reactants.

B. The concentrations of products will not change because the limiting reagent is gone.
C. The concentrations of products will not change because the forward and reverse rates are equal.
D. The concentrations of products will change continually because of reversibility.

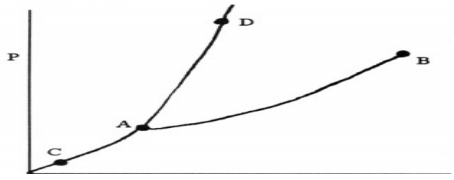
8. Which of the following are equal for a chemical system at equilibrium?
   A. The concentrations of reactant and products are equal
   B. The rate constants for the forward and reverse reactions are equal
   C. The time that a particular atom or molecule spends as a reactant and product are equal
   D. The rate of the forward and reverse reaction
9. An equilibrium that strongly favors products has:
   A. A value of K << 1.
   B. A value of K >> 1
   C. A value of Q << 1
   D. A value of Q >> 1
10. If the reaction quotient Q has a smaller value than the related equilibrium constant, K:
   A. The reaction is at equilibrium.
   B. The reaction is not at equilibrium, and will make more products at the expense of reactants.
   C. The reaction is not at equilibrium, and will make more reactants at the expense of products.
   D. The value of K will decrease until it is equal to Q
11. If the equilibrium is established by initially adding 0.10 mol each of A and B to a 1L container, then which of the following must be true once the mixture achieves equilibrium?

$$A + 2B \rightleftharpoons 2C, \quad K = 320$$

   A. [A] = [B]
   B. [B] = 2[C]
   C. [A] = [B] = [C]
   D. [A] > [B]
12. For the chemical equilibrium: $A + 2B \rightleftharpoons 2C$, the value of the equilibrium constant, K, is 10.What is the value of the equilibrium constant for the reaction written in reverse?
   $2C \rightleftharpoons A + 2B$, K = ??? Given that: $A + 2B \rightleftharpoons 2C$, K = 10
   A. 0.10 B. 100 C. 10 D. –10 E. 1
13. In which of the following does the reaction go farthest to completion?
   A. $K = 10^5$ B. $K = 10^{-5}$ C. K = 1000 D. K = 100 E. K = 1
14. Consider the equilibrium $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ at a certain temperature. An equilibrium mixture in a 4.00-L vessel contains 1.60 mol $NH_3$, 0.800 mol $N_2$, and 1.20 mol $H_2$. What is the value of Kc?
   A. 9.00 B.29.6 C.3.37 D.17.1 E.7.41
15. For the reaction system: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$, Kc = 0.020 at 720 K. If the initial concentrations of HI, $H_2$, and $I_2$ are all $1.50 \times 10^{-3}$ M at 720 K, which one of the following statements is correct?
   A. The system is at equilibrium.
   B. The concentrations of HI and $I_2$ will increase as the system is approaching equilibrium.
   C. The concentrations of $H_2$ and HI will decrease as the system is approaching equilibrium.
   D. The concentration HI will increase as the system is approaching equilibrium.
   E. The concentrations of $H_2$ and $I_2$ will increase as the system is approaching equilibrium.

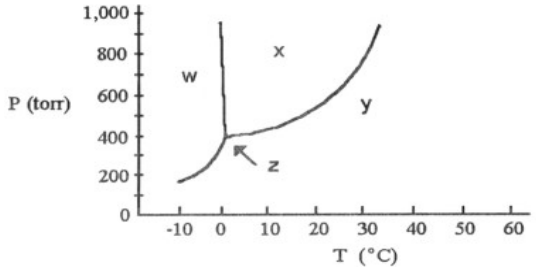
16. Exactly 1.0 mol $N_2O_4$ is placed in an empty 1.0-L container and is allowed to reach equilibrium described by the equation:$N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$. If at equilibrium the $N_2O_4$ is 20% dissociated, what is the value of the equilibrium constant (in units of mol/L) for the reaction under these conditions?
    A. 0.05 B.0.2 C.0.5 D.20 E.400
17. For the equilibrium:$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; Kc = 4.0 at 228˚C.
    Pure $PCl_5$ is added to the reaction system. At equilibrium there is 0.040 M $PCl_5$. What is the concentration of $PCl_3$ in this system?
    A. 0.16 M B. 0.20 M C. 0.40 M D. 0.80 M E. 1.6 M
18. For which of the following reactions are the numerical values of Kp and Kc the same?
    A. $2\ CO(g) + O_2(g) \rightleftharpoons 2\ CO_2(g)$ C. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
    B. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ D. $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$
19. Which of the following equilibria would not be affected by volume changes at constant temperature?
    A. $2\ NO_2(g) \rightleftharpoons N_2O_4(g)$ C. $2\ NO(g) + 3\ F_2(g) \rightleftharpoons 2\ F_3NO(g)$
    B. $F_3(g) + NH_3(g) \rightleftharpoons H_3NBF_3(s)$ D. $O_3(g) + NO(g) \rightleftharpoons NO_2(g) + O_2(g)$
20. Gibbs phase rule for general system:
    A. P+F=C-1 B. P+F=C+1 C. P+F=C-2 D. P+F=C+2
21. In a single-component condensed system, if degree of freedom is zero, maximum number of phases that can co-exist:
    A. 0 B.1 C.2 D. 3
22. Based on the equilibrium constants given, in which of these reactions are the products most favoured over the reactants?
    A. Keq = 0.002 B. Keq = 0.0 C. Keq = 3.5 D. Keq = $6.0 \times 10^{-4}$
23. Which of the statements regarding the effect of reactant or product concentration changes on equilibrium is false?
    A. Adding a reactant always shifts a reversible reaction in the direction of reactants.
    B. Removing a reactant always shifts a reversible reaction in the direction of reactants.
    C. Adding a product causes a reversible reaction to shift in the direction of the formation of the reactants.
    D. Removing a product shifts a reversible reaction in the direction of formation of products.
24. Which of the following statements correctly describes the effect of an increase in temperature on the position of equilibrium for an exothermic reaction?
    A. The position of equilibrium does not change if you change the temperature.
    B. According to Le Châtelier's Principle, the position of equilibrium will move to the left if the temperature is increased.
    C. If you increase the temperature, the position of equilibrium will move in such a way as to increase the temperature again.
    D. Equilibrium will shift to favour the reaction which releases heat in this context.

25. Which explanation best describes why a catalyst does not affect the position of equilibrium?
    A. A catalyst will increase the activation energy in both directions; therefore, no shift in the position of equilibrium will result.
    B. The position of equilibrium is not affected by adding a catalyst since a catalyst speeds up both the forward and back reactions by exactly the same amount.
    C. Equilibrium constants are not affected by adding a catalyst since no shift in the position of equilibrium occurs.
    D. Not all chemical reactions respond to catalysts.
26. Which one of the following statements regarding a dynamic equilibrium is false?
    A. At equilibrium, there is no net change in the system
    B. At equilibrium, the concentration of reactants and products stays the same
    C. At equilibrium, the forward and back reactions cease to occur
    D. At equilibrium, the rates of the forward and back reactions are identic
27. $K_1$ and $K_2$ are the velocity constants of the forward and back ward reactions. The equilibrium constant K of the reaction is:
    A. $K_1xK_2$ B.$K_1$-$K_2$ C.$K_1/K_2$ D.$\frac{K1+K2}{K1-K2}$
28. The rate of $Kp/Kc$ for the reaction: CO (g) + ½ $O_2$ (g) ⇌$CO_2$ (g)is:
    A. 1 B. $(RT)^{1/2}$ C. RT D.$(RT)^{-1/2}$
29. Equilibrium constant greater than 1 means:
    A. Equilibrium constant lies to the right , products predominate.
    B. Equilibrium constant lies to the left, reactants predominate.
    C. Equilibrium constant lies to the right, reactants predominate.
    D. Equilibrium constant lies to the left, products predominate
30. Equilibria in which all substances are in the same phases are called
    A. Homogeneous equilibria. C. Heterogeneous equilibria.
    B. Equilibrium constant D. Equilibrium constant expression
31. Which of the following statements is NOT true in relation to the triple point on a single component phase diagram?
    A. The point at which the solid, liquid and gaseous phases for a substance co-exist
    B. The triple point exists for a substance occurs at a specific temperature and pressure
    C. The triple point exists at a single temperature and is independent of pressure
    D. The system must be enclosed so that no vapour can escape
32. On the phase diagram shown below, segment _____corresponds to the conditions of temperature and pressure under which the solid and the gas of the substance are in equilibrium.



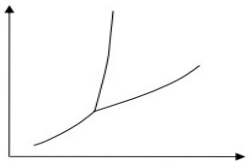

    A. AD B.BC C.AC D. AB
33. On the phase diagram shown above(Question number 32), the coordinates of point correspond to the critical temperature and pressure.
    A. A B.B C.C D. D

34. According to the phase diagram shown below, the normal boiling point of this substance is:




A. 10 B. -3 C. 29 D. 38 E. 0

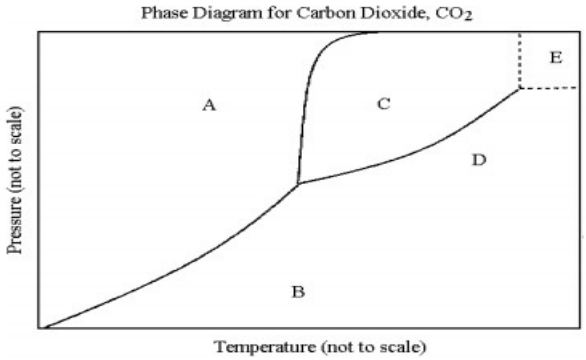
35. The phase diagram of oxygen ($O_2$) includes the following points:
- Critical point: Tc = 154.5 K, Pc = 49.3 atm
- Triple point: $T_{t.p.}$ = 54.33 K, Pt.p. = 0.00150 atm
- Normal melting point: $T_{fus}$ = 54.8 K
- Normal boiling point: $T_{vap}$ = 90.2 K
- You may wish to use the sketch below to help you answer the question.



Under which one of the following conditions is oxygen a liquid?

A. T = 50. K, P = 0.80 atm
B. T = 90. K, P = 0.20 atm
C. T = 150. K, P = 1.0 atm
D. T = 60. K, P = 0.50 atm
E. T = 100. K, P = 0.050 atm

36. Consider the phase diagram for $CO_2$.




In going from phase A to phase B,

A. Gaseous $CO_2$ becomes solid.
B. Solid $CO_2$ becomes liquid.
C. Liquid $CO_2$ becomes gaseous.
D. Solid $CO_2$ becomes gaseous.
E. Liquid $CO_2$ becomes solid.

37. Consider the phase diagram for $CO_2$ above (question number 36).
The point on the graph labelled E represents $CO_2$as:

A. Gas.
B. Solid.
C. Supercritical fluid.
D. $CO_2$ cannot exist at that temperature and pressure.

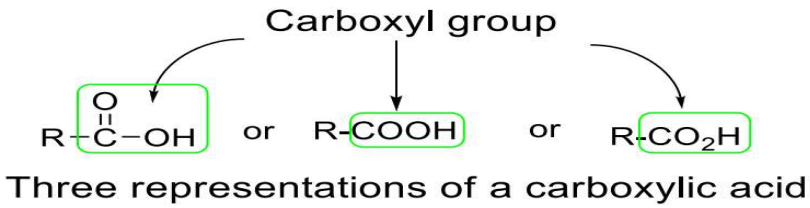
# UNIT 6

## Carboxylic Acids, Esters, Fats and Oils

***Main* topics**

- Carboxylic Acids
- Esters
- Fats and Oils

**Carboxylic acids** are organic compounds containing the carboxyl group (-COOH), wherein the hydroxyl group (-OH) is directly attached to the carbonyl (C=O) group.



Three representations of a carboxylic acid

**Nomenclature of Carboxylic Acids**

The common names of some basic carboxylic acids are derived from Latin names that indicate the first original natural source of the carboxylic acid.

| Structure of Acid | Natural Source | Common Name |
|---|---|---|
| $H-\overset{O}{\overset{\|}{C}}-OH$ | Ants (Formica) | Formic acid |
| $CH_3-\overset{O}{\overset{\|}{C}}-OH$ | Vinegar (Acetum) | Acetic acid |
| $CH_3CH_2-\overset{O}{\overset{\|}{C}}-OH$ | Basic Fat (Propio) | Propionic acid |
| $CH_3CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$ | Rancid butter (Butyrum) | Butyric acid |
| $CH_3CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$ | Present in aValerian herb | Valeric acid |
| $CH_3CH_2CH_2CH_2CH_2-\overset{O}{\overset{\|}{C}}-OH$ | Goat (Caper) | Caproic acid |

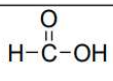
**Common Names of Carboxylic Acids**

The common name of a carboxylic acid (R-COOH) is derived by adding the suffix –ic acid to a prefix representing the chain length of the carboxylic acid.

| # of Carbons | Prefix | Common Name of Acid |
|---|---|---|
| 1 | Form- | Formic acid |
| 2 | Acet- | Acetic acid |
| 3 | Propion- | Propionic acid |
| 4 | Butyr- | Butyric acid |
| 5 | Valer- | Valeric acid |
| 6 | Capro- | Caproic acid |
| Aromatic acid | Benzo- | Benzoic acid |

**IUPAC Nomenclature of Aliphatic Carboxylic Acids**

IUPAC names of straight chain aliphatic carboxylic acids are derived by adding the suffix –oic acid to the systematic name of the parent hydrocarbon. They are named as alkanoic acids

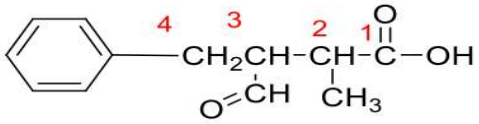
| # of Carbons | Structure & IUPAC Name of Alkane | Structure & IUPAC Name of Acid |
|---|---|---|
| 1 |  Methane |  Methan**oic acid** |
| 2 | $CH_3-CH_3$ Ethane | $CH_3-C(=O)-OH$ Ethan**oic acid** |
| 3 | $CH_3CH_2-CH_3$ Propane | $CH_3CH_2-C(=O)-OH$ Propan**oic acid** |

**Systematic Nomenclature of Substituted Carboxylic Acids**

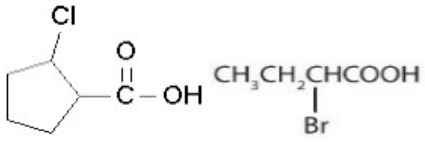
The systematic names of substituted aliphatic carboxylic acids are derived by:

i. First identifying the parent chain that contains most, if not all, the carboxyl groups.
ii. Number the parent chain from the carbon of the carboxyl group i.e the carboxyl carbon is C-1.
iii. Identify the substituents and assign each substituent a locator/address number (2,3,4…etc.) consistent with the numbering in the parent chain.
iv. Arrange the names of the substituents in alphabetical order in the systematic name of the poly-substituted carboxylic acid.

**Examples:**



3-Formyl-2-methyl-4-phenylbutanoic acid



2-chlorocyclopentanoic acid

$ClCH_2CH_2CH_2COOH$

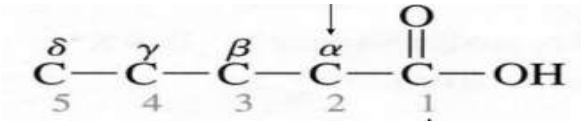
4-chlorobutanoic acid

**Naming using Greek letters α β γ δ ε**

There are two ways to identify substituent carbons in carboxylic acid:

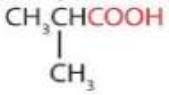
- ✓ numbers or
- ✓ Greek letters.

Using numbers, the carboxyl group carbon is given the number one.

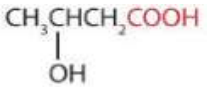



Greek letters are used to designate the position of substituent relative to the carbon of the carboxyl group. The carbon of the carboxyl group is NOT given a Greek letter.

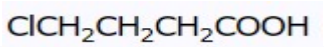
**Examples:**



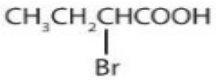

α-Methylpropionic acid




β-Hydroxybutyric acid




γ-chlorobutyric acid

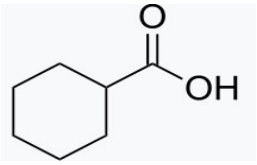



α-bromobutyric acid

**Systematic Nomenclature of Cyclic Carboxylic Acids**

The systematic name of a carboxylic acid in which the COOH group is attached directly to a ring is derived by adding a suffix – carboxylic acid to the name of the attached cycloalkane or cycloalkene or arene.

**Example:**

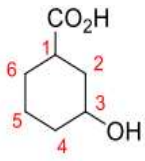



**Cyclohexanecarboxylic acid**

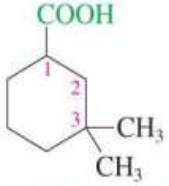
When such carboxylic acids are substituted, the carbon of the COOH group is itself not numbered, but it is, by convention, taken to be attached to C-1 of the ring.

**Systematic Nomenclature of Substituted Cyclic Carboxylic Acids**

For substituted carboxylic acids with the carboxyl group attached directly to a ring, the carbon of the COOH group is itself not numbered, but it is, by convention, taken to be attached to C-1 of the ring.

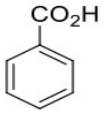



3-Hydroxycyclohexanecarboxylic acid




3,3-dimethylcyclohexanecarboxylic acid

Under this system of nomenclature, benzoic acid would be named as benzenecarboxylic acid.

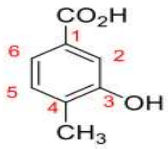



Benzenecarboxylic acid (benzoic acid)

**IUPAC Nomenclature of Substituted Aromatic Carboxylic Acids**

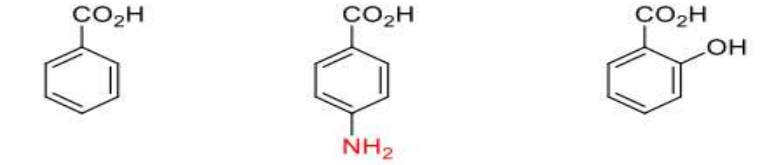
Substituted aromatic acids with one carboxyl group are named as derivatives of benzoic acid, with the position of substituents being cited using the locators (2,3etc) according to their position on the benzene ring relative to the carboxyl group. The carbon on which the carboxyl group is attached is by convention C-1

Example:




3-Hydroxy-4-methylbenzoic acid or 3-Hydroxy-4-methylbenzenecarboxylic acid

Typically aromatic acids of the form Ar-CO2H are named as derivatives of benzoic acids, with ortho, meta and para indicating the location relative to the carboxyl group. (Recall that this is non-IUPAC).




*benzoic acid* *p-aminobenzoic acid* *o-hydroxybenzoic acid*

**Systematic Nomenclature of Dicarboxylic Acids**

The systematic name of an open chain aliphatic dicarboxylic acid is derived by adding a suffix -dioic acid to the name of the parent hydrocarbon i.e. alkanedioic acid.

| Systematic Name | Common Name | Structure |
|---|---|---|
| Ethanedioic acid | Oxalic acid | $HO_2C\text{-}CO_2H$ |
| Propanedioic acid | Malonic acid | $HO_2CCH_2CO_2H$ |
| Butanedioic acid | Succinic acid | $HO_2C(CH_2)_2CO_2H$ |
| Pentanedioic acid | Glutaric acid | $HO_2C(CH_2)_3CO_2H$ |
| Hexanedioic acid | Adipic acid | $HO_2C(CH_2)_4CO_2H$ |
| Heptanedioic acid | Pimelic acid | $HO_2C(CH_2)_5CO_2H$ |

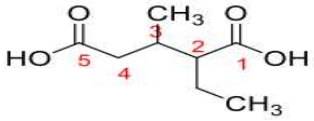
**Systematic Nomenclature of Substituted Dicarboxylic Acids**

The systematic name of an aliphatic dicarboxylic acid is derived by:

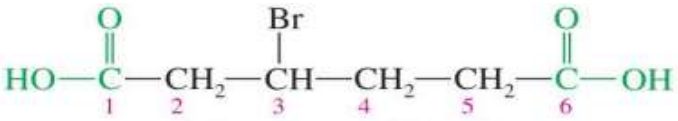
i. First identifying the parent chain that contains the two carboxylic acid groups and then adding a suffix -dioic acid to the name of the parent hydrocarbon.

ii. The parent chain is numbered from the end that gives the substituents in the chain the lowest possible address number.
iii. The substituents are arranged in alphabetical order in the full name of the dicarboxylic acid.

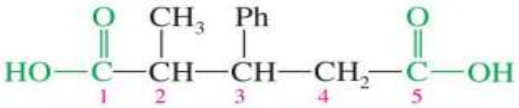
**Examples:**



**2-Ethyl-3-Methylpentanedioic acid**



3-bromohexanedioic acid



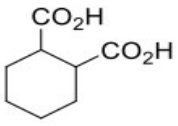
2-methyl-3-phenylpentanedioic acid

**Systematic Nomenclature of Cyclic Dicarboxylic Acids**

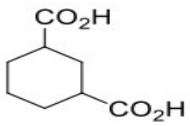
The systematic name of a cyclic aliphatic or aromatic dicarboxylic acid is derived by adding a suffix -dicarboxylic acid to the name of the parent cycloalkane or arene i.e.

**cycloalkanedicarboxylic acid or arenedicarboxylic acid.**

**Examples**



Cyclohexane-1,2-dicarboxylic acid



Cyclohexane-1,3-dicarboxylic acid



4-Methylbenzene-1,3-dicarboxylic acid



4-Methylbenzene-1,2-dicarboxylic acid

The positions of the two carboxyl groups are cited with the lowest possible address numbers to differentiate between isomers.

**Exercise**

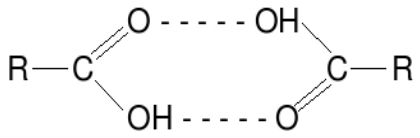
1. Draw the structure for each compound.
   a. heptanoic acid
   b. 2,3-dibromobenzoic acid
   c. 3-methylbutanoic acid
   d. β-hydroxybutyric acid
2. Draw the structure for each compound.
   a. *o*-nitrobenzoic acid
   b. 3-chloropentanoic acid
   c. *p*-chlorobenzoic acid
   d. α-chloropropionic acid

3. Name each compound with either the IUPAC name, the common name, or both.
   a. $(CH_3)_2CHCH_2COOH$ c. $(CH_3)_3CCH(CH_3)CH_2COOH$
   b. $CH_2OHCH_2CH_2COOH$
4. Name each compound with its IUPAC name.
   a. $CH_3(CH_2)_8COOH$ c. $(CH_3)_2CHCCl_2CH_2CH_2COOH$
   b. $CH_3CHOHCH(CH_2CH_3)CHICOOH$

**Properties of Carboxylic Acids**

**Physical Properties of Carboxylic Acids**

- ✓ Carboxylic acids hydrogen bond to themselves to form a dimer:




- ✓ Carboxylic acids also form hydrogen bonds to water molecules:
- ✓ Since carboxylic acids can form more than one set of hydrogen bonds, their boiling points are usually higher than those of other molecules of the same molecular weight (MW).
- ✓ Low-MW carboxylic acids are generally liquids at room temp. (often, they are somewhat oily); higherMW carboxylic acids are generally waxy solids.
- ✓ Carboxylic acids with 12 to 20 carbon atoms are often referred to as fatty acids, since they are found in the triglycerides in fats and oils (more later).
- ✓ Short-chain carboxylic acids are also generally more soluble in water than compounds of similar MW, since they can hydrogen bond to more than one water molecule.
- ✓ As the number of carbons in a carboxylic acid series becomes greater, the boiling point increases and the solubility in water decreases.
- ✓ Many carboxylic acids that are liquids at room temperature have characteristically sharp or unpleasant odors.

  Ethanoic acid/acetic acid is the main ingredient in vinegar.

  Butanoic acid is partially responsible for the odor of locker rooms and unwashed socks.

  Hexanoic acid is responsible for the odor of Limburger cheese.
- ✓ Like most acids, carboxylic acids tend to have a sour taste (e.g., vinegar, citric acid, etc.)

**Exercise: Predicting Physical Properties**

Arrange the following compounds in order of increasing boiling point. (All of the compounds have about the same molecular weight.)

a. 1-pentanol b. hexane c. butanoic acid d. pentanal

b. Which member of each of the following pairs of compounds would you expect to have a higher solubility in water?

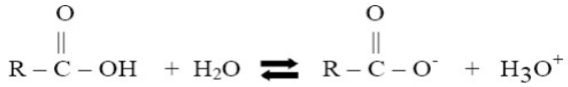
   2-butanone or propanoic acid hexanoic acid or ethanoic acid

**Reactions of Carboxylic Acids**

The reactions of carboxylic acids can be directed to various sites on the carboxyl group Reactions of carboxylic acids can be placed into four categories:

i. Reactions at the acidic hydrogen on the carboxyl group.
ii. Reactions at the carbonyl group
iii. Reactions at the carboxylate oxygen
iv. Reactions that lead to loss of the carboxyl group as $CO_2$

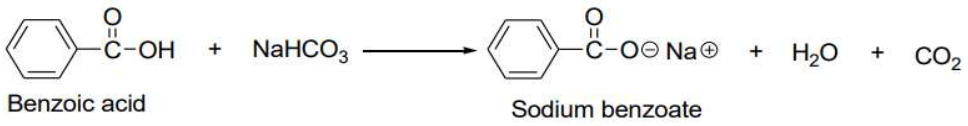
**Reaction with water**



**Reaction of Carboxylic Acids with Sodium Bicarbonate**

Most carboxylic acids (pKa≈ 5) are stronger acids than carbonic acid ($H_2CO_3$ ) (pKa 6.4). Consequently they displace carbonic acid from its salts (hydrogen carbonates). The most reliable test for carboxylic acids employs $NaHCO_3$ leading to evolution of $CO_2$ . This is commonly called the bicarbonate test for carboxylic acids.

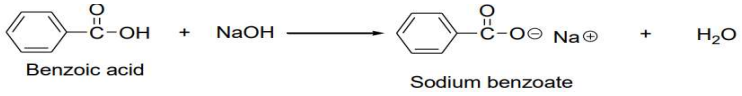
Example:




**Reactions of Carboxylic Acids with Strong Bases**

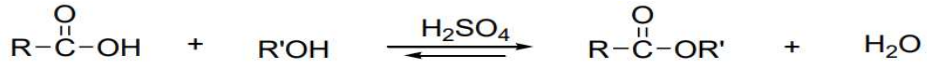
Bases such as metal hydroxides (NaOH and KOH) and amines abstract the acidic proton on carboxylic acids to form carboxylate salts.

**Example**

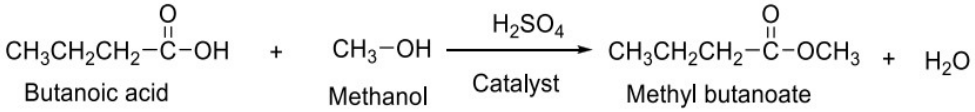



**Acid-Catalysed Esterification of Carboxylic Acids**

The traditional method for converting carboxylic acids to esters is through an acid-catalyzed esterification in the presence of an alcohol: Commonly referred to as the Fischer esterification.



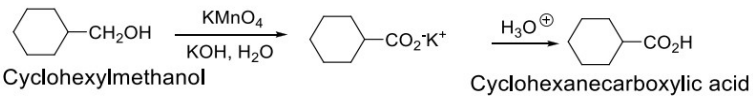
**Example:**

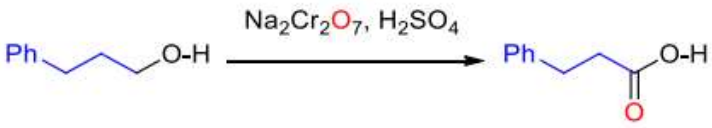



**Synthesis of Carboxylic Acids**

**A. Oxidation of Primary Alcohols to Carboxylic Acids**

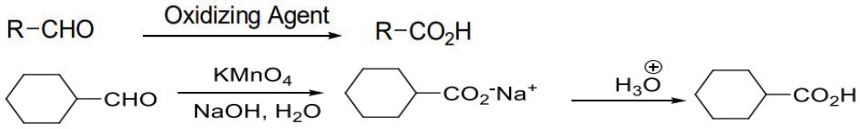
The best conditions for the oxidation of primary alcohols to carboxylic acids is under the basic conditions employing potassium permanganate.





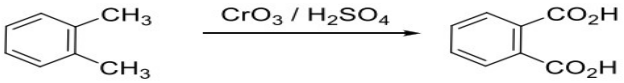

### B. Oxidation of Aldehydes to Carboxylic Acids

Aldehydes can be oxidised to carboxylic acids by a variety of oxidizing agents. Both strong and mild oxidizing agents may be employed successfully.




### C. Side-Chain Oxidation of Alkylbenzenes to Benzoic Acids

Oxidation of alkylbenzenes using strong oxidizing agents provides benzoic acids. The entire alkyl chain, regardless of its length, is oxidised to a carboxyl (-COOH) group




**Fatty acids**

- ✓ These are monocarboxylic organic acids, which usually contain an even number of carbon atoms.
- ✓ The general formula of fatty acid is R-COOH
  **Example:** $CH_3 – CH_2 – CH_2 – CH_2 – CH_2 – COOH$
- ✓ They are further classified into:Saturated & Unsaturated fatty acidsaccording to absence or presence of double bonds.

**A.** Saturated fatty acids

- They have no double bonds.
- They have the general formula : $CH_3 – (CH_2)_n – COOH$.
- They are further classified, according to the number of carbon atoms, into: Short chain & Long chain fatty acids.

| | Short chain FA | Long chain FA |
|---|---|---|
| Number of carbon atoms | Less than 10 carbons ( 2C to 10C ) | More than 10 carbons |
| Consistency at room temperature | Liquid | Solid |
| Volatility | Volatile | Nonvolatile |
| Solubility in water | Soluble | Insoluble |
| Examples | Acetic (2 C)<br>Butyric (4 C) | Palmetic (16 C)<br>Stearic (18 C) |

The following table shows the formula of the most common saturated fatty acids.

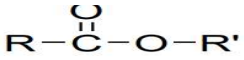
| Common name | Formula |
|---|---|
| Acetic acid (2C) | $CH_3 - COOH$ |
| Butyric acid (4C) | $CH_3 - (CH_2)_2 - COOH$ |
| Caproic acid (6C) | $CH_3 - (CH_2)_4 - COOH$ |
| Palmitic acid (16C) | $CH_3 - (CH_2)_{14} - COOH$ |
| Stearic acid (18C) | $CH_3 - (CH_2)_{16} - COOH$ |
| Arachidic acid (20C) | $CH_3 - (CH_2)_{18} - COOH$ |
| Lignoceric acid (24C) | $CH_3 - (CH_2)_{22} - COOH$ |

**B. Unsaturated fatty acids**

- They have one or more double bonds.
- Most of the double bonds are of cis type

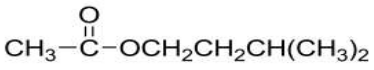
**Esters**

Structurally, an ester is a compound that has an alkoxy (OR) group attached to the carbonyl group.

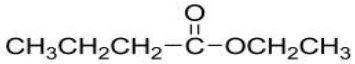


R may be H, alkyl or aryl, while R' may be alkyl or aryl only. Esters are widespread in nature. Many of the fragrances of flowers and fruits are due to the esters present. Ethyl butanoate is the chief component that accounts for the pineapple-like aroma and flavour of pineapples.

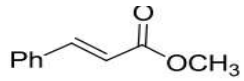
**Examples**



Isopentyl ethanoate
(Banana aroma)



Ethyl butanoate
(Pineapple aroma)

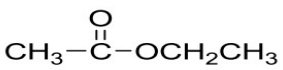


Methyl *trans*-cinnamate
(Strawberry aroma)

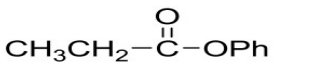
**Nomenclature of Esters**

- Names of esters consist of two words that reflect the composite structure of the ester The first word is derived from the alkyl group of the alcohol component, and the second word from the carboxylate group of the carboxylic acid component of the ester.
- The name of the carboxylate portion is derived bysubstituting the -ic acid suffix of the parent carboxylic acid with the –ate suffix.
- The alkyl group is cited first followed by the carboxylate group separated by a space. An ester is thus named as an alkyl alkanoate.

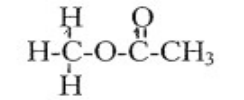
**Examples**



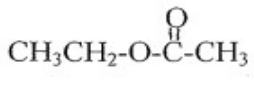
Ethyl ethanoate



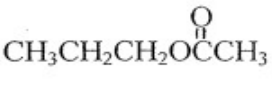
Phenyl propanoate



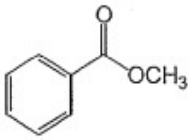
Methyl ethanoate or Methyl acetate



ethyl ethanoate or ethyl acetate



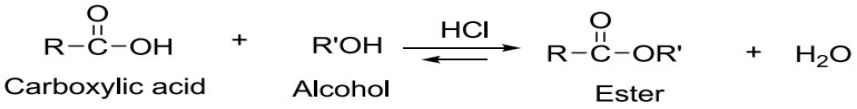
propyl ethanoate or propyl acetate



Methyl benzoate

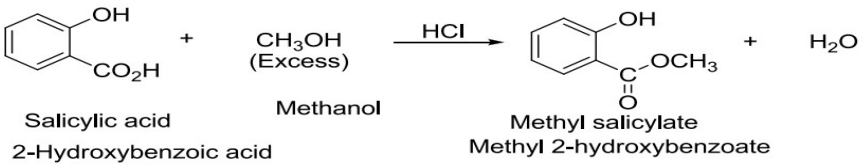
**Synthesis of Esters**

**Acid-Catalysed Esterification of a Carboxylic Acid and an Alcohol**




The acid-catalysed reaction of carboxylic acids and alcohols provides esters. Typically, a catalytic amount of a strong inorganic (mineral) acid such as $H_2SO_4$ ,HCl and $H_3PO_4$ is used.

**Examples:**




$CH_3COOH + C_2H_5OH \Leftrightarrow CH_3COOC_2H_5 + H_2O$

$C_6H_5COOH + C_2H_5OH \Leftrightarrow C_6H_5COOC_2H_5 + H_2O$

**Physical properties**

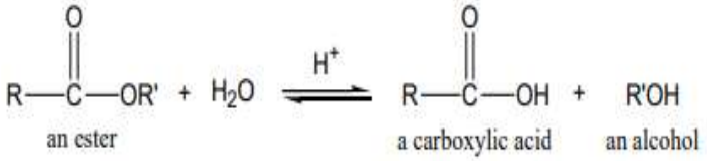
- Most of the esters are liquids with much lower boiling point than those of the acids or alcohols of nearly equal weight, this is due to the absence of the polar hydroxyl group which found in alcohols and acids and leads to the association of the alcohol and carboxylic acid molecules with hydrogen bonds.
- Esters have a neutral effect on litmus.
- The boiling point of the ester is less than the boiling point of the acid and alcoholforming it due to the absence of polar hydroxyl group (presents in alcohols and acids) which has the ability to form hydrogen bonds between molecules and water.
- The solubility degree of ester in water is less than that of the corresponding acid due to the absence of polar hydroxyl group (presents in alcohols and acids) which has the ability to form hydrogen bonds between molecules and water.

Reactions of Ester

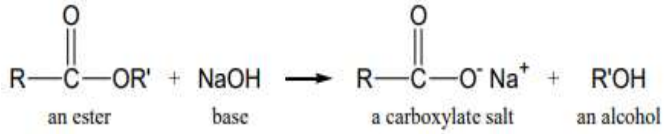
Hydrolysis of esters: Alcohol and acid are produced from the hydrolysis of ester, this reaction reverse to ester formation, Hydrolysis may take place by the use of dilute mineral acids as a as

a catalyst and is called acid hydrolysis, Dilute mineral acid ($H^+$) is used to prevent the reversible reaction.
This is essentially the reverse reaction of the synthesis of esters from carboxylic acids and alcohols.

Example: $CH_3COOC_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$




Hydrolysis of esters may also be carried out by heating with aqueous alkalies, to produce the alcohol and the salt of the acid, this is called alkaline-hydrolysis or saponification, (since soap is the sodium salt of high carboxylic acids), NaOH is added to react with the produced acid converting it to salt and prevent the reversible reaction.



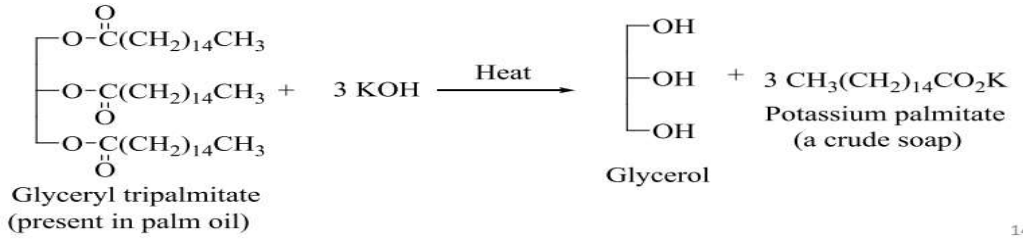

**Examples:**

$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

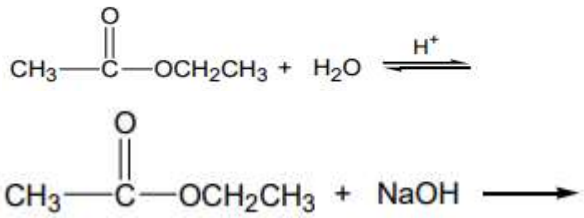
$C_6H_5COOC_2H_5 + NaOH \rightarrow C_6H_5COONa + C_2H_5OH$

For historical reasons, ester hydrolysis in aqueous hydroxide (KOH or NaOH) is called saponification because it was used in the manufacture of soap through the reaction of oils or fats (triesters or triglycerides) with lye (contains mainly KOH).

- Hydrolysis of esters is the reaction of the ester with water (in an acidic medium) to form acid and alcohol
- Saponification is the heating of ester with aqueous alkalis to produce the alcohol and the salt of the acid, Soap is the sodium salt of high fatty carboxylicacids**.**



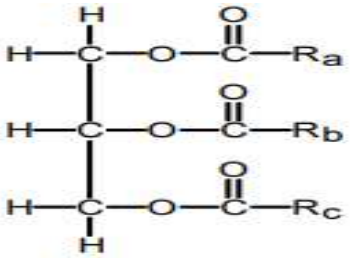

**Exercise: Complete the following reactions**




**Fats and Oils**

Fats and oils belong to a group of biological substances called lipids. Lipids are biological chemicals that do not dissolve in water. Fats differ from oils only in that they are solid at room

temperature, while oils are liquid. Fats and oils share a common molecular structure, which is represented by the formula below.



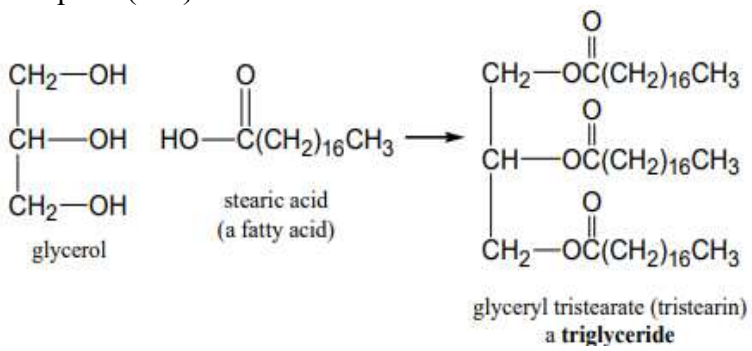
This structural formula shows that fats and oils contain three ester functional groups. Fats and oils are esters of the tri-alcohol, glycerol (or glycerine). Therefore, fats and oils are commonly called triglycerides, although a more accurate name is triacylglycerols. One of the reactions of triglycerides is hydrolysis of the ester groups.

Fats and oils:

- ❖ They are estersof fatty acids with glycerol.
- ❖ They are similar chemically, but they differ in physical properties as oils are liquid while fats are solid at room temperature.
- ❖ They are called triglycerides because they are triesters formed of glycerol and 3 fatty acids.

**Triglycerides**

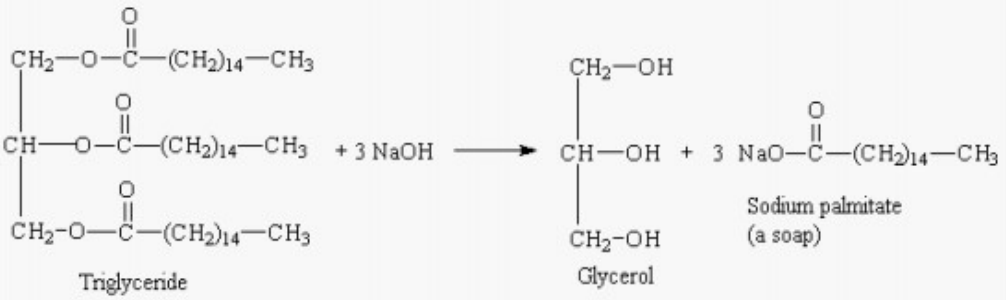
- Fats and oils are both triglycerides; the only difference is that fats are solids at room temperature and oils are liquids at room temperature.
- Long-chain carboxylic acids, often referred to as fatty acids, are stored by living organisms by combining them with glycerol to produce tri-esters called triglycerides.
- Triglycerides at room temperature are usually either solids or semi-solids (fats), or viscous liquids (oils).



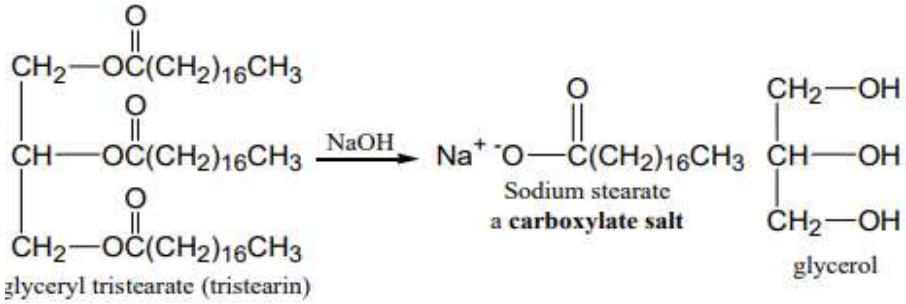

**Hydrolysis of triglycerides**

The hydrolysis of triglycerides can be carried out with base and this is the common way of doing it on an industrial scale. The hydrolysis and neutralization are carried out simultaneously and produces soap in a one step reaction called **saponification.**

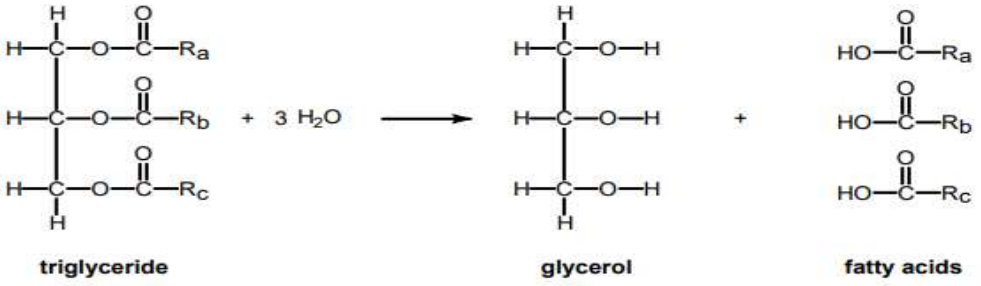
Triglycerides can be broken apart under basic conditions (a saponification reaction) to produce long-chain carboxylate salts




**Example:**




**Triglycerides** (fats) can be hydrolyzed to produce glycerol and 3 fatty acids in the presence of acid and heat or with a suitable lipase enzyme under biological conditions.




This hydrolysis reaction produces glycerol and fatty acids, which are carboxylic acids derived from fats and oils. In the fatty acids, Ra, Rb, and Rc, represent groups of carbon and hydrogen atoms in which the carbon atoms are attached to each other in an unbranched chain.

The hydrolysis reaction is promoted by acids and by bases. When a strong base such as NaOH (lye) is used, the product contains salts of the fatty acids. These salts of fatty acids are the functional ingredient in soap. The ingredients lists of some soaps include sodium tallowate, a generic name for the mixture of fatty acid salts obtained from tallow (animal fat), and sodium cocoate, obtained from coconut oil.

**Hardening of oils**

Chemically, the hydrogenation of oils is the reduction of the double bonds in unsaturated fatty acids to single saturated bonds, by the reaction of hydrogen gas in the presence of a metal catalyst.

**Rancidity**

Rancidity is a condition in which fat attains a bad taste and disagreeable odour.

### Types of rancidity

There are 2 types of rancidity:

1. Hydrolytic rancidity
2. Oxidative rancidity

**Hydrolytic rancidity:** Fats are hydrolyzed into glycerol and fatty acids in presence of moisture .warm temperature and bacterial enzymes.

**Oxidative rancidity:** It occurs by oxidation of unsaturated fatty acidspresent in fats and oils forming lipid peroxides, fatty aldehydes, ketones and short chain fatty acids.

Rancidity is predisposed by: light, moisture, warm and temperature

Rancidity leads to:

- Fats and oils attain bad taste.
- Fats and oils attain disagreeable odour.
- Production of toxic compounds as lipid peroxidies, aldehydes and ketones.

Preventionof rancidity:

- Avoid exposure of fats to light, moisture and hightemperature.
- Addition of antioxidants to fats and oils.

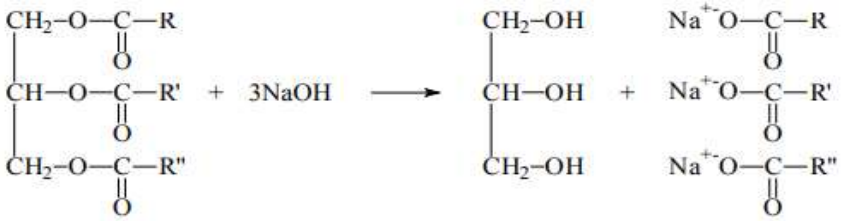
**Soaps and detergents**

**Soaps** are water-soluble sodium or potassium salts of fatty acids. Soaps are made from fats and oils, or their fatty acids, by treating them chemically with a strong alkali.

Saponification of fats and oils is the most widely used soapmaking process.

Soaps are the product of the reaction between a fat and sodium hydroxide:

**fat + 3NaOH → glycerine + 3 soap**

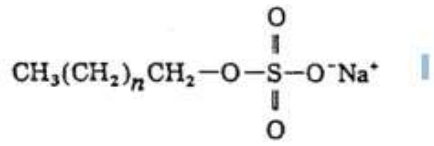



**Detergent**

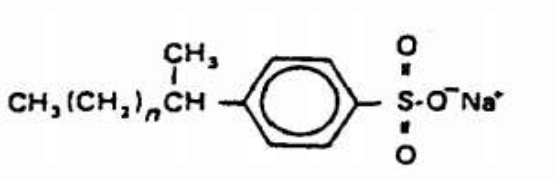
Detergents are complex formulations that contain more than 25 different ingredients, which can be categorized into the following main groups:

1. Surfactants
2. Bleaching agents
3. Builders
4. Additives

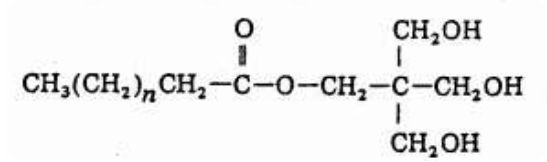
Detergents are structurally similar to soaps, but differ in the water-soluble portion. Three examples of detergents are shown below.



a sodium alkyl sulfate



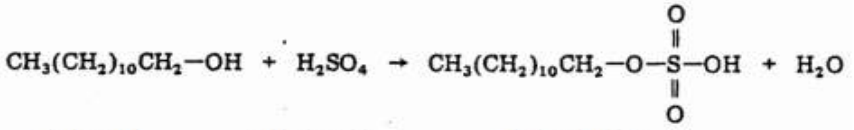
a sodium alkylbenzene sulfonate



a glycerol (a non-ionic detergent)

**Preparation of a detergent**

A synthetic detergent, a sodium alkyl sulfate called sodium dodecylsulfate, will be prepared by reacting dodecyl alcohol (dodecanol) with sulfuric acid.



dodecanol sulfuric acid dodecylsulfate

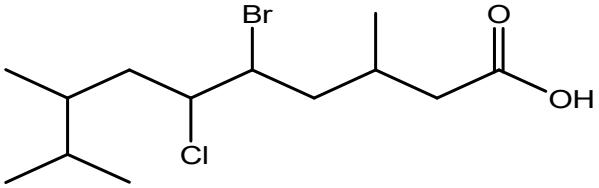
When a soap or detergent is added to water, a polar solvent, the molecules form clusters, known as **micelle**s, in which the polar ends of the molecules are on the outside of the cluster and the non-polar ends are in the middle.

The cleaning action of both soaps and detergents results from their ability to emulsify or disperse water-insoluble materials (dirt, oil, grease, etc.) and hold them in suspension in water. This ability comes from the molecular structure of soaps and detergents. When a soap or detergent is added to water that contains oil or other water-insoluble materials, the soap or detergent molecules surround the oil droplets. The oil or grease is “dissolved” in the alkyl groups of the soap molecules while the ionic end allows the micelle to dissolve in water. As a result, the oil droplets are dispersed throughout the water (this is referred to as emulsification ) and can be rinsed away.

## Review Exercise

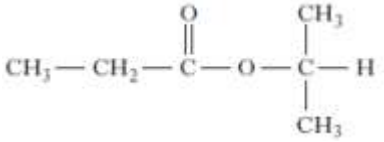
**Choose the correct answer for the following questions**

1. Which of the following statements is **true** about ester?
   A. Ester form intermolecular hydrogen bonding to each other
   B. Ester molecules can form intra molecular hydrogen bonds
   C. Ester have higher boiling point than alcohols of comparable molecular weight
   D. Ester molecules cannot form intra molecular hydrogen bonds
2. A chemical name for Asprin is;
   A. Salicyclic acid C. Methyl salicylate
   B. Acetyl salicyclic acid D. Sodium salicylate
3. Detergents are preferable to hard soap for washing (cleaning process). This because detergents
   A. Made with chemicals that are not affected by hard water.
   B. Work equally well with hard and soft water
   C. Are cheaper in price than hard soap
   D. Are manufactured more easily than soaps
4. $C_{57}H_{104}O_6 + 3H_2 \xrightarrow{Ni} C_{57}H_{110}O_6$
   Olein Stearin
   Which of the following is false from the above reaction?
   A. Stearin is a saturated glyceride C. Olein is solid at ordinary temperature
   B. Olein is an unsaturated glyceride D. The reaction is hydrogenation reaction
5. Which of the following is an acceptable IUPAC name for the organic compound shown below?



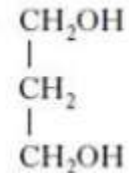
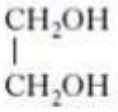
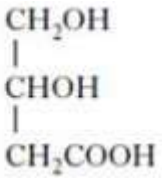
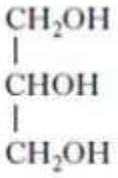

   A. 5-chloro-6-bromo-3, 8, 9-trimethyl dodecanoic acid.
   B. 5-chloro-6, 3, 8-trimethyl-5-bromo decanoic acid.
   C. 5-bromo-6-chloro-3, 8-dimethyl nonanoic acid.
   D. 5-bromo-6-chloro-3, 8, 9-trimethyl decanoic acid.
6. A lipid is any substance of biochemical origin that is;
   A. Soluble in both water and non-polar solvents
   B. Insoluble in both water and non-polar solvents
   C. Soluble in water but insoluble in non-polar solvents
   D. Soluble in non-polar solvents but insoluble in water
7. Fats and oils develop unpleasant odour due to:
   A. Rusting C. Solidification
   B. Evaporation D. Rancidity
8. Which of the following occurs when a **greasy cloth** is placed in soapy water?
   A. The hydrophobic tail of the soap bonds to grease
   B. The hydrophilic head bonds to grease
   C. Non – polar tails are embedded in to water
   D. Charged head groups are embedded to grease

9. Which of the following is true about the chemical decomposition of Fats and Oils?
   A. Oxidative rancidity occurs when the double bond of an unsaturated fatty acid react chemically with hydrogen
   B. Microbial rancidity refers to a process in which microorganisms use their enzymes to break down chemical structure in the fat or oil
   C. Rancidity result in a pleasant odor and fruity smell
   D. The spoilage of fat and oil is hardening of oil
10. The chemical makeup of fats is:
   A. Esters of glycerol with three identical saturated fatty acids.
   B. Esters of glycerol with three predominantly saturated fatty acids.
   C. Esters of glycerol with three predominantly unsaturated fatty acids.
   D. Esters of glycerol with three identical unsaturated fatty acids.
11. Example of saturated fatty acid:
   A. Arachidonic acid B.Oleic acid C.palmitic acid D. Linoleic acid
12. Rancidity is a process of oxidation concerning :
   A. Short chain fatty acid C. Saturated fatty acid
   B. Hydroxy fatty acid D. Unsaturated fatty acid
13. Which reaction can be used to convert oils into fats?
   A. Esterification C. Saponification
   B. Dehydration D. Hydrogenation
14. Soaps are .
   A. Alkali metal salts of long chain carboxylic acids
   B. Alkali metal salts of glycerol
   C. Esters of a long chain fatty alcohol with a long chain fatty acid
   D. Long chain fatty alcohols
15. An ester has the structural formula:

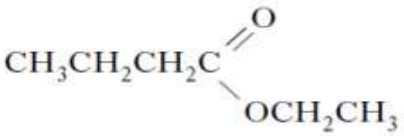


   On hydrolysis, the ester would produce:
   A. Pthanoic acid and propan-1-ol C.Ethanoic acid and propan-2-ol
   B. propanoic acid and propan-1-ol D. Propanoic acid and propan-2-ol.
16. An ester has the following structural formula, $CH_3CH_2CH_2COOCH_2CH_3$.
   The name of this ester is:
   A. Propyl propanoate C. Ethyl butanoate
   B. Butyl ethanoate D.Ethyl propanoate.
17. Esters are formed by the reaction between which two functional groups?
   A. A hydroxyl group and a carboxyl group
   B. A hydroxyl group and a carbonyl group
   C. A hydroxide group and a carboxyl group
   D. A hydroxide group and a carbonyl group

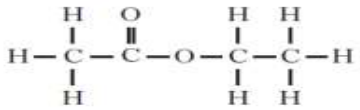
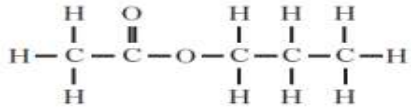
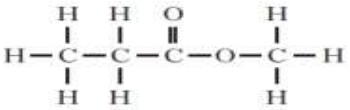
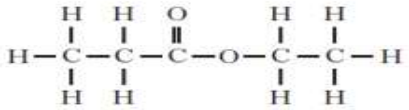
18. Oils are generally:
    A. Solid at room temperature and contain a high proportion of unsaturated molecules
    B. Solid at room temperature and contain a high proportion of saturated molecules
    C. Liquid at room temperature and contain a high proportion of unsaturated molecules
    D. Liquid at room temperature and contain a high proportion of saturated molecules.
19. What is the structural formula for glycerol?

A 
B 
C 
D 

20. Rum flavouring is based on the compound with the formula shown.

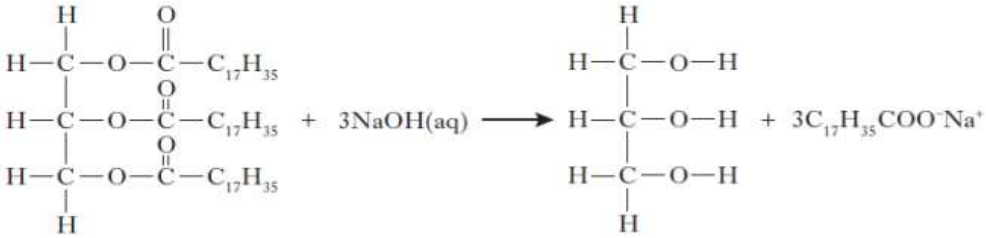


It can be made from:
    A. Ethanol and butanoic acid
    B. Butanol and methanoic acid
    C. Propanol and ethanoic acid
    D. Propanol and propanoic acid
21. Which of the following reactions takes place during the „hardening" of vegetable oil?
    A. Addition B.Hydrolysis C.Dehydration D. Oxidation
22. Fats have higher melting points than oils because comparing fats and oils
    A. Fats have more hydrogen bonds
    B. Fat molecules are more saturated
    C. Fat molecules are more loosely packed
    D. Fats have more cross-links between molecules
23. Hydrolysis of an ester gave an alcohol and a carboxylic acid both of which had the same molecular mass of 60. The structure of the ester was:

A 
B 
C 
D 

24. Fats are formed by the condensation reaction between glycerol molecules and fatty acid molecules. In this reaction the mole ratio of glycerol molecules to fatty acid molecules is:
    A. 1 : 1 B. 1 : 2 C. 1 : 3 D. 3 : 1
25. Which of the following fatty acids is unsaturated?
    A. $C_{19}H_{39}COOH$
    B. $C_{17}H_{31}COOH$
    C. $C_{21}H_{43}COOH$
    D. $C_{13}H_{27}COOH$
26. Which molecule is a fatty acid?
    A. $(CH3)_2CH(CH_2)_3COOH$
    C. $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

27. Triglycerides belong to which general class of organic molecules.
    A. Ketones B.Esters C. Alcohols D. Carboxylic acids
28. The saponification reaction used to form soaps can be more specifically described as:
    A. Dehydration C.Acid hydrolysis.
    B. Hydrogenation D. Basic hydrolysis
29. In chemical terms, soaps can best be described as:
    A. Simple esters of fatty acids C. Salts of carboxylic acids
    B. Long chain acids D. Bases formed from glycerol
30. The hydrocarbon end of a soap molecule is
    A. Hydrophobic and attracted to grease
    B. Hydrophilic and attracted to water
    C. Hydrophobic and attracted to water hydrophilic and attracted to grease
    D. Neither hydrophobic nor hydrophilic
31. Which of the following is the residual product in the formation of soap?
    A. Glyceraldehyde B.Glycerol C.Glycerine D. Acrylonitrile
32. Which of the following is a typical soap molecule?
    A. Calcium stearate C.Potassium permanganate
    B. Sodium bicarbonate D.Sodium stearate
33. Soaps are produced by the following reaction




This reaction is an example of:
A. Condensation B. Esterification C. Hydrolysis D. oxidation

## Answers to Review Exercise

### Unit 5

| | | | | |
|---|---|---|---|---|
| **1. C** | 9. **B** | **17. C** | **25. B** | **33. B** |
| **2. B** | 10. **B** | **18. D** | **26. C** | **34. D** |
| **3. D** | 11. **D** | **19. D** | **27. C** | **35. D** |
| **4. B** | 12. **A** | **20. D** | **28. D** | **36. D** |
| **5. C** | 13. **A** | **21. D** | **29. A** | **37. C** |
| **6. E** | 14. **B** | **22. C** | **30. A** | |
| **7. C** | 15. **D** | **23. A** | **31. D** | |
| **8. D** | 16. **B** | **24. B** | **32. C** | |

### Unit 6

| | | | |
|---|---|---|---|
| **1. D** | **9. B** | 17. **A** | **25. B** |
| **2. C** | **10. B** | 18. **C** | **26. C** |
| **3. A** | **11. C** | 19. **D** | **27. B** |
| **4. C** | **12. D** | 20. **A** | **28. D** |
| **5. D** | **13. D** | 21. **A** | **29. C** |
| **6. D** | **14. A** | 22. **C** | **30. A** |
| **7. D** | **15. D** | 23. **B** | **31. B** |
| **8. A** | **16. C** | 24. **C** | **32. D** |
| | | | **33. C** |

**Dear Students:**

**KEEP SAFE, BE HEALTHY AND STAY AT HOME DURING THIS UNCERTAIN TIME.**

Reference

M. L. and G.T