# Chemical Kinetics and Thermodynamics

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# CHAPTER

# Chemical Kinetics

## CONTENTS

So far we have studied equilibrium reactions. In these reactions, the rates of the two opposing reactions are equal and the concentrations of reactants or products do not change with lapse of time. But most chemical reactions are **spontaneous reactions.** These reactions occur from left to right till all the reactants are converted to products. A spontaneous reaction may be slow or it may be fast. For example, the reactions between aqueous sodium chloride and silver nitrate is a fast reaction. The precipitate of AgCl is formed as fast as $AgNO_3$ solution is added to NaCl solution. On the contrary, the rusting of iron is a slow reaction that occurs over the years.

The branch of Physical chemistry which deals with the rate of reactions is called Chemical Kinetics. The study of Chemical Kinetics includes :

(1) The rate of the reactions and rate laws.
(2) The factors as temperature, pressure, concentration and catalyst, that influence the rate of a reaction.
(3) The mechanism or the sequence of steps by which a reaction occurs.

The knowledge of the rate of reactions is very valuable to understand the chemical of reactions. It is also of great importance in selecting optimum conditions for an industrial process so that it proceeds at a rate to give maximum yield.

## REACTION RATE

The rate of a reaction tells as to what speed the reaction occurs. Let us consider a simple reaction

$$\text{A} \longrightarrow \text{B}$$

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

Thus

$$\begin{aligned}\text{rate of reaction} &= \text{rate of disappearance of } A\\ &= \text{rate of appearance of } B\end{aligned}$$

or

$$\begin{aligned}\text{rate} &= -\frac{d[A]}{dt}\\ &= +\frac{d[B]}{dt}\end{aligned}$$

where [ ] represents the concentration in moles per litre whereas ‘d’ represents infinitesimally small change in concentration. Negative sign shows the concentration of the reactant A decreases whereas the positive sign indicates the increase in concentration of the product B.

## UNITS OF RATE

Reactions rate has the units of concentration divided by time. We express concentrations in moles per litre (mol/litre or mol/1 or mol $1^{-1}$) but time may be given in any convenient unit second (s), minutes (min), hours (h), days (d) or possible years. Therefore, the units of reaction rates may be

| | | |
|---|---|---|
| mole/litre sec | or | mol $1^{-1}$ s |
| mole/litre min | or | mol $1^{-1}$ min$^{-1}$ |
| mole/litre hour | or | mol $1^{-1}$ h$^{-1}$ and, so on |

### Average Rate of Reaction is a Function of Time

Let us consider the reaction between carbon monoxide (CO) and nitrogen dioxide.

$$\text{CO}(g) + \text{NO}_2(g) \longrightarrow \text{CO}_2(g) + \text{NO}(g)$$

The average rate of reaction may be expressed as

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

The concentration of CO was found experimentally every 10 seconds. The results of such an experiment are listed below.

| Conc. of CO | 0.100 | 0.067 | 0.050 | 0.040 | 0.033 |
|---|---|---|---|---|---|
| Time (sec) | 0 | 10 | 20 | 30 | 40 |

The results are also shown graphically in Fig. 20.1.

As the reaction proceeds the concentration of CO decreases rapidly in the initial stages of the reaction. Then the concentration of CO decreases more and more slowly. Obviously the rate of reaction is a function of time.

Over the first 10 seconds, the average rate is

$$\frac{-d[\text{CO}]}{dt} = \frac{-(0.067-0.100)}{(10-0)} = \frac{0.033}{10} = 0.0033\,\text{mol}\,1^{-1}\,\text{s}^{-1}$$

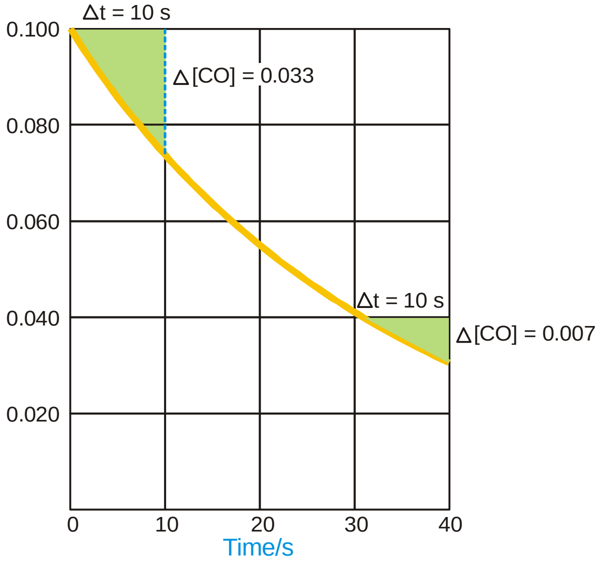


**Figure 20.1**
**Graph of CO concentrations *versus time*. The average rate is equal to the slope of the curve. The average rates for the first 10 and the last 10 seconds are shown.**

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

$$\frac{-d[\mathrm{CO}]}{dt} = \frac{-(0.033-0.040)}{(40-30)} = \frac{0.007}{10} = 0.0007\,\mathrm{mol1}^{-1}\,\mathrm{s}^{-1}$$

The reaction in indeed slowing down with time.

We shall see that average rates are not always useful. They cover a large time interval during which the rate of reaction changes significantly. So, a better way to estimate the rate of reaction, we need to make the time interval as small as possible.

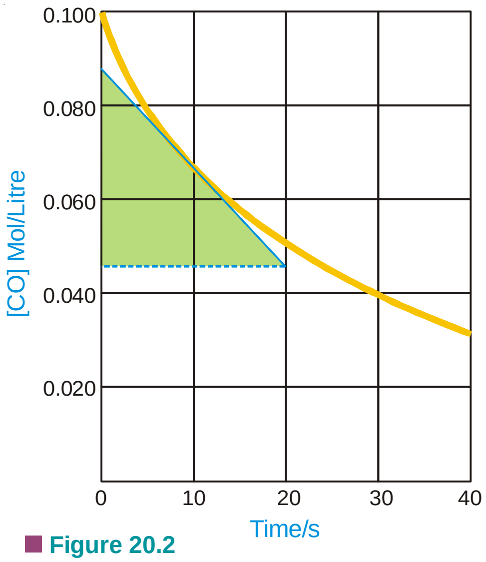


**Figure 20.2**
**The slope of tangent at 10 seconds is equal to the instantaneous rate.**

## Instantaneous Rate of Reaction

The average rates obtained by finding the slope of the curve are not always useful. They cover a large time interval during which the rate of reaction changes significantly. So, a better way to estimate the rate of a reaction is to make the time interval as small as possible. If the interval be infinitesimally small (that is as $\Delta t$ approaches zero), the rate is referred to as the **instantaneous rate** and is written in calculus as

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

where $[\ ]_t$ is the concentration at time $t$. In the present case,

$$\text{the instantaneous rate} = \frac{-d[\mathrm{CO}]_t}{dt}$$

**Thus at any time the instantaneous rate is equal**

**to the slope of a straight line drawn tangent to the curve at that time.** For example, in Fig. 20.2 the instantaneous rate at 10 seconds is found to be 0.0022 mol $l^{-1}$ $s^{-1}$.

## RATE LAWS

At a fixed temperature the rate of a given reaction depends on concentration of reactants. The exact relation between concentration and rate is determined by measuring the reaction rate with different initial reactant concentrations. By a study of numerous reactions it is shown that : **the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.**

Thus for a substance A undergoing reaction,

rate $$\text{rate} \propto [A]^n$$

or $$\text{rate} = k\,[A]^n \qquad ...(1)$$

For a reaction

$$2A + B \longrightarrow \text{products}$$

the reaction rate with respect to *A* or *B* is determined by varying the concentration of one reactant, keeping that of the other constant. Thus the rate of reaction may be expressed as

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(2)$$

Expressions such as (1) and (2) tell the relation between the rate of a reaction and reactant concentrations.

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

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

**Examples of rate law :**

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

In these rate laws where the quotient or concentration is not shown, it is understood to be 1. That is $[H_2]^1 = [H_2]$.

It is apparent that the rate law for a reaction must be determined by experiment. It cannot be written by merely looking at the equation with a background of our knowledge of Law of Mass Action. However, for some elementary reactions the powers in the rate law may correspond to coefficients in the chemical equation. **But usually the powers of concentration in the rate law are different from coefficients.** Thus for the reaction (4) above, the rate is found to be proportional to $[H_2]$ although the quotient of $H_2$ in the equation is 2. For NO the rate is proportional to $[NO]^2$ and power '2' corresponds to the coefficient.

## ORDER OF A REACTION

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

Let us consider the example of a reaction which has the rate law

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(1)$$

The order of such a reaction is (*m* + *n*).

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is $m$ and with respect to B it is $n$. The **overall order of reaction** ($m + n$) may range from 1 to 3 and can be fractional.

**Examples of reaction order :**

| RATE LAW | REACTION ORDER |
|---|---|
| rate = $k\,[N_2O_5]$ | 1 |
| rate = $k\,[H_2]\,[I_2]$ | $1 + 1 = 2$ |
| rate = $k\,[NO_2]^2$ | 2 |
| rate = $k\,[[H_2]\,[NO]^2$ | $1 + 2 = 3$ |
| rate = $k\,[CHCl_3]\,[Cl_2]^{1/2}$ | $1 + \frac{1}{2} = 1\frac{1}{2}$ |

Reactions may be classified according to the order. If in the rate law (1) above

$m + n$ = 1, it is **first order reaction**

$m + n$ = 2, it is **second order reaction**

$m + n$ = 3, it is **third order reaction**

## ZERO ORDER REACTION

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus $[A]^0 = 1$.

**A zero order reaction is one whose rate is independent of concentration.** For example, the rate law for the reaction

$$NO_2 + CO \longrightarrow NO + CO_2$$

at 200° C is

$$\text{rate} = k\,[NO_2]^2$$

Here the rate does not depend on [CO], so this is not included in the rate law and the power of [CO] is understood to be zero. The reaction is **zeroth order** with respect to CO. The reaction is second order with respect to $[NO_2]$. The overall reaction order is $2 + 0 = 2$.

## MOLECULARITY OF A REACTION

Chemical reactions may be classed into two types :

(*a*) Elementary reactions

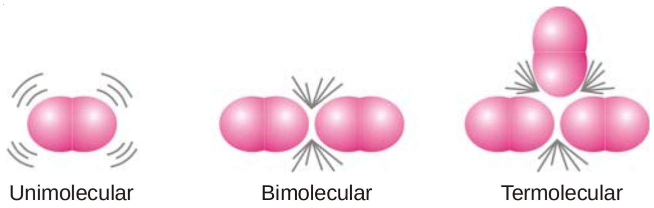
(*b*) Complex reactions

An **elementary reaction** is a simple reaction which occurs in a single step.

A **complex reaction** is that which occurs in two or more steps.

### Molecularity of an Elementary Reaction

The molecularity of an elementary reaction is defined as : **the number of reactant molecules involved in a reaction.**



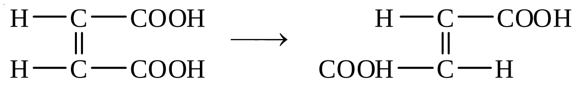
Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called **unimolecular, bimolecular and termolecular** respectively. Thus we have :

(*a*) **Unimolecular reactions :** (molecularity = 1)

$$A \longrightarrow \text{product}$$

Examples are : (*i*) $Br_2 \longrightarrow 2Br$

(*ii*)



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array} \longrightarrow \begin{array}{c} H-C-COOH \\ \| \\ COOH-C-H \end{array}$$

maleic acid fumaric acid

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

$$A + B \longrightarrow \text{products}$$
$$A + A \longrightarrow \text{products}$$

Examples are :

(*i*) $\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} + H_2O \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$

(*ii*) $2HI \longrightarrow H_2 + I_2$

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

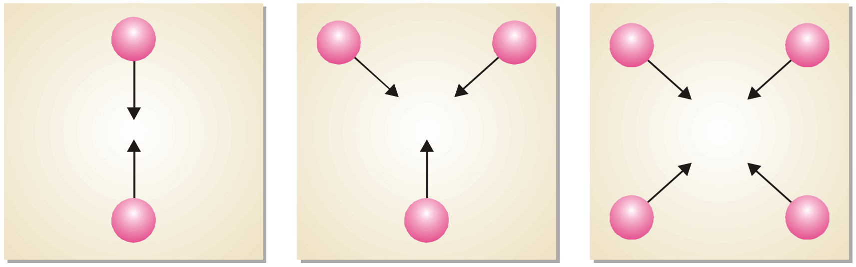
$$A + B + C \longrightarrow \text{products}$$

Examples are :

$$2NO + O_2 \longrightarrow 2NO_2$$
$$2NO + Cl_2 \longrightarrow 2NOCl$$

### Why High Molecularity Reactions are Rare ?

Most of the reactions involve one, two or at the most three molecules. The reactions involving four or more molecules are very rare. The rarity of reactions with high molecularity can be explained on the basis of the kinetic molecular theory. According to this theory, the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules. The chances of simultaneous collision of reacting molecules will go on decreasing with increase in number of molecules. Thus the possibility of three molecules colliding together is much less than in case of bimolecular collision. For a reaction of molecularity 4, the four molecules must come closed and collide with one another at the same time. The possibility of their doing so is much less than even in the case of termolecular reaction. Hence the reactions involving many molecules proceed through a series of steps, each involving two or three or less number of molecules. Such a reaction is called a complex reaction and the slowest step determines the overall rate of the reactions.



Common Less common Rare

**Figure 20.3**
**Chances of simultaneous collision between reacting molecules decrease as the molecularity increases.**

### Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products is called the **mechanism of the reaction.** In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the **rate-determining step** of the reaction.

The decomposition of $N_2O_5$,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

is an example of a complex reaction. It occurs by the following steps :

*Step 1* $\quad 2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (*slow*)

*Step 2* $\quad NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ (*slow*)

*Step 3* $\quad NO + NO_3 \longrightarrow 2NO_2$ (*fast*)

*Overall reaction* $\quad 2N_2O_5 \longrightarrow 4NO_2 + O_2$

Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each, perhaps with a different molecularity. At best could be thought of as : **the number of molecules or atoms taking part in the rate-determining step.**

Thus step 2 in the above mechanism is rate-determining and has molecularity ‘2’ which could be considered as the molecularity of the decomposition reaction of $N_2O_5$.

## MOLECULARITY *VERSUS* ORDER OF REACTION

The term molecularity is often confused with order of a reaction.

The total number of molecules or atoms which take part in a reaction as represented by the chemical equation, is known as the **molecularity of reaction.**

The sum of the powers to which the concentrations are raised in the rate law is known as the **order of reaction.**

### Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction.

$$2A + B \longrightarrow \text{products}$$

$$\text{rate} \propto [A][A][B]$$

or

$$\text{rate} = k[A]^2[B] \qquad (\textit{rate law})$$

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is 2 + 1 = 3. The sum of powers in the rate law is 2 + 1 and hence the reaction order is also 3. Thus **the molecularity and order for an elementary reaction are equal.**

**TABLE 20.1. MOLECULARITY AND ORDER FOR ELEMENTARY REACTIONS.**

| Reactions | Molecularity | Rate law | Order |
|---|---|---|---|
| $A \longrightarrow$ products | 1 | rate = $k[A]$ | 1 |
| $A + A \longrightarrow$ products | 2 | rate = $k[A]^2$ | 2 |
| $A + B \longrightarrow$ products | 2 | rate = $k[A][B]$ | 2 |
| $A + 2B \longrightarrow$ products | 3 | rate = $k[A][B]^2$ | 3 |
| $A + B + C \longrightarrow$ products | 3 | rate = $k[A][B][C]$ | 3 |

### Differences Between Order and Molecularity

| Order of a Reaction | Molecularity of a Reaction |
|---|---|
| 1. It is the **sum of powers** of the concentration terms in the rate law expression. | 1. It is number of **reacting species** undergoing simultaneous collision in the elementary or simple reaction. |
| 2. It is an **experimentally** determined value. | 2. It is a **theoretical** concept. |
| 3. It can have **fractional** value. | 3. It is always a **whole number.** |
| 4. It can assume **zero value.** | 4. It **can not have zero value.** |
| 5. Order of a reaction **can change** with the conditions such as pressure, temperature, concentration. | 5. Molecularity is **invariant** for a chemical equation. |

## PSEUDO–ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. **The experimental order which is not the actual one is referred to as the pseudo order.** Since for elementary reactions molecularity and order are identical, pseudo-order reactions may also be called **pseudo molecular reactions.**

Let us consider a reaction

$$A + B \longrightarrow \text{products}$$

in which the reactant B is present in a large excess. Since it is an elementary reaction, its rate law can be written as

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

As B is present in large excess, its concentration remains practically constant in the course of reaction. Thus the rate law can be written as

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

where the new rate constant $k' = k\,[B]$. Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a **pseudo-first order.**

### Examples of Pseudo-order Reactions

(1) **Hydrolysis of an ester.** For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + \underset{\text{(excess)}}{H_2O} \longrightarrow \underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

Here a large excess of water is used and the rate law can be written as

$$\begin{aligned}\text{rate} &= k\,[CH_3COOH]\,[H_2O]\\ &= k'\,[CH_3COOH]\end{aligned}$$

The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.

(2) **Hydrolysis of sucrose.** Sucrose upon hydrolysis in the presence of a dilute mineral acid gives glucose and fructose.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + \underset{\text{(excess)}}{H_2O} \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

If a large excess of water is present, $[H_2O]$ is practically constant and the rate law may be written as

$$\begin{aligned}\text{rate} &= k\,[C_{12}H_{22}O_{11}]\,[H_2O]\\ &= k\,[C_{12}H_{22}O_{11}]\end{aligned}$$

The reaction though of second-order is experimentally found to be first-order. Thus it is a pseudo-first-order reaction.

## ZERO ORDER REACTIONS

In a zero order reaction, rate is independent of the concentration of the reactions. Let us consider a zero-order reaction of the type

| | A | $\longrightarrow$ | Products |
|---|---|---|---|
| Initial conc. | $a$ | | 0 |
| Final conc. | $a-x$ | | $x$ |

$$\text{Rate of reaction} = \frac{-d[A]}{dt} = k_0\,[A]^\circ$$

or
$$\frac{dx}{dt} = \frac{-d\ (a-x)}{dt} = k_0\,(a-x)^\circ = k_0$$

On integrating we get

$$k_0 = \frac{x}{t} \quad \text{or} \quad x = k_0 t$$

where $k_0$ is the rate constant of a zero-order reaction, the unit of which is concentration per unit time. In zero order reaction, the **rate constant is equal to the rate of reaction at all concentrations.**

## FIRST ORDER REACTIONS

Let us consider a first order reaction

$$\text{A} \longrightarrow \text{products}$$

Suppose that at the beginning of the reaction ($t = 0$), the concentration of A is $a$ moles litre$^{-1}$. If after time $t$, $x$ moles of A have changed, the concentration of A is $a - x$. We know that for a first order reaction, the rate of reaction, $dx/dt$, is directly proportional to the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k\,(a-x)$$

or
$$\frac{dx}{a-x} = k\,dt \qquad \text{...(1)}$$

Integration of the expression (1) gives

$$\int \frac{dx}{a-x} = \int k\,dt$$

or
$$-\,\text{1n}\,(a-x) = kt + \text{I} \qquad \text{...(2)}$$

where I is the constant of integration. The constant $k$ may be evaluated by putting $t = 0$ and $x = 0$.

Thus,

$$\text{I} = -\,\text{1n}\,a$$

Substituting for I in equation (2)

$$\text{1n}\frac{a}{a-x} = kt \qquad \text{...(3)}$$

or
$$k = \frac{1}{t}\,\text{1n}\frac{a}{a-x}$$

Changing into common logarithms

$$k = \frac{2.303}{t} \log \frac{a}{a - x} \qquad \text{...(4)}$$

The value of $k$ can be found by substituting the values of $a$ and $(a - x)$ determined experimentally at time interval $t$ during the course of the reaction.

Sometimes the integrated rate law in the following form is also used :

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

where $x_1$ and $x_2$ are the amounts decomposed at time intervals $t_1$ and $t_2$ respectively from the start.

### Examples of First order Reactions

Some common reactions which follow first order kinetics are listed below :

(1) **Decomposition of $N_2O_5$ in $CCl_4$ solution.** Nitrogen pentoxide in carbon tetrachloride solution decomposes to form oxygen gas,

$$N_2O_5 \longrightarrow 2NO_2 + \tfrac{1}{2}O_2$$

The reaction is carried in an apparatus shown in Fig. 20.4. The progress of the reaction is monitored by measuring the volume of oxygen evolved from time to time.

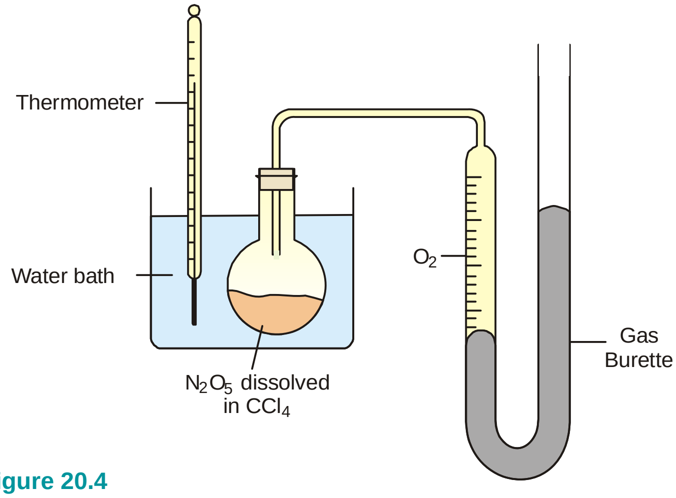


**Figure 20.4**

**An apparatus for monitoring the volume of $O_2$ evolved in the decomposition of $N_2O_5$ dissolved in carbon tetrachloride.**

If $V_t$ be the volume of $O_2$ at any time t and $V_\infty$ the final volume of oxygen when the reaction is completed, the $V_\infty$ is a measure of the initial concentration of $N_2O_5$ and $(V_\infty - V_t)$ is a measure of undecomposed $N_2O_5$ $(a - x)$ remaining at time $t$. Thus,

$$k = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

On substituting values of $V_\infty$, $(V_\infty - V_t)$ at different time intervals, $t$, the value of $k$ is found to be constant. Thus it is a reaction of the first order.

**SOLVED PROBLEM.** From the following data for the decomposition of $N_2O_5$ in $CCl_4$ solution at 48°C, show that the reaction is of the first order

| *t* (mts) | 10 | 15 | 20 | $\infty$ |
|---|---|---|---|---|
| Vol of $O_2$ evolved | 6.30 | 8.95 | 11.40 | 34.75 |

**SOLUTION**

For a first order reaction the integrated rate equation is

$$\frac{1}{t}\log\frac{V_\infty}{V_\infty - V_t} = k$$

In this example, $V_\infty = 34.75$

| $t$ | $V_\infty - Vt$ | $\frac{1}{t}\log\frac{V_\infty}{V_\infty - V_t}$ | $=$ | $k$ |
|---|---|---|---|---|
| 10 | 28.45 | $\frac{1}{10}\log\frac{34.75}{28.45}$ | $=$ | 0.00868 |
| 15 | 25.80 | $\frac{1}{15}\log\frac{34.75}{25.80}$ | $=$ | 0.00862 |
| 20 | 23.35 | $\frac{1}{20}\log\frac{34.75}{23.35}$ | $=$ | 0.00863 |

Since the value of *k* is fairly constant, it is a **first order reaction**.

(2) **Decomposition of $H_2O_2$ in aqueous solution.** The decomposition of $H_2O_2$ in the presence of Pt as catalyst is a first order reaction.

$$H_2O_2 \xrightarrow{\text{Pt}} H_2O + O$$

The progress of the reaction is followed by titrating equal volumes of the reaction mixture against standard $KMnO_4$ solution at different time intervals.

**SOLVED PROBLEM.** A solution of $H_2O_2$ when titrated against $KMnO_4$ solution at different time intervals gave the following results :

| *t* (minutes) | 0 | 10 | 20 |
|---|---|---|---|
| Vol $KMnO_4$ used<br>for 10 ml $H_2SO_4$ | 23.8 ml | 14.7 ml | 9.1 ml |

Show that the decomposition of $H_2O_2$ is a first order reaction.

**SOLUTION**

The integrated rate equation for first order reaction is

$$k = \frac{2.303}{t}\log\frac{a}{a-x}$$

Since volume of $KMnO_4$ used in the titration is measure of concentration of $H_2O_2$ in solution,

$a = 23.8$ ml

$(a-x) = 14.7$ when $t = 10$ mts

$(a-x) = 9.1$ when $t = 20$ mts

Substituting these values in the rate equation above, we have

$$k = \frac{2.303}{10}\log\frac{23.8}{14.7}$$

$$= 0.2303\,(\log 23.8 - \log 14.7)$$

$$= 0.2303\,(1.3766 - 1.1673)$$
$$= 0.04820$$

and
$$k = \frac{2.303}{20} \log \frac{23.8}{9.1}$$
$$= 0.10165\,(\log 23.8 - \log 9.1)$$
$$= 0.10165\,(1.3766 - 0.9595) = 0.04810$$

Since the value of $k$ is almost constant, the decomposition of $H_2O_2$ is a **first order reaction**.

(3) **Hydrolysis of an Ester.** The hydrolysis of ethyl acetate or methyl acetate in the presence of a mineral acid as catalyst, is a first order reaction.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} \underset{\text{acetic acid}}{CH_3COOH} + C_2H_5OH$$

For studying the kinetics of the reaction, a known volume of ethyl acetate is mixed with a relatively large quantity of acid solution, say N/2 HCl. At various intervals of time, a known volume of the reaction mixture is titrated against a standard alkali solution. Hydrolysis of the ester produces acetic acid. Therefore as the reaction proceeds, the volume of alkali required for titration goes on increasing.

**SOLVED PROBLEM.** The following data was obtained on hydrolysis of methyl acetate at 25°C in 0.35N hydrochloric acid. Establish that it is a first order reaction.

| $t$ (secs) | 0 | 4500 | 7140 | ∞ |
|---|---|---|---|---|
| ml alkali used | 24.36 | 29.32 | 31.72 | 47.15 |

**SOLUTION**

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

At any time, the volume of alkali used is needed for the acid present as catalyst and the acid produced by hydrolysis.

The volume of alkali used for total change from $t_0$ to $t_\infty$ gives the initial concentration of ester. Thus,

$a = 47.15 - 24.36 = 22.79$ ml

$(a - x)$ after 4500 sec $= 47.15 - 29.32 = 17.83$ ml

$(a - x)$ after 7140 sec $= 47.15 - 31.72 = 15.43$ ml

Substituting values in the rate equation above, we have

$$k = \frac{2.303}{4500} \log \frac{22.79}{17.83} = 0.00005455$$

$$k = \frac{2.303}{7140} \log \frac{22.79}{15.43} = 0.0000546$$

Since the values of $k$ in the two experiments are fairly constant, the reaction is of the first order.

(4) **Inversion of Cane sugar (sucrose).** The inversion of cane sugar or sucrose catalyzed with dil HCl,

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$

follows the first order kinetics. The progress of the reaction is followed by noting the optical rotation of the reaction mixture with the help of a polarimeter at different time intervals. The optical rotation goes on changing since D-glucose rotates the plane of polarised light to the right and D-fructose to the left. **The change in rotation is proportional to the amount of sugar decomposed.**

Let the final rotation be $r_\infty$, the initial rotation $r_0$ while the rotation at any time $t$ is $r_t$

The initial concentration, a is ∞ $(r_0 - r_\infty)$.

The concentration at time $t$, $(a - x)$ is ∝ $(r_t - r_\infty)$

Substituting in the first order rate equation,

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

we have

$$k = \frac{2.303}{t} \log_{10} \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$$

If the experimental values of $t$ $(r_0 - r_\infty)$ and $(r_t - r_\infty)$ are substituted in the above equation, a constant value of $k$ is obtained.

**SOLVED PROBLEM.** The optical rotation of sucrose in 0.9N HCl at various time intervals is given in the table below.

| time (min) | 0 | 7.18 | 18 | 27.1 | ∞ |
|---|---|---|---|---|---|
| rotation (degree) | +24.09 | +21.4 | +17.7 | +15 | –10.74 |

Show that inversion of sucrose is a first order reaction.

**SOLUTION**

The available data is substituted in the first order rate equation for different time intervals.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$r_0 - r_\infty = 24.09 - (-10.74) = 34.83$ for all time intervals. Thus, the value of rate constant can be found.

| time ($t$) | $r_t = r_\infty$ | $k = \frac{1}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)}$ |
|---|---|---|
| 7.18 | 32.14 | $k = \frac{1}{7.18} \log \frac{34.83}{32.14} = 0.0047$ |
| 18 | 28.44 | $k = \frac{1}{18} \log \frac{34.83}{28.44} = 0.0048$ |
| 27.1 | 25.74 | $k = \frac{1}{27.1} \log \frac{34.83}{25.74} = 0.0048$ |

Since the value of $k$ comes out to be constant, the inversion of sucrose is a **first order reaction**.

## SECOND ORDER REACTIONS

Let us take a second order reaction of the type

$$2A \longrightarrow \text{products}$$

Suppose the initial concentration of A is $a$ moles litre$^{-1}$. If after time $t$, $x$ moles of A have reacted, the concentration of A is $(a - x)$. We know that for such a second order reaction, rate of reaction is proportional to the square of the concentration of the reactant. Thus,

$$\frac{dx}{dt} = k\,(a - x)^2 \qquad \text{...(1)}$$

where $k$ is the rate constant, Rearranging equation (1), we have

$$\frac{dx}{(a-x)^2} = k\,dt \qquad \text{...(2)}$$

On integration, it gives

$$\frac{1}{a-x} = kt + I \qquad \text{...(3)}$$

where $I$ is is integration constant. $I$ can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{a} \qquad \text{...(4)}$$

Substituting for I in equation (3)

$$\frac{1}{a-x} = kt + \frac{1}{a}$$

$$kt = \frac{1}{a-x} - \frac{1}{a}$$

Thus $$k = \frac{1}{t}.\frac{x}{a(a-x)}$$

This is the integrated rate equation for a second order reaction.

### Examples of Second order Reaction

**Hydrolysis of an Ester by NaOH.** This is typical second order reaction.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow CH_3COONa + \underset{\text{ethyl alcohol}}{C_2H_5OH}$$

The reaction is carried in a vessel at a constant temperature by taking. equimolar amounts of ethyl acetate and NaOH. Measured volumes of the reaction mixture (say, 25 ml) are withdrawn at various times and titrated against a standard acid. The volume of the acid used is a measure of the concentration of NaOH or ester. Thus the volume of the acid used when $t = 0$, gives the initial concentration ($a$) of the reactants. The volume of acid consumed at any other time $t$ gives $(a - x)$. The value of $x$ can be calculated. The rate constant $k$ can be determined by substituting values in the second order integrated rate equation.

**SOLVED PROBLEM.** Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants, was studied by titrating 25ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.

| $t$ (mts) | 0 | 5 | 15 | 25 |
|---|---|---|---|---|
| ml acid used | 16.00 | 10.24 | 6.13 | 4.32 |

**SOLUTION**

The second order integrated rate equation is

$$k = \frac{1}{at}.\frac{x}{a(a-x)} \qquad \text{...(1)}$$

The volume of acid used at any time is a measure of concentration of the unreacted substances at that time.

Therefore,

$a$, initial concentration = 16.00

after 5 mts $(a - x)$ = 10.24 and $x = 5.76$

after 15 mts $(a-x) = 6.13$ and $x = 9.85$

after 25 mts $(a-x) = 4.32$ and $x = 11.68$

Substituting values in the rate equation (1), we have

$$k = \frac{1}{16 \times 5} \cdot \frac{5.76}{10.24} = 0.0070$$

$$k = \frac{1}{16 \times 15} \cdot \frac{9.85}{6.13} = 0.0067$$

$$k = \frac{1}{16 \times 25} \cdot \frac{11.68}{4.32} = 0.00675$$

The values of $k$ being fairly constant, this reaction is of the second order.

## THIRD ORDER REACTIONS

Let us consider a simple third order reaction of the type

$$3\text{A} \longrightarrow \text{products}$$

Let the initial concentration of A be $a$ moles litre$^{-1}$ and after time $t$, $x$, moles have reacted. Therefore, the concentration of A becomes $(a-x)$. The rate law may be written as :

$$\frac{dx}{dt} = k(a-x)^3 \qquad ...(1)$$

Rearranging equation (1), we have

$$\frac{dx}{(a-x)^3} = k\,dt \qquad ...(2)$$

On integration, it gives

$$\frac{1}{2(a-x)^2} = kt + I \qquad ...(3)$$

where $I$ is the integration constant. $I$ can be evaluated by putting $x = 0$ and $t = 0$. Thus,

$$I = \frac{1}{2a^2}$$

By substituting the value of $I$ in (3), we can write

$$kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

Therefore,

$$k = \frac{1}{t} \cdot \frac{x(2a-x)}{2a^2(a-x)^2}$$

This is the integrated rate equation for a third order reaction.

### Examples of Third order Reactions

There are not many reactions showing third order kinetics. A few of the known examples are :

(*i*) $2\text{FeCl}_3(aq) + \text{SnCl}_2(aq) \longrightarrow 2\text{FeCl}_2 + \text{SnCl}_4$

(*ii*) $2\text{NO}(g) + \text{O}_2(g) \longrightarrow 2\text{NO}_2(g)$

(*iii*) $2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$

## UNITS OF RATE CONSTANT

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

### Units of Zero order Rate constant

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

$$k = \frac{d[\mathrm{A}]}{dt} = \frac{\text{mol}}{\text{litre}} \times \frac{1}{\text{time}}$$

Thus the units of $k$ are

**mol l$^{-1}$ time$^{-1}$**

Time may be given in seconds, minutes, days or years.

### Units of First order Rate constant

The rate constant of a first order reaction is given by

$$k = \frac{2.303}{t} \log \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t}$$

Thus the rate constant for the first order reaction is independent of the concentration. It has the unit

**time$^{-1}$**

### Units of Second order Rate constant

The rate constant for a second order reaction is expressed as

$$k = \frac{1}{t} \times \frac{x}{[\mathrm{A}]_0\,([\mathrm{A}]_0 - x)}$$

or

$$= \frac{\text{concentration}}{\text{concentration} \times \text{concentration}} \times \frac{1}{\text{time}}$$

$$= \frac{1}{\text{concentration}} \times \frac{1}{\text{time}}$$

$$= \frac{1}{\text{mole/litre}} \times \frac{1}{\text{time}}$$

$$= \text{mol}^{-1}\,\text{l}\,\text{time}^{-1}$$

Thus the units for $k$ for a second order reactions are

**mol$^{-1}$ 1 time$^{-1}$**

### Units of Third order Rate constant

The rate constant for a third order reaction is

$$k = \frac{1}{t} \cdot \frac{x(2a - x)}{2a^2 (a - x)^2}$$

or

$$k = \frac{\text{concentration} \times \text{concentration}}{(\text{concentration})^2 \times (\text{concentration})^2} \times \frac{1}{\text{time}}$$

$$= \frac{1}{(\text{concentration})^2} \times \frac{1}{\text{time}}$$

$$= \frac{1}{(\text{mol/litre})^2} \times \frac{1}{\text{time}}$$

Thus the units of $k$ for third order reaction are

**mol$^{-2}$ l$^2$ time$^{-1}$**

## HALF–LIFE OF A REACTION

Reaction rates can also be expressed in terms of **half-life** or **half-life period.** It is defined as : **the time required for the concentration of a reactant to decrease to half its initial value.**

In other words, half-life is the time required for one-half of the reaction to be completed. It is represented by the symbol $t_{1/2}$ or $t_{0.5}$.

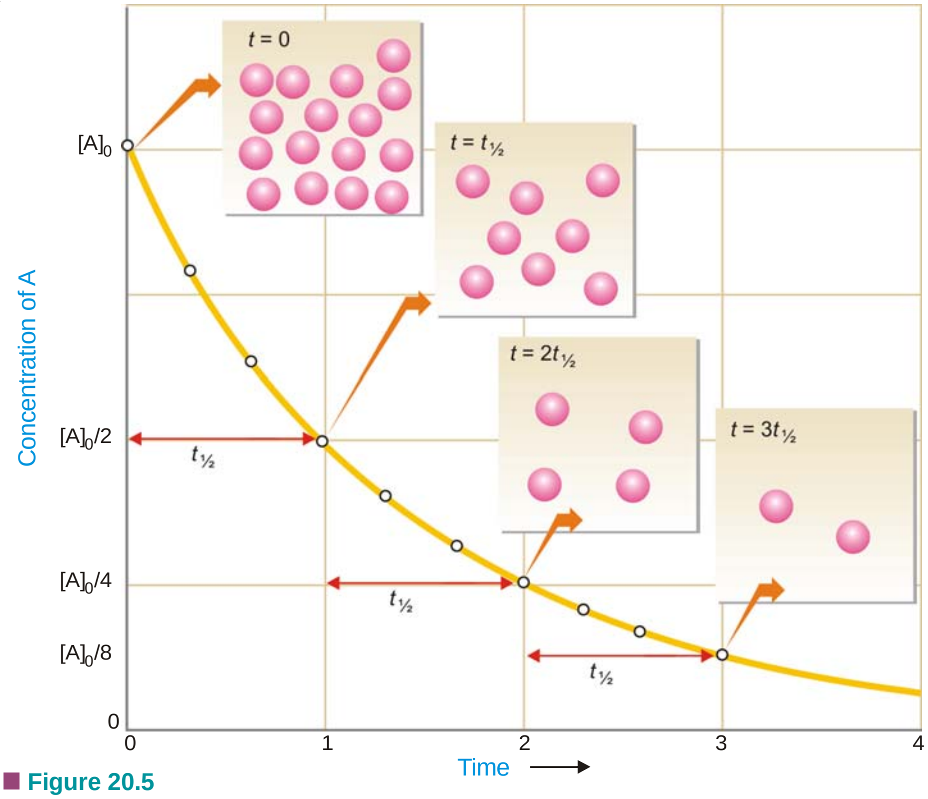


**Figure 20.5**
**First-order half-life. Concentration of a reactant A as a function of time for a first-order reaction. The concentration falls from its initial value, $[A]_0$, to $[A]_0/2$ after one half-life, to $[A]_0/4$ after a second half-life, to $[A]_0/8$ after a third half-life, and so on. For a first-order reaction, each half-life represents an equal amount of time.**

### Calculation of Half-life of a First order Reaction

The integrated rate equation (4) for a first order reaction can be stated as :

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

where $[A]_0$ is initial concentration and [A] is concentration at any time $t$. Half-life, $t_{1/2}$, is time when initial concentration reduces to $\frac{1}{2}$ *i.e.*,

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

Substituting values in the integrated rate equation, we have

$$k = \frac{2.303}{t_{1/2}} \log \frac{[A]_0}{1/2[A]_0} = \frac{2.303}{t_{1/2}} \log 2$$

or $$t_{1/2} = \frac{2.303}{k} \log\ 2 = \frac{2.303}{k} \times 0.3010$$

or $$t_{1/2} = \frac{0.693}{k}$$

It is clear from this relation that :

(1) half-life for a first order reaction is **independent of the initial concentration.**

(2) it is **inversely proportional ot $k$,** the rate-constant.

### Calculation of Time for Completing any Fraction of the Reaction

As for half-change, we can calculate the time required for completion of any fraction of the reaction. For illustration, let us calculate the time in which two-third of the reaction is completed. First order integrated rate equation is

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

Here, the initial concentration has $\frac{2}{3}$ reacted reducing it to $\frac{1}{3}$. Thus,

$$[A] = \frac{1}{3}[A]_0$$

Substituting values in the rate equation

$$t_{3/4} = \frac{2.303}{k} \log \frac{[A]_0}{1/3[A]_0} = \frac{2.303}{k} \log 3$$

$$= \frac{\mathbf{2.303}}{\boldsymbol{k}} \times \mathbf{0.4771}$$

**SOLVED PROBLEM 1.** Compound A decomposes to form B and C the reaction is first order. At 25°C the rate constant for the reaction is 0.450 $s^{-1}$. What is the half-life of A at 25°C ?

**SOLUTION**

We know that for a first order reaction, half-life $t_{1/2}$, is given by the expression

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

where $k$ = rate constant

Substituting the value of k = 0.450 $s^{-1}$, we have

$$t_{1/2} = \frac{0.693}{0.450\,s^{-1}} = \mathbf{1.54\ s}$$

Thus half-life of the reaction $A \rightarrow B + C$ is 1.54 seconds.

**SOLVED PROBLEM 2.** The half-life of a substance in a first order reaction is 15 minutes. Calculate the rate constant.

**SOLUTION**

For a first order reaction

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

Putting $t_{1/2}$ = 15 min in the expression and solving for $k$, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{15\,\text{min}} = \mathbf{4.62 \times 10^{-2}\ min^{-1}}$$

**SOLVED PROBLEM 3.** For the reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

the rate is directly proportional to $[N_2O_5]$. At 45°C, 90% of the $N_2O_5$ reacts in 3600 seconds. Find the value of the rate constant $k$.

**SOLUTION**

Since rate is $\propto [N_2O_5]$ it is first order reaction. The integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]}$$

When 90% of $N_2O_5$ has reacted, the initial concentration is reduced to $\frac{1}{10}$ That is,

$$[N_2O_5] = \frac{1}{10}[N_2O_5]_0$$

Substituting values in the rate equation,

$$k = \frac{2.303}{3600} \log \frac{[N_2O_5]_0}{\frac{1}{10}[N_2O_5]_0}$$

$$= \frac{2.303}{3600} \log 10 = \frac{2.303}{3600} \times 1$$

Thus $$k = \frac{2.303}{3600} = \mathbf{6.40 \times 10^{-4}\ s^{-1}}$$

**SOLVED PROBLEM 4.** The rate law for the decomposition of $N_2O_5$ ($l$) is : rate $= k\,[N_2O_5]$ where $k = 6.22 \times 10^{-4}$ sec$^{-1}$. Calculate half-life of $N_2O_5$ ($l$) and the number of seconds it will take for an initial concentration of $N_2O_5$ ($l$) of 0.100 M to drop to 0.0100 M.

**SOLUTION**

**Calculation of half-life**

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.22 \times 10^{-4}\ \text{sec}^{-1}} = 1.11 \times 10^3 \text{ sec}$$

**Calculation of time in seconds for drop of $[N_2O_5]$ from 0.100 M to 0.0100 M**

From first order integrated rate equation,

$$t = \frac{2.303}{t} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

or $$t = \frac{2.303}{k} \log \frac{[N_2O_5]_0}{[N_2O_5]_t}$$

Substituting values

$$t = \frac{2.303}{6.22 \times 10^{-4}} \log \frac{0.100}{0.0100}$$

$$= \frac{2.303}{6.22 \times 10^{-4}} \times 1$$

$$= \mathbf{3.70 \times 10^3\ sec}$$

**SOLVED PROBLEM 5.** For a certain first order reaction $t_{0.5}$ is 100 sec. How long will it take for the reaction to be completed 75% ?

**SOLUTION**

**Calculation of *k***

For a first order reaction

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

or $$100 = \frac{0.693}{k}$$

∴ $$k = \frac{0.693}{100} = 0.00693 \text{ sec}^{-1}$$

**Calculation of time for 75% completion of reaction**

The integrated rate equation for a first order reaction is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

or $$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

When $\frac{3}{4}$ initial concentration has reacted, it is reduced to $\frac{1}{4}$

Substituting values in the rate equation

$$t_{3/4} = \frac{2.303}{0.00693} \log \frac{[A]_0}{\frac{1}{4}[A]_0}$$

$$= \frac{2.303}{0.00693} \log 4 = \mathbf{200\,sec}$$

**SOLVED PROBLEM 6.** A first order reaction is one-fifth completed in 40 minutes. Calculate the time required for its 100% completion.

**SOLUTION**

**Calculation of *k***

For a first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

After 40 mts, the initial concentration is reduced to $\frac{4}{5}$ That is,

$$[A] = \frac{4}{5}[A]_0$$

Substituting values in the equation above

$$k = \frac{2.303}{40} \log \frac{[A]_0}{\frac{4}{5}[A]_0}$$

or $$k = \frac{2.303}{40} \log 5 - \log 4 = 0.00558 \text{ mt}^{-1}$$

**Calculation of time required for 100% completion**

We know that for first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

If reaction is 100% complete in, say, $t_1$ time, we have, [A] = 0. Thus,

$$t_1 = \frac{2.303}{0.00558} \log \frac{[A]_0}{0} = \propto$$

**SOLVED PROBLEM 7.** 50% of a first order reaction is complete in 23 minutes. Calculate the time required to complete 90% of the reaction.

**SOLUTION**

**Calculation of *k***

$$t_{0.5} = \frac{0.693}{k}$$

or

$$k = \frac{0.693}{t_{0.5}} = \frac{0.693}{23} = 0.0301304 \text{ mt}^{-1}$$

**Calculation of time for 90% completion of the reaction**

For first order reaction, integrated rate equation is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} \qquad \text{...(1)}$$

or

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]} \qquad \text{...(2)}$$

When 90% of the initial concentration has reacted, 10% of it is left. That is.

$$[A] = \frac{1}{10}[A]_0$$

Substituting values in equation (2)

$$t = \frac{2.303}{0.0301304} \log \frac{[A]_0}{\frac{1}{10}[A]_0} = \frac{2.303}{0.0301304} \log 10$$

$$= \frac{2.303}{0.0301304} = \mathbf{76.4\ min}$$

## Half-life for a Second order Reaction

For the simple second order reaction 2A ⟶ Products, the integrated rate equation is

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

where $[A]_0$ is the initial concentration and [A] is the concentration when time *t* has elapsed.

When one-half life has elapsed.

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

and we have

$$k\,t_{1/2} = \frac{1}{\frac{1}{2}[\text{A}]_0} - \frac{1}{[\text{A}]_0}$$

or
$$k\,t_{1/2} = \frac{2}{[\text{A}]_0} - \frac{1}{[\text{A}]_0}$$

Solving for $t_{1/2}$ we find that

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

As in case of a first order reaction, half-life for a second order reaction is inversely proportional to rate constant ***k***. While half-life of a first order reaction is independent of initial concentration, **half-life of a second order reaction depends on initial concentration.** This fact can be used to distinguish between a first order and a second order reaction.

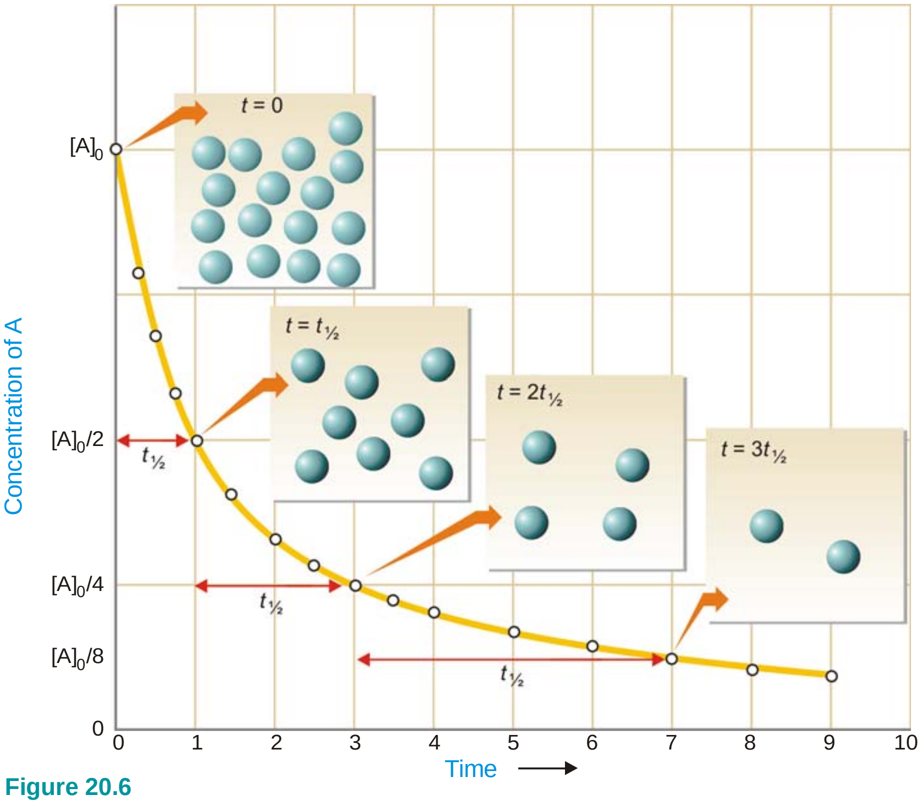


**Figure 20.6**
**Second-order half-life. Concentration of a reactant A as a function of time for a second-order reaction. Note that each half-life is twice as long as the preceding one because $t_{½} = 1/k[A]_0$ and the concentration of A at the beginning of each successive half-life is smaller by a factor of 2.**

## HOW TO DETERMINE THE ORDER OF A REACTION

There are at least four different methods to determine the order of a reaction.

### (1) Using integrated rate equations

The reaction under study is performed by taking different initial concentrations of the reactant ($a$) and noting the concentration ($a - x$) after regular time intervals ($t$). The experimental values of $a$,

$(a - x)$ and $t$ are then substituted into the integrated rate equations for the first, second and third order reactions. **The rate equation which yields a constant value of *k* corresponds to the correct order of the reaction.** This method of ascertaining the order of a reaction is essentially a method of hit-and-trial but was the first to be employed. It is still used extensively to find the order of simple reactions.

### (2) Graphical method

For reactions of the type A ⟶ products, we can determine the reaction order by seeing whether a graph of the data fits one of the integrated rate equations.

**In case of First order**

We have already derived the integrated rate equation for first order as

$$1\text{n}\,\frac{a}{a-x} = kt$$

Simplifying, it becomes

$$\begin{array}{ccccc} 1\text{n}\,(a-x) & = & -\,kt & + & 1\text{n}\,a \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

Thus the two variables in the first order rate equation are :

$$1\text{n}\,\frac{a}{a-x} \text{ and } t$$

Hence, if $1\text{n}\,\dfrac{a}{a-x}$ is plotted against $t$ and straight line results (Fig. 20.7), the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order.

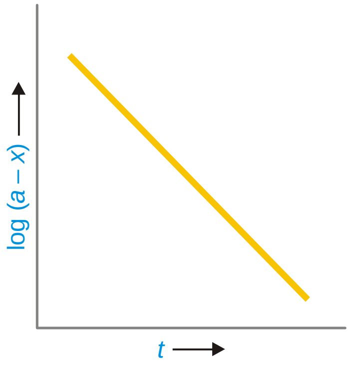


**Figure 20.7**
**Plot of log($a$ – $x$) against $t$ for a first order reaction.**

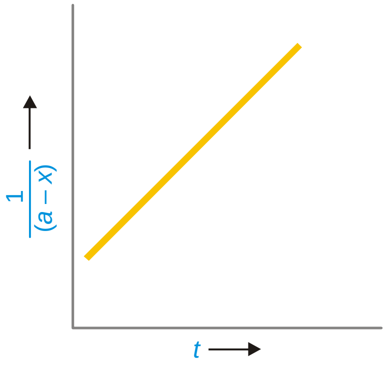


**Figure 20.8**
**Plot of 1/($a$ – $x$) against $t$ for a second order reaction.**

**In case of Second order**

We have already shown that second order rate equation can be written as

$$\begin{array}{ccccc} \dfrac{1}{a-x} & = & kt & + & \dfrac{1}{a} \\ \uparrow & & \uparrow & & \uparrow \\ y & = & mx & + & b \end{array}$$

This is the equation of a straight line, $y = mx + b$. Here the two variables are

$$\frac{1}{a-x} \text{ and } t$$

Thus when $\dfrac{1}{a-x}$ is plotted against t and we get a straight line (Fig. 20.8), the reaction is second order. In case a curve is obtained, the reaction is not second order.

### (3) Using half-life period

Two separate experiments are performed by taking different initial concentrations of a reactant. The progress of the reaction in each case is recorded by analysis. When the initial concentration is reduced to one-half, the time is noted. Let the initial concentrations in the two experiments be $[A_1]$ and $[A_2]$, while times for completion of half change are $t_1$ and $t_2$ respectively.

**Calculation of order of reaction.** We know that half-life period for a first order reaction is independent of the initial concentration, [A]. We also know :

$$\text{half-life} \propto \frac{1}{[A]} \quad \text{for 2nd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^2} \quad \text{for 3rd order reaction}$$

$$\text{half-life} \propto \frac{1}{[A]^{n-1}} \quad \text{for } n\text{th order reaction}$$

Substituting values of initial concentrations and half-life periods from the two experiments, we have

$$t_1 \propto \frac{1}{[A_1]^{n-1}} \qquad t_2 \propto \frac{1}{[A_2]^{n-1}}$$

and

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1}$$

$$(n-1)\log\left[\frac{A_2}{A_1}\right] = \log\left[\frac{t_1}{t_2}\right]$$

Solving for $n$, the order of reaction

$$n = 1 + \frac{\log\,[t_1/t_2]}{\log\,[A_2/A_1]}$$

**SOLVED PROBLEM.** In the reduction of nitric oxide, 50% of reaction was completed in 108 seconds when initial pressure was 336 mm Hg and in 147 seconds initial pressure was 288 mm Hg. Find the order of the reaction.

**SOLUTION**

We know that

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2}\right]^{n-1} \qquad \text{...(1)}$$

where $t_1$ and $t_2$ are half-life periods and $[A_1]$ and $[A_2]$ are the corresponding initial concentrations, while $n$ is the order of the reaction.

Taking logs of the expression (1), we have

$$n = 1 + \frac{\log\,[t_2/t_1]}{\log\,[A_1/A_2]} \qquad \text{...(2)}$$

Substituting values in expression (2),

$$n = 1 + \frac{\log\ 108/147}{\log\ 288/336}$$

$$= 1 + \frac{0.1339}{0.0669} = 1 + 2 = 3$$

Therefore, the reaction is of the **third order**.

### (4) The Differential method

This method was suggested by van't Hoff and, therefore, it is also called **van't Hoff's differential method.** According to it, the rate of a reaction of the *n*th order is proportional to the *n*th power of concentration.

$$-\frac{dC}{dt} = k\,C^n$$

where $C$ = concentration at any instant. In two experiments performed with different initial concentrations, we can write

$$-\frac{dC_1}{\mathrm{dt}} = k\,C_1^n \qquad \text{...(1)}$$

$$-\frac{dC_2}{\mathrm{dt}} = k\,C_2^n \qquad \text{...(2)}$$

Taking logs of the expression (1) and (2)

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n\log C_1 \qquad \text{...(3)}$$

$$\log\left(-\frac{dC_2}{dt}\right) = \log k + n\log C_2 \qquad \text{...(4)}$$

On substracting (4) from (3), we get

$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2} \qquad \text{...(5)}$$

To find $n$, $\left(-\frac{dC}{dt}\right)$ in the two experiments is determined by plotting concentrations against time ($t$). The slope, $\left(-\frac{dC}{dt}\right)$ at a given time interval is measured by drawing tangents. Using the values of slopes $\left(-\frac{dC_1}{dt}\right)$ and $\left(-\frac{dC_2}{dt}\right)$ in the equation (5), $n$ can be calculated.

### (5) Ostwald's Isolation method

This method is employed in determining the order of complicated reactions by 'isolating' one of the reactants so far as its influence on the rate of reaction is concerned. Suppose the reaction under consideration is :

$$A + B + C \longrightarrow \text{products}$$

The order of the reaction with respect to $A$, $B$ and $C$ is determined. For the determination of the order of reaction with respect to $A$, $B$ and $C$ are taken in a large excess so that their concentrations are not affected during the reaction. The order of the reaction is then determined by using any of the methods described earlier. Likewise, the order of the reaction with respect to $B$ and $C$ is determined. If $n_A$, $n_B$ and $n_C$ are the orders of the reaction with respect to $A$, $B$ and C respectively, the order of the reaction $n$ is given by the expression.

$$n = n_A + n_B + n_C$$

## COLLISION THEORY OF REACTION RATES

According to this theory, **a chemical reaction takes place only by collisions between the reacting molecules.** But not all collisions are effective. Only a small fraction of the collisions produce a reaction. The two main conditions for a collision between the reacting molecules to be productive are :

(1) The colliding molecules must posses sufficient kinetic energy to cause a reaction.

(2) The reacting molecules must collide with proper orientation.

Now let us have a closer look at these two postulates of the collision theory.

### (1) The molecules must collide with sufficient kinetic energy

Let us consider a reaction

$$\text{A}-\text{A} \quad + \quad \text{B}-\text{B} \longrightarrow 2\text{A}-\text{B}$$

A chemical reaction occurs by breaking bonds between the atoms of the reacting molecules and forming new bonds in the product molecules. The energy for the breaking of bonds comes from the kinetic energy possessed by the reacting molecules before the collision. Fig. 20.9 shows the energy of molecules $A_2$ and $B_2$ as the reaction $A_2 + B_2 \rightarrow 2AB$ progresses.

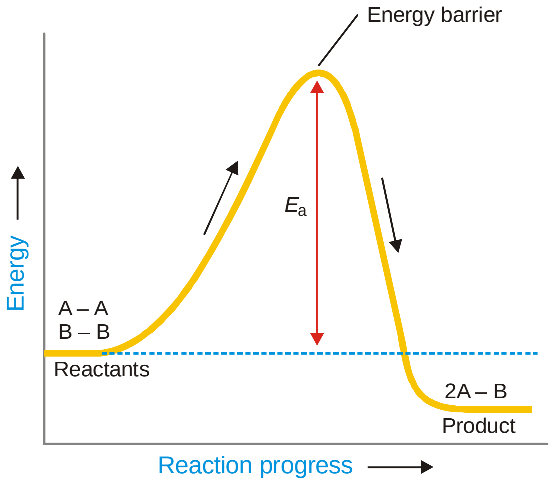


**Figure 20.9**

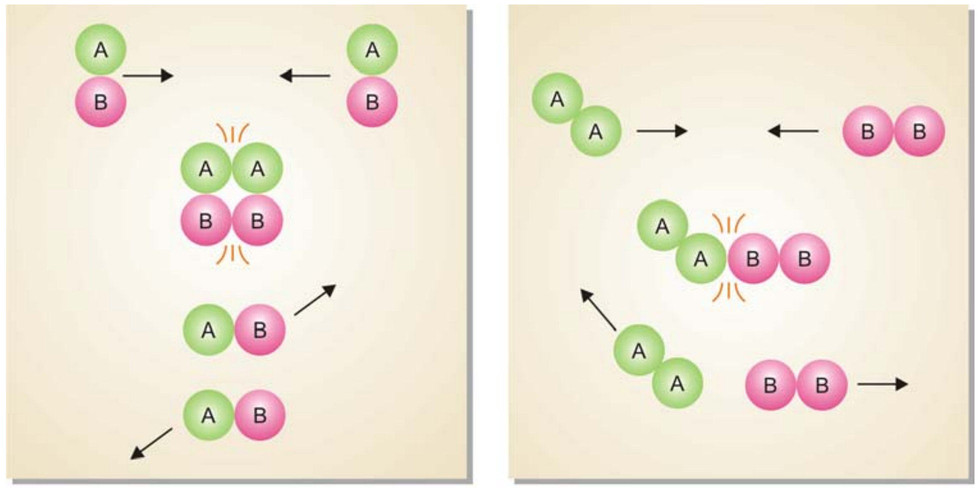
**The energy of the colliding molecules as the reaction $A_2 + B_2 \rightarrow 2AB$ proceeds. The activation energy $E_a$ provides the energy barrier.**

The Fig. 20.9 also shows the **activation energy,** $E_a$, that is the minimum energy necessary to cause a reaction between the colliding molecules. Only the molecules that collide with a kinetic energy greater than $E_a$, are able to get over the barrier and react. The molecules colliding with kinetic energies less that $E_a$ fail to surmount the *barrier*. The collisions between them are unproductive and the molecules simply bounce off one another.

### (2) The molecules must collide with correct orientation

The reactant molecules must collide with favourable orientation (relative position). **The correct orientation is that which ensure direct contact between the atoms involved in the breaking and forming of bonds.** (Fig. 20.10)

From the above discussion it is clear that : **Only the molecules colliding with kinetic energy greater that $E_a$ and with correct orientation can cause reaction.**



Effective collision

Ineffective collision

**Figure 20.10**
**Orientations of reacting molecules $A_2$ and $B_2$ which lead to an effective and ineffective collision.**

### Collision Theory and Reaction Rate Expression

Taking into account the two postulates of the collision theory, the reaction rate for the elementary process.

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

is given by the expression

$$\text{rate} = f \times p \times z$$

where $f$ = fraction of molecules which possess sufficient energy to react; $p$ = probable fraction of collisions with effective orientations, and $z$ = collision frequency.

## EFFECT OF INCREASE OF TEMPERATURE ON REACTION RATE

It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as **Temperature Coefficient.**

$$i.e., \text{ Temperature Coefficient } = \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}}$$

$$= 2 \text{ to } 3$$

It has been found that **generally an increase of temperature increases the rate of reaction.** As a rule, an increase of temperature by 10°C doubles the reaction rate.

### Temperature Dependence of Reaction Rate and Arrhenius Equation

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system is increased, more and more molecules will acquire necessary energy greater that $E_a$ to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested as simple relationship between the rate constant, $k$, for a reaction and the temperature of the system.

$$k = A\, e^{-E_a/RT} \qquad ...(1)$$

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

Taking natural logs of each side of the Arrhenius equation, it can be put in a more useful form :

$$1\text{n}\,k = -\frac{E_a}{RT} + 1\text{n}\ A \qquad \text{...(2)}$$

$$\log k = \frac{-E_a}{2.303\,RT} + \log A \qquad \text{...(3)}$$

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

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right] \qquad \text{...(4)}$$

Arrhenius equation is valuable because it can be used to calculate the activation energy, $E_a$ if the experimental value of the rate constant, $k$, is known.

## Calculation of $E_a$ Using Arrhenius Equation

In slightly rearranged form Arrhenius equation (2) can be written as

$$\underset{\underset{y}{\uparrow}}{1\text{n}\ k} = \underset{\underset{mx}{\uparrow}}{-\frac{E_a}{R}\left(\frac{1}{T}\right)} + \underset{\underset{b}{\uparrow}}{1\text{n}\ A} \qquad \text{...(3)}$$

You can see that the equation (3) is that of a straight line, $y = mx + b$. The two variables in this equation are 1n $k$ and $1/T$.

Thus if we plot the natural logarithm of $k$ against $1/T$, we get a straight line (Fig. 20.11). From the slope of the line, we can calculate the value of $E_a$.

$$\text{Slope} = -\frac{E_a}{R}$$

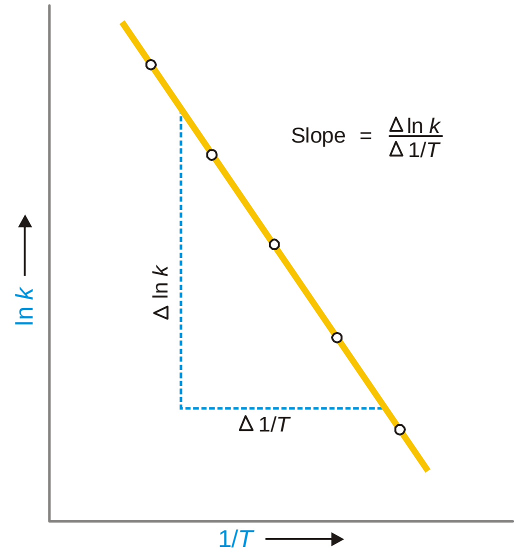


**Figure 20.11**

**The plot of In *k* versus I/*T* gives a straight line. The slope of line Δ In *k* /Δ I/*T* gives $E_a$ using the expression given above.**

**SOLVED PROBLEM.** The values of the rate constant (*k*) for the reaction $2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$ were determined at several temperatures. A plot of 1n k *versus* 1/*T* gave a straight line of which the slope was found to be – 1.2 × $10^4$ K. What is the activation energy of the reaction ?

**SOLUTION**

We know that

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -R \times (\text{slope})$$

Substituting the values, we have

$$E_a = (-8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\,(-1.2 \times 10^4\ \text{K})$$

$$= 1.0 \times 10^5\ \text{J mol}^{-1}$$

Thus the activation energy for the reaction is **$1.0 \times 10^5$ J mol$^{-1}$**

### Calculation of $E_a$ from the Values of *k* at Two Temperatures

The rate constant , *k*, is measured at two temperatures. $E_a$, is then calculated using the formula that can be derived as follows from equation (3) above.

At temperature $T_1$, where the rate constant is $k_1$,

$$1\text{n}\, k_1 = -\frac{E_a}{RT_1} + 1\text{n}\, A \qquad \text{...(1)}$$

At temperature $T_2$, where the rate constant is $k_2$,

$$1\text{n}\, k_2 = -\frac{E_a}{RT_2} + 1\text{n}\, A \qquad \text{...(2)}$$

Subtracting the equation (1) from the equation (2), we have

$$1\text{n}\, k_2 - 1\text{n}\, k_1 = \left(-\frac{E_a}{RT_2} + 1\text{n}\, A\right) - \left(-\frac{E_a}{RT_1} + 1\text{n}\, A\right)$$

$$= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1}$$

or $$1\text{n}\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \text{or} \quad \log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Thus the values of $k_1$ and $k_2$ measured at $T_1$ and $T_2$ can be used to find $E_a$.

**SOLVED PROBLEM.** The gas-phase reaction between methane ($CH_4$) and diatomic sulphur ($S_2$) is given by the equation

$$CH_4\,(g) + 2S_2\,(g) \longrightarrow CS_2\,(g) + 2H_2S\,(g)$$

At 550°C the rate constant for this reaction is 1.1 *l* mol$^{-1}$ sec and at 625°C the rate constant is 6.4 1 mol$^{-1}$ sec. Calculate $E_a$ for this reaction.

**SOLUTION**

Here $\quad k_1 = 1.1$ 1itre mol$^{-1}$ sec. $\quad T_1 = 550 + 273 = 823$ K

$k_2 = 6.4$ 1itre mol$^{-1}$ sec. $\quad T_2 = 625 + 273 = 898$ K

Substituting the values in the equation

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

$$1\text{n}\left(\frac{6.4}{1.1}\right)=\frac{E_a}{8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}}\left(\frac{1}{823\,\text{K}}-\frac{1}{898\,\text{K}}\right)$$

Solving for $E_a$, gives

$$E_a=\frac{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\;1\text{n}\left(\frac{6.4}{1.1}\right)}{\left(\frac{1}{823\,\text{K}}-\frac{1}{898\,\text{K}}\right)}$$

$$= \mathbf{1.4 \times 10^5\ J/mol}$$

## SIMULTANEOUS REACTIONS

Sometimes there are some side reactions accompanying the main chemical reaction. Such reactions are known as **complex reactions** as these do not take place in a single step. In other words, such complex reactions proceed in a series of steps instead of a single step and the rate of overall reaction is in accordance with the stoichiometric equation for that reaction. Generally, following types of complications occur.

(1) **Consecutive reactions**

(2) **Parallel reactions**

(3) **Reversible or opposing reactions**

These are discussed as follows :

### (1) Consecutive Reactions

The reactions in which the final product is formed through one or more intermediate steps are called **consecutive reactions.** These are also known as **sequential** reactions. In such reactions the product formed in one of the elementary reactions acts as the reactant for some other elementary reaction. Various step reactions can be written for the overall reaction as shown below :

$$\begin{array}{lccccc} & \text{A} & \xrightarrow{k_1} & \text{B} & \xrightarrow{k_2} & \text{C} \\ \text{Initial conc.} & [\text{A}]_0 & & 0 & & 0 \\ \text{Conc. after time } t & [\text{A}] & & [\text{B}] & & [\text{C}] \end{array}$$

In the above reaction the product C is formed from the reactant A through intermediate B. In this reaction each stage has its own different rate constants $k_1$ for the first step and $k_2$ for the second step. The net or overall rate of reaction depends upon the magnitude of these two rate constants. The initial concentration and concentration after time $t$ are shown below each species in above reaction under consideration.

It is clear that

$$[\text{A}]_0 = [\text{A}]+[\text{B}]+[\text{C}]$$

The differential rate expressions are

$$\frac{-\,d[\text{A}]}{dT}=k_1[\text{A}]$$

$$\frac{d[\text{B}]}{dT}=k_1[\text{A}]-k_2[\text{B}]$$

and

$$\frac{d[\text{C}]}{dT}=k_2[\text{B}]$$

During the course of the reaction the concentration of A, B and C vary as shown in the Fig. 20.12

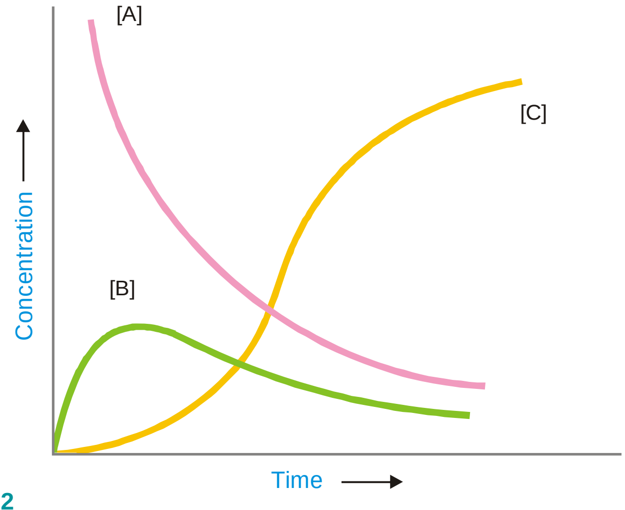


**Figure 20.12**
**Variation of concentration of reactants and products in a consecutive reaction.**

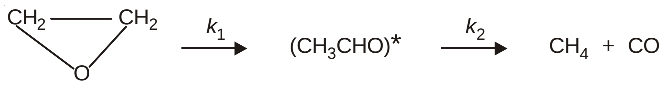
From the Fig 20.12 it is clear that the concentration of A decreases exponentially, the concentration of B first increases and then decreases and that of C increases (from zero) with time and finally attains the value equal to $[A]_0$ (initial concentration A) when all A has changed into the final product C.

### Examples of First Order Consecutive Reactions

(*a*) Decomposition of dimethyl ether is gaseous phase

$$CH_3COCH_3 \xrightarrow{k_1} CH_4 + HCHO \xrightarrow{k_2} H_2 + CO$$

(*b*) Decomposition of Ethylene oxide



(*c*) Any radioactive decay of the type

$$^{218}_{84}Po \xrightarrow{-\alpha} {}^{214}_{82}Pb \xrightarrow{-\beta} {}^{214}_{83}Bi \xrightarrow{-\beta} {}^{214}_{84}Po$$

### (2) Parallel or Side Reactions

In these reactions the reacting substance follows two or more paths to give two or more products. The preferential rate of such may be changed by varying the conditions like pressure, temperature or catalyst. The reaction in which the maximum yield of the products is obtained is called the main or major reaction while the other reaction (or reactions) are called side or parallel reactions. For example,

$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow[k_2]{} C \end{cases}$$

In the above reaction the reactant A gives two products B and C separately in two different reactions with rate constants $k_1$ and $k_2$ respectively. If $k_1 > k_2$ the reaction A $\longrightarrow$ B will be the major reaction and A $\longrightarrow$ C will be the side or parallel reaction. Let us assume that both these reactions are of first order and concentration of A is [A] at the time t. The differential rate expressions are

$$r_1 = \frac{-\,d[\mathrm{A}]}{dT} = k_1[\mathrm{A}] \qquad ...(i)$$

and

$$r_2 = \frac{-\,d[\mathrm{A}]}{dT} = k_2[\mathrm{A}] \qquad ...(ii)$$

The total rate of disappearance of A is given by

$$\frac{-\,d[\mathrm{A}]}{dT} = r_1 + r_2 = k_1[\mathrm{A}] + k_2[\mathrm{A}]$$

$$= (k_1 + k_2)[\mathrm{A}]$$

$$= k'[\mathrm{A}] \qquad ...(iii)$$

where $k'$ is the first order rate constant. It is equal to the sum of the two constants $k_1$ and $k_2$ of two side reactions.

Integrating equation (*iii*), we get

$$\int \frac{-\,d[\mathrm{A}]}{dT} = \int k'[\mathrm{A}]$$

applying the limits $[A_0]$ & $[A]_t$ and 0 & $t$, we have

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{-\,d[\mathrm{A}]}{dt} = k' \int_0^t dt$$

$$1n\,\frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = k't + (k_1 + k_2)t \qquad ...(iv)$$

where $[A]_0$ is the initial concentration of the reactant A and $[A]_t$ is concentration of A at time t.

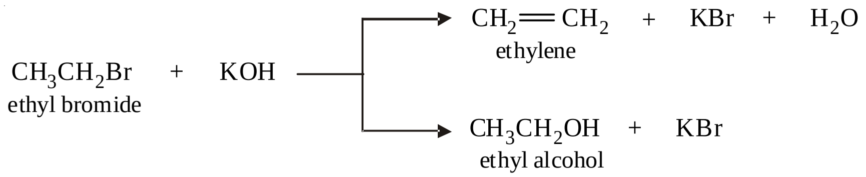
The ratio of the rates of two side reactions is obtained by dividing equations (*i*) by (*ii*), we have

$$\frac{r_1}{r_2} = \frac{k_1[\mathrm{A}]}{k_2[\mathrm{A}]} = \frac{k_1}{k_2} \qquad ...(v)$$

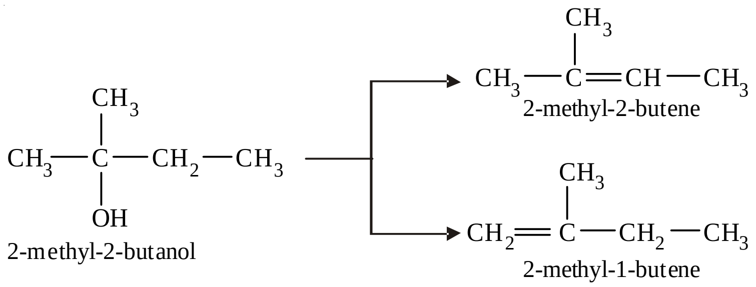
From equations (*iv*) and (*v*) we can calculate the individual rate constant $k_1$ and $k_2$.

### Examples of Parallel or Side Reactions

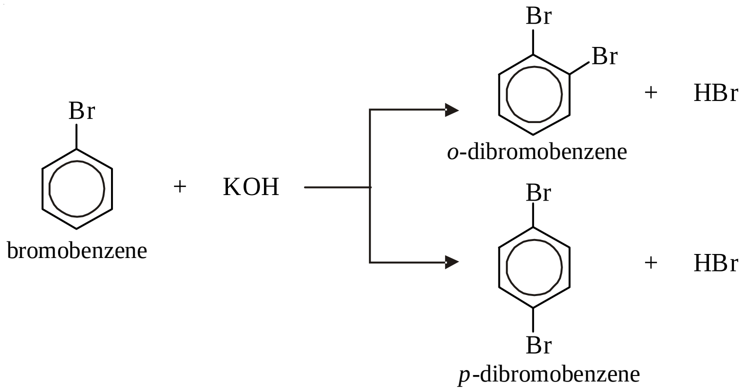
(*a*) Reaction of ethyl bromide with potassium hydroxide



(*b*) Dehydration of 2-methyl–2–butanol



(*c*) Bromination of bromobenzene



### (3) Reversible or Opposing Reactions

In reversible or opposing reactions the products formed also react to give back the reactants. Initially, the rate of forward reaction is very large which decreases with passage of time and the rate of backward or reverse reaction is zero which increases with passage of item. A stage is reached when two rates become equal. This situation is called the chemical equilibrium. It is dynamic in nature *i.e.*, all the species are reaching at the rate at which they are being formed. A reaction of this type may be represented as

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}$$

| | A | B |
|---|---|---|
| Initial concentration | $[\mathrm{A}]_0$ | 0 |
| Conc. after time t | [A] | [B] |

where $k_f$ and $k_b$ are the rate constants of the forward and backward reactions respectively.

The overall rate of reaction is given by

Rate of Reaction = Rate of forward reaction – Rate of backward reaction

*i.e.*,
$$\frac{-d[\mathrm{A}]}{dt} = \frac{d[\mathrm{B}]}{dt} = k_f[\mathrm{A}] - k_b[\mathrm{B}] \qquad \text{...}(i)$$

If $[\mathrm{A}]_0$ is the initial concentration of A and $x$ moles of it have reacted in time $t$

then $$[\mathrm{A}]_t = [\mathrm{A}]_0 - x$$

and $$[\mathrm{B}] = x$$

Substituting these in equation (*i*), we get

$$\frac{dx}{dt} = k_f([\mathrm{A}]_0 - x) - k_b x \qquad \text{...}(ii)$$

At equilibrium $$\frac{dx}{dt} = 0$$

Hence $$k_f([\mathrm{A}]_0 - x_{eq}) = k_b x_{eq} \qquad \text{...}(iii)$$

where $x_{eq}$. is the concentration of A that has reacted into B at equilibrium. From equation (*iii*) we have

$$k_b = k_f\left(\frac{[\mathrm{A}]_0 - x_{eq}}{x_{eq}}\right)$$

Substituting the value of $k_b$ in equation (*ii*), we get

$$\frac{dx}{dt} = k_f([A]_0 - x) - k_f\left(\frac{[A]_0 - x_{eq}}{x_{eq}}\right)x$$

Integrating this equation between the limits $t = 0, x = 0$ and $t = t, x = x_{eq}$, we have

$$\int_0^x \frac{dx}{x_{eq} - x} = k_f \frac{[A_0]}{x_{eq}} \int_0^t dt$$

$$= -\mathrm{1n}\,(x_{eq} - x) + \mathrm{1n}\,x_{eq} = k_f \frac{[A]_0\,t}{x_{eq}}$$

or
$$\mathrm{1n}\,\frac{x_{eq}}{x_{eq} - x} = k_f \frac{[A]_0}{x_{eq}}\,t$$

From this equation we can find the value of $k_f$ from the quantities $[A]_0$, $x_{eq}$ and $x$ at time t. All these quantities can be measured easily. From the value of $k_f$ the value of $k_b$ can be calculated by using the relation.

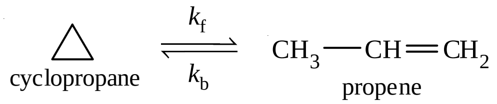
$$k_b = k_f\left(\frac{[A_0] - x_{eq}}{x_{eq}}\right)$$

### Examples of Opposing Reactions

(*a*) Dissociation of hydrogen iodides

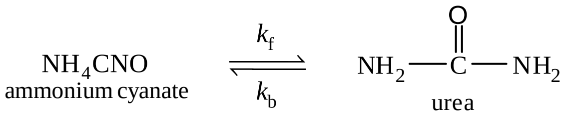
$$2HI \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2 + I_2$$

(*b*) Isomerisation of cyclopropane into propene



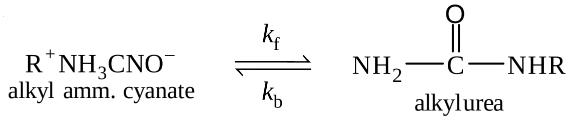
$$\text{cyclopropane} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CH_3{-}CH{=}CH_2$$

(*c*) Isomerisation of ammonium cyanate into urea in aqueous solution.



$$\underset{\text{ammonium cyanate}}{NH_4CNO} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{urea}}{NH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2}$$

(*d*) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution



$$\underset{\text{alkyl amm. cyanate}}{R^+NH_3CNO^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{alkylurea}}{NH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHR}$$

(*e*) Reaction between gaseous CO and $NO_2$

$$CO(g) + NO_2(g) \underset{k_b}{\overset{k_f}{\rightleftharpoons}} CO_2(g) + NO(g)$$

### Limitations of the Collision Theory

The collision theory of reaction rates is logical and correct. However, it has been oversimplified and suffers from the following weaknesses.

(1) **The theory applies to simple gaseous reactions only.** It is also valid for solutions in which the reacting species exist as simple molecules.

(2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. **For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.**

(3) There is no method for determining the steric effect (*p*) for a reaction whose rate constant has not been determined experimentally.

(4) In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.

(5) **The collision theory is silent on the cleavage and formation of bonds involved in the reaction.**

The various drawbacks in the simple collision theory do not appear in the modern transition-state theory.

## TRANSITION STATE THEORY

The **transition state** or **activated complex theory** was developed by Henry Erying (1935). This theory is also called the **absolute rate theory** because with its help it is possible to get the absolute value of the rate constant. The transition state theory assume that simply a collision between the reactant molecules does not really causes a reaction. During the collision, **the reactant molecules form a transition state or activated complex which decomposes to give the products.**

Thus,

$$\underbrace{\text{A} + \text{B—C}}_{\text{Reactants}} \longrightarrow \underset{\substack{\text{Activated}\\ \text{complex}}}{\text{ABC}^{\ddagger}} \longrightarrow \underbrace{\text{A—B} + \text{C}}_{\text{Products}}$$

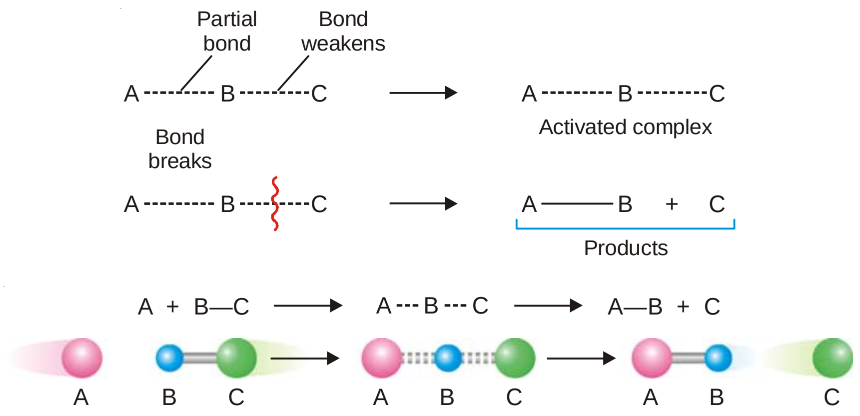
The double dagger superscript (‡) is used to identify the activated complex.

The transition state theory may be summarised as follows :

(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process **the kinetic energy of the two molecules is converted into potential energy.**

(2) As the molecules come close, **the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.**

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an **activated complex** or **transition state.** The activated complex is momentary and decomposes to give the products (A–B + C)



The activated complex theory may be illustrated by the **reaction energy diagram** (Fig. 20.13).

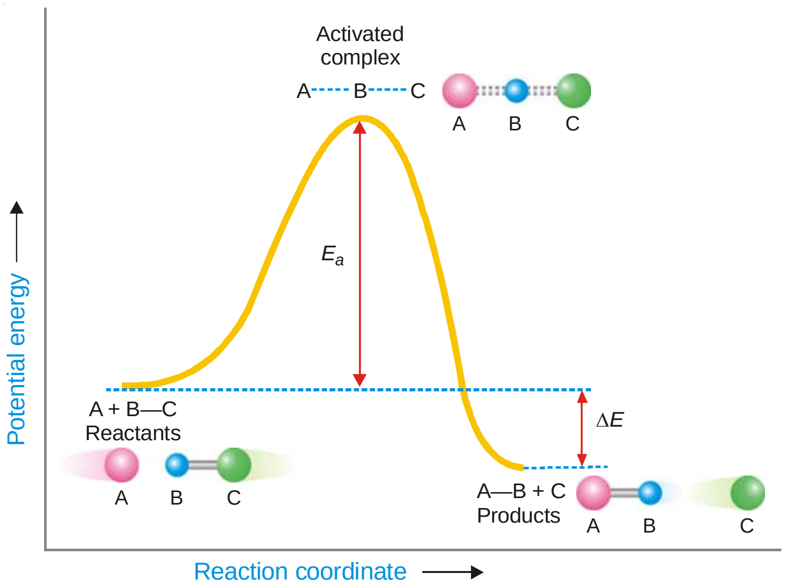


**Figure 20.13**
**Change of potential energy during a collision between the reactant molecules for an exothermic reaction.**

Here the potential energy of the system undergoing reaction is plotted against the **reaction coordinate** (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the **activation energy,** $E_a$.The reactants must have this minimum energy to undergo the reaction through the transition state.

As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 20.14) the energy obtained in going from the activated complex to products will be more than the activation energy ($E_a$). Thus such a reaction will be **exothermic.**

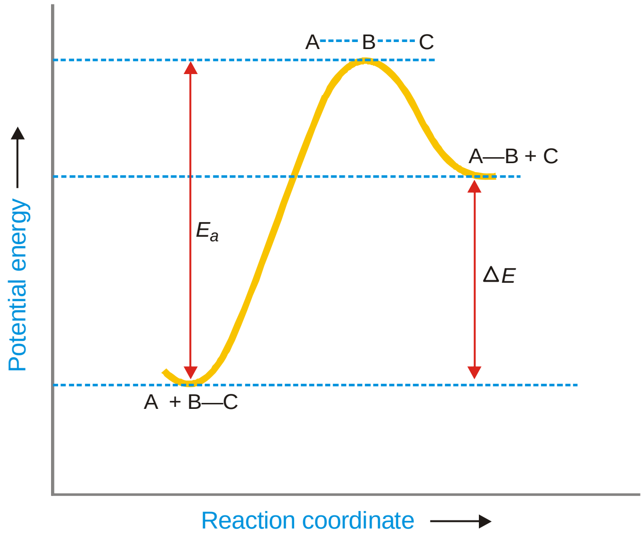


**Figure 20.14**
**A potential energy diagram for an endothermic reaction.**

On the other hand, if the potential energy of the products is greater than that of the reactants, the energy released in going from the activated complex to products will be less than the activation energy and the reaction will be **endothermic.**

## ACTIVATION ENERGY AND CATALYSIS

We know that for each reaction a certain energy barrier must be surmounted. As shown in the energy diagram shown in Fig. 20.15, the reactant molecules must possess the activation energy, $E_a$, for the reaction to occur.

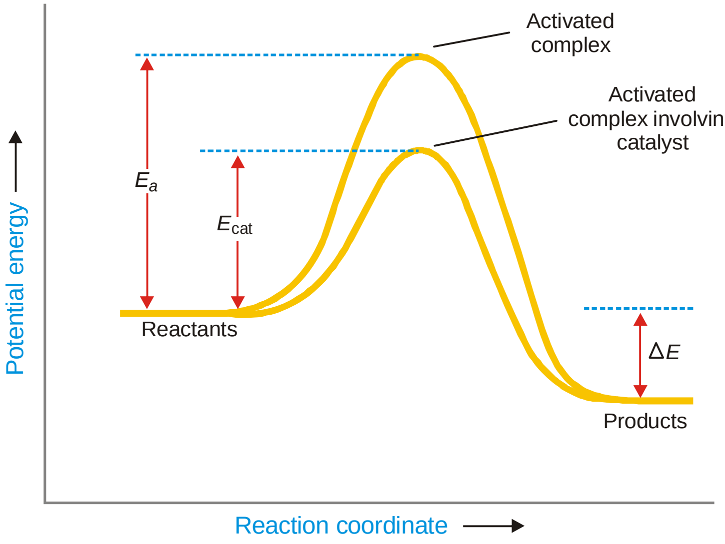


**Figure 20.15**
**Energy diagram for a catalysed and uncatalysed reaction showing a lowering of activation energy by a catalyst.**

**The catalyst functions by providing another pathway with lower activation energy,** $E_{cat}$. Thus a much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same. It may be noted from the above diagram that although a catalyst lowers the activation energy, the energy difference, $\Delta E$, between products and reactants remains the same.

## LINDEMAN'S THEORY OF UNIMOLECULAR REACTIONS

A number of unimolecular reactions, for example,

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

are found to be of the first order. It is difficult to account for such reactions using the collision theory and the absolute reaction rate theory. If two molecules must collide in order to provide necessary activation energy, a second order rate law should result. In 1922, Lindeman explained this anomaly by assuming that **there existed a time lag between activation and reaction of molecules.** During this time lag, the activated molecules could either react or be deactivated. Thus,

$$A + A \longrightarrow A + A^* \qquad \textit{activation} \;...(1)$$

$$A + A^* \longrightarrow A + A \qquad \textit{deactivation} \;...(2)$$

$$A^* \longrightarrow \text{products} \qquad \textit{reaction} \;...(3)$$

If the time lag is long, step (3) is slow, the reaction should follow first order kinetics. However, if $A$ reacts as soon as formed, step (2) is the slow step, then the reaction should be second order.

The proof of Lindeman's theory is provided by studying the effect of change of pressure on the reaction. At high pressure the rate of deactivation will be dominant. On the other hand, at sufficiently low pressure all the activated molecules will react before they can be deactivated. Therefore the reaction kinetics should change from first order to second order with decreasing pressure. Several gases are known to exhibit this behaviour.

## EXAMINATION QUESTIONS

**1.** Define or explain the following terms :

| | | | |
|---|---|---|---|
| (*a*) | Rate of reaction | (*b*) | Order of a reaction |
| (*c*) | Molecularity of a reaction | (*d*) | Rate constant |
| (*e*) | Half life of a reaction | (*f*) | Arrhenius equation |

**2.** Derive mathematical expression for the rate constant of a reaction (A + B $\longrightarrow$ Products) of the second order.

**3.** The first order rate constant for the decomposition of $N_2O_2$ of 0°C is $5.2 \times 10^{-6}$ min$^{-1}$. If the energy of activation is 6200 joules per mole, calculate the rate constant at 25°C.

**Answer.** $7.385 \times 10^{-6}$

**4.** (*a*) Define order of a reaction, molecularity of a reaction and half life period. Show that for first order reactions the half life period is independent of the initial concentration.

(*b*) The rate constant of a reaction is $1.2 \times 10^{-3}$ sec$^{-1}$ at 303 K. Calculate the rate constant at 313 K, if the activation energy for the reaction is 44.12 kJ mol$^{-1}$.

**Answer.** $1.47 \times 10^{-3}$

**5.** (*a*) Explain why the rate of a reaction cannot be measured by dividing the amount of reactants reacted by the time taken.

(*b*) What is activation energy? How is it determined?

**6.** (*a*) For the kinetics of bimolecular reactions briefly discuss the "Collision Theory".

(*b*) Derive an expression for the half life period of the following reaction:

$A \longrightarrow B,\ \text{rate} \propto [A]$

(*c*) With the help of two examples, show that the rate can be independent of initial concentration of the reactants. What is the order of such reactions?

(*d*) If the rate constant at one temperature alongwith the activation energy is given, how can the rate constant at any other temperature be determined?

**7.** Explain Arrhenius equation. Discuss Arrhenius concept of activation energy. Give graphical representation of activation energy diagram. (*Jiwaji BSc, 2000*)

**8.** (*a*) Explain, with examples, zero-order reaction. Write rate law expression for it.

(*b*) The reaction, A + B + C $\longrightarrow$ Products, is found to obey the rate law

$$r = \frac{-d[A]}{dt} = k\,[A]^2\,[B]^{3/2}\,[C]^{-1/2}$$

What is the order of overall reaction? (*Purvanchal BSc, 2000*)

**9.** Derive an expression for rate constant of a bimulecular gaseous reaction on the basis of collision theory. (*Allahabad BSc, 2001*)

**10.** Distinguish between reaction rate and rate constant of a reaction. Derive the integrated rate law for first order reaction. (*kathmandu BSc, 2001*)

**11.** (*a*) Explain briefly the collision theory of reaction rates. What are its limitations and how far they are overcome by theory of absoulte reaction rates?

(*b*) Write unit of rate constant for zero order reaction. (*Jamia Millia BSc, 2001*)

**12.** (*a*) A reactant R is converted into product by the following mechanism :

$$R \rightarrow x \rightarrow P$$

where both the steps are of first order. Find out how the concentration of x varies with time and give a physical interpretation of the resulting expression.

(*b*) A solution containing equal concentrations of ethyl acetate and NaOH is 25% saponified in 5 minutes. What will be the % saponification after 10 minutes.

**Answer.** $1.11 \times 10^{-5}$ (*Vidyasagar BSc* (*H*), *2002*)

**13.** Deduce the rate expression for second order reaction where both the concentration terms are same. What is half-life period of the second order reaction? (*Arunachal BSc (H), 2002*)

**14.** (*a*) Explain various methods of determining the order of a reaction.

(*b*) Derive an expression for the dependence of rate constant of a reaction with temperature.

(*c*) Explain how the acid catalysed hydrolysis of an ester is followed experimentally to show it to follow first order kinetics.

(*d*) What are zero order reactions? Give one example. (*Sri Venkateswara BSc, 2002*)

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

**Answer.** 37.75% (*Vidyasagar BSc, 2002*)

**16.** Discuss the kinetics of hydrolysis of ethyl acetate in acidic medium. (*Jamia Millia BSc, 2002*)

**17.** Write short notes on :

(*a*) Activation energy (*b*) Energy barrier (*MD Rohtak BSc, 2002*)

**18.** Derive the rate equation for the first order reaction and show that :

(*i*) Half-life is independent of initial concentration.

(*ii*) The rate constant is independent of concentration. (*MD Rohtak BSc, 2002*)

**19.** The velocity constant for a certain reaction is $5.25 \times 10^{-3}$ at 303 K and $11.1 \times 10^{-3}$ at 314 K. Calculate the energy of activation of the reaction.

**Answer.** 53.849 kJ (*Mumbai BSc, 2002*)

**20.** (*a*) Describe the expression for the rate constant of the reaction $A + B \rightarrow$ Products. The initial concentrations of A and B are different.

(*b*) Describe the graphical method for the determination of order of reaction.

(*c*) Obtain the unit of the second order rate constant from the rate expression. (*HS Gaur BSc, 2002*)

**21.** The energy of activation for a reaction is 105 kJ $mol^{-1}$. Calculate the specific reaction rate for the reaction at 300 K, if the frequency factor is $2.5 \times 10^{15}$ $sec^{-1}$.

**Answer.** $1.3 \times 10^{-3}$ $sec^{-1}$ (*Mumbai BSc, 2002*)

**22.** (*a*) Derive the integrated Arrhenius equation of activation energy. How is the energy of activation determined from the plot?

(*b*) The value of rate constant for the decomposition of nitrogen pentoxide ($N_2O_5 \rightarrow N_2O_4 + ½O_2$) is $4.346 \times 10^{-5}$ at 25°C and $4.87 \times 10^{-3}$ at 65°C. Calculate the energy of activation for the reaction. ($R = 8.314$ $JK^{-1}$ $mol^{-1}$)

**Answer.** 103.585 kJ (*Arunachal BSc (H), 2002*)

**23.** (*a*) Discuss the collision theory of Bimolecular reactions.

(*b*) Define collision number. (*Nagpur BSc, 2002*)

**24.** (*a*) Name different methods to determine the order of a reactions and describe the half-life method in detail.

(*b*) Give theory of absolute reaction rates. (*Jamia Millia BSc, 2002*)

**25.** If the half-life of a first order reaction in A is 15 min., how long it will take for [A] to reach 10 percent of the initial concentration?

**Answer.** 2990 sec (*Arunachal BSc, 2002*)

**26.** The rate constant of a second order reaction is $5.70 \times 10^{-5}$ dm$^3$ mol$^{-1}$ sec$^{-1}$ at 25°C and $1.64 \times 10^{-4}$ dm$^3$ mol$^{-1}$ sec$^{-1}$ at 40°C. Calculate the activation energy of the reaction. ($R$ = 8.314 JK$^{-1}$ mol$^{-1}$)

**Answer.** 54.645 kJ (*Mizoram BSc (H), 2002*)

**27.** Explain the term collision frequency. On what factors does it depend? What is meant by collision diameter?

(*Guru Nanak Dev BSc, 2002*)

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

**Answer.** 450 sec (*Allahabad BSc, 2002*)

**29.** How is the order of the reaction determined by Differential method and Half-life method?

(*Arunachal BSc, 2002*)

**30.** A second order reaction, in which the initial concentration of both the reactants is the same, is 25% completed in 600 sec. How long will it take for the reaction to go to 75% completion?

**Answer.** 5400 sec (*Jamia Millia BSc, 2002*)

**31.** Explain the following :

(*i*) If a reaction is pseudo order, the half life is always defined with respect to the species present in the smallest amount.

(*ii*) Under certain situation the rate of reaction and specific reaction rate become identical.

(*Delhi BSc, 2002*)

**32.** (*a*) Derive the Arrhenius equation and discuss how it is useful to calculate the energy of activation.

(*b*) Give one example each for pseudo unimolecular, second order, third order and zero order reactions.

(*Madurai BSc, 2002*)

**33.** Explain, with examples, the functions of catalytic promoters and poisons in chemical reactions.

(*Panjab BSc, 2002*)

**34.** The activation energy of a non-catalysed reaction at 37°C is 83.68 kJ mol$^{-1}$ and the activation energy for the same reaction catalysed by enzymes is 25.10 kJ mol$^{-1}$. Calculate the ratio of the two rate constants.

**Answer.** 0.9975 (*Kalyani BSc, 2003*)

**35.** (*a*) Derive an expression for rate constant ($k$) for the reaction $A + B \longrightarrow$ Products on the basis of collision theory. Express the value of $k$ in cm$^3$ mol$^{-1}$ s$^{-1}$.

(*b*) The rate constants for a reaction at 27°C and 37°C are $4.5 \times 10^{-5}$ sec$^{-2}$ and $9.0 \times 10^{-5}$ sec$^{-2}$. Evaluate the activation energy of the reaction.

**Answer.** 53.598 kJ (*Punjabi BSc, 2003*)

**36.** Write short notes on:

(*i*) Transition state theory of reaction rates

(*ii*) Parallel reactions

(*iii*) Opposing reactions (*Allahabad BSc, 2003*)

**37.** A ln $k$ versus 1/$T$ graph was plotted to calculate the activation energy of a reaction using Arrhenius equation for the effect of temperature on reaction rate. The slope of the straight line was found to be $-2.55 \times 10^4$. Calculate the activation energy of the reaction.

**Answer.** $21.2007 \times 10^4$ J (*Guru Nanak Dev BSc, 2003*)

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

**Answer.** 53.598 kJ (*Arunachal BSc, 2003*)

**39.** What do you understand by the term: 'rate determining step' of a complex reaction? What is steady–state hypothesis? (*Arunachal BSc, 2003*)

**40.** What would be the units of the rate constant in the following rate law :

rate = $k$ [A][B]

if the concentration is expressed in moles litre$^{-1}$ and time in seconds. (*Delhi BSc, 2003*)

**41.** Show that

(*i*) for a first order reaction $t_{\frac{1}{2}} = \frac{0.693}{k}$

(*ii*) for a second order reaction $t_{\frac{1}{2}} = \frac{1}{k_2\, a}$ (*Allahabad BSc, 2003*)

**42.** Derive the equation

$$k = \frac{1}{t}\ \frac{x}{a\,(a-x)}$$

for a second order reaction where ‘*k*’ is second order rate constant, ‘*x*’ is in the amount of product formed after time ‘*t*’ and ‘*a*’ is the initial amount of reactants. What is the unit of *k* in the equation?

(*Nagpur BSc, 2003*)

**43.** Write down the rate and the differential rate expression for A + 2B ⟶ Products.

(*Guru Nanak Dev BSc, 2003*)

**44.** Explain the following with examples:

(*a*) Parallel Reactions

(*b*) Reversible Reactions

(*c*) Consecutive Reactions (*Purvanchal BSc, 2003*)

**45.** Derive the rate expression for an opposing reaction in which the forward as well as reverse reactions are both first order. (*Kalyani BSc, 2003*)

**46.** (*a*) What are pseudo and true unimolecular reactions? Explain with examples.

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

**Answer.** (*b*) 85 min (*Purvanchal BSc, 2003*)

**47.** (*a*) Derive an expression for the rate constant of a second order reaction, involving one reactant only. Also write how the equation you, derive, is employed in the graphical method to confirm second order.

(*b*) Describe the activated complex theory of bimolecular reactions. What are the advantages of this theory over collision theory? (*Guru Nanak Dev BSc, 2004*)

**48.** (*a*) Derive a second order rate equation for the reaction

$$2\,\text{A} \longrightarrow \text{Product.}$$

Explain that half-life period depends upon initial concentration of the reactants.

(*b*) Calculate the activation energy of a reaction whose rate constant at 27°C gets doubled for 10°C rise in temperature.

**Answer.** (*b*) 12804.5 cal (*Agra BSc, 2004*)

**49.** (*a*) Derive an expression for the rate constant for 2nd order reaction assuming the initial concentration to be the same.

(*b*) 50% of a first order reaction is completed in 23 minutes. Calculate the time required to complete 90% of the reaction.

**Answer.** (*b*) 76.43 min (*Madras BSc, 2004*)

**50.** A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?

**Answer.** 112.79 min (*Patna BSc, 2004*)

**51.** Calculate the half-life period for the first order reaction whose rate constant is $1.052 \times 10^{-3}$ $\text{sec}^{-1}$.

**Answer.** 659 sec (*Indore BSc, 2004*)

**52.** An acid solution of sucrose was hydrolysed to the extent of 54% after 67 minutes. Assuming the reaction to be of first order, calculate the time taken for 80% hydrolysis.

**Answer.** 124.4 min (*Allahabad BSc, 2005*)

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

**Answer.** 2700 min (*Purvanchal BSc, 2005*)

**54.** For a certain reaction, it takes 5 minutes for the initial concentration of 0.5 mol $lit^{-1}$ to become 0.25 mol $lit^{-1}$ and another 5 minutes to became 0.125 mol $lit^{-1}$. (a) What is the order of the reaction ? (b) What is the rate contant of the reaction ?

**Answer.** (a) One (b) 0.136 $min^{-1}$ (*Mizoram BSc, 2005*)

**55** If the half life of a first order in A is 2 min, how long will it take A to reach 25% of its initial concentration.

**Answer.** 4 min (*Delhi BSc, 2006*)

**56.** A reaction that is first order with respect to the reactant A has a rate constant of 6 $min^{-1}$. If we start $[A] = 5.0$ mol $lit^{-1}$ when would $[A]$ reach the value of 0.05 mol $lit^{-1}$ ?

**Answer.** 0.7676 min (*Mysore BSc, 2006*)

**57.** The rate of a particular reaction becomes three times when the temperature is increased from 298 K to 308 K. Calculate the energy of activation for the reaction.

**Answer.** 83.8 kJ $mol^{-1}$ (*Himachal BSc, 2006*)

**58.** Calculate the half life of a first order reaction where the specific rate constant is (a) 200 $sec^{-1}$ (b) 2 $min^{-1}$.

**Answer.** (a) 0.00346 $sec^{-1}$ ; (b) 0.3465 $min^{-1}$ (*Panjab BSc, 2006*)

## MULTIPLE CHOICE QUESTIONS

**1.** Which of the following includes all the aims of kinetics?

(*i*) to measure the rate of a reaction
(*ii*) to be able to predict the rate of a reaction
(*iii*) to be able to establish the mechanism by which a reaction occurs
(*iv*) to be able to control a reaction

(*a*) (*i*), (*ii*) and (*iii*)
(*b*) (*i*) and (*ii*)
(*c*) (*i*) and (*iii*)
(*d*) (*i*), (*ii*), (*iii*) and (*iv*)

**Answer.** (*d*)

**2.** Reaction rates can change with

(*a*) temperature
(*b*) the addition of a catalyst
(*c*) reactant concentrations
(*d*) all of these

**Answer.** (*d*)

**3.** Reaction rates generally

(*a*) are constant throughout a reaction
(*b*) are smallest at the beginning and increase with time
(*c*) are greatest at the beginning of a reaction and decrease with time
(*d*) no such generalisations can be made

**Answer.** (*d*)

**4.** Consider the reaction in which nitric oxide is oxidized to nitrogen dioxide,

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$, for which the rate law is = $k\,[NO]^2\,[O_2]$. If this reaction takes place in a sealed vessel and the partial pressure of nitric oxide is doubled, what effect would this have on the rate of reaction?

(*a*) the reaction rate would triple
(*b*) the reaction rate would double
(*c*) the reaction rate would quadruple
(*d*) there would be no effect on the reaction rate

**Answer.** (*c*)

**5.** Which three factors affect the rate of a chemical reaction?

(*a*) temperature, pressure and humidity

(*b*) temperature, reactant concentration and catalyst

(*c*) temperature, reactant concentration and pressure

(*d*) temperature, product concentration and container volume

**Answer.** (*b*)

**6.** For first-order reactions the rate constant, *k*, has the unit(s)

(*a*) l $\text{mol}^{-1}$ (*b*) $\text{time}^{-1}$

(*c*) $(\text{mol/l})^{-1}\ \text{time}^{-1}$ (*d*) time mol $\text{l}^{-1}$

**Answer.** (*b*)

**7.** What are the units of the rate constant for a reaction in solution that has an overall reaction order of two? (M is molarity, s is seconds.)

(*a*) $\text{M}^{-1}\ \text{s}^{-1}$ (*b*) $\text{M}^{-1}$

(*c*) $\text{s}^{-1}$ (*d*) $\text{M s}^{-1}$

**Answer.** (*a*)

**8.** The reaction A $\rightarrow$ B is a second-order process. When the initial concentration of A is 0.50 M, the half-life is 8.0 minutes. What is the half-life if the initial concentration of A is 0.10 M?

(*a*) 1.6 minutes (*b*) 8.0 minutes

(*c*) 40.0 minutes (*d*) 16.0 minutes

**Answer.** (*c*).

**9.** The quantity *k* in a rate law expression

(*a*) is independent of concentration (*b*) is called the Arrhenius constant

(*c*) is dimensionless (*d*) is independent of the temperature

**Answer.** (*a*)

**10.** The first-order rate constant for the decomposition of $N_2O_5$ to $NO_2$ and $O_2$ at 70°C is $6.82 \times 10^{-3}\ \text{s}^{-1}$. Suppose we start with 0.300 mol of $N_2O_5$(g) in a 0.500 L container. How many moles of $N_2O_5$ will remain after 1.5 min?

(*a*) 0.081 mol (*b*) 0.555 mol

(*c*) 0.325 mol (*d*) 0.162 mol

**Answer.** (*d*)

**11.** As the temperature of a reaction is increased, the rate of the reaction increases because the

(*a*) reactant molecules collide with greater energy

(*b*) reactant molecules collide less frequently

(*c*) reactant molecules collide less frequently and with greater energy

(*d*) activation energy is lowered

**Answer.** (*d*)

**12.** In a series of reactions, which is the rate-determining step?

(*a*) the simplest reaction (*b*) the main reaction involving the major reactant

(*c*) the slowest reaction (*d*) the fastest reaction

**Answer.** (*c*)

**13.** Beaker A contains a 1 gram piece of zinc and beaker B contains 1 gram of powdered zinc. If 100 milliliters of 0.1 M HCl is added to each of the beakers, how is the rate of reaction in beaker A compared to the rate of reaction in beaker B?

(*a*) the rate in A is greater due to the smaller surface area of the zinc

(*b*) the rate in A is greater due to the greater surface area of the zinc

(*c*) the rate in B is greater due to the smaller surface area of the zinc

(*d*) the rate in B is greater due to the greater surface area of the zinc

**Answer.** (*d*)

**14.** The decomposition of ethylene oxide at 652 K

$(CH_2)_2O(g) \longrightarrow CH_4(g) + CO(g)$

is first-order with $k = 0.0120\ min^{-1}$. The activation energy of the reaction is 218 kJ/mol. Calculate the rate constant of the reaction at 525 K.

| | | | |
|---|---|---|---|
| (*a*) | $7.11 \times 10^{-7}\ min^{-1}$ | (*b*) | $202\ min^{-1}$ |
| (*c*) | $8.7 \times 10^{-6}\ min^{-1}$ | (*d*) | $-14.2\ min^{-1}$ |

**Answer.** (*a*)

**15.** Here is a second order reaction $A \longrightarrow P$. If the initial concentration of A 0.0818 M goes down 30.0% in 3.15 minutes, what is the rate constant for the reaction?

| | | | |
|---|---|---|---|
| (*a*) | $0.0078\ l\ mol^{-1}\ s^{-1}$ | (*b*) | $1.7\ l\ mol^{-1}\ s^{-1}$ |
| (*c*) | $9.1\ l\ mol^{-1}\ s^{-1}$ | (*d*) | $16\ l\ mol^{-1}\ s^{-1}$ |

**Answer.** (*b*)

**16.** For a first–order reaction of the form $A \longrightarrow P$, $t_{1/2} = 9$ hours. If the concentration of A is 0.0013 M right now, what is the best estimate of what it was the day before yesterday?

| | | | |
|---|---|---|---|
| (*a*) | 0.0026 M | (*b*) | 0.0065 M |
| (*c*) | 0.0052 M | (*d*) | 0.042 M |

**Answer.** (*d*)

**17.** The rate law relates the rate of a chemical reaction to

| | | | |
|---|---|---|---|
| (*a*) | the concentrations of reactants | (*b*) | the temperature |
| (*c*) | the activation energy | (*d*) | the reaction mechanism |

**Answer.** (*a*)

**18.** Rate laws for chemical reactions are determined

(*a*) by examining the coefficients in the balanced chemical equation

(*b*) from the equilibrium constant

(*c*) from the rates of the forward and reverse reactions of the system at equilibrium

(*d*) by experiment

**Answer.** (*d*)

**19.** For a reaction, $A \longrightarrow$ products, a graph of [A] versus time is found to be a straight line. What is the order of this reaction?

| | | | |
|---|---|---|---|
| (*a*) | zero order | (*b*) | first order |
| (*c*) | second order | (*d*) | third order |

**Answer.** (*a*)

**20.** To study the rate of a reaction, it is necessary to

(*a*) identify the reactants

(*b*) know the relative amounts of reactants used

(*c*) know the overall chemical equation for the reaction

(*d*) all of the above are necessary

**Answer.** (*d*)

**21.** Why do most chemical reaction rates increase rapidly as the temperature rises?

(*a*) the fraction of the molecules with kinetic energy greater than the activation energy increases rapidly with temperature

(*b*) the average kinetic energy increases as temperature rises

(*c*) the activation energy decreases as temperature rises

(*d*) more collisions take place between particles so that the reaction can occur

**Answer.** (*a*)

**22.** The rate constant for a reaction depends upon each of the following, EXCEPT:

(*a*) solvent for solutions (*b*) temperature

(*c*) concentration of reactants (*d*) nature of reactants

**Answer.** (*c*)

**23.** All of the following are true statements concerning reaction orders EXCEPT:

(*a*) the rate of a zero-order reaction is constant

(*b*) after three half-lives, a radioactive sample will have one-ninth of its original concentration

(*c*) the units for the rate constant for first order reactions are $sec^{-1}$

(*d*) if doubling the concentration of a reactant doubles the rate of the reaction, then the reaction is first order in that reactant

**Answer.** (*b*)

**24.** The powers in the rate law are determined by

(*a*) the principle of detailed balance

(*b*) the physical states of the reactants and products

(*c*) experiment

(*d*) the coefficients in the balanced chemical reaction

**Answer.** (*c*)

**25.** Consider the reaction $3A \longrightarrow 2B$.

The average rate of appearance of B is given by [B]/*t*. How is the average rate of appearance of B related to the average rate of disappearance of A?

(*a*) $-2[A]/3t$ (*b*) $[A]/t$

(*c*) $-[A]/t$ (*d*) $-3[A]/2t$

**Answer.** (*a*)

**26.** Which one of the following is incorrect for the reaction $A \longrightarrow B$?

(*a*) the half-life of a second-order reaction depends on the initial concentration

(*b*) the half-life is the time for one half of the reactant to be consumed

(*c*) the second-order rate constant can be found by plotting $1/[A]^2$ versus time, where [A] is the concentration of reactant

(*d*) the initial rates for a second-order reaction depend on the concentration of the reactant squared

**Answer.** (*c*)

**27.** Consider the reaction in which ammonia is synthesized from nitrogen and hydrogen gases :

$N_2(g) + 3\,H_2(g) \longrightarrow 2NH_3(g)$

How is the rate of formation of ammonia related to the rate of consumption of hydrogen?

(*a*) the rate of formation of ammonia is half the rate of consumption of hydrogen

(*b*) the rate of formation of ammonia is twice the rate of consumption of hydrogen

(*c*) the rate of formation of ammonia is equal to the rate of consumption of hydrogen

(*d*) the rate of formation of ammonia is two-thirds the rate of consumption of hydrogen

**Answer.** (*d*)

**28.** Which concentration plot is linear for a first-order equation? (A is one of the reactants).

(*a*) [A] versus time (*b*) square root of [A] versus time

(*c*) In[A] versus time (*d*) $[A]^2$ versus time

**Answer.** (*c*)

**29.** A reaction in which all reactants are in the same phase is called

(*a*) elementary (*b*) bimolecular

(*c*) homogeneous (*d*) heterogeneous

**Answer.** (*c*)

**30.** As temperature increases, the reaction rate .....

(*a*) decrease than increase
(*b*) decreases
(*c*) increases
(*d*) stays the same

**Answer.** (*c*)

**31.** For the reaction $2NO_2 + O_3 \rightarrow N_2O_5 + O_2$ the following observations are made :
Doubling the concentration of $[NO_2]$ doubles the rate, and doubling the concentration of $[O_3]$ doubles the rate. What is the rate law for the reaction?

(*a*) rate = $k\,[NO_2]$
(*b*) rate = $k\,[NO_2]^2\,[O_3]$
(*c*) rate = $k\,[NO_2]^2\,[O_3]^2$
(*d*) rate = $k\,[NO_2]\,[O_3]$

**Answer.** (*d*)

**32.** The half-life of a first-order process

(*a*) depends on the reactant concentration raised to the first power
(*b*) is inversely proportional to the square of the reactant concentration
(*c*) is inversely proportional to the reactant concentration
(*d*) is totally independent of the reactant concentration

**Answer.** (*d*)

**33.** The reaction, $2NO(g) \rightarrow N_2(g) + O_2(g)$, proceeds in a single elementary step. This reaction is thus

(*a*) the molecularity cannot be determined from the given information
(*b*) termolecular
(*c*) bimolecular
(*d*) unimolecular

**Answer.** (*c*)

**34.** Why is a minimum energy needed for an effective collision?

(*a*) energy is needed to break bonds
(*b*) energy is needed to orient the particles correctly
(*c*) a minimum energy is needed, so that the particles will collide many times per second
(*d*) enough energy is needed to give off heat in a reaction

**Answer.** (*a*)

**35.** Species that are formed in one step of reaction mechanism and used up in another step are called

(*a*) catalysts
(*b*) intermediates
(*c*) inhibitors
(*d*) activated complexes

**Answer.** (*b*)

**36.** For a certain reaction, the rate = $k\,[NO]^2\,[O_2]$, when the initial concentration of NO is tripled, the initial rate

(*a*) decreases by a factor of nine
(*b*) increases by a factor of three
(*c*) increases by a factor of six
(*d*) increases by a factor of nine

**Answer.** (*d*)

**37.** Which of the following statements associated with mechanisms of chemical reactions is incorrect?

(*a*) intermediates do not appear in the net chemical equation or overall rate law
(*b*) the first step in a mechanism always determines the rate of the reaction
(*c*) in elementary reactions, coefficients give the order with respect to reactants and products
(*d*) a plausible mechanism must account experimentally determined rate law

**Answer.** (*b*)

**38.** What happens in a steady state?

(*a*) product is being formed faster than reactants are regenerated
(*b*) heat is evolved

(*c*) the concentration of an intermediate is constant
(*d*) nothing is happening
**Answer.** (*c*)

**39.** What happens when molecules collide with less than the activation energy needed for the reaction?
(*a*) they stick together but do not react
(*b*) they react, but more slowly
(*c*) they react if the bonds are arranged in the correct orientation
(*d*) they do not react; they simply bounce off of each other
**Answer.** (*d*)

**40.** Why do fine iron wires burst into flame when lighted, while an iron frying pan does not?
(*a*) the finely divided iron has lower internal free energy than the frying pan
(*b*) the frying pan has much greater mass than the finely divided wires
(*c*) the frying pan is more dense than the wires
(*d*) the wires have greater surface area, enabling more iron particles to react more quickly
**Answer.** (*d*)

**41.** Which of the following terms describes a process in which two particles come together to form an activated complex?
(*a*) reaction mechanism (*b*) elementary process
(*c*) rate determining step (*d*) unimolecular
**Answer.** (*b*)

**42.** A + B + C $\rightarrow$ products is :
(*a*) unimolecular (*b*) trimolecular
(*c*) bimolecular (*d*) tetramolecular
**Answer.** (*b*)

**43.** Based on the collision model, the atoms at the top of the potential energy “hill” are called:
(*a*) top of the hill (*b*) activation energy
(*c*) transition state (*d*) steric factor
**Answer.** (*c*)

**44.** According to chemical kinetic theory, a reaction can occur
(*a*) if the reactants collide with the proper orientation
(*b*) if the reactants possess sufficient energy of collision
(*c*) if the reactants are able to form a correct transition state
(*d*) all of the above
**Answer.** (*d*)

**45.** What does termolecular refer to?
(*a*) 2 molecules colliding (*b*) 4 molecules colliding
(*c*) 3 molecules colliding (*d*) 1 molecule dissociating
**Answer.** (*c*)

**46.** What is the order of the absorption process for alcohol through the lining of the stomach and small intestine?
(*a*) zero order (*b*) first order
(*c*) second order (*d*) third order
**Answer.** (*b*)

**47.** The decomposition of nitrogen dioxide to nitrogen and oxygen is second-order with a rate constant $k$ = 12.5 $M^{-1}\ s^{-1}$. What is the half-life for the reaction if $[NO_2]_0$ = 0.00260 M?
(*a*) 0.0554 sec (*b*) 30.8 sec

(*c*) 385 sec (*d*) 61.5 sec

**Answer.** (*b*)

**48.** A first order reaction requires 8.96 months for the concentration of reactant to be reduced to 25.0% of its original value. What is the half life of the reaction?

(*a*) 4.48 months (*b*) 2.24 months

(*c*) 8.96 months (*d*) 17.9 months

**Answer.** (*a*)

**49.** In a reaction, the initial concentration of the reactant is 2.34 M. The equilibrium mixture contains 1.12 M of the reactant. Equilibrium was achieved in 523 sec. What is the average rate of the reaction?

(*a*) $4.45 \times 10^{-3}$ M/sec (*b*) $2.14 \times 10^{-3}$ M/sec

(*c*) $2.33 \times 10^{-3}$ M/sec (*d*) 429 M/sec

**Answer.** (*c*)

**50.** The half-life for a first order reaction is 2768 years. If the concentration after 11,072 years is 0.0216 M, what was the initial concentration?

(*a*) 0.0690 M (*b*) 0.345 M

(*c*) 0.173 M (*d*) 1.000 M

**Answer.** (*b*)

**51.** For the hypothetical gas-phase reaction $3A(g) \rightarrow 2B(g)$, the number of moles of A present at 25 min is found to be 0.022. If the initial number of moles of A and B were 0.050 mol and 0.00 mol, respectively, how much B is present at 25 min?

(*a*) 0.022 mol (*b*) 0.056 mol

(*c*) 0.028 mol (*d*) 0.019 mol

**Answer.** (*d*)

**52.** The number of undecayed nuclei in a sample of Bromine-87 decreased by a factor of 4 over a period of 112 sec. What is the rate constant for the decay of Bromine-87?

(*a*) 56 sec (*b*) $6.93 \times 10^{-1}$ sec$^{-1}$

(*c*) $1.24 \times 10^{-2}$ sec$^{-1}$ (*d*) $6.19 \times 10^{-3}$ sec$^{-1}$

**Answer.** (*c*)

**53.** The half-life of radioactive sodium is 15.0 hours. How many hours would it take for a 64 g sample to decay to one-eighth of its original concentration?

(*a*) 3 (*b*) 15

(*c*) 30 (*d*) 45

**Answer.** (*d*)

**54.** The decomposition of NOBr is second-order with respect to NOBr and second-order overall. If the initial concentration of NOBr is 0.102 M and the rate constant is 25 M$^{-1}$ min$^{-1}$, what is [NOBr] after 1.0 min?

(*a*) 9.8 M (*b*) $2.9 \times 10^{-2}$ M

(*c*) $4.0 \times 10^{-2}$ M (*d*) 35 M

**Answer.** (*b*)

**55.** For a reaction of the type A + B + C going to product, the following observations are made: Doubling the concentration of A doubles the rate, doubling concentration of B has no effect on the rate, and tripling the concentration of C increases the rate by a factor of 9. What is the rate law for the reaction?

(*a*) rate = $k\,[A]^2\,[B]\,[C]^2$ (*b*) rate = $k\,[A]\,[C]^2$

(*c*) rate = $k\,[A]^2\,[B]\,[C]$ (*d*) rate = $k\,[A]\,[B]\,[C]$

**Answer.** (*b*)

**56.** If we have the reaction $A(g) \rightarrow 2B(g)$ and the number of moles of A is as follows,

| time | 0 | 5 min | 10 min |
|---|---|---|---|

| | | | |
|---|---|---|---|
| moles A | 0.100 | 0.085 | 0.070 |

what is the number of moles of B at 10 min?

(*a*) 0.030 mol
(*b*) 0.140 mol
(*c*) 0.060 mol
(*d*) 0.200 mol

**Answer.** (*c*)

**57.** From a plot or reasonable estimate, what is the instantaneous rate of change of A versus time at 10 min?

| Time | 0 | 2.50 | 5.00 | 7.50 | 10.0 | 12.5 |
|---|---|---|---|---|---|---|
| [A] | 0.500 | 0.389 | 0.303 | 0.236 | 0.184 | 0.143 |

(*a*) – 0.0209
(*b*) – 0.0164
(*c*) – 0.0316
(*d*) – 0.0184

**Answer.** (*d*)

**58.** A reaction requires 279 minutes in order to reach equilibrium. The concentration of one reactant changed from 2.13 M to 0.24 M. What is the average rate of the reaction?

(*a*) $7.63 \times 10^{-3}$ M/min
(*b*) $6.77 \times 10^{-3}$ M/min
(*c*) 2.13 M/min
(*d*) 148 M/min

**Answer.** (*b*)

**59.** In a first-order reaction, A $\longrightarrow$ products, [A] = .0620 M initially and 0.520 M after 15.0 min. What is the half-life, $t_{1/2}$, of this reaction?

(*a*) 7.50 min
(*b*) 46.5 min
(*c*) 29.6 min
(*d*) 59.2 min

**Answer.** (*d*)

**60.** In a first-order reaction, A $\longrightarrow$ product, [A] = 0.620 M initially and 0.520 M after 15.0 min. What is the value of the rate constant?

(*a*) $9.12 \times 10^{-2}$ $\text{min}^{-1}$
(*b*) $5.09 \times 10^{-3}$ $\text{min}^{-1}$
(*c*) 0.0117 $\text{min}^{-1}$
(*d*) 0.154 $\text{min}^{-1}$

**Answer.** (*c*)

**61.** In a lab, each of the following factors will vary to affect reaction rate EXCEPT:

(*a*) catalyst used
(*b*) concentration of reactants
(*c*) identity of reactants
(*d*) oxygen availability

**Answer.** (*d*)

**62.** In a first-order reaction, A $\longrightarrow$ products, $k$ = 0.0150 $\text{min}^{-1}$. If [A] is 0.400 M initially, what will [A] be after 2.00 h?

(*a*) 0.388 M
(*b*) $1.92 \times 10^{-3}$ M
(*c*) 0.487 M
(*d*) 0.0661 M

**Answer.** (*d*)

**63.** In a second-order reaction the rate constant is $4.0 \times 10^{-4}$ $\text{M}^{-1}$ $\text{s}^{-1}$. What will be the concentration of reactant after 10 min if the initial concentration is 0.800 M?

(*a*) 1.49 M
(*b*) 0.671 M
(*c*) 0.629 M
(*d*) 0.300 M

**Answer.** (*b*)

**64.** In the reaction 2A + B $\longrightarrow$ 2C + D, $-\Delta[\text{A}]/t$ is found to be 5.0 M $\text{min}^{-1}$. What is the rate of change of B?

(*a*) 2.5 M/min
(*b*) 10 M/min
(*c*) 25 M/min
(*d*) 5.0 M/min

**Answer.** (*a*)

**65.** The reaction A $\longrightarrow$ P is a second-order process with $t_{1/2}$ = 23.0 minutes at an initial concentration of A = 0.500 M. What is the concentration of A after 1.00 hour elapses?

(*a*) 0.263 M
(*b*) 0.139 M

(*c*) 0.0822 M (*d*) 0.175 M

**Answer.** (*b*)

**66.** The thermal decomposition of $N_2O_5$(g) to form $NO_2$(g) and $O_2$(g) is a first-order reaction. The rate constant for the reaction is $5.1 \times 10^{-4}$ $s^{-1}$ at 318 K. What is the half-life of this process?

(*a*) $3.9 \times 10^3$ s (*b*) $2.0 \times 10^3$ s

(*c*) $1.0 \times 10^{-3}$ s (*d*) $1.4 \times 10^3$ s

**Answer.** (*d*)

**67.** If the reaction, 2A + 3D $\longrightarrow$ products, is first-order in A and second-order in D, then the rate law will have the form : rate =

(*a*) $k$ [A] $[D]^2$ (*b*) $k$ $[A]^2$ [D]

(*c*) $k$ $[A]^2$ $[D]^2$ (*d*) $k$ [A] [D]

**Answer.** (*a*)

**68.** If the reaction below is carried out in a closed, rigid container, how could you best follow the rate of the reaction?

$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(*a*) monitor the density of the mixture (*b*) monitor the temperature

(*c*) monitor the pressure (*d*) monitor the change in concentration

**Answer.** (*c*)

**69.** Which of the following does NOT affect the rate of a chemical reaction?

(*a*) enthalpy of the reaction (*b*) concentration of reactants

(*c*) temperature (*d*) surface area

**Answer.** (*a*)

**70.** Which of the following rate laws is third-order overall?

(*a*) rate = $k$ $[A]^3$ $[B]^1$ (*b*) rate = $k$ $[A]^3$ $[B]^3$

(*c*) rate = $k$ $[A]^5$ $[B]^2$ (*d*) rate = $k$ [A] $[B]^2$

**Answer.** (*d*)

**71.** For a certain reaction, a plot of In [A] versus *t* gives a straight line with a slope of –1.46 $s^{-1}$. The order of the reaction in A is:

(*a*) 0 (*b*) 3

(*c*) 2 (*d*) 1

**Answer.** (*d*)

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# 7

# CHAPTER

# First Law of Thermodynamics – Basic Concepts

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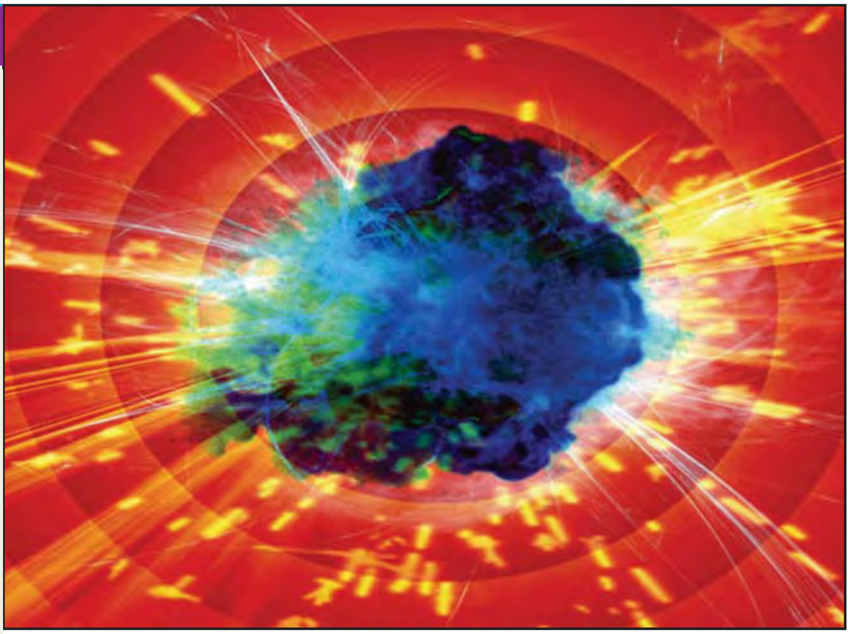


**The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation, is called Thermodynamics.**

In studying and evaluating the flow of energy into or out of a system, it will be useful to consider changes in certain properties of the system. These properties include temperature, pressure, volume and concentration of the system. Measuring the changes in these properties from the initial state to the final state, can provide information concerning changes in energy and related quantities such as heat and work.

## THE THREE EMPIRICAL LAWS

The study of thermodynamics is based on three broad generalisations derived from well established experimental results. These generalisations are known as **the First, Second and Third law of thermodynamics.** These laws have stood the test of time and are independent of any theory of the atomic or molecular structure. The discussion of these laws will be the subject of our study in the two chapters on thermodynamics.

### Scope of Thermodynamics

(1) Most of the important laws of Physical Chemistry, including the van't Hoff law of lowering of vapour pressure, Phase Rule and the Distribution Law, can be derived from the laws of thermodynamics.

(2) It tells whether a particular physical or chemical change can occur under a given set of conditions of temperature, pressure and concentration.

(3) It also helps in predicting how far a physical or chemical change can proceed, until the equilibrium conditions are established.

### Limitations of Thermodynamics

(1) **Thermodynamics is applicable to macroscopic systems** consisting of matter in bulk and not to microscopic systems of individual atoms or molecules. **It ignores the internal structure of atoms and molecules.**

(2) Thermodynamics does not bother about the time factor. That is, it does not tell anything regarding the rate of a physical change or a chemical reaction. **It is concerned only with the initial and the final states of the system.**

## THERMODYNAMIC TERMS AND BASIC CONCEPTS

An important part of the study of thermodynamics is a few terms and definitions which must be understood clearly.

## SYSTEM, BOUNDARY, SURROUNDINGS

**A system is that part of the universe which is under thermodynamic study and the rest of the universe is surroundings.**

**The real or imaginary surface separating the system from the surroundings is called the boundary.**

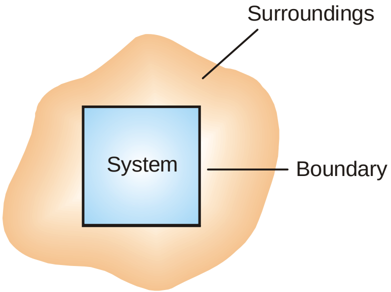


**Figure 7.1**
**Thermodynamic system.**

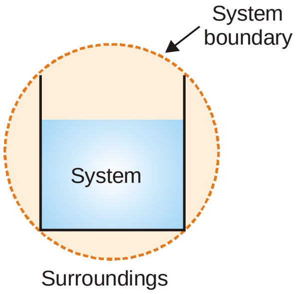


**Figure 7.2**
**Water contained in a beaker constitutes a system.**

In experimental work, a specific amount of one or more substances constitutes the system. Thus 200 g of water contained in a beaker constitutes a thermodynamic system. The beaker and the air in contact, are the surroundings.

Similarly 1 mole of oxygen confined in a cylinder fitted with a piston, is a thermodynamic system. The cylinder and the piston and all other objects outside the cylinder, form the surroundings. Here the boundary between the system (oxygen) and the surroundings (cylinder and piston) is clearly defined.

## HOMOGENEOUS AND HETEROGENEOUS SYSTEMS

**When a system is uniform throughout, it is called a Homogeneous System.** Examples are : a pure single solid, liquid or gas, mixtures of gases, and true solution of a solid in a liquid. A homogeneous system is made of one phase only. A **phase** is defined as a homogeneous, physically distinct and mechanically separable portion of a system.

**A heterogeneous system is one which consists of two or more phases.** In other words it is not uniform throughout. Examples of heterogeneous systems are : ice in contact with water, ice in contact with vapour etc. Here ice, water and vapour constitute separate phases.

## TYPES OF THERMODYNAMIC SYSTEMS

There are three types of thermodynamic systems depending on the nature of the boundary. If the boundary is closed or sealed, no *matter* can pass through it. If the boundary is insulated, no *energy* (say heat) can pass through it.

### (1) Isolated System

When the boundary is both sealed and insulated, no interaction is possible with the surroundings. Therefore, **an isolated system is one that can transfer neither matter nor energy to and from its surroundings.**

Let us consider a system 100 ml of water in contact with its vapour in a closed vessel which is insulated. Since the vessel is sealed, no water vapour (matter) can escape from it. Also, because the vessel is insulated, no heat (energy) can be exchanged with the surroundings.

A substance, say boiling water, contained in a *thermos flask*, is another example of an isolated system.

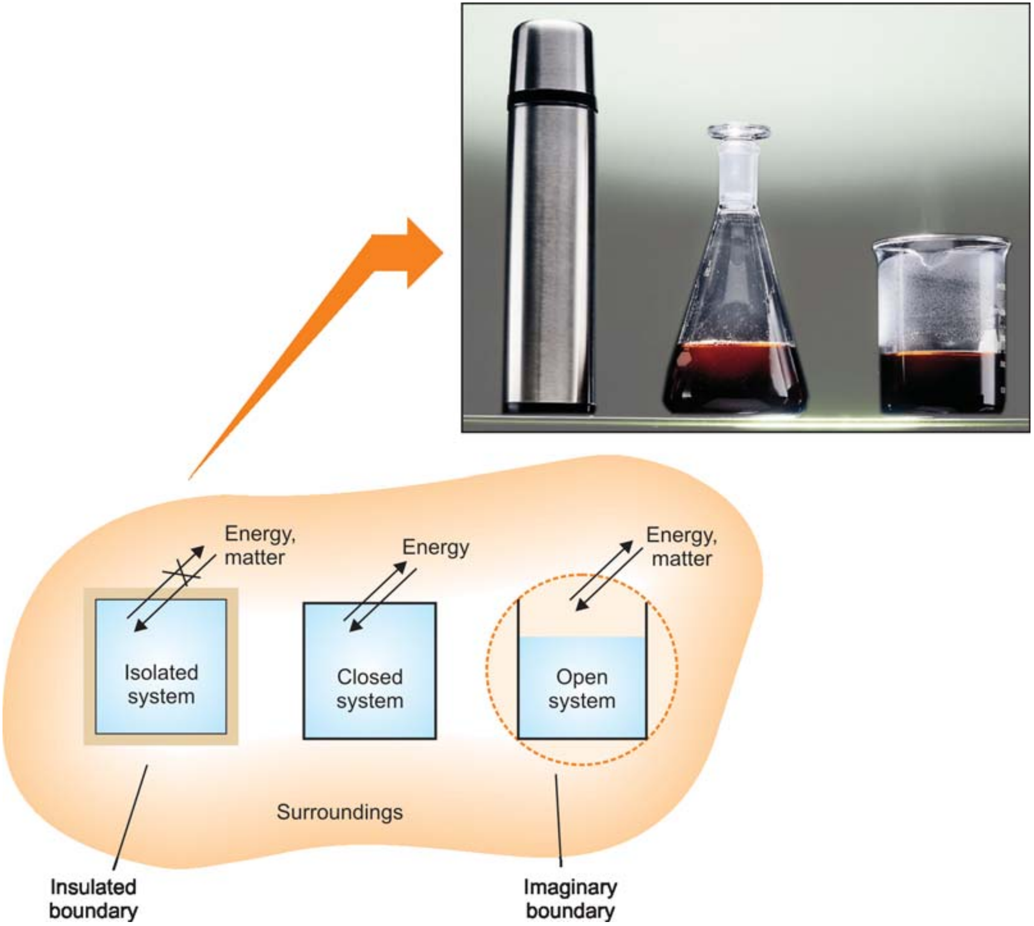


**Figure 7.3**
**Three types of thermodynamic systems.**

### (2) Closed System

Here the boundary is sealed but not insulated. Therefore, **a closed system is one which cannot transfer matter but can transfer energy in the form of heat, work and radiation to and from its surroundings.**

A specific quantity of hot water contained in a sealed tube, is an example of a closed system. While no water vapour can escape from this system, it can transfer heat through the walls of the tube to the surroundings.

A gas contained in a cylinder fitted with a piston constitutes a closed system. As the piston is raised, the gas expands and transfers heat (energy) in the form of work to the surroundings.

### (3) Open System

In such a system the boundary is open and un-insulated. Therefore, **an open system is one which can transfer both energy and matter to and from its surroundings.**

Hot water contained in a beaker placed on laboratory table is an open system. The water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

Zinc granules reacting with dilute hydrochloric acid to produce hydrogen gas in a beaker, is another example of open system. Hydrogen gas escapes and the heat of the reaction is transferred to the surroundings.

### What are Adiabatic Systems ?

**Those systems in which no thermal energy passes into or out of the system, are said to be adiabatic systems.**

## INTENSIVE AND EXTENSIVE PROPERTIES

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes :

(*a*) Intensive properties
(*b*) Extensive properties

### Intensive Properties

**A property which does not depend on the quantity of matter present in the system, is known as Intensive Property.**

Some examples of intensive properties are *pressure*, *temperature*, *density*, and *concentration*. If the overall temperature of a glass of water (our system) is 20ºC, then any drop of water in that glass has a temperature of 20ºC. Similarly if the concentration of salt, NaCl, in the glass of water is 0.1 mole/litre, then any drop of water from the glass also has a salt concentration of 0.1 mole/litre.

### Extensive Properties

**A property that does depend on the quantity of matter present in the system, is called an Extensive Property.**

Some examples of extensive properties are *volume, number of moles, enthalpy, entropy, and Gibbs' free energy*. Some of these properties are unfamiliar to you but these will be defined and illustrated later.

By definition, **the extensive properties are additive while intensive properties are not.** Let us consider the system 'a glass of water'. If we double the mass of water, the volume is doubled and so is the number of moles and the internal energy of the system.

**TABLE 7.1.** COMMON PROPERTIES OF A SYSTEM.

| Intensive properties | | Extensive properties |
|---|---|---|
| Temperature | Surface tension | Mass |
| Pressure | Refractive index | Volume |
| Density | Viscosity | Internal energy |
| Boiling point | Freezing point | Enthalpy, Entropy |

## STATE OF A SYSTEM

**A thermodynamic system is said to be in a certain state when all its properties are fixed.**

The fundamental properties which determine the state of a system are pressure ($P$), temperature ($T$), volume ($V$), mass and composition. Since a change in the magnitude of such properties alters the state of the system, these are referred to as **State variables** or **State functions** or **Thermodynamic parameters.** It also stands to reason that a change of system from the *initial state* to the *final state* (2nd state) will be accompanied by change in the state variables.

It is not necessary to state all the properties (state variables) to define a system completely. For a pure gas, the composition is fixed automatically, as it is cent per cent. The remaining state variables $P$, $V$, $T$ are interrelated in the form of an algebraic relationship called the **Equation of State.** Thus for one mole of a pure gas, the equation of state is :

$$PV = RT$$

where $R$ is gas constant. If of the three state variables ($P$, $V$, $T$), $P$ and $T$ are specified, the value of third ($V$) is fixed automatically and can be calculated from the equation of state. The variables ($P$ and $T$) which must be necessarily specified to define the state of a system, are designated as **Independent state variables.** The remaining state variable ($V$) which depends on the value of $P$ and $T$, is called **Dependent state variable.**

An important characteristic of a state variable (or state function) is that when the state of a system is altered, the change in the variable depends on the initial and final states of the system. For example, if we heat a sample of water from 0º C to 25º C, the change in temperature is equal to difference between the initial and final temperatures.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 25°\text{C}$$

The way in which the temperature change is brought about has no effect on the result.

## EQUILIBRIUM AND NON-EQUILIBRIUM STATES

**A system in which the state variables have constant values throughout the system is said to be in a state of thermodynamic equilibrium.**

Suppose we have a gas confined in a cylinder that has a frictionless piston. If the piston is stationary, the state of the gas can be specified by giving the values of pressure and volume. The system is then in a *state of equilibrium*.

**A system in which the state variables have different values in different parts of the system is said to be in a non-equilibrium state.**

If the gas contained in a cylinder, as stated above, is compressed very rapidly by moving down the piston, it passes through states in which pressure and temperature cannot be specified, since these properties vary throughout the gas. The gas near the piston is compressed and heated and that at the far end of the cylinder is not. The gas then would be said to be in non-equilibrium state.

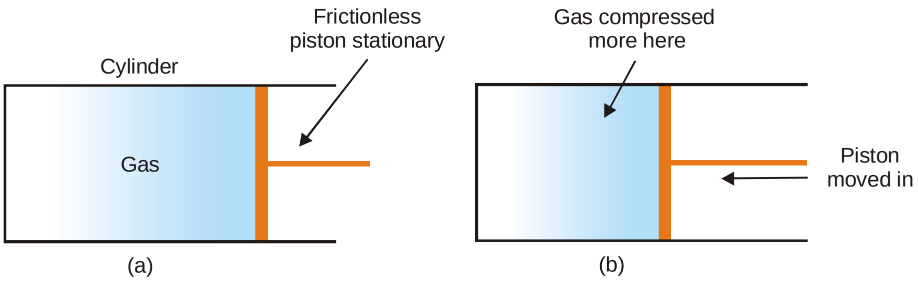


**Figure 7.4**
**(*a*) Gas in equilibrium state; (*b*) Rapidly compressed gas in non-equilibrium state.**

Thermodynamics is concerned only with equilibrium states.

### The Criteria for Equilibrium

(1) **The temperature of the system must be uniform and must be the same as the temperature of the surroundings (thermal equilibrium).**

(2) **The mechanical properties must be uniform throughout the system (mechanical equilibrium).** That is, no mechanical work is done by one part of the system on any other part of the system.

(3) **The chemical composition of the system must be uniform with no net chemical change (chemical equilibrium).**

If the system is heterogeneous, the state variables of each phase remain constant in each phase.

## THERMODYNAMIC PROCESSES

**When a thermodynamic system changes from one state to another, the operation is called a Process.** These processes involve the change of conditions (temperature, pressure and volume). The various types of thermodynamic processes are :

### (1) Isothermal Processes

**Those processes in which the temperature remains fixed, are termed isothermal processes.** This is often achieved by placing the system in a thermostat (a constant temperature bath).

For an isothermal process $dT = 0$

### (2) Adiabatic Processes

**Those processes in which no heat can flow into or out of the system, are called adiabatic processes.** Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos' bottle. High vacuum and highly polished surfaces help to achieve thermal insulation.

For an adiabatic process $dq = 0$

### (3) Isobaric Processes

**Those processes which take place at constant pressure are called isobaric processes.** For example, heating of water to its boiling point and its vaporisation take place at the same atmospheric pressure. These changes are, therefore, designated as isobaric processes and are said to take place isobarically.

For an isobaric process $dp = 0$

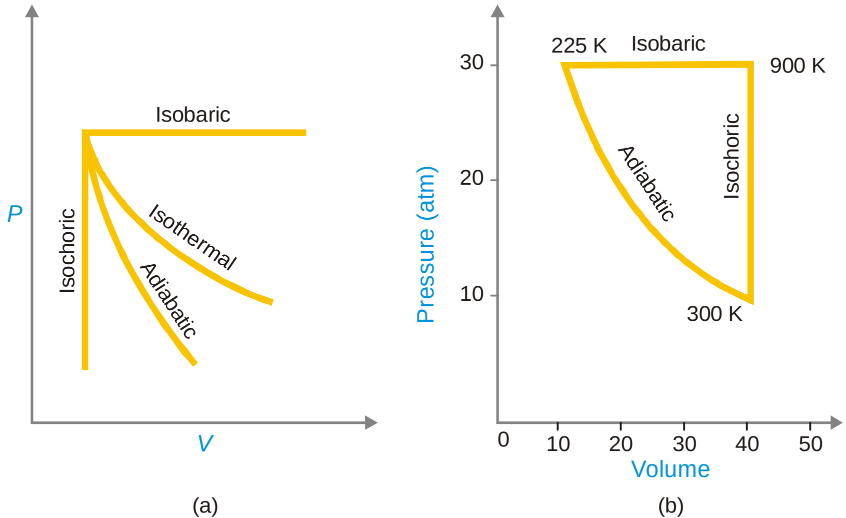


**Figure 7.5**
**(*a*) Four basic thermodynamic processes; (*b*) A cyclic process.**

### (4) Isochoric Processes

**Those processes in which the volume remains constant are known as isochoric processes.** The heating of a substance in a non-expanding chamber is an example of isochoric process.

For isochoric processes $dV = 0$.

### (5) Cyclic Process

**When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.**

For a cyclic process $dE = 0$, $dH = 0$.

## REVERSIBLE AND IRREVERSIBLE PROCESSES

**A thermodynamic reverse process is one that takes place infinitesimally slowly and its direction at any point can be reversed by an infinitesimal change in the state of the system.**

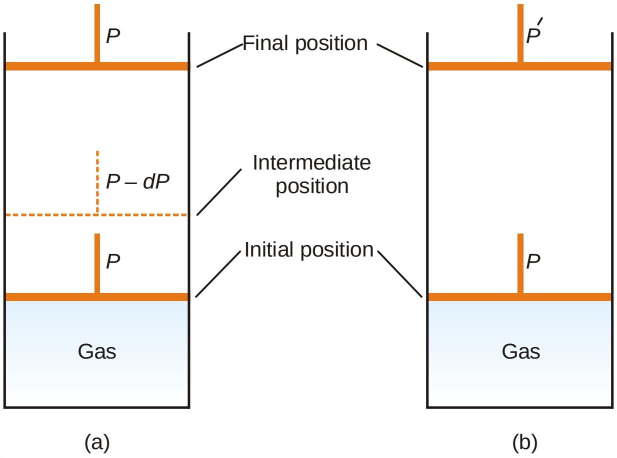


**Figure 7.6**
**(*a*) Reversible expansion occurs by decreasing the pressure on the piston by infinitesimal amounts. (*b*) Irreversible expansion occurs by sudden decrease of pressure from P to P′ when the gas expands rapidly in a single operation.**

In fact, a reversible process is considered to proceed from the initial state to the final state through an infinite series of infinitesimally small stages. At the initial, final and all intermediate stages, the system is in equilibrium state. This is so because an infinitesimal change in the state of the system at each intermediate step is negligible.

**When a process goes from the initial to the final state in a single step and cannot be carried in the reverse order, it is said to be an irreversible process.** Here the system is in equilibrium state in the beginning and at the end, but not at points in between.

Consider a certain quantity of a gas contained in a cylinder having a weightless and frictionless piston. The expansion of the gas can be carried by two methods illustrated in Fig. 7.6.

Let the pressure applied to the piston be $P$ and this is equal to the internal pressure of the gas. Since the external and internal pressures are exactly counterbalanced, the piston remains stationary and there is no change in volume of the gas. Now suppose the pressure on the piston is decreased by an infinitesimal amount $dP$. Thus the external pressure on the piston being $P - dP$ , the piston moves up and the gas will expand by an infinitesimal small amount. The gas will, therefore, be expanded infinitely slowly *i.e.*, by a thermodynamically *reversible process*. At all stages in the expansion of the gas, $dP$ being negligibly small the gas is maintained in a state of equilibrium throughout. If at any point of the process the pressure is increased by $dP$, the gas would contract reversibly.

On the other hand, the expansion is irreversible (Fig. 7.6 *b*) if the pressure on the piston is decreased suddenly. It moves upward rapidly in a single operation. The gas is in equilibrium state in the initial and final stages only. The expansion of the gas, in this case, takes place in an irreversible manner.

## DIFFERENCES BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

| Reversible Process | Irreversible Process |
|---|---|
| 1. It takes place in infinite number of infinitesimally small steps and it would take *infinite time* to occur. | 1. It takes place *infinite time*. |
| 2. It is *imaginary* as it assumes the presence of frictionless and weightless piston. | 2. It is *real* and can be performed actually. |
| 3. It is in equilibrium state at *all stages* of the operation. | 3. It is in equilibrium state only at the *initial and final stages* of the operation. |
| 4. All changes are *reversed* when the process is carried out in reversible direction. | 4. After this type of process has occurred all changes *do not return* to the initial state by themselves. |
| 5. It is extremely slow. | 5. It proceeds at *measureable speed*. |
| 6. Work done by a reversible process is *greater* than the corresponding irreversible process. | 6. Work done by a irreversible process is *smaller* than the corresponding reversible process. |

## NATURE OF HEAT AND WORK

When a change in the *state* of a system occurs, energy is transferred to or from the surroundings. This energy may be transferred as heat or mechanical work.

**We shall refer the term 'work' for mechanical work which is defined as force × distance.**

### Units of Work

In CGS system the unit of work is erg which is defined as the work done when a resistance of 1 dyne is moved through a distance of 1 centimeter. Since the erg is so small, a bigger unit, the **joule (J)** is now used.

$$1 \text{ joule} = 10^7 \text{ ergs}$$

or

$$1 \text{ erg} = 10^{-7} \text{ J}$$

We often use **kilojoule** (kJ) for large quantities of work

$$1 \text{ kJ} = 1000 \text{ J}$$

### Units of Heat

The unit of heat, which was used for many years, is **calorie** (cal). A calorie is defined as the quantity of heat required to raise the temperature of 1 gram of water by 1° C in the vicinity of 15°C.

Since heat and work are interrelated, **SI unit of heat is the joule (J).**

$$1 \text{ joule} = 0.2390 \text{ calories}$$

$$1 \text{ calorie} = 4.184 \text{ J}$$

or

$$1 \text{ kcal} = 4.184 \text{ kJ}$$

### Sign Convention of Heat

The symbol of heat is $q$. If the heat flows from the surroundings into the system to raise the energy of the system, it is taken to be positive, $+q$. If heat flows from the system into the surroundings, lowering the energy of the system, it is taken to be negative, $-q$.

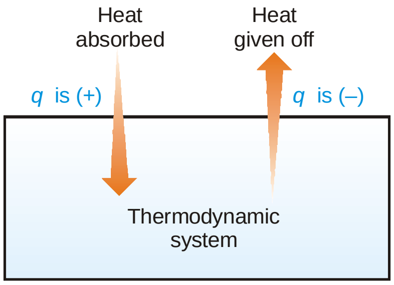


**Figure 7.7**
**Sign convention for heat flow in a thermodynamic system.**

### Sign Convention of Work

The symbol of work is $w$. If work is done on a system by the surroundings and the energy of the system is thus increased, it is taken to be positive, $+w$. If work is done by the system on the surroundings and energy of the system is decreased, it is taken to be negative, $-w$.

### Summary of Sign Conventions

| | |
|---|---|
| Heat flows into the system, $q$ is +ve | Heat flows out of the system, $q$ is –ve |
| Work is done on the system, $w$ is +ve | Work is done by the system, $w$ is –ve |

## PRESSURE–VOLUME WORK

In physics, mechanical work is defined as force multiplied by the distance through which the force acts. In elementary thermodynamics the only type of work generally considered is the work done in expansion (or compression) of a gas. This is known as **pressure-volume work** or **PV work** or **expansion work.**

Consider a gas contained in a cylinder fitted with a frictionless piston. The pressure (force per unit area) of the gas, *P*, exerts a force on the piston. This can be balanced by applying an equal but opposite pressure from outside on the piston. Let it be designated as $P_{ext}$. **It is important to remember that it is the external pressure, $P_{ext}$, and not the internal pressure of the gas itself which is used in evaluating work.** This is true whether it be expansion or contraction.

If the gas expands at constant pressure, the piston would move, say through a distance *l*. We know that

$$work = force \times distance \quad \text{(by definition)}$$

or
$$w = f \times l \qquad \text{...(1)}$$

Since pressure is force per unit area,

$$f = P_{ext} \times A \qquad \text{...(2)}$$

where *A* is the cross-section area of the piston.

From (1) and (2), we have

$$\begin{aligned} w &= P_{ext} \times A \times l \\ &= P_{ext} \times \Delta V \end{aligned}$$

where $\Delta V$ is the increase in volume of the gas.

Since the system (gas) is doing work on the surroundings (piston), it bears negative sign. Thus,

$$w = -P_{ext} \times \Delta V$$

Proceeding as above the work done in compression of a gas can also be calculated. In that case the piston will move down and sign of the work will be positive.

$$w = P_{ext} \times \Delta V$$

As already stated, work may be expressed in dynes-centimetres, ergs, or joules. *PV* work can as well be expressed as the product of pressure and volume units *e.g.*, in litre or atmospheres.

It may be noted that **the work done by a system is not a state function.** This is true of the mechanical work of expansion. We shall show presently that the work is related to the process carried out rather than to the internal and final states. This will be evident from a consideration of the *reversible expansion* and an *irreversible process*.

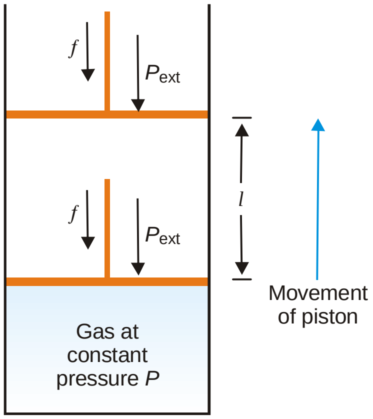


**Figure 7.8**
**Pressure volume work of a system (gas) confined by a frictionless piston.**

**SOLVED PROBLEM.** Calculate the pressure-volume work done when a system containing a gas expands from 1.0 litre to 2.0 litres against a constant external pressure of 10 atmospheres. Express the answer in calories and joules.

**SOLUTION**

$$\begin{aligned} w &= -P_{ext}(V_2 - V_1) \\ &= -(10 \text{ atm})(2\,l - 1\,l) \\ &= -10\,l \text{ atm} \end{aligned}$$

$$= -(10\ l\ \text{atm})\left(\frac{1.987\ \text{cal}}{0.082\ l\ \text{atm}}\right)$$

$$= -242\ \text{cal}$$

But 1 calorie = 4.184 J

$$w = \mathbf{-\ 1012.528\ J}$$

## ISOTHERMAL REVERSIBLE EXPANSION WORK OF AN IDEAL GAS

Consider an ideal gas confined in a cylinder with a frictionless piston. Suppose it expands in a reversible manner from volume $V_1$ to $V_2$ at a constant temperature. The pressure of the gas is successively reduced from $P_1$ to $P_2$.

The reversible expansion of the gas takes place in a finite number of infinitesimally small intermediate steps. To start with the external pressure, $P_{ext}$, is arranged equal to the internal pressure of the gas, $P_{gas}$, and the piston remains stationary. If $P_{ext}$ is decreased by an infinitesimal amount $dP$ the gas expands reversibly and the piston moves through a distance $dl$.

Since $dP$ is so small, for all practical purposes,

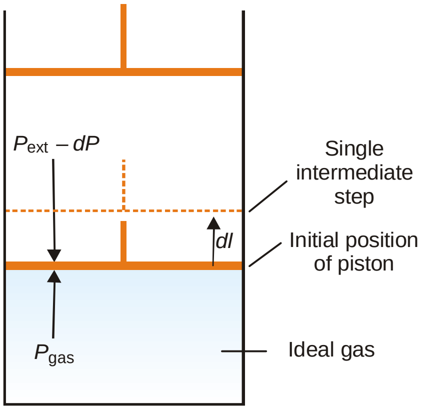


**Figure 7.9**
**Isothermal reversible expansion work.**

$$P_{ext} = P_{gas} = P$$

The work done by the gas in one infinitesimal step $dw$, can be expressed as

$$dw = P \times A \times dl \qquad (A = \text{cross-sectional area of piston})$$
$$= P \times dV$$

where $dV$ is the increase in volume

The total amount of work done by the isothermal reversible expansion of the ideal gas from $V_1$ to $V_2$ is, therefore,

$$w = -\int_{V_1}^{V_2} P dV \qquad ...(1)$$

By the ideal gas equation

$$P = \frac{nRT}{V}$$

$$\therefore \qquad w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$= -\ nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

which integrates to give

$$w = -\ nRT\ 1n\frac{V_2}{V_1}$$

Since $$P_1V_1 = P_2V_2$$
$$V_2/V_1 = P_1/P_2$$

$\therefore$ $$w = -\,nRT\ \text{In}\ \frac{P_1}{P_2} = -2.303\ nRT\ \log\ \frac{P_1}{P_2}$$

*Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with the sign changed. Here the pressure on the piston, $P_{ext}$, is increased by dP which reduces the volume of the gas.*

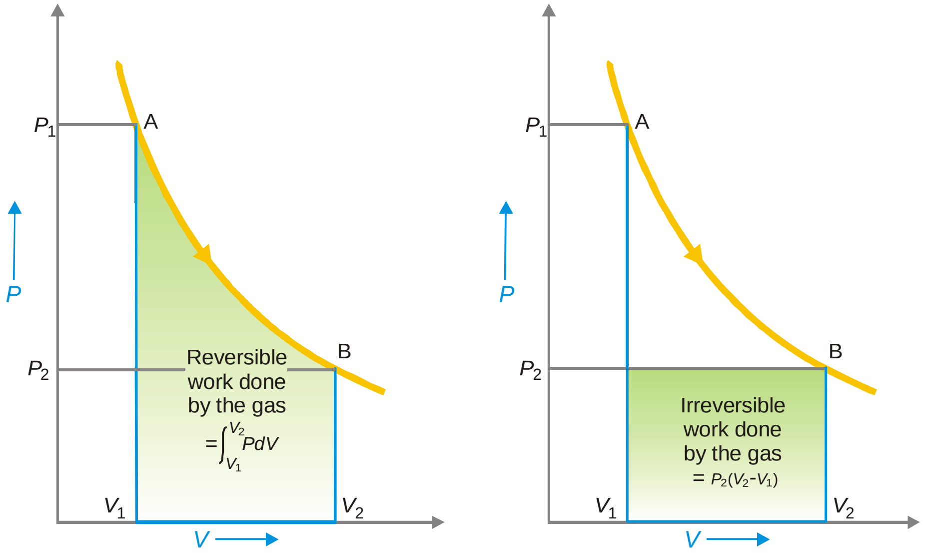
## ISOTHERMAL IRREVERSIBLE EXPANSION WORK OF AN IDEAL GAS

Suppose we have an ideal gas contained in a cylinder with a piston. This time the process of expansion of the gas is performed irreversibly *i.e.*, by instantaneously dropping the external pressure, $P_{\text{ext}}$, to the final pressure $P_2$. The work done by the system is now against the pressure $P_2$ throughout the whole expansion and is given by the following expression :

$$w = -\,P_{\text{ext}} \int_{v_1}^{v_2} dV$$
$$= P_2\,(V_2 - V_1)$$
$$= P_2\,dV$$

## MAXIMUM WORK DONE IN REVERSIBLE EXPANSION

The isothermal expansion of an ideal gas may be carried either by the *reversible process* or *irreversible process* as stated above.



(a) (b)

**Figure 7.10**

**(*a*) The reversible work of expansion; (*b*) The irreversible work done by the gas when the external pressure is at once dropped to the final value $P_2$.**

The reversible expansion is shown in Fig. 7.10 in which the pressure is falling as the volume increases. The reversible work done by the gas is given by the expression

$$-\,w_{irr} = \int_{v_1}^{v_2} PdV$$

which is represented by the shaded area.

If the expansion is performed irreversibly by suddenly reducing the external pressure to the final pressure $P_2$, the irreversible work is given by

$$-w_{in} = P_2 (V_2 - V_1)$$

which is shown by the shaded area in Fig. 7.10 (*b*).

In both the processes, the state of the system has changed from *A* to *B* but the work done is much less in the irreversible expansion than in the reversible expansion. **Thus mechanical work is not a state function as it depends on the path by which the process is performed rather than on the initial and final states. It is a path function.**

It is also important to note that **the work done in the reversible expansion of a gas is the maximum work that can be done by a system (gas) in expansion between the same initial (A) and final state (B).** This is proved as follows :

We know that the work always depends on the external pressure, $P_{ext}$; the larger the $P_{ext}$ the more work is done by the gas. But the $P_{ext}$ on the gas cannot be more than the pressure of the gas, $P_{gas}$ or a compression will take place. Thus the largest value $P_{ext}$ can have without a compression taking place is equal to $P_{gas}$. But an expansion that occurs under these conditions is the reversible expansion. Thus, maximum work is done in the reversible expansion of a gas.

**SOLVED PROBLEM 1.** One mole of an ideal gas at 25ºC is allowed to expand reversibly at constant temperature from a volume of 10 litres to 20 litres. Calculate the work done by the gas in joules and calories.

**SOLUTION**

$$w = -\,nRT\ \text{1n}\ \frac{V_2}{V_1} = -2.303\ nRT\ \log\frac{V_2}{V_1}$$

$$= -2.303 \times 8.314 \times 298 \log\frac{20}{10} = -1717.46\ \text{J}$$

$$= -1717.46\ \text{J} \times \frac{1.987\ \text{cal}}{8.314\ \text{J}} = \mathbf{-410.46\ cal}$$

**Notes.** (1) 1n $x = 2.303 \log x$

(2) The units of $R$ will determine the units of $w$ in this expression.

(3) The temperature must be expressed in degrees Kelvin.

**SOLVED PROBLEM 2.** Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25ºC.

**SOLUTION**

$$w = -\,nRT\ \text{1n}\ \frac{P_1}{P_2}$$

$$= -1 \times 8.314 \times 298 \times 2.303 \log 5$$

$$= -3988\ \text{J}$$

$$= \mathbf{-\ 3.988\ kJ}$$

## INTERNAL ENERGY

A thermodynamic system containing some quantity of matter has within itself a definite quantity of energy. This energy includes not only the translation kinetic energy of the molecules but also other molecular energies such as rotational, vibrational energies. The kinetic and potential energy of the nuclei and electrons within the individual molecules also contribute to the energy of the system.

**The total of all the possible kinds of energy of a system, is called its Internal Energy.**

The word 'internal' is often omitted and the energy of a system always implies internal energy.

The internal energy of a system, like temperature, pressure, volume, etc., is determined by the state of a system and is independent of the path by which it is obtained. **Hence internal energy of a system is a state function.**

For example, we consider the heating of one mole of liquid water from 0º to 100º C. The change in energy is 1.8 kcal and is the same regardless of the form in which this energy is transferred to the water by heating, by performing work, by electrical means or in any other way.

Since the value of internal energy of a system depends on the mass of the matter contained in a system, it is classed as an **extensive property.**

### Symbol Representation of Internal Energy and Sign Conventions

The internal energy of a system is represented by the symbol *E* (Some books use the symbol *U*). It is neither possible nor necessary to calculate the absolute value of internal energy of a system. In thermodynamics we are concerned only with the energy changes when a system changes from one state to another. If $\Delta E$ be the difference of energy of the initial state ($E_{in}$) and the final state ($E_f$), we can write

$$\Delta E = E_f - E_{in}$$

$\Delta E$ is +ve if $E_f$ is greater than $E_{in}$ and –ve if $E_f$ is less than $E_{in}$.

A system may transfer energy to or from the surroundings as heat or as work, or both.

## UNITS OF INTERNAL ENERGY

The SI unit for internal energy of a system is the joule (J). Another unit of energy which is not an SI unit is the calorie, 1 cal = 4.184 J.

## FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is, in fact, an application of the broad principle known as the Law of Conservation of Energy to the thermodynamic system. It states that :

**the total energy of an isolated system remains constant though it may change from one form to another.**

When a system is changed from state *A* to state *B*, it undergoes a change in the internal energy from $E_A$ to $E_B$. Thus, we can write

$$\Delta E = E_B - E_A$$

This energy change is brought about by the evolution or absorption of heat and/or by work being done by the system. Because the total energy of the system must remain constant, we can write the **mathematical statement of the First Law** as :

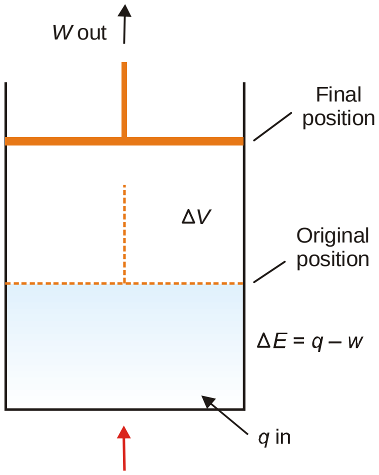


**Figure 7.11**
**Illustration of First Law. Heat adds to internal energy, while work subtracts.**

$$\Delta E = q - w \qquad \text{...(1)}$$

where $q$ = the amount of heat supplied to the system
$w$ = work done by the system

Thus First Law may also be stated as : **the net energy change of a closed system is equal to the heat transferred to the system minus the work done by the system.**

To illustrate the mathematical statement of the First Law, let us consider the system 'expanding hot gas' (Fig. 7.11).

The gas expands against an applied constant pressure by volume $\Delta V$. The total mechanical work done is given by the relation

$$w = P \times \Delta V \qquad \text{...(2)}$$

From (1) and (2), we can restate

$$\Delta E = q - P \times \Delta V$$

### Other Definitions of First Law of Thermodynamics

(1) Whenever energy of a particular type disappears equivalent amount of another type must be produced.

(2) Total energy of a system and surroundings remains constant (or conserved)

(3) It is impossible to construct a perpetual motion machine that can produce work without spending energy on it.

### Some Special Forms of First Law of Thermodynamics

Mathematical statement of the First law of Thermodynamics is

$$\Delta E = q - w$$

**Case 1 :** For a cyclic process involving isothermal expansion of an ideal gas

$$\Delta E = o$$

$$\therefore \quad q = w$$

**Case 2 :** For an isochoric process (no change in volume) there is no work of expansion *i.e.* $w = 0$. Hence

$$\Delta E = q_v$$

**Case 3 :** For an adiabatic process there is no change in heat gained or lost *i.e.* $q = 0$. Hence

$$\Delta E = -w$$

In other words, the decrease in internal energy is exactly equal to the work done on the system by surroundings.

**Case 4 :** For an isobaric process there is no change in pressure, *i.e.* $P$ remains constant. Hence

$$\Delta E = q - w$$

or $$\Delta E = q - P\Delta V$$

**SOLVED PROBLEM 1.** Find $\Delta E$, $q$ and $w$ if 2 moles of hydrogen at 3 atm pressure expand isothermally at 50°C and reversibly to a pressure of 1 atm.

**SOLUTION**

Since the operation is isothermal and the gas is ideal

$$\Delta E = 0$$

From the First Law

$$\Delta E = q - w$$

$\therefore$ $$q - w = 0$$

when $$\Delta E = 0$$

or $$q = w$$

For a reversible process

$$w = -nRT\,1\text{n}\,(P_1/P_2) \text{ or } -2.303\,nRT \log \frac{P_1}{P_2}$$

$$= -2 \times 1.987 \times 323 \times 2.303 \times \log 3$$
$$= -1410 \text{ cals}$$

Since $q = w$

$$q = \mathbf{-\ 1410\ cals}$$

**SOLVED PROBLEM 2.** 1g of water at 373 K is converted into steam at the same temperature. The volume of water becomes 1671 ml on boiling. Calculate the change in the internal energy of the system if the heat of vaporisation is 540 cal/g.

**SOLUTION**

As the vaporisation takes place against a constant pressure of 1 atmosphere, work done for an irreversible process, *w*, is

$$\begin{aligned} w &= P\,(V_2 - V_1) \\ &= nRT \\ &= \frac{1}{18} \times 1.987 \times 373 \\ &= 41 \text{ cal/g} \end{aligned}$$

Now $q = 540$ cal/g

Since $\Delta E = q - w$ (First Law)

$$= 540 - 41$$

$\therefore$ $\Delta E = \mathbf{499\ cal/g}$

**SOLVED PROBLEM 3.** A gas contained in a cylinder fitted with a frictionless piston expands against a constant external pressure of 1 atm from a volume of 5 litres to a volume of 10 litres. In doing so it absorbs 400 J thermal energy from its surroundings. Determine $\Delta E$ for the process.

**SOLUTION**

$$\Delta E = q - w \qquad ...(1)$$

Here $q = 400$ J

$$\begin{aligned} w &= -P\,(V_2 - V_1) = -(1)\,(10 - 5) \\ &= -5\ l \text{ atm} \\ &= -506 \text{ J} \qquad [\because 1\ l \text{ atm} = 101.2 \text{ J}] \end{aligned}$$

Substituting values in (1)

$$\begin{aligned} \Delta E &= 400 \text{ J} - (-506 \text{ J}) \\ &= 400 \text{ J} + 506 \text{ J} \\ &= \mathbf{906\ J} \end{aligned}$$

**SOLVED PROBLEM 4.** Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to one atmosphere at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy ? Also calculate '*q*'.

**SOLUTION.** We know

$$w = 2.303\, nRT \log \left(\frac{P_1}{P_2}\right)$$

Here $n = \frac{10}{2} = 5$ moles; $T = 273$ K

$$P_1 = 20 \text{ atm}; P_2 = 1 \text{ atm}.$$

Substituting the values we get

$$w = -2.303 \times 5 \times 1.987 \times 273 \log \frac{20}{1}$$

$$= \mathbf{-\ 8126.65\ cals.}$$

Since there is no change in temperature

$$\Delta E = 0$$

Hence $$q = \Delta E + w$$

$$= 0 + (-8126.65)$$

$$= \mathbf{-\ 8126.65\ cals.}$$

## ENTHALPY OF A SYSTEM

In a process carried at constant volume (say in a sealed tube), the heat content of a system is the same as internal energy (*E*), as no *PV* work is done. But in a constant-pressure process, the system (a gas) also expends energy in doing *PV* work. Therefore, **the total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy.** This is called the **Enthalpy** (Greek *en* = in; *thalpos* = heat) of the system and is represented by the symbol *H*. Thus enthalpy is defined by the equation :

$$H = E + PV \qquad ...(1)$$

### Enthalpy – A Function of State

In the equation (1) above, *E*, *P*, *V* are all state functions. Thus *H*, the value of which depends on the values of *E*, *P*, *V* must also be a function of state. Hence its value is independent of the path by which the state of the system is changed.

### Change in Enthalpy

If Δ *H* be the difference of enthalpy of a system in the final state ($H_2$) and that in the initial state ($H_1$),

$$\Delta H = H_2 - H_1 \qquad ...(2)$$

Substituting the values of $H_2$ and $H_1$, as from (1) and (2), we have

$$\Delta H = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$= (E_2 - E_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta E + \Delta PV$$

If *P* is constant while the gas is expanding, we can write

$$\Delta H = \Delta E + P\Delta V$$

or $$\Delta H = \Delta E + w \ \ (w = \text{work}) \qquad ...(3)$$

According to the First Law,

$$\Delta E = q - w \qquad ...(4)$$

where $q$ = heat transferred

From equations (3) and (4)

$\Delta H = q$ when change in state occurs at constant pressure

This relationship is usually written as

$$\Delta H = q_p$$

where subscript *p* means constant pressure.

Thus Δ *H* can be measured by measuring the heat of a process occurring at constant pressure.

## Units and Sign Conventions of Enthalpy

Since

$$\Delta H = H_2 - H_1$$

$\Delta H$ is positive if $H_2 > H_1$ and the process or reaction will be endothermic. $\Delta H$ is negative if $H_1 > H_2$ and the reaction will be exothermic.

In case of a chemical reaction carried in the laboratory in an open vessel,

$$\Delta H = H \text{ products} - H \text{ reactants} = q_p$$

The heat of reaction at one atmosphere pressure is usually shown along with the equation. Thus,

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 68.32 \text{ kcal}$$

The quantity of heat 68.32 kcal on the right hand represents $-\Delta H$ of the reaction.

The units of $\Delta H$ are kilocalories (kcal) or kilojoules (kJ).

## Relation Between $\Delta H$ and $\Delta E$

Calorific values of many gaseous fuels are determined in constant volume calorimeters. These values are, therefore, given by the expression

$$q_v = \Delta E$$

When any fuel is burnt in the open atmosphere, additional energy of expansion, positive or negative, against the atmosphere is also involved. The value of $q$ thus actually realised, *i.e.*, $q_p = \Delta H$, may be different from the equation

$$\Delta H = \Delta E + P\Delta V \qquad \text{...(1)}$$

If gases are involved in a reaction, they account for most of the volume change as the volumes of solids and liquids are negligibly small in comparison.

Suppose we have $n_1$ moles of gases before reaction, and $n_2$ moles of gases after it. Assuming ideal gas behaviour, we have

$$P V_2 = n_2 RT$$

$$P V_1 = n_1 RT$$

$$\therefore \qquad P(V_2 - V_1) = (n_2 - n_1) RT$$

or $$P\Delta V = \Delta n \, RT$$

Substituting in equation (1) we have,

$$\Delta H = \Delta E + \Delta n \, RT$$

**SOLVED PROBLEM.** For the reaction

$$H_2F_2(g) \longrightarrow H_2(g) + F_2(g)$$

$$\Delta E = -14.2 \text{ kcal/mole at } 25° \text{C}$$

Calculate $\Delta H$ for the reaction.

**SOLUTION**

$$\Delta H = \Delta E + \Delta n RT$$

$$\Delta n = n_2 - n_1$$

Now $$n_2 = 1 + 1 = 2$$

$$n_1 = 1$$

$$n_2 - n_1 = 2 - 1 = 1$$

$$\therefore \quad \Delta H = \Delta E + 1 \times 1.987 \times 298/1000$$
$$= -14.2 + 0.592$$
$$= \mathbf{-13.6\ kcal/mole}$$

## MOLAR HEAT CAPACITIES

By heat capacity of a system we mean the capacity to absorb heat and store energy. As the system absorbs heat, it goes into the kinetic motion of the atoms and molecules contained in the system. This increased kinetic energy raises the temperature of the system.

If $q$ calories is the heat absorbed by mass $m$ and the temperature rises from $T_1$ to $T_2$, the heat capacity ($c$) is given by the expression

$$c = \frac{q}{m \times (T_2 - T_1)} \qquad \text{...(1)}$$

*Thus heat capacity of a system is the heat absorbed by unit mass in raising the temperature by one degree (K or ° C) at a specified temperature.*

When mass considered is 1 mole, the expression (1) can be written as

$$C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T} \qquad \text{...(2)}$$

where $C$ *is denoted as Molar heat capacity.*

**The molar heat capacity of a system is defined as the amount of heat required to raise the temperature of one mole of the substance (system) by 1 K.**

Since the heat capacity ($C$) varies with temperature; its true value will be given as

$$C = \frac{dq}{dT}$$

where $dq$ is a small quantity of heat absorbed by the system, producing a small temperature rise $dT$.

**Thus the molar heat capacity may be defined as the ratio of the amount of heat absorbed to the rise in temperature.**

### Units of Heat Capacity

The usual units of the molar heat capacity are calories per degree per mole (cal $K^{-1}$ $mol^{-1}$), or joules per degree per mole (J $K^{-1}$ $mol^{-1}$), the latter being the SI unit.

**Heat is not a state function, neither is heat capacity.** It is, therefore, necessary to specify the process by which the temperature is raised by one degree. The two important types of molar heat capacities are those : (1) at constant volume; and (2) at constant pressure.

### Molar Heat Capacity at Constant Volume

According to the first law of thermodynamics

$$dq = dE + PdV \qquad \text{...}(i)$$

Dividing both sides by $dT$, we have

$$\frac{dq}{dT} = \frac{dE + PdV}{dT} \qquad \text{...}(ii)$$

At constant volume $dV = 0$, the equation reduces to

$$C_V = \left(\frac{dE}{dT}\right)_V$$

**Thus the heat capacity at constant volume is defined as the rate of change of internal energy with temperature at constant volume.**

### Molar Heat Capacity at Constant Pressure

Equation (*ii*) above may be written as

$$C = \frac{dE}{dT} + \frac{PdV}{dT} \qquad \text{...}(iii)$$

We know $H = E + PV$

Differentiating this equation w.r.t $T$ at constant pressure, we get

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dE}{dT}\right)_p + P\left(\frac{dV}{dT}\right)_p \qquad \text{...}(iv)$$

comparing it with equation (*iii*) we have

$$C_p = \left(\frac{dH}{dT}\right)_p$$

**Thus heat capacity at constant pressure is defined as the rate of change of enthalpy with temperature at constant pressure.**

### Relation Between $C_p$ and $C_v$

From the definitions, it is clear that two heat capacities are not equal and $C_p$ is greater than $C_v$ by a factor which is related to the work done. At a constant pressure part of heat absorbed by the system is used up in increasing the internal energy of the system and the other for doing work by the system. While at constant volume the whole of heat absorbed is utilised in increasing the temperature of the system as there is no work done by the system. Thus increase in temperature of the system would be lesser at constant pressure than at constant volume. Thus **$C_p$ is greater than $C_v$.**

We know $$C_p = \frac{dH}{dT} \qquad \text{...}(i)$$

and $$C_v = \frac{dE}{dT} \qquad \text{...}(ii)$$

By definition $H = E + PV$ for 1 mole of an ideal gas

or $H = E + RT$ $\qquad (\because PV = RT)$

Differentiating w.r.t. temperature, $T$, we get

$$\frac{dH}{dT} = \frac{dE}{dT} + R$$

or $C_p = C_v + R$ $\qquad$ [By using equations (*i*) and (*ii*)]

or $C_p - C_v = R$

Thus $C_p$ is greater than $C_v$ by a gas constant whose value is 1.987 cal $K^{-1}$ $mol^{-1}$ or 8.314 J $K^{-1}$ $mol^{-1}$ in S.I. units.

### Calculation of ΔE and ΔH

(A) $\Delta E$ : For one mole of an ideal gas, we have

$$C_v = \frac{dE}{dT}$$

or $dE = C_v \times dT$

For a finite change, we have

$$\Delta E = E_2 - E_1 = C_v (T_2 - T_1)$$

and for $n$ moles of an ideal gas we get

$$\Delta E = E_2 - E_1 = n \times C_v \times (T_2 - T_1)$$

(B) $\Delta H$ : We know

$$\begin{aligned} \Delta H &= \Delta(E + PV) \\ &= \Delta E + \Delta(PV) \\ &= \Delta E + \Delta RT && [\because\ PV = RT] \\ &= \Delta E + R\,\Delta T \\ &= C_v(T_2 - T_1) + R(T_2 - T_1) \\ &= (C_v + R)(T_2 - T_1) \\ &= C_p(T_2 - T_1) && [\because\ C_p - C_v = R] \end{aligned}$$

and for *n* moles of an ideal gas we get

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

**SOLVED PROBLEM 1.** Calculate the value of $\Delta E$ and $\Delta H$ on heating 64.0 g of oxygen from 0°*C* to 100°*C*. $C_v$ and $C_p$ on an average are 5.0 and 7.0 cal mol$^{-1}$ degree$^{-1}$.

**SOLUTION.** We know

$$\Delta E = n \times C_v \times (T_2 - T_1) \qquad ...(i)$$

and

$$\Delta H = n \times C_p \times (T_2 - T_1) \qquad ...(ii)$$

Here

$$n = \frac{64}{16} = 4 \text{ moles; } T_2 = 100°C = 373\text{ K}$$

$$T_1 = 0°\,C = 273\text{ K}$$

On substitution we get

$$\begin{aligned} \Delta E &= 4 \times 5.0 \times (373 - 273) \\ &= 4 \times 5.0 \times 100 = \mathbf{2000\ cals} \end{aligned}$$

and

$$\begin{aligned} \Delta H &= 4 \times 7.0 \times (373 - 273) \\ &= 4 \times 7 \times 100 \\ &= \mathbf{2800\ cals} \end{aligned}$$

**SOLVED PROBLEM 2.** Calculate the amount of heat necessary to raise 213.5 g of water from 25° to 100°C. Molar heat capacity of water is 18 cal mol$^{-1}$ K$^{-1}$.

**SOLUTION**

By definition

$$C = \frac{q}{T_2 - T_1}$$

or

$$q = C(T_2 - T_1) \qquad \text{– for 1 mole}$$

$$q = n\,C(T_2 - T_1) \qquad \text{– for } n \text{ moles} \qquad ...(1)$$

In the present case

$$\begin{aligned} n &= 213.5/18 \\ C &= 18 \text{ cal mol}^{-1}\text{ K}^{-1} \\ T_2 - T_1 &= (373 - 298)\text{K} \end{aligned}$$

Substituting the value in (1)

$$\begin{aligned} q &= \frac{213.5}{18} \times 18 \times (373 - 298) \\ &= \mathbf{16{,}012\ cals = 16.012\ kcals} \end{aligned}$$

**SOLVED PROBLEM 3.** Three moles of an ideal gas ($C_v = 5$ cal deg$^{-1}$ mol$^{-1}$) at 10.0 atm and 0° are converted to 2.0 atm at 50°. Find $\Delta E$ and $\Delta H$ for the change.

$$R = 2 \text{ cal mol}^{-1} \text{ deg}^{-1}$$

**SOLUTION.**

(*a*)

$$\begin{aligned} \Delta E &= n\,C_v dT \\ &= 3 \times 5 \times (323 - 273) \\ &= \mathbf{750\ cals} \end{aligned}$$

(*b*)

$$\begin{aligned} \Delta H &= n\,C_p dT = n\,(C_v + R)\,dT \\ &= 3 \times (5 + 2) \times (323 - 273) \\ &= \mathbf{1050\ cals} \end{aligned}$$

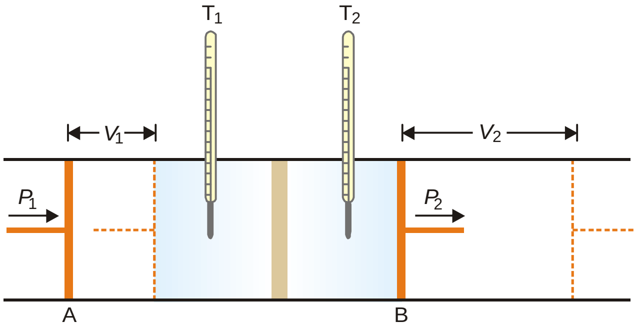
## JOULE-THOMSON EFFECT

Joule and Thomson (later Lord Kelvin) showed that when a compressed gas is forced through a porous plug into a region of low pressure, there is appreciable cooling.

**The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure, is known as Joule-Thomson Effect or Joule-Kelvin Effect.**

### Joule-Thomson Experiment

The apparatus used by Joule and Thomson to measure the temperature change on expansion of a given volume of gas is illustrated in Fig. 7.12. An insulated tube is fitted with a porous plug in the middle and two frictionless pistons *A* and *B* on the sides. Let a volume $V_1$ of a gas at pressure $P_1$ be forced through the porous plug by a slow movement of piston *A*. The gas in the right-hand chamber is allowed to expand to volume $V_2$ and pressure $P_2$ by moving the piston *B* outward. The change in temperature is found by taking readings on the two thermometers.



■ **Figure 7.12**
**Joule-Thomson experiment.**

Most gases were found to undergo cooling on expansion through the porous plug. Hydrogen and helium were exceptions as these gases showed a warming up instead of cooling.

**Explanation.** The work done on the gas at the piston *A* is $P_1V_1$ and the work done by the gas at the piston *B* is $P_2V_2$. Hence the net work ($w$) done by the gas is

$$\begin{aligned} w &= P_2V_2 - P_1V_1 \\ \Delta E &= q - w \quad \text{(First Law)} \end{aligned}$$

But the process is adiabatic and, therefore, $q = 0$

$$\therefore \qquad \Delta E = E_2 - E_1 = -w = -(P_2V_2 - P_1V_1)$$

$$\text{or} \qquad E_2 - E_1 = -(P_2V_2 - P_1V_1)$$

Rearranging,

$$E_2 + P_2V_2 = E_1 + P_1V_1$$

$$H_2 = H_1 \text{ or } \Delta H = 0$$

Thus the process in Joule-Thomson experiment takes place at constant enthalpy.

### Joule-Thomson Coefficient

**The number of degrees temperature change produced per atmosphere drop in pressure under constant enthalpy conditions on passing a gas through the porous plug, is called Joule-Thomson coefficient.** It is represented by the symbol $\mu$. Thus,

$$\mu = \frac{dT}{dP}$$

If $\mu$ is positive, the gas cools on expansion; if $\mu$ is negative, the gas warms on expansion. The temperature at which the sign changes is called the **Inversion temperature.** Most gases have positive Joule-Thomson coefficients and hence they cool on expansion at room temperature. Thus liquefaction of gases is accomplished by a succession of Joule-Thomson expansion.

The inversion temperature for $H_2$ is –80ºC. Above the inversion temperature, $\mu$ is negative. Thus at room temperature hydrogen warms on expansion. Hydrogen must first be cooled below –80ºC (with liquid nitrogen) so that it can be liquefied by further Joule-Thomson expansion. So is the case with helium.

### Explanation of Joule-Thomson Effect

We have shown above that Joule-Thomson expansion of a gas is carried at constant enthalpy. But

$$H = E + PV$$

Since $H$ remains constant, any increase in $PV$ during the process must be compensated by decrease of $E$, the internal energy. This leads to a fall in temperature *i.e.*, $T_2 < T_1$. For hydrogen and helium $PV$ decreases with lowering of pressure, resulting in increase of $E$ and $T_2 > T_1$. Below the inversion temperature, $PV$ increases with lowering of pressure and cooling is produced.

## ADIABATIC EXPANSION OF AN IDEAL GAS

A process carried in a vessel whose walls are perfectly insulated so that no heat can pass through them, is said to be **adiabatic.** In such a process there is no heat exchange between a system and surroundings, and $q = 0$.

According to the First law

$$\Delta E = q - w = 0 - w$$

$$\text{or} \qquad \Delta E = -w \qquad \text{...(1)}$$

Since the work is done at the expense of internal energy, the internal energy decreases and the temperature falls.

Consider 1 mole of an ideal gas at pressure $P$ and a volume $V$. For an infinitesimal increase in volume $dV$ at pressure $P$, the work done by the gas is $-PdV$. The internal energy decreases by $dE$.

According to equation (1)

$$dE = -PdV \qquad \text{...(2)}$$

By definition of molar heat capacity at constant volume

$$dE = C_v dT \qquad \text{...(3)}$$

From (2) and (3)

$$C_v dT = -PdV$$

For an ideal gas

$$P = RT/V$$

and hence

$$C_v dT = -RT\frac{dV}{V}$$

or
$$C_v \frac{dT}{T} = -R\frac{dV}{V}$$

Integrating between $T_1$, $T_2$ and $V_1$, $V_2$ and considering $C_v$ to be constant,

$$C_v \int_{T_2}^{T_1} \frac{dT}{T} = -R\int_{V_2}^{V_1} \frac{dV}{V}$$

Thus

$$C_v \ln\frac{T_2}{T_1} = -R\ln\frac{V_2}{V_1}$$

Since $R = C_p - C_v$, this equation may be written as

$$\ln\frac{T_2}{T_1} = -\frac{(C_p - C_v)}{C_v}\ln\frac{V_2}{V_1} \qquad \text{...(4)}$$

The ratio of $C_p$ to $C_v$ is often written as $\gamma$,

$$\gamma = \frac{C_p}{C_v}$$

and equation (4) thus becomes

$$\ln\frac{T_2}{T_1} = -(\gamma - 1)\ln\frac{V_2}{V_1}$$

Replacing – ve sign by inverting $V_2/V_1$ to $V_1/V_2$ and taking antilogarithms

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \text{...(5)}$$

$$T_2V_2^{\gamma-1} = T_1V_1^{\gamma-1}$$

or
$$TV^{\gamma-1} = \text{a constant}$$

We can also eliminate the temperature by making use of the ideal gas relationship

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1} = \left[\frac{V_1}{V_2}\right]^{\gamma-1} \qquad \text{...(6)}$$

Equating the right-hand sides of equations (5) and (6)

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} \qquad \text{or} \qquad PV^{\gamma} = k$$

### Comparison between Isothermal and Adiabatic Expansions

Boyle's law describes pressure-volume relations of an ideal gas under isothermal conditions ($T$, constant). This is similar to the relation derived for adiabatic expansion.

$$PV = \text{constant} \qquad (\text{Boyle's law})$$
$$PV^{\gamma} = \text{constant} \qquad (\text{Adiabatic expansion})$$

$\gamma$ for an ideal monoatomic gas = 1.67. The difference between the two processes is : **in an isothermal process, temperature of a system remains constant while in an adiabatic process, temperature must change.**

**Explanation.** In an isothermal process heat is absorbed to make up for the work done by the gas in expansion and the temperature remains unchanged. On the other hand, adiabatic expansion takes place at the expense of internal energy which decreases and the temperature falls. For the same reason, the curve for the adiabatic process (Fig. 7.13) is steeper than that for the isothermal process.

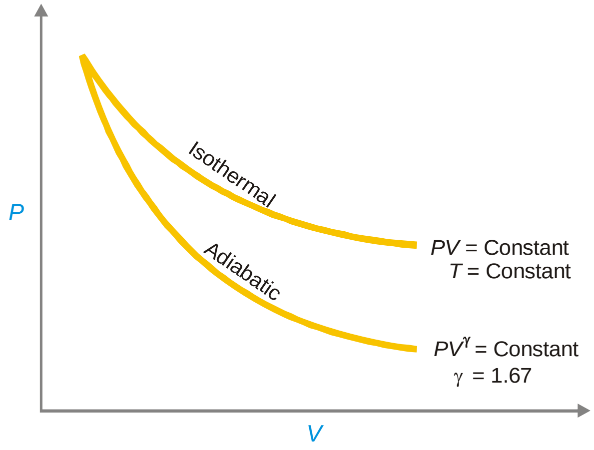


**Figure 7.13**
**Curves for isothermal and adiabatic expansions for a monoatomic ideal gas.**

## WORK DONE IN ADIABATIC REVERSIBLE EXPANSION

**Step 1. Value of VdP from adiabatic equation**

For an adiabatic process

$$PV^{\gamma} = \text{constant}$$

Differentiating it, we have

$$\gamma PV^{\gamma-1}\,dV + V^{\gamma}\,dp = 0$$

Dividing by $V^{\gamma-1}$, we get

$$\gamma PdV + VdP = 0$$

or $$VdP = -\gamma PdV \qquad ...(1)$$

**Step 2. Value of *VdP* from ideal gas equation**

For 1 mole of an ideal gas

$$PV = RT$$

Complete differentiation gives

$$PdV + VdP = RdT$$
$$VdP = RdT - PdV \qquad ...(2)$$

**Step 3. Substitution**

Substituting the value of *VdP* from (1) in (2) we get

$$RdT - PdV = -\gamma\, PdV$$

or
$$RdT = P\,(1-\gamma)\, dV$$

or
$$PdV = \frac{RdT}{1-\gamma}$$

If there are *n* moles of a gas

$$PdV = \frac{n\,R\,d\,T}{1-\gamma}$$

**Step 4. Integration**

Integrating from $T_1$, $V_1$ to $T_2$, $V_2$ with γ constant

$$\begin{aligned} w_{\max} &= P\,(V_2 - V_1) \\ &= \int_{T_1}^{T_2} \frac{n\,RdT}{1-\gamma} \\ &= \frac{n\,R\,(T_2 - T_1)}{1-\gamma} \end{aligned}$$

When $T_2 > T_1$, $w_{\max}$ *is negative* because $1 - \gamma$ is negative. This means that work is done on the gas. On the other hand, when $T_2 < T_1$, $w_{\max}$ is positive which means that work is done by the gas.

**SOLVED PROBLEM.** Calculate *w* for the adiabatic reversible expansion of 2 moles of an ideal gas at 273.2 K and 20 atm to a final pressure of 2 atm.

**SOLUTION**

Given
$$\begin{aligned} C_p &= 5R/2,\ \text{mole}^{-1}\text{deg}^{-1} \\ C_v &= 3R/2,\ \text{mole}^{-1}\text{deg}^{-1} \\ R &= 8.314\text{J mole}^{-1}\text{deg}^{-1} \end{aligned}$$

**Step 1.** To calculate the value of $T_2$, the final temperature, using the equation

$$(T_2 / T_1)^{\gamma} = (P_2 / P_1)^{\gamma - 1}$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

Substituting the value of γ in (1)

$$(T_2 / 273.2)^{5/3} = (2/20)$$

Solving it, we get

$$T_2 = \mathbf{108.8\ K}$$

**Step 2.** To calculate maximum work under adiabatic conditions

$$\begin{aligned} w_{\max} &= \frac{nR\,(T_2 - T_1)}{1-\gamma} \\ &= \frac{2 \times 8.314\,(108.8 - 273.2)}{1 - 5/3} \\ &= 4100\text{ J} = \mathbf{4.1\ kJ} \end{aligned}$$

### ALTERNATIVE SOLUTION

The work done under adiabatic conditions may be obtained by calculating decrease in internal energy.

$$\begin{aligned} w &= -\Delta E = -nC_v\,(T_2 - T_1) \\ &= -2 \times 3/2 \times 8.314\,(108.8 - 273.2) \\ &= 4100\text{ J} = 4.1\text{ kJ} \end{aligned}$$

**SOLVED PROBLEM.** At 25ºC for the combustion of 1 mole of liquid benzene the heat of reaction at constant pressure is given by

$$C_6H_6\,(l) + 7\tfrac{1}{2}\,O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(1)\ \Delta H = -780980\text{ cal}$$

What would be the heat of reaction at constant volume ?

**SOLUTION.** We have

$$\Delta H = \Delta E + \Delta n\,R\,T$$

Here $\Delta n = n_p - n_R = 6 - 7.5 = -1.5$

Thus

$$\begin{aligned} \Delta E &= \Delta H - \Delta n\,(RT) \\ &= -780980 - (-1.5) \times (2 \times 298) \\ &= -780980 + 894 \\ &= -780086\text{ cals} \\ &= \mathbf{-\ 780.086\ kcals} \end{aligned}$$

## EXAMINATION QUESTIONS

1. Define or explain the following terms :
   - (*a*) First law of thermodynamics
   - (*b*) An isothermal reversible expansion
   - (*c*) Irreversible expansion
   - (*d*) Internal energy
   - (*e*) Enthalpy
   - (*f*) Molar heat capacities
   - (*g*) Molar heat capacity
   - (*h*) Adiabatic expansion
   - (*i*) Ideal gas
2. Explain the following terms :
   - (*a*) State of a System
   - (*b*) Extensive Properties
   - (*c*) Closed System
   - (*d*) Isothermal Process
3. What do you understand by $C_P$ and $C_V$ of gases? Why is the value of $C_P$ always greater than that of $C_V$? How are they related?
4. State the first law of thermodynamics in as many ways as possible. Obtain the mathematical expression for the law with sign conventions.
5. Give a concise statement of the first law of thermodynamics. Deduce its mathematical form and explain the terms involved.
6. (*a*) What do you understand by thermodynamic system and surroundings?
   (*b*) Which of the following are intensive properties :
   - (*i*) Density
   - (*ii*) Surface Tension
   - (*iii*) Volume
   - (*iv*) Entropy
7. (*a*) Show thermodynamically that for an ideal gas $C_P - C_V = R$

(*b*) A dry gas at NTP is expanded adiabatically from 1 litre to 5 litre. Calculate the final temperature and pressure assuming ideal behaviour ($C_P/C_V = 1.4$)

**Answer.** (*b*) $T_2 = 143.31$ K; $P_2 = 0.105$ atm

**8.** (*a*) State and explain First law of Thermodynamics

(*b*) Prove that $Q_V = \Delta E$ and $Q_P = \Delta H$ and discuss the relation amongst heat, internal energy and work.

**9.** Derive the relationship $\Delta H = \Delta E + \Delta n\,RT$

**10.** Explain heat capacity at constant volume thermodynamically.

**11.** Distinguish between isothermal and adiabatic process.

**12.** How would the energy of an ideal gas change if it is made to expand into vacuum at constant temperature.

**13.** (*a*) Derive the expression for maximum work done when *n* moles of an ideal gas are expanded isothermally and reversibly from $V_1$ to $V_2$ volume.

(*b*) Describe different types of thermodynamic processes.

**14.** (*a*) Explain the term enthalpy.

(*b*) State the first law of thermodynamics.

(*c*) Define $C_P$ and $C_V$. State their relation.

**15.** (*a*) What are state functions? How do these differ from path functions.

(*b*) State the first law of thermodynamics. Give its mathematical statement and explain each term involved.

**16.** (*a*) Describe open, closed and isolated systems.

(*b*) What do you understand by the terms : Extensive properties and Intensive properties. Give two examples of each category.

(*c*) Calculate the work of expansion of one mole of an ideal gas at 25°C under isothermal conditions, the pressure being changed from 1 to 5 atmosphere.

**Answer.** (*c*) –3988.2 J

**17.** (*a*) Give two definitions of First law of thermodynamics.

(*b*) State "Kirchoff's Law". Derive it with the help of first law of thermodynamics.

(*c*) Calculate the value of $\Delta E$ and $\Delta H$ on heating 64.0 grams of oxygen from 0°C to 1000°C. $C_V$ and $C_P$ on an average are 5.0 and 7.0 cal. $\text{mol}^{-1}\ \text{deg}^{-1}$ respectively.

**Answer.** (*c*) 1000 cals; 1400 cals

**18.** (*a*) Under what conditions $\Delta E = \Delta H$ for a chemical reaction?

(*b*) One mole of an ideal gas expands isothermally and reversibly from 1 litre to 100 litres at 27°C. Calculate *w*, *q*, $\Delta E$, $\Delta H$ and $\Delta S$ for the process.

**Answer.** (*b*) 2745.63 cal; 2745.63 cal; zero; 596.1 cal, 9.152 cal $K^{-1}$

**19.** State the first law of thermodynamics. With the help of this law show that:

(*i*) Heat absorbed by a system at constant volume is equal to increase in internal energy of the system.

(*ii*) Heat absorbed by a system at constant pressure is equal to the increase in the enthalpy.

**20.** Explain the difference between isothermal and adiabatic processes.

**21.** (*a*) Distinguish between open, closed and isolated system. Give examples.

(*b*) Differentiate between reversible and irreversible processes.

**22.** (*a*) Prove that the value of Joule Thomson coefficient is zero for an ideal gas.

(*b*) Explain First law of Thermodynamics. Calculate the work done in an isothermal and reversible expansion process of an ideal gas.

**23.** (*a*) Derive an expression for the work done by a gas in isothermal reversible expansion of an ideal gas.

(*b*) One mole of an ideal gas at 25°C is allowed to expand reversibly at constant temperature from volume 10 litres to 20 litres. Calculate the work done by the gas in Joules and calories.

**Answer.** (*b*) –1717.46 J or –410.46 cal (*Guru Nanak Dev BSc, 2002*)

**24.** Calculate the work done in expanding 2 moles of an ideal gas from 2L to 5L at 273°C.

**Answer.** –5683.5 J (*Andhra BSc, 2002*)

**25.** Distinguish between

(*a*) Isothermal and adiabatic process (*b*) State function and path function

(*c*) Reversible and irreversible process (*d*) Gibbs and Helmholtz free energy

(*Andhra BSc, 2002*)

**26.** (*a*) Write short notes on following :

(*i*) Enthalpy (*ii*) Internal Energy

(*iii*) Free Energy

(*b*) Heat supplied to a Carnot engine is 453.6 kcal. How much useful work can be done by the engine between 0°C and 100°C?

**Answer.** (*b*) $1.216 \times 10^5$ cal (*HS Gaur BSc, 2002*)

**27.** What is the efficiency of Carnot engine working between 500 K and 850 K? If the engine absorbs 1200 cal of work, how much heat is given to sink?

**Answer.** 0.4117; 705.96 cal (*Andhra BSc, 2002*)

**28.** Calculate $q$, $w$, $\Delta H$, $\Delta S_{\text{system}}$, $\Delta S_{\text{surr}}$ and $\Delta S_{\text{universe}}$ for one mole of an ideal gas which expands from $V_1$ to $10V_1$ at 300 K isothermally under reversible conditions (Use $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

**Answer.** 5744.14 J, 5744.14 J, 0, 0, 19.147 J $\text{K}^{-1}$, –19.147 J $\text{K}^{-1}$, 0 (*Delhi BSc, 2003*)

**29.** Two moles of an ideal gas expanded isothermally and reversibly at 300 K to twice the original volume. Calculate $q$, $w$, $\Delta E$ and $\Delta H$ (Given log 2 = 0.3010, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

**Answer.** 3457.97 J, 3457.97 J, 0, 0 (*Sambalpur BSc, 2003*)

**30.** Calculate maximum amount of heat withdrawn from a hot reservoir at 410 K to obtain work equivalent to 15 kJ per cycle. The temperature of the sink is 290 K.

**Answer.** 512.50 kJ (*Sambalpur BSc, 2003*)

**31.** A gas at 10 atm pressure occupies a volume of 10 litres at 300 K. It is allowed to expand at the constant temperature of 300 K under a constant external pressure till the volume equilibrates at 100 litres. Calculate the work done.

**Answer.** 900 atm litre (*Kolkata BSc, 2003*)

**32.** What is the basic principle of Joule-Thomson effect? (*Nagpur BSc, 2003*)

**33.** Which of the following parameters are state functions : $q$, $H$, $E$ and $w$. The terms have their usual meanings. Show that the work done in an isothermal expansion of an ideal gas is greater than that of a van der Waal's gas. (*Kalyani BSc, 2003*)

**34.** Distinguish between :

(*a*) Isothermal and adiabatic process

(*b*) Reversible and Irreversible process (*Panjab BSc, 2003*)

**35.** Define heat capacity at constant pressure and heat capacity at constant volume.

(*Arunachal BSc, 2003*)

**36.** How many calories of heat are required to heat 18 grams of Argon from 40°C to 100°C at

(*i*) constant volume and (*ii*) constant pressure

Molar heat capacity of Argon at constant volume is 3 cal/degree and molar heat capacity of Argon at constant pressure is 5 cal/degree.

**Answer.** 180 cals; 300 cals (*Meerut BSc, 2004*)

**37.** (*a*) Calculate the maximum work done when 44 g of Neon gas expands reversibly and isothermally from 10 atm. to 2 atm. pressure at constant temperature 27°C. (Neon at wt. = 20; $R = 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$)

(*b*) Derive Kirchoff's equation.

**Answer.** (*a*) 2124.84 cals (*Dibrugarh BSc, 2004*)

**38.** (*a*) Explain the following :

Heat capacity, Thermodynamic state, Isolated state, Intensive properties.

(*b*) Calculate the maximum work obtained when 2 moles of nitrogen were expanded isothermally and reversibly from 10 litres to 20 litres at 25°C.

**Answer.** (*b*) 3434.9 J (*Sri Venkateswara BSc, 2004*)

**39.** (*a*) Write notes on objectives and limitations of Thermodynamics.

(*b*) Calculate $\Delta E$ and $\Delta H$ when the temperature of one mole of water is increased from 10°C to 70°C. The density of water is 0.9778 g $cm^{-3}$ and 0.9997 g $cm^{-3}$ at 70°C and 10°C respectively.

**Answer.** (*b*) 1080 cal $mol^{-1}$; 1079.99 cal $mol^{-1}$ (*Gulbarga BSc, 2004*)

**40.** Calculate $w$ and $\Delta E$ for the conversion of 1 mole of water into l mole of steam at a temperature of 373 K and 1 atm pressure. Latent heat of vaporisation of water 540 cal $g^{-1}$.

**Answer.** 8.979 kcal (*Delhi BSc, 2005*)

**41.** Calculate the work done when 5 moles of hydrogen gas expand isothermally and reversibly at 298 K from 10 to 50 litres.

**Answer.** 4.766 kcal (*Bangalore BSc, 2005*)

**42.** When one mole of liquid $Br_2$ is converted to $Br_2$ vapour at 25 ºC and 1 atm pressure, 7.3 kcal of heat is absorbed and 0.59 k cal of expansion work is done by the system. Calculate $\Delta E$ for this process.

**Answer.** + 6.7 kcal (*Nagpur BSc, 2005*)

**43.** Find the work done when 2 moles of an ideal gas expand isothermally from 2 litres to 5 litres against a constant pressure of 1 atm at 298 K.

**Answer.** 1085 cal (*Madras BSc, 2006*)

**44.** What is the maximum work which can be obtained by the isothermal reversible expansion of two moles to three moles of an ideal gas at 273 K from 1.12 litre to 11.2 litres ?

**Answer.** 1627.35 cal (*Utkal BSc, 2006*)

**45.** Calculate $\Delta E$ for the combustion of one mole of Magnesium in an open container at 298 K and 1 atm pressure, if $\Delta H_{combustion} = -143.9$ k cal ?

**Answer.** – 143.6 k cal (*Baroda BSc, 2006*)

## MULTIPLE CHOICE QUESTIONS

**1.** The study of the flow of heat or any other form of energy into or out of a system undergoing physical or chemical change is called

(*a*) thermochemistry (*b*) thermokinetics

(*c*) thermodynamics (*d*) thermochemical studies

**Answer.** (*c*)

**2.** Thermodynamics is applicable to

(*a*) microscopic systems only (*b*) macroscopic systems only

(*c*) homogeneous systems only (*d*) heterogeneous systems only

**Answer.** (*b*)

**3.** Which is not true about thermodynamics?

(*a*) it ignores the internal structure of atoms and molecules

(*b*) it involves the matter in bulk

(*c*) it is concerned only with the initial and final states of the system

(*d*) it is not applicable to macroscopic systems

**Answer.** (*d*)

**4.** A system that can transfer neither matter nor energy to and from its surroundings is called
(*a*) a closed system (*b*) an isolated system
(*c*) an open system (*d*) a homogeneous system
**Answer.** (*b*)

**5.** A thermos flask is an example of
(*a*) isolated system (*b*) closed system
(*c*) open system (*d*) heterogeneous system
**Answer.** (*a*)

**6.** A closed system is one which cannot transfer matter but transfer ________ to and from its surrounding
(*a*) heat (*b*) work
(*c*) radiations (*d*) all of these
**Answer.** (*d*)

**7.** A gas contained in a cylinder filled with a piston constitutes
(*a*) an open system (*b*) a heterogeneous system
(*c*) a closed system (*d*) an isolated system
**Answer.** (*c*)

**8.** A system that can transfer both energy and matter to and from its surroundings is called
(*a*) an isolated system (*b*) a closed system
(*c*) an open system (*d*) a heterogeneous system
**Answer.** (*c*)

**9.** Zinc granules reacting with dilute hydrochloric acid in an open beaker constitutes
(*a*) an isolated system (*b*) an open system
(*c*) a closed system (*d*) a heterogeneous system
**Answer.** (*b*)

**10.** A system in which no thermal energy passes into or out of the system is called
(*a*) adiabatic system (*b*) an open system
(*c*) a reversible system (*d*) a closed system
**Answer.** (*a*)

**11.** An intensive property does not depend upon
(*a*) nature of the substance (*b*) quantity of matter
(*c*) external temperature (*d*) atmospheric pressure
**Answer.** (*b*)

**12.** Which out of the following is not an intensive property?
(*a*) pressure (*b*) concentration
(*c*) density (*d*) volume
**Answer.** (*d*)

**13.** A property that depends upon the quantity of matter is called an extensive property. Which of the following is not an extensive property?
(*a*) mass (*b*) volume
(*c*) density (*d*) internal energy
**Answer.** (*c*)

**14.** Which of the following sets of properties constitute intensive properties?
(*a*) temperature, pressure and volume (*b*) mass, density and volume
(*c*) density, pressure and temperature (*d*) internal energy, density and pressure
**Answer.** (*c*)

**15.** A system in which state variables have constant values throughout the system is called in a state of

(*a*) equilibrium (*b*) non-equilibrium

(*c*) isothermal equilibrium (*d*) none of these

**Answer.** (*a*)

**16.** In an adiabatic process _______ can flow into or out of the system.

(*a*) no heat (*b*) heat

(*c*) matter (*d*) no matter

**Answer.** (*a*)

**17.** Which of the following conditions holds good for an adiabatic process?

(*a*) $dq < 0$ (*b*) $dq > 0$

(*c*) $dq = 0$ (*d*) $dq = \alpha$

**Answer.** (*c*)

**18.** An isobaric process takes place at constant _______.

(*a*) temperature (*b*) pressure

(*c*) volume (*d*) concentration

**Answer.** (*b*)

**19.** Which is true for an isobaric process?

(*a*) $dp > 0$ (*b*) $dp < 0$

(*c*) $dp = \alpha$ (*d*) $dp = 0$

**Answer.** (*d*)

**20.** An isochoric process takes place at constant_______.

(*a*) volume (*b*) temperature

(*c*) pressure (*d*) concentration

**Answer.** (*a*)

**21.** For a cyclic process, the change in internal energy of the system is

(*a*) always positive (*b*) always negative

(*c*) equal to zero (*d*) equal to infinity

**Answer.** (*c*)

**22.** Which out of the following is incorrect?

(*a*) heat flow into the system is +ve (*b*) heat flow out of the system is –ve

(*c*) work done on the system is –ve (*d*) none of these

**Answer.** (*c*)

**23.** The units erg, joule and calorie are interconvertible, which of the following is incorrect?

(*a*) $10^7$ ergs = 1 Joule (*b*) 4.184 J = 1 cal

(*c*) 1 Joule = 0.2390 cal (*d*) 1 erg = 4.184 cal

**Answer.** (*d*)

**24.** A gas expands from 10 litres to 20 litres against a constant external pressure of 10 atm. The pressure-volume work done by the system is

(*a*) 100 lit atm (*b*) –100 lit atm

(*c*) 10 lit atm (*d*) –10 lit atm

**Answer.** (*b*)

**25.** Which out of the following is incorrect, for an ideal gas?

(*a*) $PV = nRT$ (*b*) $V = \frac{nRT}{P}$

(*c*) $P = \frac{nRT}{V}$ (*d*) all are correct

**Answer.** (*d*)

**26.** The work done in the reversible expansion of a gas from the initial state A to final state B is

(*a*) maximum (*b*) minimum

(*c*) equal to zero (*d*) equal to infinity

**Answer.** (*a*)

**27.** The first law of thermodynamics is

(*a*) the total energy of an isolated system remains constant though it may change from one form to another

(*b*) total energy of a system and surroundings remains constant

(*c*) whenever energy of one type disappears, equivalent amount of another type is produced

(*d*) all of the above

**Answer.** (*d*)

**28.** The mathematical relation for the first law of thermodynamics is

(*a*) $\Delta E = q - w$ (*b*) $\Delta E = 0$ for a cyclic process

(*c*) $\Delta E = q$ for an isochoric process (*d*) all of these

**Answer.** (*d*)

**29.** For an adiabatic process, according to first law of thermodynamics,

(*a*) $\Delta E = -w$ (*b*) $\Delta E = w$

(*c*) $\Delta E = q - w$ (*d*) none of these

**Answer.** (*a*)

**30.** The change in internal energy for an isobaric process is given by

(*a*) $\Delta E = q + p\,\Delta v$ (*b*) $\Delta E = q - p\,\Delta v$

(*c*) $\Delta E = q$ (*d*) $\Delta E = p\,\Delta v$

**Answer.** (*b*)

**31.** Which of the following properties is not a function of state?

(*a*) concentration (*b*) internal energy

(*c*) enthalpy (*d*) entropy

**Answer.** (*a*)

**32.** The change in enthalpy of a system is measured by measuring

(*a*) heat of the process at constant volume (*b*) heat of the process at constant temperature

(*c*) heat of the process at constant pressure (*d*) none of these

**Answer.** (*c*)

**33.** The enthalpy change, $\Delta H$ of a process is given by the relation

(*a*) $\Delta H = \Delta E + p\,\Delta v$ (*b*) $\Delta H = \Delta E + \Delta n\,R\,T$

(*c*) $\Delta H = \Delta E + w$ (*d*) all of these

**Answer.** (*b*)

**34.** The amount of heat required to raise the temperature of one mole of the substance by 1 K is called

(*a*) heat capacity (*b*) molar heat capacity

(*c*) molar heat (*d*) molar capacity

**Answer.** (*b*)

**35.** Which of the following statements is not correct?

(*a*) heat is not a state function (*b*) heat capacity is not a state function (*c*) neither of these (*d*) both

**Answer.** (*c*)

**36.** Heat capacity at constant pressure is the change in

(*a*) internal energy with temperature at constant volume

(*b*) internal energy with temperature at constant pressure

(*c*) enthalpy with temperature at constant volume

(*d*) enthalpy with temperature at constant pressure

**Answer.** (*d*)

**37.** Heat capacity at constant volume is the change in

(*a*) internal energy with temperature at constant volume

(*b*) internal energy with temperature at constant pressure

(*c*) enthalpy with temperature at constant volume

(*d*) enthalpy with temperature at constant pressure

**Answer.** (*a*)

**38.** Which of the following relations is true ?

(*a*) $C_p > C_v$ (*b*) $C_v > C_p$

(*c*) $C_p = C_v$ (*d*) $C_p = C_v = 0$

**Answer.** (*a*)

**39.** The heat capacity at constant pressure is related to heat capacity at constant volume by the relation

(*a*) $C_p - R = C_v$ (*b*) $C_v - R = C_p$

(*c*) $C_p - C_v = R$ (*d*) $R - C_p = C_v$

**Answer.** (*c*)

**40.** The phenomenon of lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as

(*a*) First law of thermodynamics (*b*) Second law of thermodynamics

(*c*) Le Chatlier's principle (*d*) Joule Thomson effect

**Answer.** (*d*)

**41.** Which of the following relations is applicable to adiabatic expansion of an ideal gas?

(*a*) $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$ (*b*) $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

(*c*) both (*d*) none of these

**Answer.** (*c*)

**42.** In an adiabatic process ________ must change

(*a*) pressure (*b*) volume

(*c*) concentration (*d*) temperature

**Answer.** (*d*)

**43.** The enthalpy change of a reaction is independent of

(*a*) state of the reactants and products

(*b*) nature of the reactants and products

(*c*) initial and final enthalpy change of the reaction

(*d*) different intermediate reaction

**Answer.** (*d*)

**44.** Which of the following is not correct?

(*a*) $H = E + P V$ (*b*) $H - E = P V$

(*c*) $H - E - P V = 0$ (*d*) $H = E - P V$

**Answer.** (*d*)

**45.** When the total energy change in an isothermal cycle is zero, it represents

(*a*) a reversible cycle
(*b*) an adiabatic change
(*c*) a thermodynamic equilibrium
(*d*) an irreversible cycle

**Answer.** (*a*)

**46.** One mole of an ideal gas at 300 K is expanded isothermally from 1 litre volume to 10 litre volume. $\Delta E$ for this process is ($R = 2$ cal $K^{-1}$ $mol^{-1}$)

(*a*) 300 cal
(*b*) 600 cal
(*c*) 1200 cal
(*d*) 0 cal

**Answer.** (*d*)

**47.** A system absorbs 100 kJ heat and performs 50 kJ work on the surroundings. The increase in internal energy of the system is

(*a*) 50 kJ
(*b*) 100 kJ
(*c*) 150 kJ
(*d*) 5000 kJ

**Answer.** (*a*)

**48.** For the reaction $H_2 + I_2 \rightleftharpoons 2HI$, $\Delta H$ is equal to

(*a*) $\Delta E + 2RT$
(*b*) $\Delta E - 2RT$
(*c*) $\Delta E$
(*d*) $\Delta E + RT$

**Answer.** (*c*)

**49.** The work done when 1 mole of a gas expands reversibly and isothermally from 5 atm to 1 atm at 300 K is

(*a*) – 4015 J
(*b*) +4015 J
(*c*) zero
(*d*) 150 J

**Answer.** (*a*)

**50.** Three moles of an ideal gas ($C_v = 5$ cal $K^{-1}$ $mol^{-1}$) at 10.0 atm and 0° are converted to 2.0 atm at 50°. The $\Delta E$ for the process is

(*a*) 150 cal
(*b*) 300 cal
(*c*) 750 cal
(*d*) 1500 cal

**Answer.** (*c*)

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# 8

# CHAPTER

# Thermochemistry

CONTENTS

It is noticed that energy in the form of heat (thermal energy) is generally evolved or absorbed as a result of a chemical change.

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

We have studied in the previous chapter that every substance has a definite amount of energy known as the **intrinsic energy or internal energy, E.** Its exact value cannot be determined but the change in internal energy, $\Delta E$, can be accurately measured experimentally.

When the internal energy of reactants ($E_r$) is greater than the internal energy of the products ($E_p$), the difference of internal energy, $\Delta E$, is released as heat energy.

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

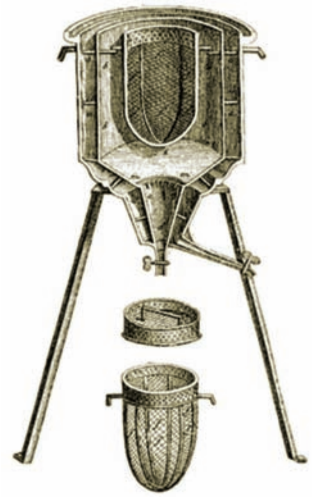
or

$$\Delta E = E_p - E_r$$

Such a reaction is called **exothermic reaction.** If the internal energy of the products ($E_p$) is greater than that of the reactants ($E_r$), heat is absorbed from the surroundings. Such a reaction is called **endothermic reaction.** The amount of heat released or absorbed in a chemical reaction is termed the **heat of reaction.**

## HISTORY OF THERMOCHEMISTRY

In 1782 Antoine Lavoisier and Pierre-Simon Laplace laid the foundations of "thermochemistry" by showing that the heat evolved in a reaction is equal to the heat absorbed in the reverse reaction. They also investigated the specific heat and latent heat of a number of substances, and amounts of heat evolved in combustion. Similarly, in 1840 Swiss chemist Germain Hess formulated the principle that the evolution of heat in a reaction is the same whether the process is accomplished in one-step or in a number of stages. This known as Hess's law. With the advent of the mechanical theory of heat in the early 19th century, Hess's law came to be viewed as a consequence of the law of conservation of energy.



The world's first ice-calorimeter, used in the winter of 1782-83, by Antoine Lavoisier and Pierre-Simon Laplace, to determine the heat evolved in various chemical changes.

The energy changes in chemical reactions are largely due to the breaking of existing bonds between the atoms and the formation of new bonds. **Thus thermochemistry provides useful information regarding the bond energies.**

## UNITS OF ENERGY CHANGES

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

## ENTHALPY OF A REACTION

Thermochemical measurements are made either at (*a*) constant volume or (*b*) constant pressure. The magnitudes of changes observed under the two conditions are different.

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

However at constant pressure not only does the change in internal energy take place but work is also involved because of expansion or contraction. In the laboratory most of the chemical reactions are carried out at constant pressure (atmospheric pressure) rather than at constant volume. In order to study the heat changes for reactions taking place at constant pressure and constant temperature, chemists have introduced a new term called **enthalpy.**

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

$$H = E + PV$$

where $E$ is the internal energy, $P$ is the pressure and $V$ is the volume of the system. It is also called **Heat content.**

Just like internal energy, enthalpy is also a function of the state and it is not possible to measure its absolute value. However a change in enthalpy ($\Delta H$) accompanying a process can be measured accurately and is given by the expression

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$
$$= H_{\text{p}} - H_{\text{r}}$$

Thus if $\Delta V$ be the change in volume in case of a reaction at constant temperature and pressure, the thermal effect observed will be the sum of the change in internal energy ($\Delta E$) and the work done in expansion or contraction. That is,

$$\Delta H = \Delta E + P \times \Delta V$$

**Therefore, while the heat change in a process is equal to its change in internal energy $\Delta E$ at constant volume, it gives at constant pressure the enthalpy change $\Delta H$.** That is,

$\Delta E$ = Heat change in a reaction at constant volume

$\Delta H$ = Heat change in a reaction at constant pressure

For reactions involving solids and liquids only the change in volume ($\Delta V$) is very small and the term $P \times \Delta V$ is negligible. For such reactions $\Delta H$ is equal to $\Delta E$. In case of gases, however, we must specify whether the reaction has taken place at constant volume or at constant pressure because the value of $P \times \Delta V$ is appreciable. Most of such reactions are, however, studied at constant pressure and change in enthalpy ($\Delta H$) is involved.

## EXOTHERMIC AND ENDOTHERMIC REACTIONS

Let us consider a general reaction at constant pressure,

$$\text{A} + \text{B} \longrightarrow \text{C} + \text{D}$$

If $H_A$, $H_B$, $H_C$ and $H_D$ be the enthalpies of A, B, C and D respectively, the heat of reaction at constant pressure *viz*., $\Delta H$ is equal to the difference in enthalpies of the products and the reactants *i.e.*,

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

The value of $\Delta H$ may be either zero, negative or positive. Where $\Delta H$ is zero, the enthalpies of the products and reactants being the same, the heat is evolved or absorbed. In case $\Delta H$ is negative, the sum of enthalpies of the products is less than that of the reactants and the difference in enthalpy is given out in the form of heat.

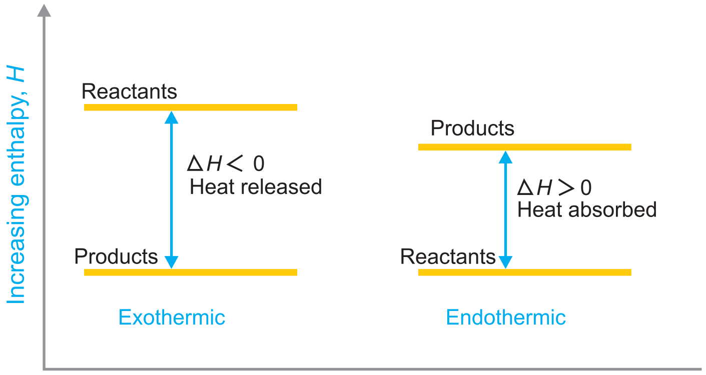


**Figure 8.1**
**Enthalpy diagram for an exothermic and endothermic reaction.**

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

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

## EXAMPLES OF EXOTHERMIC AND ENDOTHERMIC PROCESSES

When trying to classify a process as exothermic or endothermic, watch how the temperature of the surroundings changes. An exothermic process releases heat, and causes the temperature of the immediate surroundings to rise. An endothermic process absorbs heat and cools the surroundings.

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

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

Thus for an exothermic reaction $H_p < H_r$ and $\Delta H = -$ ve, for an endothermic reaction $H_p > H_r$ and $\Delta H = +$ve.

### Sign of $\Delta H$ and $\Delta E$

A negative sign of $\Delta H$ or $\Delta E$ shows that heat is evolved and the reaction is exothermic. A positive sign of $\Delta H$ or $\Delta E$ indicates that heat energy is absorbed and the reaction is endothermic.

**TABLE 8.1. SIGN CONVENTIONS FOR ENERGY**

| Energy | Terms used | Sign |
|---|---|---|
| Released | Exothermic | – |
| Absorbed | Endothermic | + |

### Calculation of ΔH from ΔE and *vice versa*

The enthalpy change of a reaction at constant pressure ($\Delta H$) and internal energy change ($\Delta E$) are related to each other as

$$\Delta H = \Delta E + P \times \Delta V \qquad \dots (i)$$

where $\Delta V$ is the change in volume due to expansion or contraction when measurement is done at constant pressure, $P$. Though heat changes of reactions are usually measured at constant pressure, it is sometimes necessary to carry out the reaction at constant volume as, for example, in the measurement of heat of combustion in a bomb calorimeter. The above relationship can be used, if desired, for the conversion of $\Delta H$ into $\Delta E$ and *vice versa*.

Let us consider a reaction

$$\text{aA} + \text{bB} \longrightarrow \text{cC} + \text{dD}$$

Change in number of moles

$$\begin{aligned} &= \text{No. of moles of products} - \text{No. of moles of reactants} \\ &= (\text{c} + \text{d}) - (\text{a} + \text{b}) \\ &= \Delta n \end{aligned}$$

Let the volume occupied by one mole of the gas be $V$. Then, change in volume, $\Delta V$ = change in No. of moles × volume occupied by one mole of the gas.

$$\Delta V = \Delta n \times V$$

or $$P \times \Delta V = P\,(\Delta n \times V)$$

$$P \times \Delta V = PV \times \Delta n \qquad ...(ii)$$

But $$PV = RT \qquad \text{(for one mole of gas)}$$

Putting $RT$ in place of $PV$ in equation (*ii*) we get

$$P\Delta V = RT\,\Delta n$$

Substituting the value of $P\Delta V$ in equation (*i*) we get

$$\Delta H = \Delta E + \Delta n\,RT$$

It may be pointed out that while determining the value of $\Delta H$, only the number of moles of gaseous reactants and products are taken into consideration. The value of gas constant $R$ is taken either in calories or joules per degree per mol and is 1.987 cal (approximately 2 calories) or 8.314 joules.

**SOLVED PROBLEM 1.** The heat of combustion of ethylene at 17ºC and at constant volume is – 332.19 kcals. Calculate the heat of combustion at constant pressure considering water to be in liquid state. ($R$ = 2 cal degree$^{-1}$ mol$^{-1}$)

**SOLUTION**

The chemical equation for the combustion of ethylene is

$$\underset{\text{1 mole}}{C_2H_4(g)} + \underset{\text{3 moles}}{3O_2(g)} \longrightarrow \underset{\text{2 moles}}{2CO_2(g)} + \underset{\text{negligible volume.}}{2H_2O(l)}$$

No. of moles of the products = 2

No. of moles of the reactants = 4

∴ $\Delta n = (2 - 4) = -2$

We know that $\Delta H = \Delta E + \Delta n\,RT$

Given that $\Delta E = -332.19$ kcal

$T = 273 + 17 = 290$ K

$R = 2$ cals $= 2 \times 10^{-3}$ kcals

∴ $\Delta H = -332.19 + 2 \times 10^{-3} \times -2 \times 290$

**= – 333.3 kcal**

**SOLVED PROBLEM 2.** The heat of combustion of carbon monoxide at constant volume and at 17°C is – 283.3 kJ. Calculate its heat of combustion at constant pressure ($R = 8.314$ J degree$^{-1}$ mol$^{-1}$).

**SOLUTION**

$$\underset{1\text{ mole}}{CO(g)} + \underset{\frac{1}{2}\text{ mole}}{\tfrac{1}{2}\,O_2(g)} \longrightarrow \underset{1\text{ mole}}{CO_2(g)}$$

$$\text{No. of moles of products} = 1$$

$$\text{No. of moles of reactants} = 1\tfrac{1}{2}$$

$$\Delta n = \text{No. of moles of products} - \text{No. of moles of reactants}$$

$$= 1 - 1\frac{1}{2} = -\frac{1}{2}$$

Given that $\Delta E = -283.3$ kJ

$T = (273 + 17) = 290$ K

and $R = 8.314$ J or $8.314 \times 10^{-3}$ kJ

Substituting these values in the equation

$$\Delta H = \Delta E + \Delta n \times RT$$

we get
$$\Delta H = -283.3 + \left[-\frac{1}{2} \times (8.314 \times 10^{-3}) \times 290\right]$$

$$= -283.3 - 1.20$$

$$= -284.5 \text{ kJ}$$

∴ Heat of combustion of CO at constant pressure is – **284.5 kJ.**

**SOLVED PROBLEM 3.** The heat of formation of methane at 298 K at constant pressure is – 17.890 kcal. Calculate its heat of formation at constant volume. ($R = 1.987$ cal degree$^{-1}$ mol$^{-1}$)

**SOLUTION**

The thermochemical equation for the heat of formation of methane at 298 K at constant pressure is :

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = -17.890 \text{ kcal}$$

No. of moles of gaseous products = 1

No. of moles of the gaseous reactants = 2

Change in No. of moles, $\Delta n = 1 - 2 = -1$

Given that $\Delta H = -17.890$ kcal; $T = 25 + 273 = 298$ K

and $R = 1.987$ cal $= 1.987 \times 10^{-3}$ kcal

Substituting these values in the equation

$$\Delta H = \Delta E + \Delta n \times RT$$

$$\Delta E = -17.89 + [-1 \times (1.987 \times 10^{-3}) \times 298]$$

$$= -18.482 \text{ kcal}$$

∴ The heat of formation of methane at constant volume is – **18.482 kcal.**

## HOT PACKS / COLD PACKS

Heat therapy has become a standard treatment for ailing muscles among athletes, the disabled and elderly people. Heat packs provide relief by dilating the blood vessels of nearby muscles and allowing the soft tissue to stretch, and cold packs reduce the swelling and inflammation of injured body parts.Chemical advances have led to the development of very convenient types of heat packs and cold packs, which can now be found in most emergency first aid kits.

### Hot Packs

There are a number of types of chemical heat packs used. Some packs consist of two plastic bags, the inner bag contains water, and the area between the inner bag and the outer bag is filled with a dry salt. When the inside bag is broken, the solid and the water react in an exothermic reaction, releasing heat. However, the most frequently used heat packs today involve one sealed plastic pouch containing a metal disk and a salt solution; commonly calcium chloride, magnesium sulfate, or sodium acetate.

### Cold Packs

A cold pack comes in a plastic bag made of tough white plastic. This bag is filled with a smaller bag and ammonium nitrate crystals. The smaller bag contains water, and is made of a thin weak plastic, so it is easy to break. When a cold pack is used, it must be "broken" by rupturing the inner bag. Breaking the bag releases the water, which dissolves the ammonium nitrate. The water and ammonium nitrate react completely, and within fifteen to twenty the cold pack will no longer feel cold.

Cold packs make use of the heat transfer that occurs during chemical reactions, but in contrast to heat packs, utilize endothermic reactions. In the endothermic reaction between ammonium nitrate crystals and water, the heat required for the reaction to proceed from reactants to products is absorbed from the surrounding environment, resulting in a decrease in temperature of the pack noticeable to the touch.

## THERMOCHEMICAL EQUATIONS

There are a number of factors which affect the quantity of heat evolved or absorbed during a physical or chemical transformation. One of these factors has already been discussed *viz.*, whether the change occurs at constant pressure or constant volume. The other factors are :

(1) Amount of the reactants and products
(2) Physical state of the reactants and products
(3) Temperature
(4) Pressure

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

It must essentially : (*a*) be balanced; (*b*) give the value of $\Delta E$ or $\Delta H$ corresponding to the quantities of substances given by the equation; (*c*) mention the physical states of the reactants and products. The physical states are represented by the symbols (*s*), (1), (*g*) and (aq) for solid, liquid, gas and gaseous states respectively.

### Example of Thermochemical Equation

The equation :

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -68.32 \text{ kcal}$$

indicates that when 1 mole of hydrogen reacts with 0.5 mole of oxygen, one mole of water is formed and 68.32 kcal of heat is evolved at constant pressure. If two moles of hydrogen are burnt, the heat evolved would be (2 × 68.32) kcals. This equation, however, is not a complete thermochemical equation because it does not specify whether water is in the form of steam or liquid. There is difference in the value of $\Delta H$ if water is in the liquid or gaseous state as shown below :

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -68.32 \text{ kcal}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -57.80 \text{ kcal}$$

## HEAT OF REACTION OR ENTHALPY OF REACTION

The heat of a reaction is simply the amount of heat absorbed or evolved in the reaction. We also know that the amount of heat absorbed or evolved at constant temperature and pressure is called enthalpy. Therefore **the amount of heat change during a reaction at constant temperature and pressure may also be called enthalpy change.** Its value depends upon the number of moles of the reactants which have reacted in the given chemical reaction. Thus,

**Heat of reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products.** For example, the heat change for the reaction of one mole of carbon monoxide with 0.5 mole of oxygen to form one mole of carbon dioxide is – 284.5 kJ. This means that 284.5 kJ of heat is evolved during the reaction and is the heat of reaction. It can be represented as

$$CO(g) + \tfrac{1}{2}O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -284.5 \text{ kJ}$$

It is very important to note that heat of reaction varies with the change in temperature. Therefore, we must mention the temperature at which the reaction is taking place. It is also convenient for comparison to fix up some temperature as standard or reference. According to the conventions prevalent in thermodynamics, the temperature of 298 K under a pressure of one atmosphere has been fixed as the *standard state*. **The heat change accompanying a reaction taking place at 298 K and one atmospheric pressure is called the standard heat change or standard enthalpy change.** It is denoted by $\Delta H^\circ$.

## VARIATION OF HEAT (OR ENTHALPY) OF REACTION WITH TEMPERATURE

The heat of reaction changes with change in temperature of a gas due to variation in its specific heat. The equations representing the variation of heat change of reaction with temperature are known as **Kirchoff's equations.**

At constant volume, the heat of reaction, $\Delta E$, is given by the relation

$$\Delta E = E_2 - E_1$$

where $E_1$ and $E_2$ are the internal energies of the reactants and products.

Differentiating this equation with respect to temperature at constant volume, we get

$$\left[\frac{d(\Delta E)}{dT}\right]_v = \left(\frac{dE_2}{dT}\right)_v - \left(\frac{dE_1}{dT}\right)_v \qquad ...(1)$$

But we have already seen that

$$\left(\frac{dE}{dT}\right)_v = C_v$$

$$\therefore \qquad \frac{d(\Delta E)}{dT} = (C_v)_2 - (C_v)_1 = \Delta C_v \qquad ...(2)$$

where $(C_v)_2$ and $(C_v)_1$ are heat capacities of the products and reactants respectively. Or, **change in heat of reaction at constant volume per degree change in temperature is equal to the difference in heat capacities at constant volume of products and reactants.**

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

$$\Delta E_2 - \Delta E_1 = \int_{T_1}^{T_2} \Delta C_v \, dT$$

or $$\Delta E_2 - \Delta E_1 = \Delta C_v [T_2 - T_1] \qquad ...(3)$$

where $\Delta E_2$ and $\Delta E_1$ are heats of reaction at temperatures $T_2$ and $T_1$ respectively.

Similarly, at **constant pressure** the heat of reaction $\Delta H$ is given by the reaction

$$\Delta H = H_2 - H_1$$

where $H_2$ is the heat content (enthalpy) of the products and $H_1$ being that of the reactants.

Differentiating with respect to temperature at constant pressure, we have

$$\left(\frac{d(\Delta H)}{dT}\right)_P = \left(\frac{dH_2}{dT}\right)_P - \left(\frac{dH_1}{dT}\right)_P \qquad ...(4)$$

According to the equation, Chapter 7, we have

$$\left(\frac{dH}{dT}\right)_P = C_P$$

$$\therefore \qquad \left(\frac{d(\Delta H)}{dT}\right)_P = (C_P)_2 - (C_P)_1 = \Delta C_P \qquad ...(5)$$

where $(C_P)_2$ and $(C_P)_1$ are the heat capacities of products and reactants respectively.

or $$d(\Delta H) = \Delta C_P \times dT$$

**Change in heat of reaction at constant pressure per degree change of temperature is equal to difference in heat capacities of products and reactants at constant pressure.**

Integrating the equation between temperature $T_1$ and $T_2$, we have

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

or $$\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1] \qquad ...(6)$$

The relations (2), (3), (5) and (6) were first derived by Kirchoff and are called **Kirchoff's equations.** These equations may be used for calculating heat of reaction at a given temperature when it is known at some other temperature and when the heat capacities of products and reactants are known.

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

**SOLUTION**

Here,

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl \qquad \Delta H = -22.1 \text{ kcal}$$

$\Delta C_p$ = Heat capacities of products – Heat capacities of reactants

$$= 6.80 - \left[\frac{1}{2}(6.82) + \frac{1}{2}(7.70)\right]$$

$$= 6.80 - 7.26 = -0.46 \text{ cal} = -0.46 \times 10^{-3} \text{ kcal}$$

$$T_2 = 273 + 77 = 350 \text{ K}; T_1 = 273 + 27 = 300 \text{ K}$$

$$T_2 - T_1 = (350 - 300) \text{ K} = 50 \text{ K}$$

Substituting these values in Kirchoff's equation, we have

$$\begin{aligned} \Delta H_2 - \Delta H_1 &= \Delta C_p (T_2 - T_1) \\ &= -22.1 + (-0.46 \times 10^{-3}) \times 50 \\ &= -22.1 + (-0.023) \\ &= -22.123 \text{ kcal} \end{aligned}$$

∴ Heat of reaction at 77ºC is – **22.123 kcal**

**SOLVED PROBLEM 2.** The heat of reaction $N_2 + 3H_2 \rightarrow 2NH_3$ at 27ºC was found to be –21.976 kcal. What will be the heat of reaction at 50ºC ?

The molar heat capacities at constant pressure and at 27ºC for nitrogen, hydrogen and ammonia are 6.8, 6.77 and 8.86 cal mol$^{-1}$ degree$^{-1}$.

**SOLUTION**

Here,

$$\begin{aligned} \Delta H &= -21.976 \text{ kcal} \\ T_2 &= 273 + 50 = 323 \text{ K} \\ T_1 &= 273 + 27 = 300 \text{ K} \\ [T_2 - T_1] &= (323 - 300) \text{ K} = 23 \text{ K} \end{aligned}$$

$\Delta C_p$ = Heat capacities of products – Heat capacities of reactants

$$\begin{aligned} &= (2 \times 8.86) - [6.8 + (3 \times 6.77)] \\ &= 17.72 - (6.8 + 20.31) = -9.39 \text{ cal} \\ &= -9.39 \times 10^{-3} \text{ kcal} \end{aligned}$$

Substituting these values in Kirchoff's equation, we have

$$\begin{aligned} \Delta H_2 &= \Delta H_1 + (T_2 - T_1)\, \Delta C_p \\ &= -21.976 + [23 \times (-9.39 \times 10^{-3})] \\ &= -21.976 + (-0.216) = -22.192 \text{ kcal} \end{aligned}$$

∴ Heat of reaction at 50ºC is = **22.192 kcal**

## DIFFERENT TYPES OF HEAT (ENTHALPY) OF REACTION

The heat or enthalpy changes accompanying chemical reactions are expressed in different ways, depending on the nature of the reaction. These are discussed below.

## HEAT OF FORMATION

The heat of formation of a compound is defined as :

**The change in enthalpy that takes place when one mole of the compound is formed from its elements.**

It is denoted by $\Delta H_f$. For example, the heat of formation of ferrous sulphide and acetylene may be expressed as :

$$\text{Fe}(s) + \text{S}(s) \longrightarrow \text{FeS}(s) \qquad \Delta H_f = -24.0 \text{ kcal}$$

$$2\text{C}(s) + \text{H}_2(g) \longrightarrow \text{C}_2\text{H}_2(g) \qquad \Delta H_f = +53.14 \text{ kcal}$$

Similarly, the reaction between gaseous hydrogen and gaseous chlorine to form gaseous hydrogen chloride is represented by the equation

$$\text{H}_2(g) + \text{Cl}_2(g) \longrightarrow 2\text{HCl}(g) \qquad \Delta H = -44.0 \text{ kcal}$$

It may be noted in this case that – 44.0 kcal is not the heat of formation of hydrogen chloride because this amount of heat is evolved when two moles of hydrogen chloride are formed. The heat of formation of hydrogen chloride, therefore, would be – 44.0/2 = – 22.0 kcal and the equation can be written as

$$\tfrac{1}{2}\text{H}_2(g) + \tfrac{1}{2}\text{Cl}_2(g) \longrightarrow \text{HCl}(g) \qquad \Delta H_f = -22.0 \text{ kcal}$$

## STANDARD HEAT OF FORMATION

The standard heat of formation of a compound is defined as :

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

The standard heat of formation of some compounds are given in Table 8.2.

**TABLE 8.2.** STANDARD HEAT OF FORMATION OF SOME COMPOUNDS

| Substance | $\Delta H_f^o$ kcal mol$^{-1}$ | Substance | $\Delta H_f^o$ kcal mol$^{-1}$ |
|---|---|---|---|
| $H_2O(g)$ | – 57.84 | $CH_4(g)$ | – 17.89 |
| $H_2O(l)$ | – 68.38 | $C_2H_6(g)$ | – 20.23 |
| $HCl(g)$ | – 22.08 | $C_6H_6(g)$ | + 11.86 |
| $HBr(g)$ | – 8.70 | $C_2H_2(g)$ | + 53.14 |
| $NH_3(g)$ | – 11.02 | $CH_3OH(l)$ | – 57.17 |
| $CO_2(g)$ | – 94.13 | $C_2H_5OH(l)$ | – 66.26 |
| $SO_2(g)$ | – 71.00 | $CH_3COOH(l)$ | – 115.83 |

By convention the standard heat of formation of all elements is assumed to be zero.

### Standard Heat of Reaction ($\Delta H^o$) from Standard Heat of Formation ($\Delta H_f^o$)

We can calculate the heat of reaction under standard conditions from the values of standard heat of formation of various reactants and products. **The standard heat of reaction is equal to the standard heat of formation of products minus the standard heat of formation of reactants.**

That is,

$$\Delta H^\circ = \begin{bmatrix} \text{Total standard heat} \\ \text{of formation of products} \end{bmatrix} - \begin{bmatrix} \text{Total standard heat} \\ \text{of formation of reactants} \end{bmatrix}$$

$$\Delta H^\text{o} = \Delta H_f^o\,(\text{products}) - \Delta H_f^o\,(\text{reactants})$$

Let us consider a general reaction

$$\text{aA} + \text{bB} \longrightarrow \text{cC} + \text{dD}$$

The standard heat of reaction is given by

$$\begin{aligned} \Delta H^\text{o} &= \Delta H_f^o\,(\text{products}) - \Delta H_f^o\,(\text{reactants}) \\ &= [\text{c} \times \Delta H_f^o\,(\text{C}) + \text{d} \times H_f^o\,(\text{D})] - [\text{a} \times \Delta H_f^o\,(\text{A}) + \text{b} \times \Delta H_f^o\,(\text{B})] \end{aligned}$$

**SOLVED PROBLEM 1.** Calculate $\Delta H^\text{o}$ for the reaction

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

given that $\Delta H_f^o$ for $CO_2(g)$, $CO(g)$ and $H_2O(g)$ are – 393.5, – 111.31 and – 241.80 kJ $\text{mol}^{-1}$ respectively.

**SOLUTION**

Here we have

$$CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$$

$$\begin{aligned} \Delta H^\text{o} &= \Delta H_f^o\,(\text{products}) - \Delta H_f^o\,(\text{reactants}) \\ &= [\Delta H_f^o\,[CO\,(g)] + \Delta H_f^o\,[H_2O(g)]] - [\Delta H_f^o\,[CO_2\,(g)] + \Delta H_f^o\,[H_2(g)]] \\ &= [-111.3 + (-241.8)] - [-393.5 + 0] \\ &= -353.1 + 393.5 \\ &= \mathbf{40.4\ kJ} \end{aligned}$$

**SOLVED PROBLEM 2.** The standard heats of formation of $C_2H_5OH(l)$, $CO_2(g)$ and $H_2O(l)$ are – 277.0, –393.5 and –285.5 kJ $\text{mol}^{-1}$ respectively. Calculate the standard heat change for the reaction

$$C_2H_5OH(l) + 3O_2(l) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

**SOLUTION**

We know that :

$$\Delta H^\text{o} = \Delta H_f^o\,(\text{products}) - \Delta H_f^o\,(\text{reactants})$$

In the present case

$$\begin{aligned} \Delta H^\text{o} &= [2 \times \Delta H_f^o\,[CO_2(g)] + 3 \times \Delta H_f^o\,[H_2O(l)] \\ &\quad - \Delta H_f^o\,[C_2H_5OH(l)] + 3 \times \Delta H_f^o\,[O_2(g)] \\ &= [2 \times (-393.5) + 3 \times -285.5] - [-277.0 - 0] \\ &= -1643.5 - (-277) \\ &= \mathbf{-\ 1366.5\ kJ} \end{aligned}$$

## HEAT OF COMBUSTION

The heat of combustion of a substance is defined as : **the change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen.**

It is denoted by $\Delta H_c$. As for example, heat of combustion of methane is – 21.0 kcal (= 87.78 kJ) as shown by the equation

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -21.0 \text{ kcal}$$

Now consider the chemical equations

$$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -94.3 \text{ kcal}$$

$$C(s) + \tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = -26.0 \text{ kcal}$$

It may be noted that – 94.3 kcal and not – 26.0 kcal is the heat of combustion of carbon as the combustion is complete only in the first reaction. In the second case, oxidation has converted carbon to carbon monoxide and is by no means complete as carbon monoxide can be further oxidised to carbon dioxide.

It should be noted clearly that the **heat of combustion of a substance ($\Delta H_c$) is always negative.** Heat energy is evolved during the process of combustion *i.e.*, $\Delta H_c$ = – ve.

## APPLICATIONS OF THE HEAT OF COMBUSTION

(1) **Calculation of heat of formation.** Since the heats of combustion of organic compounds can be determined with considerable ease, these are employed to calculate their heats of formation. The direct determination of these is often impossible.

(2) **Calorific value of foods and fuels.** The calorific value is defined as : **the amount of heat produced in calories (or joules) when one gram of a substance is completely burnt.**

It is expressed in cal $g^{-1}$ or kcal $g^{-1}$ or kJ $g^{-1}$. Let us compare the calorific values of methane and ethane. Their heats of combustion are – 890.3 kJ and – 1559.7 kJ. These combustion reactions are expressed as

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H_c = -890.3 \text{ kJ}$$

$$C_2H_6(g) + 3\tfrac{1}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H_c = -1559.7 \text{ kJ}$$

In case of methane heat produced per gram is 890.3/16 = 55.64 kJ $g^{-1}$ while for ethane it is –1559.7/30 = 51.90 kJ $g^{-1}$. Thus methane has better fuel efficiency than ethane as it produces more heat per gram.

(3) **Deciding constitution.** Heat of combustion of organic compounds is to a large extent an additive property, as shown by the fact that in a homologous series the difference between the heats of combustion of successive members is nearly constant and is equal to 158 cals. Constants corresponding to the heats of combustion of various atoms and linkages have been worked out. The heat of combustion of an organic substance can be calculated from its probable structural formula by adding up the values of the constants corresponding to the atoms and linkages involved therein. If the value so obtained comes out to be the same as the experimental value of the heat of combustion of the compound, the assumed formula must be correct. In this way Kekule's formula for benzene with alternate double and single linkages has been supported as the calculated value of the heat of combustion of benzene according to this formula agrees with the actual heat of combustion. Heat of combustion of organic compounds has thus proved very valuable in deciding their chemical constitution.

**SOLVED PROBLEM.** Calculate the standard heat of formation of propane ($C_3H_8$) if its heat of combustion is – 2220.2 kJ mol$^{-1}$. The heats of formation of $CO_2(g)$ and $H_2O(l)$ are – 393.5 and – 285.8 kJ mol$^{-1}$ respectively.

**SOLUTION**

We are given

$$(i)\quad C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H_c = -2220.2\ \text{kJ}$$

$$(ii)\quad C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5\ \text{kJ}$$

$$(iii)\quad H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8\ \text{kJ}$$

We should manipulate these equations in a way so as to get the required equation

$$3C(s) + 4H_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H = ?$$

Multiplying equation (*ii*) by 3 and equation (*iii*) by 4 and adding up we get

$$3C(s) + 3O_2(g) \longrightarrow 3CO_2(g) \qquad \Delta H = -1180.5\ \text{kJ}$$

$$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l) \qquad \Delta H = -1143.2\ \text{kJ}$$

$$(iv)\quad 3C(s) + 4H_2(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l) \qquad \Delta H = -2323.7\ \text{kJ}$$

Subtracting equation (*i*) from equation (*iv*), we have

$$3C(s) + 4H_2(g) + 5O_2(g) - 5O_2(g) \longrightarrow C_3H_8(g) \qquad \Delta H = -103.5\ \text{kJ}$$

∴ The heat of formation of propane is **– 103.5 kJ mol$^{-1}$.**

## HEAT OF SOLUTION

Heat changes are usually observed when a substance is dissolved in a solvent. When a reaction takes place in solution, the heat of solution of reactants and products must be taken into consideration. The heat of solution is defined as : **the change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature.**

For example, when one mole of copper sulphate is dissolved in water so that we get one molar solution, the heat absorbed is 78.5 kJ. If the solution so obtained is further diluted, there will again be a change in enthalpy. If we go on diluting the solution, a stage will come when further dilution produces no thermal effect. This state is called the state of infinite dilution. To avoid the quantity of the solvent, we have to incorporate the idea of infinite dilution in our definition which may be stated as : **the heat of solution is the change in enthalpy when one mole of a substance is dissolved in a solvent so that further dilution does not give any change in enthalpy.**

The heat of solution can also be expressed as :

$$KCl(s) + H_2O(l) \longrightarrow KCl(aq) \qquad \Delta H = -4.4\ \text{kcal}$$

$$MgSO_4(s) + H_2O(l) \longrightarrow MgSO_4(aq) \qquad \Delta H = -20.28\ \text{kcal}$$

The heat of solution of an electrolyte may be due to energy change involved during ionisation or some hydrate formation as in case of sulphuric acid. Usually heat is absorbed when ions are torn apart from each other in the process of solution and heat is evolved during hydrate formation. With a salt as sodium chloride the heat of separation of ions just equals the heat of hydration and there is very little heat effect.

## HEAT OF NEUTRALISATION

The heat of neutralisation is defined as : **the change in heat content (enthalpy) of the system when one gram equivalent of an acid is neutralised by one gram equivalent of a base or *vice versa* in dilute solution.**

The following may be considered as typical examples of the heat of neutralisation.

$$HNO_3(aq) + NaOH(aq) \longrightarrow NaNO_3(aq) + H_2O(l) \qquad \Delta H = -13.69 \text{ kcal}$$

$$HNO_3(aq) + KOH(aq) \longrightarrow KNO_3(aq) + H_2O(l) \qquad \Delta H = -13.87 \text{ kcal}$$

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l) \qquad \Delta H = -13.68 \text{ kcal}$$

$$HCl(aq) + LiOH(aq) \longrightarrow LiCl(aq) + H_2O(l) \qquad \Delta H = -13.70 \text{ kcal}$$

It may be concluded from the above data that **the heat of neutralisation of a strong acid and strong base is –13.7 kcal, no matter which acid or base is employed.** This regularity has been explained satisfactorily with the help of the theory of ionisation. If HA and BOH represent any strong acid and any strong base respectively and equivalent amounts of these in dilute solution be mixed, we have

$$H^+(aq) + \overset{-}{A}(aq) + \overset{+}{B}(aq) + OH^-(aq) \longrightarrow \overset{-}{A}(aq) + \overset{+}{B}(aq) + H_2O(l) \qquad \Delta H = -13.7 \text{ kcal}$$

Disregarding the ions which are present on both sides of the equation, we get

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H = -13.7 \text{ kcal}$$

**Thus the heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxyl ions.**

When weak acids or weak bases are neutralised by strong bases or strong acids respectively, the heat of neutralisation differs widely from – 13.7 kcal. This is shown by the following examples :

$$HCl(aq) + NH_4OH(aq) \longrightarrow NH_4Cl(aq) + H_2O(l) \qquad \Delta H = -12.3 \text{ kcal}$$

$$HCN(aq) + NaOH(aq) \longrightarrow NaCN(aq) + H_2O(l) \qquad \Delta H = -12.3 \text{ kcal}$$

$$HNO_3(aq) + NH_4OH(aq) \longrightarrow NH_4NO_3(aq) + H_2O(l) \qquad \Delta H = -12.3 \text{ kcal}$$

$$HCOOH(aq) + NH_4OH(aq) \longrightarrow HCOONH_4(aq) + H_2O(l) \qquad \Delta H = -11.9 \text{ kcal}$$

In such cases the neutralisation process involves not only the union of hydrogen and hydroxyl ions but also the dissociation of the weak acid or base. The measured heat of neutralisation is, therefore, equal to the heat given out in the union of $H^+$ (*aq*) and $OH^-$ (*aq*) ions plus the heat accompanying the dissociation of weak acid or weak base. The neutralisation of $NH_4OH$ with HCl, for example, can be represented as :

$$NH_4OH(aq) \longrightarrow NH_4^+(aq) + OH^-(aq) \qquad \Delta H = Q \text{ kcal}$$

$$\text{and} \quad H^+(aq) + OH^-(aq) + Cl^-(aq) \longrightarrow H_2O(l) + Cl^-(aq) \qquad \Delta H = -13.7 \text{ kcal}$$

$$NH_4OH(aq) + H^+(aq) + Cl^-(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq) + H_2O(l) \quad \Delta H = Q - 13.7 \text{ kcal}$$

But the measured heat of neutralisation is – 12.3 kcals. Therefore,

$$Q - 13.7 = -12.3$$

$$Q = 13.7 - 12.3 = 1.4 \text{ kcal}$$

Hence the heat of dissociation of $NH_4OH$ is 1.4 kcal *i.e.*, 1.4 kcal of heat is absorbed when one mole of ammonium hydroxide is dissociated into ions. In general, **the heat of dissociation of a weak acid or weak base may be defined as the change in enthalpy of the system when one mole of it is dissociated into ions.**

## ENERGY CHANGES DURING TRANSITIONS OR PHASE CHANGES

The three states of matter – solid, liquid and gas differ from one another in the arrangement of their constituent particles. The magnitudes of intermolecular forces acting between the particles in these states are also different. It is a common observation that when a solid is converted into the liquid state, energy is to be supplied. This energy is spent in breaking the intermolecular forces in the solid which are of high magnitude. Whenever there is a change in the state of matter (solid → liquid or liquid → gas), the process is called phase change or transition. It is also accompanied by the change in enthalpy or heat content of the system.

## HEAT OF FUSION

It is defined as : **the heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its melting point.**

As an example, we can take the melting of one mole of ice at its melting point, 0ºC or 273 K. The process can be represented as

$$\underset{\text{ice}}{H_2O(s)} \longrightarrow \underset{\text{water}}{H_2O(l)} \qquad \Delta H = +1.43 \text{ kcal}$$

and is accompanied by the absorption of 1.43 kcal of heat. From the values of fusion of various substances we can compare their magnitudes of intermolecular forces. **Greater the heat of fusion of a substance higher the magnitude of intermolecular forces.**

## HEAT OF VAPOURISATION

The heat of vapourisation is defined as : **the heat change (or enthalpy change) when one mole of liquid is converted into vapour or gaseous state at its boiling point.**

For example, when one mole of water is converted into steam at 100ºC or 373 K, the heat absorbed is 9.71 kcal which is the heat of vaporisation of water. The change can be represented as :

$$\underset{\text{water}}{H_2O(l)} \longrightarrow \underset{\text{steam}}{H_2O(g)} \qquad \Delta H = +9.71 \text{ kcal}$$

The heats of vaporisation of ethyl alcohol ($C_2H_5OH$) and benzene ($C_6H_6$) are 7.29 kcal $mol^{-1}$ and 7.36 kcal $mol^{-1}$ respectively. The values of heats of vaporisation can also be used for the comparison of the magnitude of intermolecular forces of attraction in liquids.

## HEAT OF SUBLIMATION

Sublimation is a process when a solid changes directly into gaseous state without changing into liquid state. It occurs at a temperature below the melting point of the solid. Heat of sublimation is defined as : **the heat change (or enthalpy change) when one mole of a solid is directly converted into the gaseous state at a temperature below its melting point.**

For example, the heat of sublimation of iodine is 14.92 kcal $mol^{-1}$. It can be represented as

$$I_2(s) \longrightarrow I_2(g) \qquad \Delta H = +14.92 \text{ kcal}$$

## HEAT OF TRANSITION

The heat of transition is defined as : **the change in enthalpy which occurs when one mole of an element changes from one allotropic form to another.**

For example, the transition of diamond into amorphous carbon may be represented as

$$C_{\text{diamond}} \longrightarrow C_{\text{amorphous}} \qquad \Delta H = +3.3 \text{ kcal}$$

Similarly,

$$S_{\text{monoclinic}} \longrightarrow S_{\text{rhombic}} \qquad \Delta H = -0.016 \text{ kcal}$$

and

$$P_{\text{white}} \longrightarrow P_{\text{red}} \qquad \Delta H = -1.028 \text{ kcal}$$

where – 0.016 kcal and – 1.028 kcal are heats of transition of monoclinic sulphur to rhombic sulphur and white phosphorus to red phosphorus respectively.

## HESS'S LAW OF CONSTANT HEAT SUMMATION

We have already seen that heat changes in chemical reactions are equal to the difference in internal energy ($\Delta E$) or heat content ($\Delta H$) of the products and reactants, depending upon whether the reaction is studied at constant volume or constant pressure. Since $\Delta E$ and $\Delta H$ are functions of the state of the system, the heat evolved or absorbed in a given reaction must be independent of the manner in which the reaction is brought about. Thus it depends only on the initial state and final states of the system and not the manner or the steps in which the change takes place. This generalisation is known as **Hess's Law** and may be stated as : **If a chemical change can be made to take place in two or more different ways whether in one step or two or more steps, the amount of total heat change is same no matter by which method the change is brought about.**

The law also follows as a mere consequence of the first law of thermodynamics. Let us suppose that a substance A can be changed to Z directly.

$$\text{A} \longrightarrow \text{Z} + Q_1 \qquad \Delta H_1 = -Q_1$$

where $Q_1$ is the heat evolved in the direct change. When the same change is brought about in stages :

$$\text{A} \longrightarrow \text{B} + q_1 \qquad \Delta H_2 = -q_1$$
$$\text{B} \longrightarrow \text{C} + q_2 \qquad \Delta H_2 = -q_2$$
$$\text{C} \longrightarrow \text{Z} + q_3 \qquad \Delta H_2 = -q_3$$

the total evolution of heat = $q_1 + q_2 + q_3 = Q_2$

According to Hess's law $Q_1 = Q_2$. If it be not so, let $Q_2 > Q_1$. Then by transforming A to Z through stages and retransforming directly back to A, there would be gain of heat energy = $Q_2 - Q_1$. By repeating the process again and again an unlimited heat energy will be developed in an isolated system. This goes against the first law of thermodynamics. Hence $Q_1$ must be equal to $Q_2$.

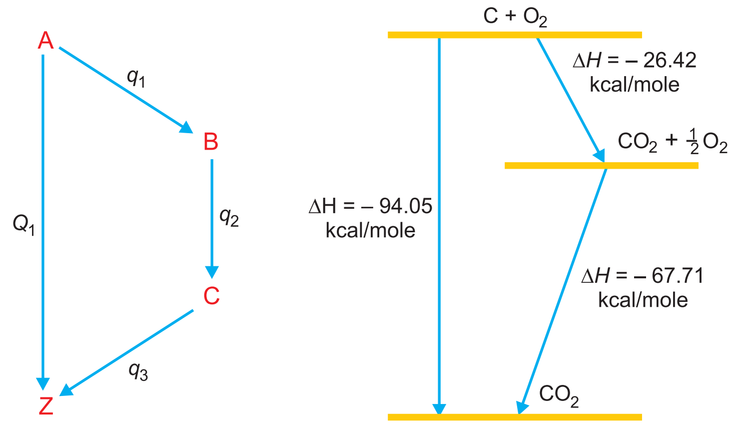


**Figure 8.2**
**Illustration of Hess's Law.**

Hess's law has been tested experimentally and shown to be true.

## Illustrations of Hess's Law

(1) **Burning of carbon to $CO_2$.** Carbon can be burnt to carbon dioxide directly or it may first be changed to carbon monoxide which may then be oxidised to carbon dioxide.

**1st way :**

$$\text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta H = -94.05 \text{ kcal}$$

**2nd way :**

$$\text{C}(s) + \tfrac{1}{2}\text{O}(g) \longrightarrow \text{CO}_2(g) \qquad \Delta H = -26.42 \text{ kcal}$$
$$\text{CO}(g) + \tfrac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g) \qquad \Delta H = -67.71 \text{ kcal}$$

---

$$\textit{overall change} \quad \text{C}(s) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) \qquad \Delta H = -94.13 \text{ kcal}$$

It is evident from above that the total heat energy evolved is the same in the two cases (Fig. 8.2)

(2) **Formation of Sodium hydroxide from Na.** The formation of sodium hydroxide from metallic sodium presents another example of Hess's law. The process can be carried out in two ways.

**1st way :**

$$\begin{array}{rcll}
2\mathrm{Na}(s)+\tfrac{1}{2}\mathrm{O_2}(g) & \longrightarrow & \mathrm{Na_2O}(s) & \Delta H = -100 \text{ kcal}\\
\mathrm{Na_2O}(s)+\mathrm{H_2O}(l) & \longrightarrow & 2\mathrm{NaOH}(aq) & \Delta H = -56 \text{ kcal}\\
\hline
2\mathrm{Na}(s)+\mathrm{H_2O}(l)+\tfrac{1}{2}\mathrm{O_2}(g) & \longrightarrow & 2\mathrm{NaOH}(aq) & \Delta H = -156 \text{ kcal}
\end{array}$$

**2nd way :**

$$\begin{array}{rcll}
2\mathrm{Na}(s)+2\mathrm{H_2O}(l) & \longrightarrow & 2\mathrm{NaOH}(aq)+\mathrm{H_2}(g) & \Delta H = -88 \text{ kcal}\\
\mathrm{H_2}(g)+\tfrac{1}{2}\mathrm{O_2}(g) & \longrightarrow & \mathrm{H_2O}(g) & \Delta H = -68.5 \text{ kcal}\\
\hline
2\mathrm{Na}(s)+\mathrm{H_2O}(l)+\tfrac{1}{2}\mathrm{O_2}(g) & \longrightarrow & 2\mathrm{NaOH}(aq) & \Delta H = -156.5 \text{ kcal}
\end{array}$$

It may be observed that the total heat evolved in carrying the reaction in two different ways is the same. The difference of 0.5 kcal is within the experimental error.

It is obvious from the above examples that by the addition of a series of chemical equations we can obtain not only the resultant products of this series of reactions but also the net heat effect. It is, therefore, clear that : **thermochemical equations may be multiplied, added or subtracted like ordinary algebraic equations.** For this reason, Hess's law has been of great service in the indirect determination of heats of formation.

## APPLICATIONS OF HESS'S LAW

(1) **Determination of heat of formation of substances which otherwise cannot be measured experimentally.** The substances like methane, carbon monoxide, benzene, etc., cannot be prepared by uniting their elements. Therefore it is not possible to measure the heats of formation of such compounds directly. These can be determined indirectly by using Hess's law. This will be illustrated by the following examples.

**SOLVED PROBLEM 1.** Calculate the heat of formation of potassium hydroxide from the following data.

$$\begin{array}{lrcll}
(i) & \mathrm{K}(s)+\mathrm{H_2O}\,(aq) & \longrightarrow & \mathrm{KOH}+\tfrac{1}{2}\mathrm{H_2} & \Delta H = -48.0 \text{ kcal}\\
(ii) & \mathrm{H_2}(g)+\tfrac{1}{2}\mathrm{O_2}(g) & \longrightarrow & \mathrm{H_2O}(l) & \Delta H = -68.5 \text{ kcal}\\
(iii) & \mathrm{KOH}(s) & \longrightarrow & \mathrm{KOH}(aq) & \Delta H = -14.0 \text{ kcal}
\end{array}$$

**SOLUTION**

We should aim at finding the value of $\Delta H$ for the equation, which is the heat of formation.

$$\mathrm{K}(s)+\tfrac{1}{2}\mathrm{O_2}(g)+\tfrac{1}{2}\mathrm{H_2}(g) \longrightarrow \mathrm{KOH}(s) \qquad \Delta H = ?$$

Adding equations (*i*) and (*ii*) and subtracting equation (*iii*) will give

$$\mathrm{K}(s)+\mathrm{H_2O}(l)+\mathrm{H_2}(g)+\tfrac{1}{2}\mathrm{O_2}(g)-\mathrm{KOH}(s) \longrightarrow \mathrm{KOH}(aq)+\tfrac{1}{2}\mathrm{H_2}(g)+\mathrm{H_2O}(l)-\mathrm{KOH}(aq)$$

$$\begin{aligned}\Delta H &= -48.0+(-68.5)-(-14.0)\\ &= -102.5 \text{ kcal}\end{aligned}$$

or $$\mathrm{K}(s)+\tfrac{1}{2}\mathrm{H_2}(g)+\tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{KOH}(s) \qquad \Delta H = -102.5 \text{ kcal}$$

Thus heat of formation of KOH is – **102.5 kcal**

**SOLVED PROBLEM 2.** The heat of combustion of ethyl alcohol is – 330 kcal. If the heat of formation of $CO_2(g)$ and $H_2O(l)$ be – 94.3 kcal and – 68.5 kcal respectively, calculate the heat of formation of ethyl alcohol.

**SOLUTION**

We are given

(*a*) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -330.0 \text{ kcal}$

(*b*) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -94.3 \text{ kcal}$

(*c*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -68.5 \text{ kcal}$

We have to manipulate these equations so as to get the required equation :

$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H = ?$$

where $\Delta H$ is the heat of formation of ethyl alcohol.

Multiplying equation (*b*) by 2 and equation (*c*) by 3 and adding up these, we get

$$2C(s) + 3H_2(g) + \tfrac{3}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$
$$\Delta H = -394.1 \text{ kcal}$$

Subtracting equation (*c*) from the above equation, we have

$$2C(s) + 3H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l)$$
$$\Delta H = -394.1 - (-330.0)$$

Thus the heat of formation of ethyl alcohol is **– 64.1 kcal.**

**SOLVED PROBLEM 3.** Determine $\Delta H$ of the reaction

$$C(s) + 2H_2(g) \longrightarrow CH_4(g)$$

from the following data :

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393.7 \text{ kJ}$

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -285.7 \text{ kJ}$

(*iii*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \quad \Delta H = -890.3 \text{ kJ}$

**SOLUTION**

Multiplying equation (*ii*) by 2 and adding to equation (*i*), we get

(*iv*) $C(s) + O_2(g) + 2H_2(g) + O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$$\Delta H = (2 \times -285.7) + (-393.7)$$
$$= -965.1 \text{ kJ}$$

On subtracting equation (*iii*) from equation (*iv*), we get

$$C(s) + 2H_2(g) = CH_4(g) \qquad \Delta H = -965.1 - (-890.3)$$
$$\Delta H = -74.8 \text{ kJ}$$

Thus the heat of formation of methane is – **74.8 kJ.**

(2) **Determination of Heat of Transition**

The heat of transition of one allotropic form to another can also be calculated with the help of Hess's law. For example, the enthalpy of transition from monoclinic sulphur to rhombic sulphur can be calculated from their heats of combustion which are :

(*i*) $S_{\text{rhombic}} + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -291.4 \text{ kJ}$

(*ii*) $S_{\text{monoclinic}} + O_2(g) \longrightarrow SO_2(g) \quad \Delta H = -295.4 \text{ kJ}$

Subtracting equation (*ii*) from (*i*) we get

$$S_{\text{rhombic}} - S_{\text{monoclinic}} + O_2(g) - O_2(g) \longrightarrow SO_2(g) - SO_2(g)$$

or

$$\Delta H = -291.4 - (-295.4)$$

$$S_{\text{rhombic}} = S_{\text{monoclinic}} \qquad \Delta H = 4.0 \text{ kJ}$$

Thus heat of transition of rhombic sulphur to monoclinic sulphur is **4.0 kJ.**

(3) **Determination of heats of various reactions**

By using Hess's law we can calculate the heats or enthalpies of many reactions which otherwise cannot be measured directly. For example, from the following equations the enthalpy of dimerisation of $NO_2$ can be calculated.

(*i*) $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g) \qquad \Delta H = 67.9 \text{ kJ}$

(*ii*) $N_2(g) + 2O_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = 9.3 \text{ kJ}$

Subtracting equation (*i*) from equation (*ii*) we have

$$2NO_2(g) \longrightarrow N_2O_4(g) \qquad \Delta H = (9.3 - 67.9) \text{ kJ}$$
$$= -58.6 \text{ kJ}$$

Thus the heat of dimerisation of $NO_2$ is – **58.6 kJ.**

## BOND ENERGY

When a bond between two atoms is formed, there is a release of energy. The same amount of energy is absorbed when the bond is broken.

**The bond energy is defined as the average amount of energy required to break all bonds of a particular type in one mole of the substance**.

Thus the bond energy of H – H bond is the energy required to break all the bonds in one mole of the gas. It is expressed in kcal $mol^{-1}$ or kJ $mol^{-1}$. For example, the bond energy of H – H bond is 433 kJ $mol^{-1}$ or 103.58 kcal $mol^{-1}$. The bond energies of some common bonds are listed below :

| Bond | Bond Energy |
|---|---|
| Cl–Cl | 243 kJ $mol^{-1}$ |
| O=O | 499.0 kJ $mol^{-1}$ |
| C–H | 414.0 kJ $mol^{-1}$ |
| O–H | 460.0 kJ $mol^{-1}$ |

### Bond Energy is a Measure of Strength of the Bond

In other words, bond energy is the force with which the atoms are bonded together. It depends upon :

(*i*) Size of the atom

(*ii*) Electronegativity

(*iii*) Bond length

A knowledge of bond enthalpy is useful for calculating heats of reaction for gaseous reactions for which no thermal data is available and which involve substances having covalent bonds.

Suppose we desire to determine the bond energy of C–H bond in methane. For this purpose we need to know the enthalpy change for the reaction

$$C(g) + 4H(g) \longrightarrow CH_4(g)$$

This is obtained by combining the heat of formation of methane from $C(s) + H_2(g)$ with the heat of sublimation of carbon *i.e.*, $C(s) \rightarrow C(g)$ and the heat of dissociation of hydrogen into atoms *i.e.*, $H_2(g)$

$\rightarrow$ 2H($g$), which have been determined by spectroscopic methods. The value so obtained is 398 kcal mol$^{-1}$ (or 1663.64 kJ mol$^{-1}$). This represents the bond energy of four C–H bonds. Since all the bonds in methane are identical, the bond energy of C–H bond is 398/4 = 99.5 kcal mol$^{-1}$.

In a similar manner the bond energies of other types of bonds have been calculated. **When a bond is broken, the bond energy is positive because heat is absorbed.** It is written with a minus sign when a bond is formed and heat is evolved. The calculation of heat of reaction with the help of bond energies is illustrated in the following examples.

**SOLVED PROBLEM 1.** Given that energies for H–H, O=O and O–H bonds are 104, 118 and 111 kcal mol$^{-1}$ respectively, calculate the heat of the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(g)$$

**SOLUTION**

In this reaction, two O–H bonds are formed and one H–H bond is broken. Therefore we can write for $\Delta H$

$$\begin{aligned}\Delta H &= -2\,\Delta H\,(\mathrm{O-H}) + \Delta H\,(H-H) + \tfrac{1}{2}\,\Delta H\,(\mathrm{O=O})\\ &= (-2\times 111) + 104 + \left(\tfrac{1}{2}\times 118\right)\\ &= -222 + 104 + 59\\ &= -59\ \text{kcal mol}^{-1}\end{aligned}$$

$\therefore$ The heat of the given reaction is – **59.0 kcal mol$^{-1}$**

**SOLVED PROBLEM 2.** Calculate the bond energy of HCl, given that H–H bond energy is 433 kJ mol$^{-1}$, Cl – Cl bond energy is 242 kJ mol$^{-1}$ and $\Delta H_f$ for HCl is – 91 kJ mol$^{-1}$.

**SOLUTION**

Given :

($i$) $\tfrac{1}{2}H_2(g) + Cl_2(g) \longrightarrow HCl(g) \qquad \Delta H = -91$ kJ

($ii$) $H_2(g) \longrightarrow 2H(g) \qquad \Delta H = +433$ kJ

($iii$) $Cl_2(g) \longrightarrow 2Cl(g) \qquad \Delta H = +242$ kJ

Multiplying equation ($i$) by 2, we get

($iv$) $H_2(g) + 2Cl_2(g) \longrightarrow 2HCl(g) \qquad \Delta H = -182$ kJ

Adding equation ($ii$) and ($iii$), we have

($v$) $H_2(g) + Cl_2(g) \longrightarrow 2H(g) + 2Cl(g) \qquad \Delta H = +675$ kJ

Subtracting equation ($iv$) from ($v$), one has

$$2HCl(g) \longrightarrow 2H(g) + 2Cl(g) \qquad \Delta H = +857\ \text{kJ}$$

Dividing this equation by 2 we get

$$HCl(g) \longrightarrow H(g) + Cl(g) \qquad \Delta H = 428.5\ \text{kJ}$$

Thus the bond energy of H–Cl is 428.5 kJ.

## MEASUREMENT OF THE HEAT OF REACTION

The experimental measurement of the heat of reaction or enthalpy change is known as **calorimetry.** The name evidently finds its origin in the unit of heat–the calorie. The heat given out or absorbed in a chemical reaction is measured in a suitable apparatus called a **calorimeter.** These calorimeters vary considerably in their construction and designs. They are adapted to suit the requirements of a particular reaction under study. For instance, to measure the heats of reactions involving (*i*) solutions only, (*ii*) gases, (*iii*) very reactive chemicals etc., different types of calorimeters are employed. We discuss below two of the common type of calorimeters.

### Water Calorimeter

This is a convenient apparatus for finding the heat changes accompanying chemical reactions taking place in solutions.

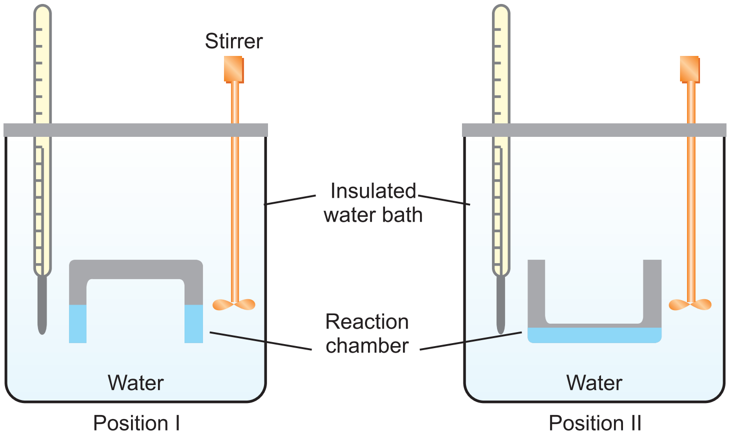


**Figure 8.3**
**Water Calorimeter.**

The apparatus consists essentially of a water-bath with thermally insulated walls. A reaction chamber consisting of two limbs is suspended in the water-bath. Through the lid of the water-bath pass (*a*) *thermometer* that records the temperature variations and (*b*) a *stirrer* that stirs water in the water-bath. A known quantity of water (say *W* gms) is taken in the water-bath and its temperature is noted. The reacting substances are filled in the two limbs as shown in Fig. 8.3. The reacting chamber is now turned upside down (position II) to allow the solutions to mix. They react and the heat produced during the reaction is taken up by water, raising its temperature. If the rise in temperature (Final reading – Initial reading) is $t$ ºC, the heat absorbed by water '$Q$' is given by

$$Q = W \times 1 \times t \text{ calories}$$

But heat produced in the reaction is equal to that absorbed by water, hence heat of the reaction can be calculated.

### Bomb Calorimeter

This apparatus was devised by Berthelot (1881) to measure the heat of combustion of organic compounds. A modified form of the apparatus shown in Fig. 8.4 consists of a sealed combustion chamber, called a *bomb*, containing a weighed quantity of the substance in a dish along with oxygen under about 20 atm pressure. The *bomb* is lowered in water contained in an insulated copper vessel. This vessel is provided with a stirrer and a thermometer reading up to 1/100th of a degree. It is also surrounded by an outer jacket to ensure complete insulation from the atmosphere. The temperature of water is noted before the substance is ignited by an electric current. After combustion, the rise in temperature of the system is noted on the thermometer and heat of combustion can be calculated from the heat gained by water and the calorimeter.

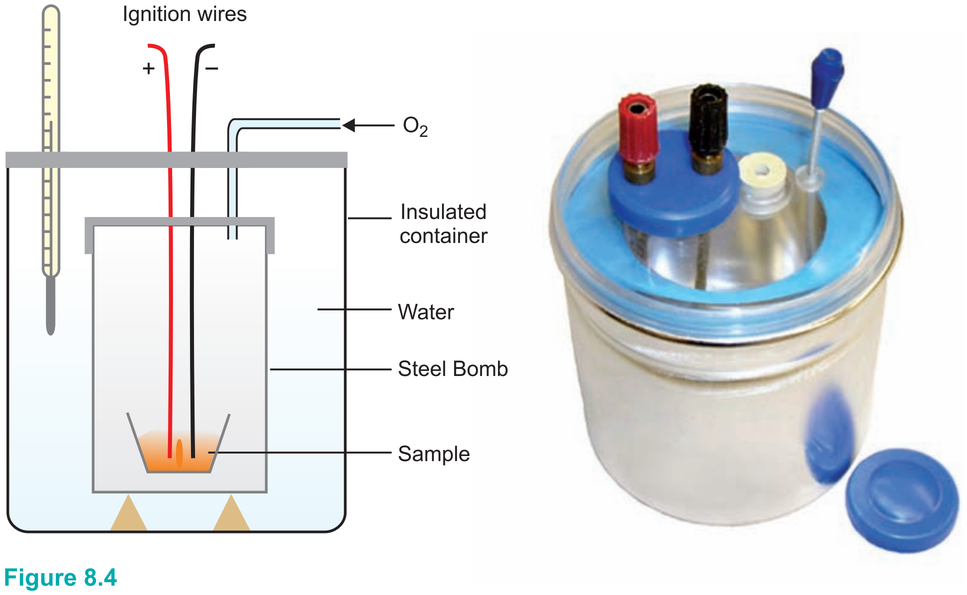


**Figure 8.4**
**Bomb Calorimeter.**

## EXAMINATION QUESTIONS

**1.** Define or explain the following terms :

(*a*) Thermochemistry
(*b*) Internal energy
(*c*) Enthalpy of a reaction
(*d*) Thermochemical equations
(*e*) Heat of reaction
(*f*) Standard heat of reaction
(*g*) Heat of formation
(*h*) Standard heat of formation
(*i*) Heat of combustion
(*j*) Heat of solution
(*k*) Heat of neutralisation
(*l*) Heat of vaporisation
(*m*) Heat of sublimation
(*n*) Heat of transition
(*o*) Hess's law
(*p*) Bond energy

**2.** (*a*) Explain the terms : heat of reaction at constant pressure and heat of reaction at constant volume. How are they related?

(*b*) If the heat of formation of methane at constant pressure is –17.9 kcal per mole at 25°C, what is its value at constant volume?

**Answer.** (*b*) –17.308 kcal

**3.** Given the heats of combustion of ethylene, hydrogen and ethane as 337.2, 68.3 and 372.8 kcal respectively, calculate the heat of reaction at 78°C for

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

**Answer.** –32.7 kcal

**4.** $\Delta H$ values for the combustion reaction of ethyl alcohol, carbon and hydrogen are –330, –94.3 and –68.5 kcal respectively. Calculate the heat of formation of ethyl alcohol.

**Answer.** – 64.1 kcal

**5.** (*a*) State Hess' Law of constant heat summation and explain some of its important applications.

(*b*) Calculate the heat of formation of benzene at 25°C, if the heats of combustion of benzene, carbon and hydrogen are – 780.98, – 94.05 and – 68.32 kcal respectively at 25°C.

**Answer.** 11.72 kcal

**6.** Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is –393.51 kJ $mol^{-1}$ and that of diamond is –395.41 kJ $mol^{-1}$. What is the enthalpy change in the process Graphite $\rightarrow$ Diamond at the same temperature?

**Answer.** 1.90 kJ $mol^{-1}$

**7.** (*a*) State and explain heat of formation, heat of combustion with examples.

(*b*) The standard heats of formation of CO(g) and $H_2O(g)$ at 25°C are 100.5 kJ and –241.8 kJ per mole respectively. Calculate the heat change of the following reaction at this temperature.

$$H_2O(g) + C(s) \rightarrow H_2(g) + CO(g)$$

**Answer.** (*b*) 342.3 kJ

**8.** The heat of combustion of liquid benzene is –326.7 kJ. The heat of formation of $CO_2$ and $H_2O$ are –393.5 kJ and –286.2 kJ respectively. Calculate the heat of formation of liquid benzene.

**Answer.** –2826.1 kJ

**9.** Explain the term enthalpy of ionisation. The enthalpy of neutralisation of HCl with NaOH is –57.3 kJ $mol^{-1}$ and that of neutralisation of $CH_3COOH$ with NaOH is –55.2 kJ $mol^{-1}$. Calculate the enthalpy of ionisation of $CH_3COOH$.

**Answer.** +2.1 kJ

**10.** Calculate the standard enthalpy of formation of naphthalene ($C_{10}H_8$) when the standard enthalpy of combustion of naphthalene is –5153 kJ and the standard enthalpies of formation of $CO_2$ and $H_2O$ are –393.5 kJ $mol^{-1}$ and –285.8 kJ $mol^{-1}$ respectively.

**Answer.** +74.8 kJ

**11.** (*a*) Discuss the variation of heat of reaction with temperature.

(*b*) Calculate the heat of formation of carbon disulphide. The heat of combustion of $CS_2$, Sulphur and Carbon are –26.5 kcal, –94.3 kcal and –71.08 kcal respectively at 25°C.

**Answer.** (*b*) –233.18 kcal

**12.** (*a*) Derive Kirchoff's equation.

(*b*) Bond energies of $F_2$ and $Cl_2$ are 36.6 and 580 kcal/mole respectively. Heat liberated in the reaction

$$F_2 + Cl_2 \rightarrow 2FCl$$

is 26.6 kcal. Find the bond energy of F—Cl bond.

**Answer.** (*b*) 295 kcal

**13.** (*a*) Define the heat of reaction. Derive the relationship between heat of reaction at constant volume and at constant pressure.

(*b*) The heat of combustion of glucose at 17°C and at constant pressure is –651000 calories. Calculate heat of combustion at constant volume at 17°C.

**Answer.** (*b*) – 651000 cals

**14.** 2.0 g of $C_6H_6$ was burnt in excess of $O_2$ in a bomb calorimeter :

$$C_6H_6(\ell) + 7\tfrac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$$

If the temperature rise is 40°C and the heat capacity of the system is 2.0 kJ $K^{-1}$, calculate the enthalpy of combustion of $C_6H_6$ at constant volume and constant pressure.

**Answer.** – 2.4414 kJ $mol^{-1}$; –24410.283 kJ $mol^{-1}$ (*Guru Nanak Dev BSc, 2002*)

**15.** The enthalpies of combustion of benzene, Carbon and hydrogen are –3267.7 kJ, –393.5 kJ and –286.2 kJ respectively. Calculate the enthalpy of formation of benzene.

**Answer.** – 48.1 kJ (*Nagpur BSc, 2002*)

**16.** Calculate heat of fusion of benzene at its freezing point, 278 K, if the rate of change of melting point with pressure is 0.0129 K $atm^{-1}$ and ΔV is 0.059 $cm^{-3}$ $g^{-1}$. (Mol. wt. of benzene is 78)

**Answer.** 99.174 kJ $mol^{-1}$ (*Aligarh BSc, 2002*)

**17.** Define enthalpy of Neutralisation. When 100 ml of 1N HCl is neutralised by equivalent amount of NaOH, 5.273 kJ of heat is evolved. Calculate the heat of neutralisation of HCl.

**Answer.** 52.73 kJ (*Nagpur BSc, 2002*)

**18.** Determine $\Delta H$ of the reaction :

$$C(s) + 2H_2(g) \rightarrow CH_4(g)$$

from the following data :

(*i*) $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.7 \text{ kJ}$

(*ii*) $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell) \qquad \Delta H = -285.7 \text{ kJ}$

(*iii*) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O \qquad \Delta H = -890 \text{ kJ}$

**Answer.** –74.9 kJ (*Guru Nanak Dev BSc, 2002*)

**19.** (*a*) State Hess's law of constant heat summation and describe its applications.

(*b*) Calculate $\Delta H$ for the reaction :

$$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$$

from the following data.

(*i*) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H = -890.35 \text{ kJ}$

(*ii*) $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell) \qquad \Delta H = -286.2 \text{ kJ}$

(*iii*) $C_{(graphite)} + O_2(g) \rightarrow CO(g) \qquad \Delta H = -393.51 \text{ kJ}$

**Answer.** –75.56 kJ (*Allahabad BSc, 2002*)

**20.** (*a*) Show that

$$\Delta H = \Delta V + \Delta nRT$$

(*b*) If the heat of formation of methane at constant pressure is –17.9 kcal per mole at 25°C, what is its value at constant volume?

**Answer.** (*b*) $-173.078 \text{ kcal mol}^{-1}$ (*Guru Nanak Dev BSc, 2002*)

**21.** Define bond energy. Calculate $\Delta H$ for the reaction :

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

from the following values of bond energies :

| *Bond* | C–H | O=O | C=O | O–H | C=C |
|---|---|---|---|---|---|
| *Bond Energy (kJ)* | 414 | 499 | 724 | 460 | 619 |

**Answer.** – 960 kJ (*Nagpur BSc, 2002*)

**22.** Calculate the standard enthalpy of formation of *n*-butane, given that the standard enthalpies of combustion of *n*-butane, $c_{(graphite)}$ and $H_2(g)$ are $-2878.5 \text{ kJ mol}^{-1}$, $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively.

**Answer.** $-124.5 \text{ kJ mol}^{-1}$ (*Delhi BSc, 2003*)

**23.** The enthalpy of formation of methane at constant volume at 25°C is –72.3 kJ. What will be the heat of formation at constant pressure? ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

**Answer.** $-74.777 \text{ kJ mol}^{-1}$ (*Arunachal BSc, 2003*)

**24.** $\Delta G°$ for the formation of CO, $H_2O$, $CO_2$ and $H_2$ gases are –32.81, –54.64, –94.26 and zero kcal $\text{mol}^{-1}$ respectively. Calculate $\Delta G°$ and $K_p$ for the forward reaction in the following equilibrium :

$$CO + H_2O \rightleftharpoons H_2 + CO_2$$

**Answer.** $28.49 \text{ kJ mol}^{-1}$ (*Delhi BSc, 2003*)

**25.** The heat of combustion of carbon, hydrogen and sucrose are –393.5, –286.2 and $-5644.2 \text{ kJ mol}^{-1}$ respectively. Calculate the heat of formation of sucrose.

**Answer.** $1566.0 \text{ kJ mol}^{-1}$ (*Jamia Millia BSc, 2003*)

**26.** Calculate enthalpy of formation of ethane from the following data :

(*i*) $C(s) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H = -393.4 \text{ kJ}$

(*ii*) $H_2(g) + ½O_2(g) \rightarrow H_2O(\ell) \qquad \Delta H = -284.61 \text{ kJ}$

(*iii*) $C_2H_6(g) + 7/2\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(\ell)$ $\Delta H = -1561.0$ kJ

**Answer.** –79.63 kJ (*Sambalpur BSc, 2003*)

**27.** Define bond energy. Explain how it can be used to calculate the heat of a reaction. Calculate the heat of reaction between propene and chlorine to give 1, 2-dichloropropane from the values of bond energies :

$$E_{C-C} = 347.3 \text{ kJ mol}^{-1}$$
$$E_{C=C} = 615 \text{ kJ mol}^{-1}$$
$$E_{C-H} = 413 \text{ kJ mol}^{-1}$$
$$E_{C-Cl} = 330.5 \text{ kJ mol}^{-1}$$
$$E_{Cl-Cl} = 242.7 \text{ kJ mol}^{-1}$$

**Answer.** –150.6 kJ mol$^{-1}$ (*Nagpur BSc, 2003*)

**28.** (*a*) Derive Kirchoff's equation when $C_P$ values are

(*i*) independent on temperature; and

(*ii*) dependent on temperature

(*b*) Calculate the enthalpy of vapourisation of $SO_2$ at –25°C if the same at its boiling point (i.e. –10°C) be 5950 cal mol$^{-1}$. Given for $SO_2$, molar heat capacities in liquid and vapour phase are 206 cal K$^{-1}$ mol$^{-1}$ and 9.3 cal K$^{-1}$ mol$^{-1}$ respectively.

**Answer.** (*b*) 6119.5 cal mol$^{-1}$ (*Delhi BSc, 2003*)

**29.** The standard enthalpy of formation ($\Delta H_f^\circ$) of $NH_3$(g) as indicated by the chemical equation is – 46.19 kJ.

$$1/2\ N_2(g) + 3/2\ H_2(g) \rightarrow NH_3(g)$$

Standard entropies of $N_2$(g), $H_2$(g) and $NH_3$(g) are 191.62, 130.60 and 192.46 JK$^{-1}$ mol$^{-1}$ respectively. Calculate the standard free energy of formation of $NH_3$(g).

**Answer.** –16.613 kJ mol$^{-1}$ (*Kalyani BSc, 2003*)

**30.** The heat of combustion of benzoic acid at constant pressure is –771400 calories at 25°C. Calculate the heat of combustion at constant volume.

**Answer.** –771103.937 cal (*Madurai BSc, 2004*)

**31.** Heats of combustion of hydrated copper sulphate and anhydrous copper sulphate are –2.80 and 15.89 kcals respectively. Calculate the heat of hydration of copper sulphate.

**Answer.** –18.69 kcal (*Delhi BSc, 2004*)

**32.** (*a*) Derive thermodynamically Kirchoff's equation.

(*b*) Calculate the heat of formation of acetic acid its heat of combustion is –869.0 kJ mol$^{-1}$. The heats of formation of $CO_2$(g) and $H_2O(\ell)$ are –390.0 kJ mol$^{-1}$ and –285.0 kJ mol$^{-1}$ respectively.

**Answer.** (*b*) – 481 kJ mol$^{-1}$ (*Agra BSc, 2004*)

**33.** (*a*) State and Explain Hess's Law.

(*b*) The heat of formation of methane at 27°C is –19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume?

**Answer.** (*b*) –18.70 kcal (*Guru Nanak Dev BSc, 2005*)

**34.** The heat of combustion of $C_2H_4(g)$, $C_2H_6(g)$ and $H_2(g)$ are –1409 kJ, –1558.3 kJ and – 285.645 respectively. Calculate the heat of hydrogenation of ethylene.

**Answer.** 136.8 kJ (*Assam BSc, 2005*)

**35.** When 2 moles of ethane are completely burnt 3129 kJ of heat is liberated. Calculate the heat of formation, $\Delta H_f$ for $C_2H_6$. $\Delta H_f$ for $CO_2(g)$ and $H_2O(l)$ are – 395 and – 286 kJ respectively.

**Answer.** – 83.5 kJ (*Purvanchal BSc, 2005*)

**36.** The bond dissociation energies of gaseous $H_2$, $Cl_2$ and HCl are 104, 58 and 103 kcal mol$^{-1}$ respectively. Calculate the enthalpy of formation of HCl.

**Answer.** – 22.0 kcal (*Madras BSc, 2005*)

**37.** In an experiment 5.48 g of formic acid, HCOOH, was burnt and the amount of heat evolved was 30.3 kJ. Calculate Δ*H* per mole of formic acid.

**Answer.** 42.79 kJ (*Nehu BSc, 2006*)

**38.** Calculate the heat of formation of ammonia from the heats of combustion of ammonia and hydrogen which are 9.06 and 68.9 kcals respectively.

**Answer.** – 94.29 kcals (*Madurai BSc, 2006*)

**39.** Calculate the standard heat of formation of carbon disulphide (*l*). Given that the standard heat of combustion of carbon(*s*), sulphur(*s*) and carbon disulphide(*l*) are –393.3, – 293.72 and – 1108.76 kJ $mol^{-1}$ respectively.

**Answer.** + 128.02 kJ (*Kerala BSc, 2006*)

**40.** The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are – 76.2, – 394.8 and –241.6 kJ $mol^{-1}$ respectively. Calculate the amount of heat evolved by burning 1 $m^3$ of methane measured under normal condition.

**Answer.** $3.58 \times 10^4$ kJ (*Delhi BSc, 2006*)

**41.** The heat of combustion of methane is – 890.65 kJ $mol^{-1}$ and heats of formation of $CO_2$ and $H_2O$ are – 393.5 and –286.0 kJ $mol^{-1}$ respectively. Calculate the heat of formation of methane.

**Answer.** –74.85 kJ $mol^{-1}$ (*Lucknow BSc, 2006*)

## MULTIPLE CHOICE QUESTIONS

**1.** The branch of chemistry which deals with the heat changes caused by chemical reactions is called

(*a*) thermodynamics (*b*) thermal chemistry
(*c*) thermochemistry (*d*) none of these

**Answer.** (*c*)

**2.** In an exothermic reaction, the internal energy of the products is _______ internal energy of the reactants

(*a*) greater than (*b*) lesser than
(*c*) equal to (*d*) none of these

**Answer.** (*a*)

**3.** In an endothermic reaction

(*a*) $E_R > E_P$ (*b*) $E_R < E_P$
(*c*) $E_R = E_P$ (*d*) None of these

**Answer.** (*a*)

**4.** The enthalpy of a system is defined by the relation

(*a*) $H = E + P V$ (*b*) $H = E - P V$
(*c*) $E = H + P V$ (*d*) $P V + E - H$

**Answer.** (*a*)

**5.** For exothermic reactions, Δ*H* is _______ while for endothermic reactions it is _______.

(*a*) positive, negative (*b*) positive, positive
(*c*) negative, negative (*d*) negative, positive

**Answer.** (*d*)

**6.** In an exothermic reaction the heat energy is _______ while in endothermic reaction it is _______.

(*a*) released, released (*b*) released, absorbed
(*c*) absorbed, released (*d*) absorbed, absorbed

**Answer.** (*b*)

**7.** Which one of the following is correct for a reaction aA + bB $\rightarrow$ cC + dD where $\Delta n = (c + d) - (a + b)$

(*a*) $P\Delta V = \Delta H - \Delta E$ (*b*) $\Delta H = \Delta E + \Delta n\,R\,T$

(*c*) $\Delta n\,R\,T = \Delta H - \Delta E$ (*d*) all of these

**Answer.** (*d*)

**8.** For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the change in enthalpy is given by

(*a*) $\Delta H = \Delta E - 2\,R\,T$ (*b*) $\Delta H = \Delta E + 2\,R\,T$

(*c*) $\Delta H = \Delta E + 3\,R\,T$ (*d*) $\Delta H = \Delta E + R\,T$

**Answer.** (*a*)

**9.** $\Delta H = \Delta E$ is true for the reaction

(*a*) $H_2 + Cl_2 \rightleftharpoons 2HCl$ (*b*) $2NO \rightleftharpoons N_2 + O_2$

(*c*) $2HI \rightleftharpoons H_2 + I_2$ (*d*) all of these

**Answer.** (*d*)

**10.** Which of the following relations holds good for the reaction

$$CO(g) + ½O_2(g) \rightarrow CO_2(g)$$

(*a*) $\Delta H = \Delta E$ (*b*) $\Delta H = \Delta E + R\,T$

(*c*) $\Delta H = \Delta E + ½\,R\,T$ (*d*) $\Delta\, H = \Delta\, E - ½\, R\, T$

**Answer.** (*d*)

**11.** The change in internal energy with temperature at a constant volume is given by the relation

(*a*) $\Delta E = \Delta C_v\,(T_1 - T_2)$ (*b*) $\Delta E = \Delta C_p\,(T_2 - T_1)$

(*c*) $\Delta E = \Delta C_v\,(T_2 - T_1)$ (*d*) $\Delta E = \Delta C_p\,(T_1 - T_2)$

**Answer.** (*c*)

**12.** The Kirchoff's equation is

(*a*) $\Delta H_2 - \Delta H_1 = \Delta C_p\,(T_2 - T_1)$ (*b*) $\Delta E_2 - \Delta E_1 = \Delta C_v\,(T_2 - T_1)$

(*c*) both (*d*) neither (*a*) nor (*b*)

**Answer.** (*c*)

**13.** The change in enthalpy that takes place when one mole of the compound is formed form its elements is called

(*a*) heat of formation of compound (*b*) heat of synthesis

(*c*) heat of combustion (*d*) standard heat of formation

**Answer.** (*a*)

**14.** By convention, the standard heat of formation of all elements is assumed to be

(*a*) zero (*b*) negative

(*c*) positive (*d*) infinity

**Answer.** (*a*)

**15.** The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air or oxygen is called

(*a*) heat of reaction (*b*) heat of formation

(*c*) heat of oxidation (*d*) heat of combustion

**Answer.** (*d*)

**16.** The calorific value is defined as the amount of heat produced in calories when _______ of a substance is completely burnt.

(*a*) one gram (*b*) one mole

(*c*) 100 grams (*d*) 1 kg

**Answer.** (*a*)

**17.** The fuel efficiency of methane (mol mass = 16) is _______ that of ethane (mol mass = 30).

(*a*) lesser than (*b*) greater than

(*c*) equal to (*d*) none of these

**Answer.** (*b*)

**18.** Which of the following always has a negative value?

(*a*) heat of formation (*b*) heat of reaction

(*c*) heat of combustion (*d*) heat of solution

**Answer.** (*c*)

**19.** The change in enthalpy when one mole of a substance is dissolved in a specified quantity of solvent at a given temperature is called

(*a*) heat of reaction (*b*) heat of combustion

(*c*) heat of solvation (*d*) heat of solution

**Answer.** (*d*)

**20.** The change in enthalpy of the system when one _________ of an acid is neutralised by one ________ of a base or *vice versa* in dilute solution is called heat of neutralisation.

(*a*) g-equivalent, mole (*b*) mole, g-equivalent

(*c*) g-equivalent, g-equivalent (*d*) mole, mole

**Answer.** (*c*)

**21.** The heat of neutralisation of a strong acid and a strong base is always

(*a*) zero (*b*) constant

(*c*) positive (*d*) changing

**Answer.** (*b*)

**22.** The heat of neutralisation is of a weak acid by a strong base is ________ that of a strong acid by a strong base.

(*a*) lesser than (*b*) greater than

(*c*) equal to (*d*) none of these

**Answer.** (*a*)

**23.** The heat change in equations $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ $\Delta H = -13.7$ kcal represents

(*a*) heat of neutralisation (*b*) heat of formation of water

(*c*) heat of dissociation of water (*d*) heat of solution

**Answer.** (*a*)

**24.** The heat change (or enthalpy change) when one mole of a solid substance is converted into the liquid state at its ________ is called heat of fusion.

(*a*) boiling point (*b*) melting point

(*c*) freezing point (*d*) evaporation point

**Answer.** (*b*)

**25.** The process depicted by the equation

$$H_2O(s) \rightarrow H_2O(\ell) \quad \Delta H = +1.43 \text{ kcal represents}$$

(*a*) melting (*b*) boiling

(*c*) evaporation (*d*) fusion

**Answer.** (*d*)

**26.** Greater the heat of fusion of a substance _______ is the magnitude of intermolecular forces

(*a*) higher (*b*) lower

(*c*) zero (*d*) infinite

**Answer.** (*a*)

**27.** The heat change when one mole of a liquid is converted into vapour or gaseous state at its boiling point is called

(*a*) heat of liquefaction (*b*) heat of fusion (*c*) heat of vaporisation (*d*) heat of sublimation

**Answer.** (*c*)

**28.** The process of sublimation for a solid occurs

(*a*) at the melting point (*b*) at a temperature below its melting point

(*c*) at a temperature above its melting point (*d*) none of these

**Answer.** (*b*)

**29.** The change in enthalpy which occurs when one mole of an element changes from one allotropic form to another is called.

(*a*) heat of allotropy (*b*) heat of transition

(*c*) heat of transformation (*d*) heat of sublimation

**Answer.** (*b*)

**30.** The thermochemical equations may be

(*a*) multiplied (*b*) added

(*c*) subtracted (*d*) all of these

**Answer.** (*d*)

**31.** In a chemical process, the amount of total heat change is same no matter by which method the change is brought about. This is statement of

(*a*) law of thermochemistry (*b*) Hess's law

(*c*) thermodynamic law (*d*) law of heat of reaction

**Answer.** (*b*)

**32.** The average amount of energy required to break all bonds of a particular type in one mole of the substance is called

(*a*) heat of reaction (*b*) bond energy

(*c*) heat of transition (*d*) heat of bond formation

**Answer.** (*b*)

**33.** The bond energy depends upon

(*a*) size of the atom (*b*) electronegativity

(*c*) bond length (*d*) all of these

**Answer.** (*d*)

**34.** When a bond is broken, the bond energy is positive because heat _______

(*a*) is evolved (*b*) is absorbed

(*c*) remains unchanged (*d*) none of these

**Answer.** (*b*)

**35.** For an endothermic reaction

(*a*) $\Delta H$ is –ve (*b*) $\Delta H$ is +ve

(*c*) $\Delta E$ is –ve (*d*) $\Delta H$ is zero

**Answer.** (*b*)

**36.** The enthalpy change in the reaction

$$2\,CO + O_2 \rightarrow 2CO_2$$

is termed as

(*a*) enthalpy of reaction (*b*) enthalpy of fusion

(*c*) enthalpy of formation (*d*) enthalpy of combustion

**Answer.** (*a*)

**37.** For a reaction

$$A_2(g) + B_2(g) \rightarrow 2AB(g) \quad \Delta H = x \text{ kcal}$$

According to this reaction, the heat of formation of AB will be

| | |
|---|---|
| (*a*) x kcal | (*b*) –x kcal |
| (*c*) x/2 kcal | (*d*) –x/2 kcal |

**Answer.** (*c*)

**38.** For a gaseous reaction

$$X(g) + Y(g) \rightarrow 4Z(g)$$

$\Delta E$ at 300 K is 20 kcal. Taking $R = 2$ cal $K^{-1}$ $mol^{-1}$, $\Delta H$ for the above reaction will be

| | |
|---|---|
| (*a*) 18.8 kcal | (*b*) 19.4 kcal |
| (*c*) 20.0 kcal | (*d*) 21.2 kcal |

**Answer.** (*d*)

**39.** The heat of neutralization of an acid A with a base B is 13.7 kcal. Which of the following is true

| | |
|---|---|
| (*a*) A is weak and B is also weak | (*b*) A is strong and B is weak |
| (*c*) A is weak nd B is strong | (*d*) A is strong and B is also strong |

**Answer.** (*d*)

**40.** For which of the following reactions, will $\Delta H$ be equal to $\Delta E$?

| | |
|---|---|
| (*a*) $N_2(g) + 3H_2(g) \rightarrow 2NH_3$ | (*b*) $2HI(g) \rightarrow H_2(g) + I_2(g)$ |
| (*c*) $2NO_2 \rightarrow N_2O_4(g)$ | (*d*) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ |

**Answer.** (*b*)

**41.** The neutralization of an acid with a base is represented by

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell) \quad \Delta H = -13.7 \text{ kcal}$$

The heat of neutralization of one mole of $H_2SO_4$ with sodium hydroxide will be

| | |
|---|---|
| (*a*) –13.7 kcal | (*b*) –27.4 kcal |
| (*c*) +27.4 kcal | (*d*) –6.85 kcal |

**Answer.** (*b*)

**42.** Given that heat neutralization of strong acid and strong base is –13.7 kcal. The heat produced when one mole of HCl is mixed with 0.5 mole of NaOH will be

| | |
|---|---|
| (*a*) 6.85 kcal | (*b*) – 6.85 kcal |
| (*c*) –27.4 kcal | (*d*) –13.7 kcal |

**Answer.** (*b*)

**43.** The apparatus used to measure heat changes during chemical reactions is called

| | |
|---|---|
| (*a*) polarimeter | (*b*) colorimeter |
| (*c*) calorimeter | (*d*) none of these |

**Answer.** (*c*)

**44.** Hess's law is used to determine

(*a*) heat of formation of substances which are otherwise difficult to measure
(*b*) heat of transition
(*c*) heats of various other reactions like dimerization
(*d*) all of the above

**Answer.** (*d*)

**45.** $\Delta H°$ represent the enthalpy change

| | |
|---|---|
| (*a*) at 0°C and 1 atm pressure | (*b*) at 0 K and 1 atm pressure |
| (*c*) at 25 K and 1 atm pressure | (*d*) none of these |

**Answer.** (*c*)

**46.** The heats of formation of CO(g) and $CO_2(g)$ are –26.4 kcal and –94.0 kcal respectively. The heat of combustion of carbon monoxide according to Hess's law will be

| | |
|---|---|
| (*a*) +26.4 kcal | (*b*) + 94.0 kcal |

(*c*) – 67.6 kcal (*d*) –120.4 kcal

**Answer.** (*c*)

**47.** The heat of combustion of ethane ($C_2H_6$) is –337.0 kcal at 25°C. The heat of the reaction when 3 g of ethane is burnt completely is

(*a*) –3.37 kcal (*b*) +3.37 kcal

(*c*) –33.7 kcal (*d*) +33.7 kcal

**Answer.** (*c*)

**48.** For the reaction $CaCO_3(s) \quad CaO(s) + CO_2(g)$ which one of the following is true?

(*a*) $\Delta H = \Delta E$ (*b*) $\Delta H > \Delta E$

(*c*) $\Delta H < \Delta E$ (*d*) $\Delta H = \frac{1}{2} \Delta E$

**Answer.** (*b*)

**49.** Consider the reaction

$$CO(g) + \frac{1}{2}O_2(g) \qquad CO_2(g)$$

at constant temperature and pressure. Which one of the following is correct?

(*a*) $\Delta H < \Delta E$ (*b*) $\Delta H > \Delta E$

(*c*) $\Delta H = \Delta E$ (*d*) none of these

**Answer.** (*a*)

**50.** The energy required to dissociate 6 g of gaseous hydrogen into free gaseous atoms is 3.12 kcal at 25°C. The bond energy of H–H bond will be

(*a*) 3.12 kcal (*b*) 1.56 kcal

(*c*) 1.04 kcal (*d*) 10.04 kcal

**Answer.** (*c*)

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CHAPTER

# Second Law of Thermodynamics

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The first law of thermodynamics states that one form of energy can change into another form but the total amount of energy remains the same. Once we specify a particular process or change, this law helps us to balance the internal energy, heat released and work done in the process. But the first law says nothing about whether the process of change we specify can, in fact, occur and if so in which direction. This question concerns the second law of thermodynamics. Before we can state the second law in a usable form, we must define some terms.

## SPONTANEOUS PROCESSES

**A process which proceeds of its own accord, without any outside assistance, is termed a spontaneous or natural process.**

**The reverse process which does not proceed on its own, is referred to as a nonspontaneous or unnatural process.**

**In general, the tendency of a process to occur naturally is called the spontaneity.**

### Examples of Spontaneous Processes

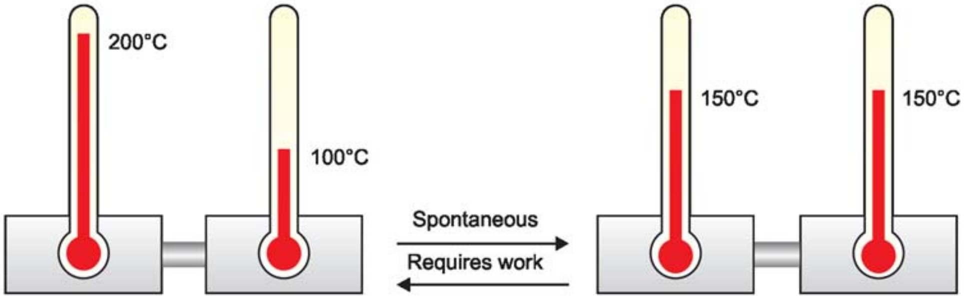
(1) **Cliff Jumping and Mountain Climbing.** Cliff jumping is a spontaneous process, whereas mountain climbing requires work.

(2) **Heat Flow.** When two balls of metal, one hot and one cold, are connected, heat flows spontaneously from the hot ball to the cold one, never from cold to hot. It requires work to transfer heat from one place to the other, say, by means of refrigerator pump.

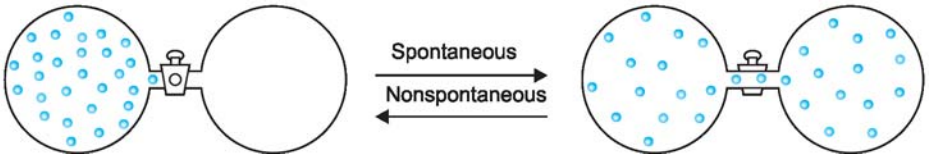
(3) **Gas Flow.** When a vessel containing a gas is connected to another evacuated vessel, the gas spreads throughout spontaneously unless the pressure is the same in both the vessels. The reverse process of compressing the gas into the original vessel cannot occur unless work is done on it.

**(a) Cliff Jumping and Mountain Climbing**

**(b) Heat Flow**



**(c) Gas Flow**



■ **Figure 9.1**
**Spontaneous processes (Illustration).**

## CRITERIA OF SPONTANEITY

Some important criteria of spontaneous physical and chemical changes are listed below.

(1) **A spontaneous change is one-way or unidirectional.** For reverse change to occur, work has to be done.

(2) **For a spontaneous change to occur, time is no factor.** A spontaneous reaction may take

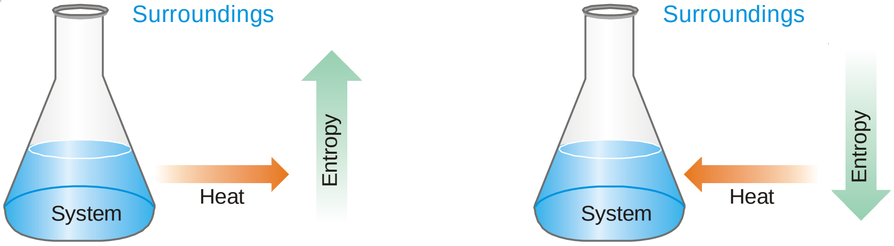
place rapidly or very slowly.

(3) **If the system is not in equilibrium state (unstable), a spontaneous change is inevitable.** The change will continue till the system attains the state of equilibrium.

(4) **Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed.** To take the system away from equilibrium, some external work must be done on the system.

(5) **A spontaneous change is accompanied by decrease of internal energy or enthalpy (Δ*H*).**

It implies that only such reactions will occur which are exothermic. But the melting of ice and evaporation of rain water are endothermic processes which proceed spontaneously. Clearly, there is some other factor in addition to Δ*H* which governs spontaneity. It is the second law of thermodynamics which introduces this new factor that is called *entropy*.



## ENTROPY

For many years scientists believed that only exothermic changes resulting in a lowering of internal energy or enthalpy could occur spontaneously. But melting of ice is an endothermic process and yet occurs spontaneously. On a warm day, ice melts by itself. The evaporation of water is another example of a spontaneous endothermic process. Thus arose the need of inventing another driving force that affects the spontaneity. This was known as the entropy change, Δ*S*.

### Spontaneity and Randomness

Careful examination shows that in each of the processes *viz*., melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer still when the water evaporates into space as now they can roam about throughout the entire atmosphere. In other words, we can say that the randomness of the water molecules increases as ice melts into water or water evaporates into space.

Melting of Ice is a classic example of 'Increasing Entropy'.

### Increase in Randomness Favours a Spontaneous Change

A change that brings about randomness is more likely to occur than one that brings about order. Let us suppose we have a suit of playing cards arranged numerically (Fig. 9.2 *a*). We can see that the sequence of cards is certainly highly organised. Now, if we throw the cards into the air, collect them and re-stack them, we will almost surely find that they have been placed at random. This is expected because when the cards are tossed, there are many ways for them to be disordered, while there is only one way for them to come together again in their original sequence. Thus on the basis of pure chance a disordered sequence is far more probable than the ordered one with which we started. The same law of chance applies to any physical or chemical process.

**Figure 9.2**
**(*a*) Cards are highly organised; (*b*) After they have been tossed, cards are placed at random.**

## DEFINITION OF ENTROPY

**Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.**

The symbol of entropy is *S*, while the change in disorder accompanying a process from start to completion is represented by Δ*S*. The entropy of a system is a state function and depends only on the initial and final states of the system. The change in entropy, Δ*S*, for any process is given by the equation,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When $S_{\text{final}} > S_{\text{initial}}$, $\Delta S$ is positive.

**A process accompanied by an increase in entropy tends to be spontaneous.** Let us consider a molecular system in states *A* and *B* (Fig. 9.3). In state *A* all the molecules are arranged and highly ordered, while in state *B* the molecules are present at random and it is highly disordered.

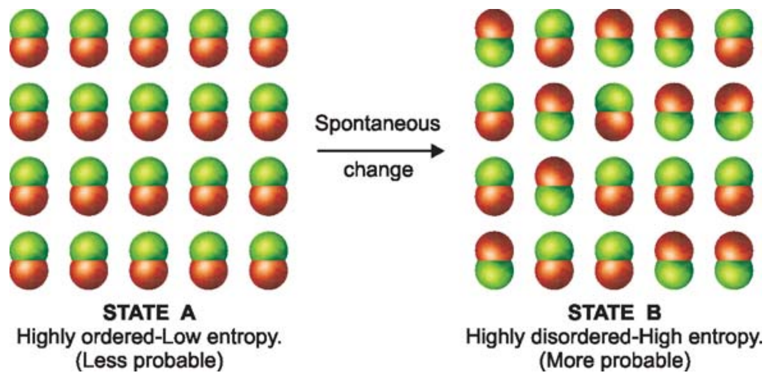


**Figure 9.3**
**(a) State A is highly ordered, low entropy and less probable;**
**(b) State B is highly disordered high entropy and more probable.**

(1) By definition, the entropy of *A* is low and that of *B* high. Thus an increase of entropy occurs in the change from *A* to *B*.

(2) According to the law of chance (probability), *A* is less probable and *B* is more probable. Therefore, the change from *A* to *B* is spontaneous.

(3) From (1) and (2), it follows that the change from *A* to *B* which is accompanied by increase of entropy will tend to be spontaneous.

Hence we can say, in general, that a change in a system which is accompanied by an increase in entropy, tends to be spontaneous.

## STATEMENT OF THE SECOND LAW

The second law of thermodynamics states that : **whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe.**

More specifically, we take the term 'universe' to mean the system and the surroundings. Thus,

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

The second law, as stated above, tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases. In other words $\Delta S_{\text{univ}} > 0$. When a reversible process occurs, the entropy of the system remains constant. $\Delta S_{\text{univ}} = 0$. Since the entire universe is undergoing spontaneous change, the second law can be most generally and concisely stated as : **the entropy of the system is constantly increasing.**

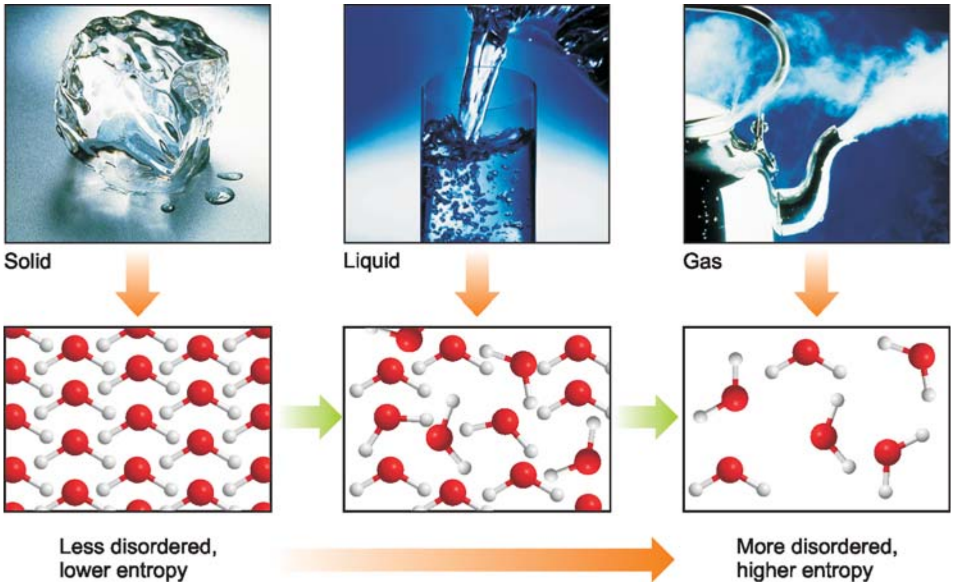


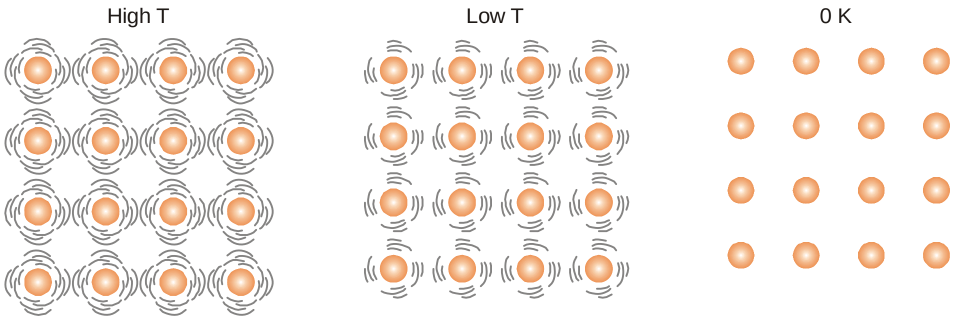
**Figure 9.4**
**Change of ice vapour to liquid and then to water vapour is accompanied by increase of entropy with increasing disorder.**

## STATEMENT OF THE THIRD LAW

The entropy of a substance varies directly with temperature. The lower the temperature, the lower the entropy. For example, water above 100ºC at one atmosphere exists as a gas and has higher entropy (higher disorder). The water molecules are free to roam about in the entire container. When the system is cooled, the water vapour condenses to form a liquid. Now the water molecules are confined below the liquid level but still can move about somewhat freely. Thus the entropy of the system has decreased. On further cooling, water molecules join together to form ice crystal. The water molecules in the crystal are highly ordered and entropy of the system is very low.

If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy. Finally, at absolute zero all molecular vibration ceases and water molecules are in perfect order. Now the entropy of the system will be zero.

This leads us to the statement of the third law of thermodynamics : **at absolute zero, the entropy of a pure crystal is also zero.** That is, $S = 0$ at $T = 0$ K.



A solid crystal; violent molecular vibrations; entropy very low.

Slow molecular vibrations; entropy very little.

No molecular vibrations; perfect order; entropy zero.

**Figure 9.5**
**Molecular states in a solid crystal (Illustration of the Third law).**

## NUMERICAL DEFINITION OF ENTROPY

We have discussed the physical definition of entropy. But classical thermodynamics does not require a physical explanation of the concept of entropy. All that we need is an operational definition so that we can calculate the entropy change of the system and the surroundings.

In 1850 Clausius introduced a numerical definition of entropy. According to him entropy of a system (not undergoing chemical or physical changes), is a constant quantity when there is no communication of heat. When heat ($q$) flows into a system, the entropy increases by $q/T$ . Heat flowing out of a system produces a corresponding decrease. Thus entropy could be precisely defined as : **for a reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temperature (T).** That is,

$$\Delta S = \frac{q}{T}$$

If heat is absorbed, then $\Delta S$ is positive and there will be increase in entropy. If heat is evolved, $\Delta S$ is negative and there is a decrease in entropy.

## UNITS OF ENTROPY

As stated above, entropy is equal to heat energy divided by absolute temperature. Therefore, it is measured in entropy units (‘*eu*’) which are calories per degree per mole *i.e.*, cal $mol^{-1}$ $K^{-1}$.

In the SI system, the units are joules per mole per degree *i.e.*, J $mol^{-1}$ $K^{-1}$. These are represented by *eu*.

$$1eu = 4.184$$

## STANDARD ENTROPY

From the third law, we know that the entropy of a pure crystal is zero at absolute zero (K) Therefore, it is possible by measurement and calculation to find the actual amount of entropy that a substance possesses at any temperature above 0 K. It is often referred to as **absolute entropy.**

**The absolute entropy of a substance at 25°C (298 K) and one atmosphere pressure is called the standard entropy; $S^o$.** The absolute entropy of elements is zero only at 0 K in a perfect crystal, and standard entropies of all substances at any temperature above 0 K always have positive values. The standard entropies of a number of elements and compounds are given in Table 9.1.

**TABLE 9.1. STANDARD ENTROPIES OF SOME SUBSTANCES (25°C, 1 ATM)**

| | Entropy, $S^o$ | | | Entropy, $S^o$ | |
|---|---|---|---|---|---|
| **Substance** | **cal $mol^{-1}$ $K^{-1}$** | **J $mol^{-1}$ $K^{-1}$** | **Substance** | **cal $mol^{-1}$ $K^{-1}$** | **J $mol^{-1}$ $K^{-1}$** |
| Ag (*s*) | 41.32 | 172.9 | $H_2$(*g*) | 31.21 | 130.6 |
| AgCl (*s*) | 58.5 | 24.5 | $H_2O$(*g*) | 45.11 | 188.7 |
| Al (*s*) | 6.77 | 28.3 | $H_2O$(*l*) | 16.72 | 69.96 |
| $Al_2O_3$ (*s*) | 12.19 | 51.0 | HCl (*g*) | 44.62 | 186.7 |
| C (*s*, graphite) | 0.58 | 2.4 | $HNO_3$ (*l*) | 37.19 | 155.6 |
| CO (*g*) | 47.30 | 197.9 | $H_2SO_4$ (*l*) | 37.5 | 157.0 |
| $CO_2$ (*g*) | 51.06 | 213.6 | Hg (*l*) | 18.2 | 76.1 |
| $CH_4$ (*g*) | 44.50 | 186.2 | K (*s*) | 38.30 | 160.2 |
| $CH_3OH$ (*l*) | 30.3 | 126.8 | KCl (*s*) | 57.24 | 239.5 |
| $CO(NH_2)_2$ (*s*) | 25.0 | 104.6 | $K_2SO_4$ (*s*) | 42.0 | 176.0 |
| $C_2H_2$ (*g*) | 48.0 | 200.8 | $N_2$ (*g*) | 45.77 | 191.5 |
| $C_2H_6$ (*g*) | 54.85 | 229.5 | $NH_3$ (*g*) | 46.01 | 192.5 |
| Ca (*s*) | 36.99 | 154.8 | Na (*s*) | 36.72 | 153.6 |
| $CaCO_3$ (*s*) | 22.2 | 92.9 | NaCl (*s*) | 17.30 | 72.88 |
| $Cl_2$ (*g*) | 53.29 | 223.0 | $O_2$ (*g*) | 49.0 | 205.0 |
| Fe (*s*) | 6.5 | 27.0 | S (*s*) | 7.62 | 31.9 |
| $Fe_2O_3$ (*s*) | 21.5 | 90.0 | $SO_2$ (*g*) | 59.40 | 248.5 |

**Once we know the entropies of a variety of substances, we can calculate the standard entropy change,** $\Delta S^o$, for chemical reactions.

$$\Delta S^o = \sum S^o \text{ (products)} - \sum S^o \text{ (reactants)}$$

## STANDARD ENTROPY OF FORMATION

**It is the entropy of formation of 1 mole of a compound from the elements under standard conditions. It is denoted $\Delta S°_f$.** We can calculate the value of entropy of a given compound from the values of $S°$ of elements.

$$S°_f = S° \text{ (compound)} - \sum S° \text{ (elements)}$$

**SOLVED PROBLEM 1.** Urea hydrolyses in the presence of water to produce ammonia and carbon dioxide.

$$CO(NH_2)_2\,(aq) + H_2O\,(l) \longrightarrow CO_2(g) + 2NH_3(g)$$

What is the standard entropy change for this reaction when 1 mole of urea reacts with water ? The standard entropies of reactants and products are listed below :

| **Substance** | **S°(cal/mole K)** |
|---|---|
| $CO(NH_2)_2$ | 41.55 |
| $H_2O\,(l)$ | 16.72 |
| $CO_2\,(g)$ | 51.06 |
| $NH_3\,(g)$ | 46.01 |

**SOLUTION**

We know that

$$\Delta S° = \sum S° \text{ (products)} - \sum S° \text{ (reactants)}$$

or

$$\Delta S° = \left(S°_{CO_2} + 2S°_{NH_3}\right) - \left(S°_{CO(NH_2)_2} + S°_{H_2O}\right)$$

$$= [51.06 + 2 \times 46.01] - [41.55 + 16.72] \text{ cal K}^{-1}$$

$$= \mathbf{84.81 \text{ cal K}^{-1}}$$

**SOLVED PROBLEM 2.** Calculate the standard entropy of formation, $\Delta S°_f$, of $CO_2(g)$. Given the standard entropies of $CO_2(g)$, $C(s)$, $O_2(g)$, which are 213.6, 5.740, and 205.0 $JK^{-1}$ respectively.

**SOLUTION**

We know that

$$S°_f = S°_{\text{compound}} - \sum S°_{\text{elements}}$$

or

$$S°_f = S°_{CO_{2(g)}} - \left[S°_{C_{(s)}} + S°_{O_{2(g)}}\right]$$

Substituting the values

$$S°_f = 213.6 - [5.740 + 205.0] \text{ JK}^{-1}$$

$$= (213.6 - 210.74) \text{ JK}^{-1} = \mathbf{2.86 \text{ JK}^{-1}}$$

## SOME USEFUL DEFINITIONS

### (1) Cyclic Process

When a system undergoes a series of changes and in the end returns to its original state, it is said to have completed as cycle. The whole process comprising the various changes is termed a **cyclic process.**

Since the internal energy of a system depends upon its state, it stands to reason that in cyclic process the net change of energy is zero. Or, we can say that the work done by the system during all these changes should be equal to the heat absorbed by the system.

$$\Delta E = 0 = q - w \text{ or } q = w$$

### (2) Heat Engines

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of a suitable device.

**A machine which can do work by using heat that flows out spontaneously from a high-temperature source to a low-temperature sink, is called a heat engine.**

A heat engine takes heat energy from a high-temperature reservoir and converts some of it into work, returning the unconverted heat to a low-temperature sink. A basic heat engine is illustrated in Fig. 9.6. A steam engine is a typical heat engine. It takes heat from the boiler (high-temperature source), converts some heat to work and returns the unused heat to the surroundings (low-temperature sink).

A heat engine running on a periodic cyclic process can yield work continuously.

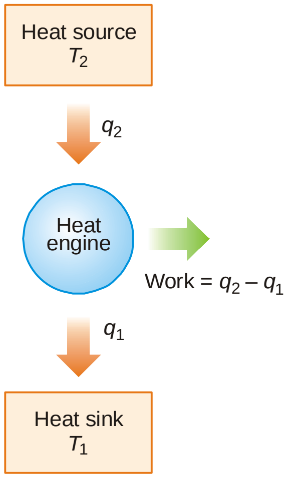


**Figure 9.6**
**Principle of heat engine (illustration).**

### (3) Efficiency of a Heat Engine

**The ratio of the work obtained in a cyclic process (*w*) to the heat taken from the high-temperature reservoir (*q*) is referred to as the efficiency of a heat engine.**

No heat engine, no matter how well constructed, can convert all the heat from the high-temperature reservoir into work. Such an engine would be 100% efficient. Sadi Carnot was the first scientist to realise this and deduce an expression showing the limitations of heat engines.

## THE CARNOT CYCLE

In 1824 Sadi Carnot proposed a theoretical heat engine to show that the efficiency was based upon the temperatures between which it operated. Carnot's imaginary engine could perform a series of operations between temperatures $T_1$ and $T_2$, so that at the end of these operations the system was restored to the original state. **This cycle of processes which occurred under reversible conditions is referred to as the Carnot cycle.** The medium employed in operating Carnot's engine was one mole of an ideal gas which could be imagined to be contained in a cylinder fitted with a frictionless piston.

The Carnot cycle comprises four operations or processes.

(1) Isothermal reversible expansion
(2) Adiabatic reversible expansion
(3) Isothermal reversible compression
(4) Adiabatic reversible compression

The above four processes are shown in the indicator diagram of Carnot cycle (Fig. 9.7).

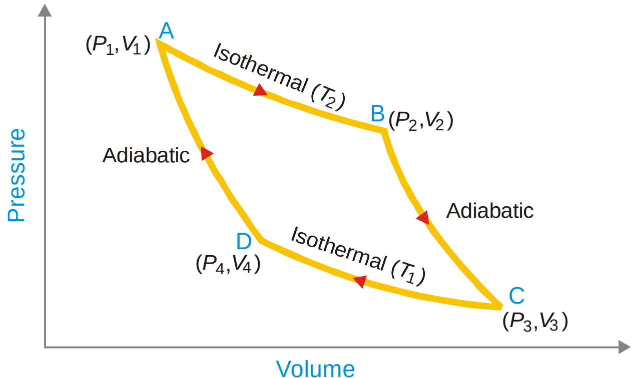


**Figure 9.7**
**Indicator diagram of the Carnot cycle.**

### First Operation – Isothermal Reversible Expansion

Let $T_2$, $P_1$ and $V_1$ be the temperature, pressure and volume respectively of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temperature ($T_2$). Now the gas is allowed to expand isothermally and reversibly so that the volume increases from $V_1$ to $V_2$. *AB* represents the path of the process in the diagram.

**Work done.** Since the process in operation 1 is isothermal, $\Delta E = 0$. If $q_2$ be the heat absorbed by the system and $w_1$ the work done by it, according to the first law equation ($\Delta E = q - w$),

$$q_2 = w_1$$

But
$$w_1 = RT_2 \text{ In } \frac{V_2}{V_1}$$

Therefore,
$$q_2 = RT_2 \text{ In } \frac{V_2}{V_1} \qquad \text{...(1)}$$

### Second Operation – Adiabatic Reversible Expansion

The gas at *B* is at a temperature $T_2$ and has volume $V_2$ under the new pressure $P_2$. The gas is now allowed to expand reversibly from volume $V_2$ to $V_3$ when the temperature drops from $T_2$ to $T_3$ (along *BC*).

**Work done.** Since this step is adiabatic, $q = 0$. If $w_2$ be the work done, according to the first law equation ($\Delta E = q - w$),

$$\Delta E = -w_2$$

or
$$w_2 = -\Delta E$$

But
$$\Delta E = C_v (T_1 - T_2)$$

Therefore,
$$w_2 = C_v (T_2 - T_1) \qquad \text{...(2)}$$

### Third Operation – Isothermal Reversible Compression

Now the cylinder is placed in contact with a heat reservoir at a lower temperature, $T_1$. The volume of the gas is then compressed isothermally and reversibly from $V_3$ to $V_4$ (represented by *CD* in diagram).

**Work done.** During compression, the gas produces heat which is transferred to the low temperature reservoir. Since the process takes place isothermally, $\Delta E = 0$. If $q_1$ is the heat given to the reservoir and $w_3$ the work done on the gas, using proper signs for $q$ and $w$, we have

$$-q_1 = -w_3 = RT_1 \text{ 1n } \frac{V_4}{V_3} \qquad \text{...(3)}$$

### Fourth Operation – Adiabatic Reversible Compression

The gas with volume $V_4$ and temperature $T_1$ at D is compressed adiabatically (along *DA*) until it regains the original state. That is, the volume of the system becomes $V_1$ and its temperature $T_2$.

**Work done.** In this step work is done on the system and, therefore, bears the negative (–) sign. If it is denoted by $w_4$, we can write

$$-w_4 = -C_v (T_2 - T_1) \qquad \text{...(4)}$$

### Net Work Done in One Cycle

Adding up the work done ($w$) in all the four operations of the cycle as shown in equations (1), (2), (3) and (4), we have

$$\begin{aligned} w &= w_1 + w_2 + (-w_3) + (-w_4) \\ &= RT_2 \text{ 1n} \frac{V_2}{V_1} + C_v\ (T_2 - T_1) + RT_1 \text{ 1n} \frac{V_4}{V_3} - C_v\ (T_2 - T_1) \end{aligned}$$

$$= RT_2 \ 1\text{n} \frac{V_2}{V_1} + RT_1 \ 1\text{n} \frac{V_4}{V_3}$$

## Net Heat Absorbed in One Cycle

If $q$ is the net heat absorbed in the whole cycle.

$$q = q_2 - q_1$$

where $q_2$ is heat absorbed by the system in operation 1 and $q_1$ is the heat transferred to the sink reservoir.

From (1) and (3)

$$q = q_2 - q_1 = RT_2 \ 1\text{n} \frac{V_2}{V_1} + RT_1 \ 1\text{n} \frac{V_4}{V_3}$$

or
$$q = RT_2 \ 1\text{n} \frac{V_2}{V_1} - RT_1 \ 1\text{n} \frac{V_3}{V_4} \qquad \text{...(5)}$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma - 1} \qquad \text{...for adiabatic expansion}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \qquad \text{...for adiabatic compression}$$

or
$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or
$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Therefore, substituting the value of $V_3/V_4$ in equation (5), the value of net heat may be given as

$$q = RT_2 \ 1\text{n} \frac{V_2}{V_1} - RT_1 \ 1\text{n} \frac{V_2}{V_1}$$

$$= R\,(T_2 - T_1) \ 1\text{n} \ \frac{V_2}{V_1} \qquad \text{...(6)}$$

## Calculation of Thermodynamic Efficiency

Since the total work done in a cycle is equal to net heat absorbed, from (6) we can write

$$w = R\,(T_2 - T_1) \ 1\text{n} \ \frac{V_2}{V_1} \qquad \text{...(7)}$$

The heat absorbed, $q_2$, at higher temperature $T_2$ is given by equation (1),

$$q_2 = RT_2 \ 1\text{n} \frac{V_2}{V_1} \qquad \text{...(8)}$$

Dividing (7) by (8)

$$\frac{w}{q_2} = \frac{R\,(T_2 - T_1) \ 1\text{n} \ V_2/V_1}{RT_2 \ 1\text{n} \ V_2/V_1} = \frac{T_2 - T_1}{T_2}$$

or
$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \text{...(9)}$$

The factor $w/q_2$ is called **thermodynamical efficiency.** It is denoted by η and gives the fraction of the heat taken from the high-temperature reservoir which it is possible to convert into work by a heat engine. Therefore, the efficiency of a Carnot engine, the most ideal of all engines, is limited by the operating temperatures of the engine. The larger the temperature difference ($T_2 - T_1$) between the high and the low temperature reservoirs, the more the heat converted to work by the heat engine. For a given temperature of the high-temperature reservoir, the lower the temperature of the sink, the greater will be the efficiency of the machine. Similarly, for a given temperature of the sink, the efficiency will be increased by using a high temperature of the source reservoir.

### Carnot Theorem

We have shown above that

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

This result deduced for a perfect gas depends upon the temperature limits between which the cycle operates. It is independent of all other factors. Thus Carnot stated an important relation known as the **Carnot theorem.** It states that : **every perfect engine working reversibly between the same temperature limits has the same efficiency, whatever be the working substance.**

## MORE STATEMENTS OF THE SECOND LAW

From equation (9)

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

Evidently $w/q_2$ is less than 1, or $q_2$ is greater than $w$. This means that heat transferred by a spontaneous process is never completely converted into work (If so, $w/q_2$ would be 1). This leads to another statement of the Second law (Lord Kelvin).

**It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.**

This statement recognises the fact that heat engines could never be 100% efficient, since some heat must be returned to a low-temperature reservoir. Another statement of the Second law was given by Clausius.

**It is impossible for a cyclic process to transfer heat from a body at a lower temperature to one at higher temperature without at the same time converting some work to heat.**

This statement recognises that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to expend some work.

**SOLVED PROBLEM 1.** An engine operating between 150ºC and 25ºC takes 500 J heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the work that can be done by this engine.

**SOLUTION**

From equation (9)

$$\text{Efficiency} = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

Here $T_2 = 423\text{ K};\ T_1 = 298\text{ K}$

Substituting the values $\frac{w}{500} = \frac{423 - 298}{423}$

$\therefore$ $w = \mathbf{147.75\ J}$

## WONDERFUL ACHIEVEMENTS IN SCIENCE AND ENGINEERING

### The Second Law of Thermodynamics

**"A spontaneous change is accompanied by an increase in the total entropy of the system and its surroundings."**

$$\Delta S_{Sys} + \Delta S_{Surr} > 0$$

**$\Delta S_{Sys}$ is the entropy change of the system.**
**$\Delta S_{Surr}$ is the entropy change of the surroundings.**

Scientists responsible for the formulation and development of the Second Law Include Rudolph Clausius (1822-1888), Lord Kelvin (1824-1907), Josiah Willard Gibbs (1839-1903) and Ludwig Boltzmann (1844-1906). The Second Law explains why the rusting of Iron is inevitable, why car engines can never be 100% efficient and why batteries eventually run down. It governs the direction of all biochemical reactions including those responsible for glucose catabolism, DNA replication and protein synthesis - even life obeys the Second Law of Thermodynamics.

**SOLVED PROBLEM 2.** The boiling point of water at a pressure of 50 atmosphere is 265ºC. Compare the theoretical efficiencies of a steam engine operating between the boiling point of water at (*i*) 1 atmosphere (*ii*) 50 atmosphere, assuming the temperature of the sink to be 35ºC in each case.

**SOLUTION**

(*i*) *At 1 atmosphere :*

$T_2$ (boiling point of water) = 100ºC or 373 K

$T_1$ (temperature of sink) = 35ºC or 308 K

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{373 - 308}{373} = 0.174$$

(*ii*) *At 50 atmosphere :*

$T_2$ (boiling point of water) = 265ºC or 538 **K**

$T_1$ (temperature of sink) = 35ºC or 308 **K**

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{538 - 308}{538} = \mathbf{0.428}$$

The possible increase of efficiency is very marked.

**SOLVED PROBLEM 3.** If a Carnot engine operating between two heat reservoirs at 227ºC and 27ºC absorbs 1000 calories from the 227ºC reservoir per cycle, how much heat is discharged into the 27ºC reservoir and how much work is done per cycle ? What is the efficiency of the cycle ?

**SOLUTION**

(*a*) We know that :

$$\text{Efficiency} = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

or $$w = \frac{q_2\,(T_2 - T_1)}{T_2}$$

$$= \frac{1000\,(500 - 300)}{500}$$

$$= 400 \text{ cal}$$

∴ The work done per cycle is **400 cal**

(*b*) The heat from the high-temperature reservoir ($q_2$) minus the heat discharged into the low-temperature reservoir ($q_1$) is converted into work ($w$). Thus,

$$q_2 - q_1 = w$$

∴ $$1000 - q_1 = 400$$

or $$q_1 = 600 \text{ cal.}$$

(*c*) Efficiency :

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$= \frac{500 - 300}{500} = \frac{200}{500}$$

$$= 0.4$$

Therefore, efficiency of the engine is **0.4**

### DERIVATION OF ENTROPY FROM CARNOT CYCLE

Because processes cannot be 100% efficient, a term to describe the energy available for doing useful work becomes necessary. Although we have discussed the concept of entropy already, its classical derivation deserves attention.

In a Carnot cycle, $q_2$ has a positive value and $q_1$ has a negative value, since former is *taken up* at a higher temperature and the latter is *given out* at the lower temperature. Thus thermodynamic efficiency may be expressed as

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or $$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or $$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

or $$\frac{q_1}{T_1} = \frac{q_2}{T_2} \quad ...(i)$$

using sign convention, heat absorbed (*i.e.*, $q_2$) is given the +ve sign and heat lost (*i.e.* $q_1$) is given the – ve sign. Equation (*i*) becomes

$$+\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$

or $$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

or $$\Sigma \frac{q}{T} = 0$$

Any reversible cycle may be regarded as made up of a number of Carnot cycles. Consider, for example, the cycle represented in Fig. 9.8 by the closed curve *ABA*. Imagine a series of isothermal

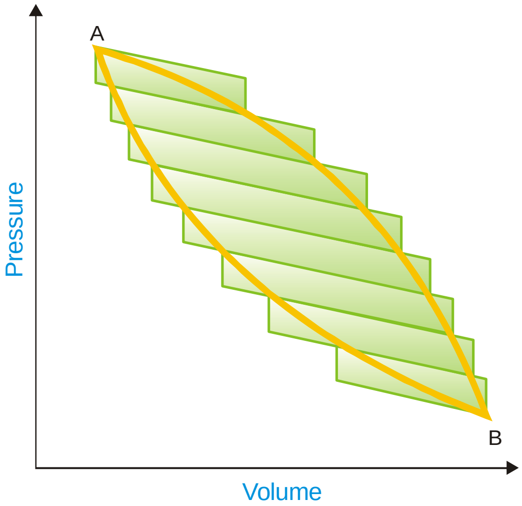


**Figure 9.8**
**Carnot cycle.**

and adiabatic curves drawn across the diagram so that a number of Carnot cycles are indicated. Starting at *A* and going through all the cycles successively from *A* to *B*, it can be shown that all paths inside the diagram cancel each other leaving only zigzag outer path. The larger the number of cycles taken in this manner, the closer will the resultant path correspond to *ABA* which represents the reversible cycle under consideration. The reversible cycle can, therefore, be regarded as being made up of an infinite number of Carnot cycles, for each of which the sum of the two *q*/*T* terms involved is zero *i.e.*,

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

For the reversible cycle *ABA* comprising a series of Carnot cycles, therefore, the above expression takes the form

$$\Sigma \frac{q}{T} = 0$$

and for an infinite number of Carnot cycles

$$\int \frac{dq}{T} = 0$$

Since the cycle is performed in two steps, *viz.*, from *A* to *B* and then back from *B* to *A*, we have:

$$\int \frac{dq}{T} = \int_A^B \frac{dq}{T} \text{ (Path I)} + \int_B^A \frac{dq}{T} \text{ (Path II)} = 0$$

$$\int_A^B \frac{dq}{T} \text{ (Path I)} = -\int_B^A \frac{dq}{T} \text{ (Path II)} = \int_A^B \frac{dq}{T} \text{ (Path II)}$$

It is evident, therefore, that both these integrals are independent of the path taken from *A* to *B*. Both depend upon the value of some function at *A* and the same function at *B*. This function is called **entropy** (*S*). Let $S_B$ be the entropy at the state *B* and $S_A$ in the state *A*. Then, the increase in entropy, Δ*S*, is given by the expression

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}$$

and for each infinitesimally small change

$$dS = \frac{dq}{T}$$

**Like $\Delta E$ and $\Delta H$, $\Delta S$ is dependent only on the state of the system and can be calculated if the substance can be brought reversibly from one state to the other.** It is independent of the path taken.

**SOLVED PROBLEM 1.** Calculate the entropy change in the evaporation of 1 mole of water at 100ºC. Latent heat of evaporation of water is 9,650 cals per mole.

**SOLUTION**

Entropy change on the evaporation of 1 mole of water is obtained by dividing the latent heat of evaporation of 1 mole of water by the absolute temperature

$$\therefore \quad \Delta S = \frac{9,650}{373} = 25.87 \text{ cal K}^{-1} \text{ mol}^{-1}$$

**SOLVED PROBLEM 2.** Calculate the increase in entropy when one gram molecular weight of ice at 0ºC melts to form water. Latent heat of fusion of ice = 80 calories.

**SOLUTION**

$$\Delta S = \frac{q}{T}$$

$$q \text{ for one mole of ice} = 80 \times 18 \text{ calories}$$

$$\text{and} \quad T = (0 + 273) = 273 \text{ K}$$

$$\therefore \quad \Delta S = \frac{80 \times 18}{273} = 5.274 \text{ cal K}^{-1} \text{ mol}^{-1}$$

## ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

The efficiency of an irreversible Carnot cycle is always less than that of a reversible one operating between the same two temperatures.

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

where $q_2$ is the heat absorbed at temperature $T_2$ and $q_1$ is the heat returned at temperature $T_1$.

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$$

In other words $\int \frac{dq}{T}$ for an irreversible cycle is always less than zero and the entropy of the final state is always greater than that of the initial state. **As most of the processes going on in nature are spontaneous and irreversible, it has been said that "the entropy of the universe always tends towards a maximum".**

## PHYSICAL SIGNIFICANCE OF ENTROPY

Entropy is a measure of disorder or randomness of a system. The entropy of the system increases if it goes from less orderly state to more orderly state and vice–versa. This concept of entropy has led to the conclusion that *all substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy*. At this state, all motion ceases. In case of a perfect crystal the entropy is zero. This is **third law of Thermodynamics.**

## ENTROPY CHANGE FOR AN IDEAL GAS

Entropy is a state function and its value depends on two of three variables $T$, $P$ and $V$.

### (*a*) *T* and *V* as Variables

Let us consider $n$ moles of an ideal gas occupying volume $V$ at pressure $P$ and temperature $T$. If the system absorbs $dq_{\text{rev}}$ heat reversibly then increase in entropy is given by

$$dS = \frac{dq_{rev}}{T} \qquad \text{...}(i)$$

According to the first law of thermodynamics

$$dq_{rev} = dE + PdV$$

Putting in equation (*i*), we get

$$dS = \frac{dE + PdV}{T} \qquad \text{...}(ii)$$

we know
$$PV = nRT$$

or
$$P = \frac{n}{V} RT$$

and
$$dE = n\,C_v\,dT \qquad \left[\because C_v = \frac{dE}{dT} \text{ for 1 mole}\right]$$

where $C_v$ is the molar heat at constant volume.

Substituting this value in equation (*ii*), we have

$$dS = \frac{n\,C_v\;dT + \left(\frac{n}{V}\,RT\right) dV}{T}$$

or
$$dS = n\,C_v \frac{dT}{T} + n\,R\frac{dV}{V}$$

Integrating between the limits $S_1, S_2$ ; $T_1, T_2$ ; and $V_1, V_2$ we get

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} n C_v \frac{dT}{T} + \int_{V_1}^{V_2} n R \frac{dV}{V}$$

or
$$\Delta S = S_2 - S_1 = n\,C_v\;1\text{n}\,\frac{T_2}{T_1} + n\,R\;1\text{n}\,\frac{V_2}{V_1} \qquad \text{...}(iii)$$

or
$$\Delta S = 2.303\,n\,C_v \log\frac{T_2}{T_1} + 2.303\,R \log\frac{V_2}{V_1} \qquad \text{...}(iv)$$

For 1 mole of an ideal gas

$$\Delta S = 2.303 C_v \log\frac{T_2}{T_1} + 2.303\;R\;\log\frac{V_2}{V_1}$$

### (*b*) *P* and *T* as Variables

Let $P_1$ be the pressure in the initial state and $P_2$ in the final state then

$$\frac{P_1\,V_1}{T_1} = \frac{P_2\,V_2}{T_2}$$

or
$$\frac{V_2}{V_1} = \frac{P_1\,T_2}{P_2\,T_1}$$

Substituting in equation (*iii*) we get

$$\begin{aligned}\Delta S &= n\,C_v\ 1\text{n}\ \frac{T_2}{T_1} + n\,R\ 1\text{n}\ \frac{P_1\,T_2}{P_2\,T_1}\\ &= n\,C_v\ 1\text{n}\ \frac{T_2}{T_1} + n\,R\ 1\text{n}\ \frac{T_2}{T_1} + n\ R\ 1\text{n}\ \frac{P_1}{P_2}\\ &= n\,(C_v + R)\ 1\text{n}\ \frac{T_2}{T_1} + n\,R\ 1\text{n}\ \frac{P_1}{P_2}\\ &= nC_P\ \text{In}\ \frac{T_2}{T_1} + n\,R\ \text{In}\ \frac{P_1}{P_2} \qquad [\because C_P = C_v + R]\end{aligned}$$

or
$$\Delta S = 2.303 \times n \times C_p \log\frac{T_2}{T_1} + 2.303 \times n \times R \log P_1/P_2 \qquad \text{...(}v\text{)}$$

For 1 mole of an ideal gas

$$\Delta S = 2.303\,C_p \log\frac{T_2}{T_1} + 2.303\,R \log\frac{P_1}{P_2}$$

From this equation entropy change can be calculated.

**Case 1.** At constant temperature for an isothermal process
In this case $T_1 = T_2$, the equation (*iv*) and (*v*) reduce to

$$\Delta S_T = 2.303 \times n \times R \log\frac{V_2}{V_1}$$

and
$$\Delta S_T = 2.303 \times n \times R \log\frac{P_1}{P_2}$$

In an isothermal expansion $V_2 > V_1$ or $P_1 > P_2$ hence $\Delta S_T$ is positive whereas in isothermal contraction $V_2 < V_1$ or $P_1 < P_2$ , $\Delta S_T$ is negative

**Case 2 :** At constant pressure (Isobaric process)
In this case $P_1 = P_2$
The equation (*iv*) reduces to

$$\Delta S_P = 2.303\,n\,C_p \log\frac{T_2}{T_1}$$

**Case 3 :** At constant volume for an isobaric process
In this case $V_1 = V_2$
The equation (*iv*) reduces to

$$\Delta S_v = 2.303 \times n \times C_v \log\frac{T_2}{T_1}$$

**SOLVED PROBLEM 1.** Calculate the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 litres to a volume of 50 litres at 303 K.

**SOLUTION.** Here $n = 2$; $V_1 = 5$ litres; $V_2 = 50$ litres

using the relation $\Delta S_T = 2.303 \times n \times R \log\dfrac{V_2}{V_1}$

on substituting the values we get

$$\begin{aligned}\Delta S_T &= 2.303 \times 2 \times 8.314 \times \log\frac{50}{5}\\ &= \mathbf{38.29\ JK^{-1}}\end{aligned}$$

**SOLVED PROBLEM 2.** Calculate the entropy change when 2 moles of an ideal gas are allowed to expand isothermally at 293 K from a pressure of 10 atmosphere to a pressure of 2 atmosphere.

**SOLUTION.** We know

$$\Delta S_T = 2.303 \times n \times R \times \log \frac{P_1}{P_2}$$

Here $n = 2;\ R = 8.314\ \text{J}$

$P_1 = 10\ \text{atm};\ P_2 = 2\ \text{atm.}$

Substituting the values we get

$$\Delta S_T = 2.303 \times 2 \times 8.314 \times \log \frac{10}{2}$$

$$= 2.303 \times 2 \times 8.314 \times 0.6990$$

$$= \mathbf{26.76\ JK^{-1}}$$

## ENTROPY CHANGE ACCOMPANYING CHANGE OF PHASE

When there is a change of state from solid to liquid or liquid to vapours or solid to vapours (melting, evaporation and sublimation respectively), there is a change in entropy. This change may be carried out at constant temperature reversibly as two phases are in equilibrium during the change.

Let us consider the process of melting of 1 mole of the substance being carried out reversibly. It would absorb molar heat of fusion at temperature equal to its melting point. The entropy change is given by

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

where $\Delta H_f$ is the Molar heat of fusion at its melting point, $T_f$ at constant pressure.

Similarly, when one mole of liquid is boiled reversibly it would absorb molar heat of vaporisation at a temperature equal to its boiling point. In this case entropy change is given by

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

where $\Delta H_v$ is Molar heat of vaporisation at its boiling point at constant pressure.

On similar lines we can calculate the change in entropy when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature. We can write

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

Where $\Delta H_t$ is the Molar heat of transition at its transition temperature $T_t$.

**SOLVED PROBLEM 1.** Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84 kJ mol$^{-1}$.

**SOLUTION.** We know

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Here $\Delta H_v = 39.84\ \text{kJ mol}^{-1}$

$= 39840\ \text{J mol}^{-1}$

$T_b = 351\ \text{K}$

$$\therefore \quad \Delta S_v = \frac{39840}{351}$$

$$= \mathbf{113.5\ JK^{-1}\ mol^{-1}}$$

**SOLVED PROBLEM 2.** 30 .4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 J mol$^{-1}$ K$^{-1}$. Calculate the melting point of sodium chloride.

**SOLUTION**

We know

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Here $\Delta S_f = 28.4 \text{ JK}^{-1} \text{ mol}^{-1}$

and $\Delta H_f = 30.4 \text{ kJ K}^{-1} \text{ mol}^{-1}$

$= 30400 \text{ JK}^{-1} \text{ mol}^{-1}$

On substitution, we get

$$T_f = \frac{\Delta H_f}{\Delta S_f} = \frac{30400}{28.4}$$

$$= \mathbf{1070.4\ K}$$

## Free Energy Function (*G*) and Work Function (*A*)

The free energy function (*G*) is defined as

$$G = H - TS$$

where *H* is the heat content or enthalpy of the system, T is its temperature and *S* its entropy. It is a single valued function of thermodynamic state of the system and is an extensive property.

Let us consider a system which undergoes a change of state from (1) to (2) at constant temperature. We have

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or $\Delta G = \Delta H - T\,\Delta\,S$

We know

$$\Delta H = \Delta E + P\Delta V$$

$\therefore$ $\Delta G = \Delta E + P\Delta V - T\Delta S$

Also $\Delta A = \Delta E - T\Delta S$

$\therefore$ $\Delta G = \Delta A + P\Delta V$ (At constant *P* & *T*)

But $P\Delta V$ represents the work done due to expansion against a constant external pressure *P*. Therefore, it is clear that the decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion. This quantity is referred to as the net work, so that

$$\text{Net work} = w - P\Delta V = -\Delta G$$

This quantity is of great importance in thermodynamics because the change in free energy is a measure of net work which may be electrical, chemical or surface work.

The work function (*A*) is defined as

$$A = E - TS$$

Where *E* is the energy content of the system, *T* its absolute temperature and *S* its entropy. Since *E*, *T* and *S* depend upon the thermodynamic state of the system only and not on its previous history, it is evident that the function *A* is also a single valued function of the state of the system.

Consider an isothermal change at temperature *T* from the initial state indicated by subscript (1) to the final state indicated by subscript (2) so that

$$A_1 = E_1 - TS_1 \qquad ...(i)$$

and $$A_2 = E_2 - TS_2 \qquad ...(ii)$$

Subtracting (*i*) from (*ii*), we have

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

$$\Delta A = \Delta E - T\Delta S \qquad ...(iii)$$

Where $\Delta A$ is the change in work function $A$, $\Delta E$ is the corresponding change in internal energy and $\Delta S$ as change in the entropy of the system.

Since $\Delta S = \frac{q_{rev}}{T}$ where $q_{\text{rev}}$ is the heat taken up when the change is carried out in a reversible manner and constant temperature, we have

$$\Delta A = \Delta E - q_{rev} \qquad ...(iv)$$

According to first law of thermodynamics

$$dE = q_{\text{rev}} - w_{\text{rev}}$$

or $$-w = \Delta E - q_{\text{rev}}$$

substituting the value in equation (*iv*), we get

$$-\Delta A = w_{\text{rev}}$$

*i.e.*, **decrease in the work function A in any process at constant temperature gives the maximum work that can be obtained from the system during any change.**

## Variation of Free Energy with Temperature and Pressure

By definition

$$G = H - TS$$

and $$H = E + PV$$

$\therefore$ $$G = E + PV - TS$$

Differentiating, we get

$$dG = dE + PdV + VdP - TdS - SdT \qquad ...(i)$$

For an infinitesimal stage of a reversible process

$$dq = dE + dw$$

and $$dS = \frac{dq}{T}$$

If the work done is restricted to work of expansion, then

$$dq = dE + PdV$$

and $$dS = dE + PdV \qquad ...(ii)$$

comparing equation (*i*) and (*ii*) we have

$$\begin{aligned} dG &= dE + PdV + VdP - dE - PdV - SdT \\ &= VdP - SdT \end{aligned}$$

If the pressure remains constant

$$dG_{\text{p}} = -SdT_{\text{p}}$$

or $$\left(\frac{dG}{dT}\right)_p = -S \qquad ...(iii)$$

But at constant temperature $dT = 0$ and we have

$$(dG)_T = VdP$$

or $$\left(\frac{dG}{dP}\right)_T = V \qquad ...(iv)$$

Equations (*iii*) and (*iv*) give the variation of free energy with temperature and pressure respectively.

## Isothermal change in Free Energy

By definition

$$G = H - TS$$

and $$H = E + PV$$

∴ $$G = E + PV - TS$$

on differentiating we get

$$dG = dE + PdV + VdP - TdS - SdT \qquad \text{... }(i)$$

and from first law of thermodynamics we have

$$dq = dE + PdV \qquad \text{...}(ii)$$

From equation (*i*) and (*ii*) we get

$$dG = dq + VdP - TdS - SdT \qquad \text{...}(iii)$$

For a reversible process

$$dS = \frac{dq}{T} \quad \text{or} \quad TdS = dq$$

Substituting this in equation (*iii*) we get

$$dG = TdS + VdP - TdS - SdT$$
$$= VdP - SdT \qquad \text{...}(iv)$$

Since the process is isothermal (there is no change in temperature) $dT = 0$, the equation (*iv*) reduces to

$$dG = VdP$$

Integrating with in the limits $G_1$ and $G_2$; $P_1$ and $P_2$, we get

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP$$

For 1 mole of the gas $PV = RT$

or $$V = \frac{RT}{P}$$

On substitution we get

$$dG = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$= RT \ 1n \frac{P_2}{P_1} \qquad \text{...}(v)$$

For *n* moles of the gas we have

$$\Delta G = nRT \ 1n \frac{P_2}{P_1} \qquad \text{...}(vi)$$

We know that $P_1 V_1 = P_2 V_2$

or $$\frac{P_2}{P_1} = \frac{V_1}{V_2}$$

From equation (*v*) we get

$$\Delta G = RT \ 1n \frac{V_1}{V_2}$$

and from equation (*vi*) we get

$$\Delta G = n\ RT\ 1n\ \frac{V_1}{V_2}$$

Changing to natural logarithms, we get

$$\Delta G = 2.303 \times nRT\ \log \frac{P_2}{P_1}$$

or
$$\Delta G = 2.303 \times nRT\ \log \frac{V_1}{V_2}$$

With the help of these equations we can calculate the change in free energy in isothermal process having an ideal gas.

**SOLVED PROBLEM 1.** Four moles of an ideal gas expand isothermally from 1 litre to 10 litres at 300 K. Calculate the change in free energy of the gas. ($R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$)

**SOLUTION**

For an isothermal process

$$\Delta G = 2.303 \times nRT\ \log \frac{V_1}{V_2}$$

Here
$V_1$ = 1 litre ; $V_2$ = 10 litres
$T$ = 300 K; $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$
$n$ = 4

Substituting the values in the formula we get

$$\begin{aligned}\Delta G &= 2.303 \times 300 \times 4 \times 8.314 \times \log \frac{1}{10}\\ &= 22976.5 \times [-1.0]\\ &= -22976.5\ \text{J}\\ &= \mathbf{-\ 22.9765\ kJ}\end{aligned}$$

**SOLVED PROBLEM 2.** Two moles of an ideal gas are allowed to expand reversibly and isothermally at 300 K from a pressure of 1 atm to a pressure of 0.1 atm. What is the change in Gibbs free energy ?

**SOLUTION.** We know for an isothermal process

$$\Delta G = 2.303 \times nRT\ \log \frac{P_2}{P_1}$$

Here
$P_1$ = 1.0 atm; $P_2$ = 0.1 atm.
$n$ = 2 moles $R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$
$T$ = 300 K

On substitution we get

$$\begin{aligned}\Delta G &= 2.303 \times 2 \times 8.314 \times 300 \times \log \frac{0.1}{1}\\ &= 11488.2 \times [-1.0]\\ &= -11488.2\ \text{J}\\ &= \mathbf{-\ 11.4882\ kJ}\end{aligned}$$

## GIBB'S HELMHOLTZ EQUATIONS

These are two equations derived by J.W. Gibbs and H.Von Helmholtz and are known as Gibbs Helmholtz equations. One equation can be expressed in terms of changes in free energy ($\Delta G$) and enthalpy ($\Delta H$), while the other can be expressed in terms of changes in internal energy ($\Delta E$) and work function ($\Delta A$). The former is generally employed and is applicable to all processes, chemical or physical, but in a closed system.

### (*a*) In Terms of Free Energy and Enthalpy

We know that

$$dG = VdP - SdT$$

At constant pressure $dP = 0$, then

$$dG = -SdT$$

Let $G_1$ be the initial free energy at temperature $T$, $G_1 + dG_1$, be the free energy at temperature $T + dT$. Then

$$dG_1 = -S_1\, dT \qquad \text{...}(i)$$

Where $S_1$ is the entropy of the system in the initial state. Now suppose the free energy of the system in the final state is $G_2$ at temperature $T$, and $G_2 + dG_2$ is the free energy at temperature $T + dT$ in the final state.

Then

$$dG_2 = -S_2\, dT \qquad \text{...}(ii)$$

where $S_2$ is the entropy of the system in the final state.

Subtracting (*i*) from (*ii*) we get

$$dG_2 - dG_1 = -(S_2 - S_1)\, dT$$

or

$$d\,(\Delta G) = -\Delta S\, dT$$

At constant pressure

$$d\left(\frac{\Delta G}{dT}\right)_p = -\Delta S \qquad \text{...}(iii)$$

We know

$$\Delta G = \Delta H - T\,\Delta S$$

or

$$-\Delta S = \frac{\Delta G - \Delta H}{T} \qquad \text{...}(iv)$$

Comparing equations (*iii*) and (*iv*)

$$\frac{\Delta G - \Delta H}{T} = d\left(\frac{\Delta G}{dT}\right)_p$$

or

$$\Delta G = \Delta H + Td\left(\frac{\Delta G}{dT}\right)_p$$

This equation is called Gibb's Helmholtz equation in terms of free energy and enthalpy change at constant pressure.

### (*b*) In terms of Internal Energy and Work Function

By definition the work function

$$A = E - TS \qquad \text{...}(i)$$

or

$$\Delta A = \Delta E - T\Delta S$$

or

$$-\Delta S = \frac{\Delta A - \Delta E}{T} \qquad \text{...}(ii)$$

Differentiating equation (*i*) we get

$$dA = dE - TdS - SdT \qquad ...(iii)$$

From the first law of thermodynamics

$$dq = dE + PdV$$

and at constant volume $dV = 0$

$$\because \qquad dq = dE$$

For a reversible change

$$dS = \frac{dq}{T}$$

$$\text{or} \qquad dq = TdS - dE \qquad ...(iv)$$

Comparing equations (*iii*) and (*iv*) we get

$$dA = -SdT$$

Let $A_1$ be the work function in its initial state at temperature $T$ and $A_1 + dA_1$ be the work function in its initial state at $T + dT$. And $A_2$ be the work function in its final state at temperature $T$ and $A_2 + dA_2$ be the work function in its final state at $T + dT$. Then

$$dA_1 = -S_1\, dT \qquad ...(v)$$

$$\text{and} \qquad dA_2 = -S_2\, dT \qquad ...(vi)$$

where $S_1$ and $S_2$ are the entropies of the system in initial and final states of the system respectively.

Subtracting equation (*v*) from equation (*vi*) we get

$$dA_2 - dA_1 = -(S_2 - S_1)\, dT$$

$$\text{or} \qquad d(\Delta A) = -\Delta S\, dT$$

At constant volume

$$d\left(\frac{\Delta A}{dT}\right)_v = -\Delta S$$

From equation (*ii*) we have

$$\frac{\Delta A - \Delta E}{T} = -\Delta S$$

On comparison we have

$$\frac{\Delta A - \Delta E}{T} = d\left(\frac{\Delta A}{dT}\right)_v$$

$$\text{or} \qquad \Delta A = \Delta E + T\, d\left(\frac{\Delta A}{dT}\right)_v$$

This equation is called Gibbs Helmholtz equation in terms of internal energy and work function at constant volume.

### Importance of Gibb's Helmholtz Equations

Gibb's Helmholtz equations are used to calculate the heats of reaction ($\Delta H$ or $\Delta E$) when $\Delta G$ or $\Delta A$ at two temperatures are given. This point is made clear in the following examples.

**SOLVED PROBLEM 1.** For the reaction

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

The values of enthalpy change and free energy change are – 68.32 and – 56.69 kcals respectively. Calculate the value of free energy change at 25ºC.

**SOLUTION.** Using the Gibb's Helmholtz equation

$$\Delta G = \Delta H + Td\left(\frac{\Delta G}{dT}\right)_{p}$$

Here $\Delta G = -56.69$ Kcal

$\Delta H = -68.32$ kcals

and $T = 273 + 25 = 298$ K

On substitution we get

$$-56.69 = -68.32 + 298\left[d\left(\frac{\Delta G}{dT}\right)_{p}\right]$$

or

$$d\left(\frac{\Delta G}{dT}\right)_{p} = \frac{-56.69 + 68.32}{298}$$

$$= 0.0390 \text{ kcal}$$

Assuming that $d\left(\frac{\Delta G}{dT}\right)_{p}$ remains constant over this temperature range. At 30ºC we can write

$$\Delta G = 68.32 + 303 \times 0.039$$

$$= -68.32 + 11.817$$

$$= \mathbf{-\ 56.503\ kcals}$$

**SOLVED PROBLEM 2.** For the following reaction

$$N_2\,(g) + 3H_2\,(g) = 2NH_3\,(g)$$

The free energy changes at 25ºC and 35ºC are – 33.089 and – 28.018 kJ respectively. Calculate the heat of reaction.

**SOLUTION.** We know

$$\Delta G = \Delta H + Td\left(\frac{\Delta G}{dT}\right)_{p}$$

Here $G_1 = -33.089$ kJ $\quad T_1 = 273 + 25 = 298$ K

$G_2 = -28.018$ kJ $\quad T_2 = 273 + 35 = 308$ K

$$\therefore \quad d\left(\frac{\Delta G}{dT}\right)_{p} = \frac{-\ 28.018 - (-33.089)}{308 - 298}$$

$$= 0.507 \text{ kJ}$$

At 35ºC $\Delta G = -28.018$ kJ

$T = 273 + 35 = 308$ K

$$\therefore \quad \Delta G = \Delta H + Td\left(\frac{\Delta G}{dT}\right)_{p}$$

$$-28.018 = \Delta H + 308 \times 0.507$$

or

$$\Delta H = 28.018 + 156.156$$

$$= \mathbf{184.174\ kJ}$$

## Conditions of Equilibrium and Criterion for a Spontaneous Process

### (*a*) In Terms of Entropy Change

The entropy of a system remains unchanged in a reversible change while it increases in an irreversible change *i.e.*

$\sum dS = 0$ For Reversible change

and $\sum dS > 0$ For Irreversible change

For a system with its surroundings we can write

$$dS_{\text{system}} + dS_{\text{surroundings}} = 0$$

and $$dS_{\text{system}} + dS_{\text{surroundings}} > 0$$

combining the two relations, we have

$$dS_{\text{system}} + dS_{\text{surroundings}} \geq 0 \qquad ...(i)$$

If we assume the change in surroundings as reversible and surroundings evolve $dq$ heat reversibly, then

$$dS_{\text{surrounding}} = -\frac{dq}{T}$$

From the first law of Thermodynamics

we know

$$dS = -\frac{dq}{T} = \frac{dE + dw}{T}$$

where $dE$ is the increase in internal energy of the system and $dw$ be the work done by the system.

From equation (*i*) we get

$$dS_{\text{system}} - \frac{dE + dw}{T} \geq 0$$

or $$TdS_{\text{system}} - dE - dw \geq 0$$

or $$TdS_{\text{system}} - dE - PdV \geq 0 \qquad ...(ii)$$

$[\because \; dw = PdV]$

**Case I**. When $E$ and $V$ are constant

In this case $dE = 0$ and $dV = 0$ the equation (*i*) reduces to

$$dS_{E.V} \geq 0$$

or $dS_{E.V} > 0$ for an irreversible change (spontaneous)

and $dS_{E.V} = 0$ for a reversible change (equilibrium)

**Case II.** When $S$ and $V$ are constant

Here $dS = 0$ and $dV = 0$

The equation (*i*) reduces to $-dE \geq 0$

or $-dE > 0$ for an irreversible change (spontaneous)

and $-dE = 0$ for a reversible change (equilibrium)

### (*b*) In Terms of Enthalpy Change

We know

$$H = E + PV$$

on differentiating

$$dH = dE + PdV + VdP$$

or $$-dE - PdV = -dH + VdP$$

Putting in equation (*ii*)

$$TdS - dH + VdP \geq 0$$

or $$dH - VdP - TdS \leq 0$$

**At constant *S* and *P***

Here $dS = 0$ and $dP = 0$

$\therefore$ we have $dH \leq 0$

or $dH < 0$ for an irreversible change (spontaneous)

and $dH = 0$ for a reversible change (equilibrium)

### (*c*) In Terms of Free Energy Change

We know

$$G = H + TS$$

or $$G = E + PV + TS \qquad [\because\ H = E + PV]$$

on differentiating we get

$$dG = dE + PdV + VdP + TdS + SdT$$

$$TdS - dE - PdV = -dG + VdP - SdT$$

Substituting in equations (*ii*) we get

$$-dG + VdP - SdT \geq 0$$

or $$dG - VdP + SdT \leq 0$$

At constant pressure in an isothermal process (*T* is also constant) this equation reduces to

$$dG \leq 0$$

or $dG < 0$ for an irreversible change (spontaneous)

and $dG = 0$ for a reversible change (equilibrium)

Thus the conditions for spontaneity and equilibrium may be summed up in the Table 9.2.

**TABLE 9.2. CONDITIONS FOR SPONTANEITY AND EQUILIBRIUM**

| Conditions | Irreversible Process (Spontaneous) | Reversible Process (Equilibrium) |
|---|---|---|
| At Constant *E*, *V* | $dS > 0$ | $dS = 0$ |
| At Constant *S*, *V* | $-dE > 0$ | $-dE = 0$ |
| At Constant *S*, *P* | $dH < 0$ | $dH = 0$ |
| At Constant *P*, *T* | $dG < 0$ | $dG = 0$ |

## THE CLAPEYRON EQUATION

A useful thermodynamic relation which gives us important information about a system consisting of any two phases of a single substance in chemical equilibrium is the Clapeyron equation. It is derived from the Gibbs-Helmholtz equation mentioned above.

Let the system studied be

$$Liquid \rightleftharpoons Vapour$$

Consider one gram mole of a liquid confined in a cylinder by a frictionless piston. Let the volume of the liquid be $V_1$ and its vapour pressure equal to $p$. Now allow the liquid to evaporate reversibly at a constant temperature $T$ and when the whole of it has vaporised, let the volume of the vapour be $V_2$.

$\therefore$ Work done during evaporation $w = p\,(V_2 - V_1)$ ...(*i*)

Differentiating equation (*i*) with respect to temperature at constant $(V_2 - V_1)$, we get,

$$\frac{dw}{dT} = (V_2 - V_1)\frac{dp}{dT} \qquad ...(ii)$$

Heat absorbed from the surroundings is the latent heat of vaporisation $L$ which on substitution in the first law equation gives us

$$\Delta E = w - L \qquad ...(iii)$$

On substitution of expressions (*ii*) and (*iii*) in the Gibbs-Helmholtz equation, we have

$$w + \Delta E = T\frac{dw}{dT}$$

$$w + (L - w) = T(V_2 - V_1)\frac{dp}{dT}$$

or

$$L = T\frac{dp}{dT}(V_2 - V_1)$$

or

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

This is the Clapeyron equation which in its general form may be written as

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_2 - V_1)} \qquad ...(1)$$

where $\Delta H$ is the heat of transition when a volume $V_1$ of a definite weight of one form changes to a volume $V_2$ of the same weight of other form at the temperature $T$.

## CLAUSIUS–CLAPEYRON EQUATION

The above equation can be simplified by neglecting the small volume of the liquid in comparison with the volume of the vapour. Equation (1) given above in such a case becomes

$$\frac{dp}{dT} = \frac{\Delta H}{TV}$$

Supposing the vapour obeys the ideal gas laws

$$V_2 = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta H\ p}{RT^2}$$

or

$$\frac{1}{p} \times \frac{dp}{dT} = \frac{\Delta H}{RT^2}$$

But

$$\frac{1}{p} \times \frac{dp}{dT} = \frac{d\ \log_e p}{dT}$$

$\therefore$

$$d\ \log_e \frac{p}{dT} = \frac{\Delta H}{RT^2} \qquad ...(2)$$

Equation (2) above is known as the **Clausius-Clapeyron equation** and though approximate is of very great value.

If $\Delta H$ is regarded as constant, we may integrate the above equation

$$d\ \log_e P = \Delta H \frac{dT}{RT^2}$$

$$\int d\ \log_e p = \frac{\Delta H}{R}\int \frac{dT}{T^2}$$

or
$$\log_e p = \frac{-\Delta H}{RT} + \text{Constant}$$

$$\log_{10} p = \frac{-\Delta H}{2.303\ RT} + C$$

If $p_1$ is the vapour pressure at $T_1$ and $p_2$ the vapour pressure at $T_2$ we have

$$\log_{10} p_1 = \frac{-\Delta H}{2.303\ RT_1} + C \qquad \text{...}(i)$$

and
$$\log_{10} p_2 = \frac{-\Delta H}{2.303\ RT_2} + C \qquad \text{...}(ii)$$

Subtracting (*i*) from (*ii*)

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H}{2.303\ R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \text{...(3)}$$

## APPLICATIONS OF CLAPEYRON-CLAUSIUS EQUATION

### (1) Calculation of Latent Heat of Vaporisation

If the vapour pressure of a liquid at two temperatures $T_1$ and $T_2$ be $p_1$ and $p_2$ respectively, the molar heat of vaporisation $\Delta H_v$ can be calculated by substituting these values in Clapeyron-Clausius equation.

**SOLVED PROBLEM.** If the vapour pressures of water at 95ºC and 100ºC are 634 and 760 mm respectively, calculate the latent heat of vaporisation per mole.

**SOLUTION**

The Clapeyron Clausius equation states that

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_v}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

In this case, we have :

$p_1$ = 634 mm
$p_2$ = 760 mm
$T_1$ = 273 + 95 = 368 K
$T_2$ = 273 + 100 = 373 K
$R$ = 1.987 cal
$\Delta H_v$ = ?

Substituting the above values in the Clapeyron-Clausius equation, we have :

$$\log \frac{760}{634} = \frac{\Delta H_v}{2.303\ R}\left[\frac{1}{368} - \frac{1}{373}\right]$$

∴
$$\Delta H_v = \mathbf{9886\ cal\ mol^{-1}}$$

In a similar manner, if the vapour pressures at two different temperatures of a solid in equilibrium with its liquid phase are known, the **latent heat of fusion** can be calculated.

### (2) Calculation of Boiling Point or Freezing Point

If the freezing point or the boiling point of a liquid at one pressure is known, it is possible to calculate it at another pressure by the use of the Clapeyron-Clausius equation.

**SOLVED PROBLEM.** At what temperature will water boil under a pressure of 787 mm? The latent heat of vaporisation is 536 cals per gram.

**SOLUTION**

The data is follows

$$p_1 = 760\,\text{mm} \qquad T_1 = 373\,\text{K}$$
$$p_2 = 787\,\text{mm} \qquad T_2 = ?$$
$$\Delta H_v = 536 \times 18\ \text{cal mol}^{-1}$$

According to Clapeyron-Clausius equation, we have :

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_v}{4.576}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Substituting the above values, we have :

$$\log_{10} \frac{787}{760} = \frac{536 \times 18}{4.576}\left[\frac{T_2 - 373}{373\ T_2}\right]$$

$$T_2 = \mathbf{374\ K}$$

∴ Water will boil at 101ºC under a pressure of 787 mm.

### (3) Calculation of Vapour Pressure at Another Temperature

If the mean heat of vaporisation is available, it is possible to calculate the vapour pressure of a liquid at given temperature if the vapour pressure at another temperature is known.

**SOLVED PROBLEM.** Calculate the vapour pressure of water at 90.0ºC if its value at 100.0ºC is 76.0cm. The mean heat of vaporisation of water in the temperature range 90º and 100ºC is 542 calories per gram.

**SOLUTION**

In this problem, we have :

$$\Delta H_v = 542 \times 18\ \text{cal per mole}$$
$$p_2 = ?$$
$$p_1 = 76.0\ \text{cm}$$
$$T_2 = 90 + 273 = 363\ \text{K}$$
$$T_1 = 100 + 273 = 373\ \text{K}$$

Using the Clapeyron-Clausius equation we have :

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_v}{4.576}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

or
$$\log_{10} \frac{p_2}{76} = \frac{542 \times 18}{4.576}\left[\frac{363 - 373}{363 \times 373}\right]$$

∴
$$p_2 = \mathbf{52.88\ cm} \ \text{ or } \ \mathbf{528.8\ mm}$$

### (4) Calculation of Molal Elevation Constant

The molal elevation constant ($K_b$) of a solvent is defined **as the elevation in boiling point which may theoretically be produced when one mole of any solute is dissolved in 1000 g of the solvent.** Accordingly, if $w$ $g$ of a solute of molecular weight $M$ is dissolved in 1000 $g$ of the solvent and $\Delta T$ is the elevation produced, the molal elevation $K_b$ is given by the equation

$$K_b = \frac{M\ \Delta T}{w}$$

Let the boiling point of the pure solvent be $T$ and that of the solvent $(T + \Delta T)$ when the atmospheric pressure is $p_1$. While $p_1$ is the vapour pressure of the solution at $(T + \Delta T)$ and is also the vapour pressure of the solvent at T, $p_2$ the vapour pressure of the solvent at $(T + \Delta T)$ can be calculated by the application of Clapeyron-Clausius equation.

$$\log_e \frac{p_2}{p_1} = \frac{L}{R}\left[\frac{1}{T} - \frac{1}{(T + \Delta T)}\right]$$

$$= \frac{L}{R}\left[\frac{\Delta T}{T\ (T + \Delta T)}\right]$$

$$= \frac{L}{R} \times \frac{\Delta T}{T^2} \text{ when } \Delta T \text{ is very small.}$$

Now $\log_e \frac{p_2}{p_1} = \log_e \left(1 + \frac{p_2 - p_1}{p_1}\right) = \frac{p_2 - p_1}{p_1}$ since $(p_2 - p_1)$ is very small and the remainder of the terms can be neglected.

According to Raoult's law, the relative lowering of vapour pressure in a dilute solute is equal to the molar fraction of the solute in solution

$$\therefore \qquad \frac{p_2 - p_1}{p_2} = \frac{n}{N}$$

When the difference between $p_2$ and $p_1$ is very small as has just been supposed, $\frac{p_2 - p_1}{p_2}$ may be taken equal to $\frac{p_2 - p_1}{p_1}$.

$$\therefore \qquad \frac{p_2 - p_1}{p_2} = \frac{n}{N} = \frac{L\ \Delta T}{RT^2}$$

$$\text{or} \qquad \Delta T = \frac{RT^2}{L} \times \frac{n}{N}$$

$$\text{But} \qquad n = \frac{w}{m} \text{ and } N = \frac{W}{M}$$

$$\therefore \qquad \Delta T = \frac{RT^2}{L} \times \frac{wM}{mW}$$

If 1 mole of the solute is dissolved in 1000 $g$ of the solvent, the above equation becomes :

$$\Delta T = \frac{RT^2}{L \times 1000}$$

$$\text{But} \qquad K_b = \frac{M\ \Delta T}{w}$$

$$\therefore \qquad K_b = \frac{M\ RT^2}{L \times 1000}$$

But $\frac{\text{L}}{\text{M}} = l$, the latent heat of vaporisation per gram of the solvent.

$$\therefore \qquad K_b = \frac{RT^2}{1000\,l}$$

Putting $R = 2$ gm cals, we have

$$K_b = \frac{0.002\,T^2}{l}$$

**SOLVED PROBLEM.** The heat of vaporisation of 1 *g* of carbon disulphide is 86.72 calories and the boiling point is 46ºC. Calculate the molal elevation constant.

**SOLUTION**

The molal elevation constant of a solvent is given by the expression

$$K_b = \frac{0.002\,T^2}{l}$$

Here $T = 273 + 46 = 319\text{ K}$

$l = 86.72$ cal

$$\therefore \qquad K_b = \frac{0.002 \times 319 \times 319}{86.72}$$

$$= \mathbf{2.34^\circ} \textbf{ per 1000 } \boldsymbol{g} \textbf{ of carbon disulphide}$$

### (5) Calculation of Molal Depression Constant

By an exactly similar reasoning, we can calculate the molal depression constant of a solvent as

$$K_f = \frac{RT^2}{1000\,l_f}$$

where $l_f$ is the latent heat of fusion per gram of the solvent,

$$\text{or} \qquad K_f = \frac{0.002\,T^2}{l_f}$$

**SOLVED PROBLEM.** The latent heat of fusion of ice per gram is 80 calories and the freezing point of water is 0ºC. Calculate the molal depression constant of water.

**SOLUTION**

The molal depression constant of a solvent is given by the expression

$$K_f = \frac{0.002\,T^2}{l_f}$$

In this problem :

$T = 0 + 273 = 273\text{ K}$

$l_f = 80$ cal

$$\therefore \qquad K_f = \frac{0.002 \times 273 \times 273}{80}$$

$$= \mathbf{1.86^\circ}$$

## FREE ENERGY AND WORK FUNCTIONS

Besides heat content (*H*), internal energy (*E*) and entropy (*S*), there are two other thermodynamic functions depending upon the state of the system which utilize *E*, *H* or *S* in their derivation and are more convenient for use. These are **Work** and **Free energy functions** represented by $A$ and $G$ respectively.

### The Work Function

The work function ($A$) is defined by

$$A = E - TS$$

where $E$ is the energy content of the system, $T$ is its absolute temperature and $S$ its entropy. Since $E$, $T$ and $S$ depend upon the thermodynamic state of the system only and not on its previous history, it is evident that the function $A$ is also a single valued function of the state of the system.

Consider an isothermal change at temperature $T$ from the initial state indicated by subscript 1 to the final state indicated by subscript 2, so that

$$A_1 = E_1 - TS_1 \qquad \text{...(1)}$$

and

$$A_2 = E_2 - TS_2 \qquad \text{...(2)}$$

Subtracting (1) from (2), we have :

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

or

$$\Delta A = \Delta E - T\Delta S \qquad \text{...(3)}$$

where $\Delta A$ is the increase in function $A$, $\Delta E$ is the corresponding increase in internal energy and $\Delta S$ is the increase in the entropy of the system.

Since $\Delta S = q_{\text{rev}}/\text{T}$ where $q_{\text{rev}}$ is the heat taken up when the change is carried out in a reversible manner at a constant temperature, we have :

$$\Delta A = \Delta E - q_{rev} \qquad \text{...(4)}$$

According to the first law of thermodynamics, $\Delta E = (q_{rev} - w_{rev})$

or

$$-w_{rev} = \Delta E - q_{rev} \qquad \text{...(5)}$$

Substituting this value in equation (4), we get

$$-\Delta A = w_{rev}$$

*i.e.*, **decrease in the work function $A$ in any process at constant temperature gives the maximum work that can be obtained from the system during any change.**

### VAN'T HOFF ISOTHERM

The van't Hoff isotherm gives the net work that can be obtained from a gaseous reactant at constant temperature when both the reactants and the products are at suitable arbitrary pressures. It can be derived by using the "equilibrium box" which is a theoretical device with the supposition that of its four walls, one is permeable to $A$, the second to $B$, the third to $C$ and the fourth to $D$ when the gaseous reaction to be considered is

$$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D}$$

Let the initial pressures of $A$ and $B$ be $p_\text{a}$ and $p_\text{b}$ and the final pressure of $C$ and $D$ be $p_\text{c}$ and $p_\text{d}$ respectively and let the equilibrium pressure of the four be $P_\text{A}$, $P_\text{B}$, $P_\text{C}$ and $P_\text{D}$ respectively.

The following theoretical operations may be performed :

(*i*) Change the pressure on $A$ from the initial pressure $p_\text{a}$ to the equilibrium pressure $P_\text{A}$.

$$\therefore \quad \text{Work done by the gas} = RT \ 1\text{n} \frac{p_a}{P_A}$$

(*ii*) Change the pressure on B from $p_\text{b}$ to $P_\text{B}$.

$$\therefore \quad \text{Work done by the gas} = RT \ 1\text{n} \frac{p_b}{P_\text{B}}$$

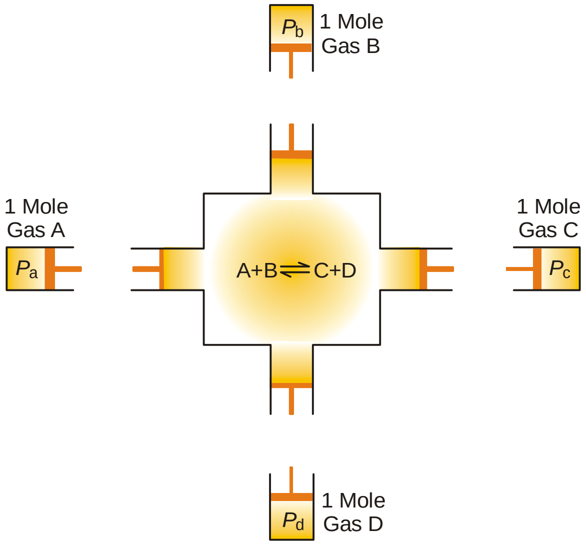


**Figure 9.9**
**van't Hoff equilibrium box.**

(*iii*) Introduce 1 gm mole of *A* and 1 gm mole of the gas *B* through their respective semipermeable membranes into the equilibrium box which contains the reactants and the products at the equilibrium pressure. This will not involve any work as the partial pressures of *A* and *B* inside the box are equal to the pressure of the gases coming in. *A* and *B* react to form 1 gm mole of *C* and 1 gm mole of *D*.

(*iv*) Withdraw 1 gm mole of *C* and 1 gm mole of *D* from the equilibrium box through their respective semipermeable walls. No work is done in this process as the gases come out at the equilibrium pressure $P_C$ and $P_D$.

(*v*) Now alter the pressure on the gas from the equilibrium pressure $P_C$ and $P_D$ to the final pressure $p_c$ and $p_d$.

$$\text{Work done by the gas } C = RT \ 1\text{n} \frac{P_C}{p_c}$$

$$\text{Work done by the gas } D = RT \ 1\text{n} \frac{P_D}{p_d}$$

As the change in free energy is equal to the total work done by the gases :

$$-\Delta G = RT \ 1\text{n} \frac{P_C \times P_D}{P_A \times P_B} - RT \ 1\text{n} \frac{p_c \times p_d}{p_a \times p_b}$$

$$= RT \ 1\text{n} \ K_p - RT \ 1\text{n} \frac{p_c \times p_d}{p_a \times p_b}$$

If the reaction is started with reactants at a partial pressure of 1 atmosphere and the resulting products are also at 1 atmosphere pressure we have,

$$-\Delta G = RT \, 1\text{n} \, K_p - RT \, 1\text{n} \, 1$$

or $$-\Delta G = RT \, 1\text{n} \, K_p$$

*i.e.*, the net work of the reaction is equal to the decrease in free energy of the system and is given by the expression, **RT 1n** $\mathbf{K_p}$ or **2.303 RT log** $\mathbf{K_p}$**.**

It will be observed that $\Delta G$ is + ve when $K_p$ is less than unity. It is – ve when $K_p$ is greater than one and is zero when $K_p = 1$.

## VAN'T HOFF ISOCHORE

The van't Hoff Isochore is obtained by combining the van't Hoff Isotherm with the Gibbs Helmholtz equation.

$$\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_{\mathrm{p}}$$

or

$$-\Delta H = T\left[\frac{d(\Delta G)}{dT}\right]_{\mathrm{p}} - \Delta G$$

Dividing both sides by $T^2$ gives

$$-\frac{\Delta H}{T^2} = \frac{T\left[d\left(\frac{\Delta G}{dT}\right)\right]_{\mathrm{p}} - \Delta G}{T^2}$$

The right-hand side of the above expression is obtained by differentiating $\Delta G/T$ w.r.t. $T$ at constant pressure

i.e.,

$$\left[\frac{d(\Delta G/T)}{dT}\right]_{\mathrm{p}} = -\frac{T\left[\frac{d(\Delta G)}{dT}\right]_{\mathrm{p}}}{T^2} - \Delta G$$

$\therefore$

$$-\frac{\Delta H}{T^2} = \left[\frac{d\ (\Delta G/T)}{dT}\right]_{\mathrm{p}} \qquad ...(i)$$

According to van't Hoff isotherm,

$$-\Delta G = RT\ 1\mathrm{n}\ K_{\mathrm{p}} \qquad ...(ii)$$

combining this with equation (*i*), we have

$$\frac{\Delta H}{T^2} = \frac{Rd\ (1\mathrm{n}\ K_p)}{dT}$$

$$\frac{\Delta H}{RT^2} = \frac{d(1\mathrm{n}\ K_p)}{dT}$$

The above equation is known as van't Hoff Isochore.

For applying the Isochore to any particular reaction, it is essential to integrate it. If $\Delta H$ remains constant over a range of temperature, we have on integration

$$1\mathrm{n}\ K_{\mathrm{p}} = \int \frac{\Delta H}{RT^2}\, dT$$

$$= \frac{-\Delta H}{RT} + Constant$$

Applying the limits $T_1$ and $T_2$ at which the equilibrium constants are $K_{p_1}$ and $K_{p_2}$ respectively, we have

$$1\mathrm{n}\ K_{\mathrm{p}_2} - 1\mathrm{n}\ K_{\mathrm{p}_1} = -\frac{\Delta H}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$1\mathrm{n}\ K_{\mathrm{p}_2} - 1\mathrm{n}\ K_{\mathrm{p}_1} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$1\mathrm{n}\ \frac{K_{\mathrm{p}_2}}{K_{\mathrm{p}_1}} = \frac{\Delta H}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

or $$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Knowing the equilibrium constant at two different temperatures it is possible, therefore, to calculate the change in heat content.

**SOLVED PROBLEM.** The equilibrium constant $K_p$ for a reaction

$A + B \rightleftharpoons C + D$ is $10^{-12}$ at 327ºC and $10^{-7}$ at 427ºC. Calculate the enthalpy of the reaction.

($R = 8.314$ JK⁻ mol⁻)

**SOLUTION**

Applying van't Hoff's equation

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303\, R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Here
$$K_{p_2} = 10^{-7}\,;\ T_2 = 427 + 273 = 700\text{ K}$$
$$K_{p_1} = 10^{-12}\,;\ T_1 = 327 + 273 = 600\text{ K}$$
$$R = 8.314\text{ JK}^{-1}\text{ mol}^{-1}$$

On substitution we get

$$\log \frac{10^{-7}}{10^{-12}} = \frac{\Delta H}{2.303 \times 8.314}\left[\frac{700 - 600}{700 \times 600}\right]$$

$$\Delta H = \log 10^5 \times \frac{2.303 \times 8.314 \times 700 \times 600}{100}$$

$$= 402089.98\text{ J}$$

$$= \mathbf{402.08998\ kJ}$$

## FUGACITY AND ACTIVITY

It has already been pointed out that equation $\Delta G = RT \log_e P_2/P_1$ is applicable only to ideal gases. When applied to real gases, particularly at higher pressures, it is found that this expression does not reproduce the change in free energy, the reason being that under these conditions $V$ is not equal to $nRT/P$. In order to apply this equation to non-ideal systems, Lewis introduced two new thermodynamic quantities, **fugacity** and **activity.**

Consider a system composed of liquid water and its vapour. Liquid water has a tendency to escape into the vapour phase while the vapour tends to escape the gaseous state and come into the liquid phase by condensation. When the system is in equilibrium, these two escaping tendencies become equal and we observe a constant vapour pressure at a constant temperature. In general, **it may be stated that each substance in a given state has a tendency to escape from that state and this escaping tendency denoted by f is called fugacity.** It is related to the free energy content ($G$) by the expression

$$G = RT\, 1\text{n}\, f + B$$

where $B$ is a constant depending upon the temperature and the nature of the substance. It is not possible to evaluate $B$ since the absolute values of the free energy are not known. To circumvent this difficulty, all free energy measurements for any given substance are referred to as standard reference point. If we represent by $G^o$ the free energy per mole and $f^o$ the fugacity in this standard state, then $G^o$ is given by

$$G^o = RT\, 1\text{n}\, f^o + B$$

If $G$ is the free energy of the substance in any state, then the free energy difference between this state and the standard state is given by

$$G - G^{o} = RT\,1n\,f/f^{o}$$

or
$$G = G^{o} + RT\,1n\,f/f^{o} \qquad ...(i)$$

The ratio $f/f^{o}$ is called **activity** and is denoted by the symbol $a$. The activity of any substance may therefore, be defined as the *ratio of fugacity of the substance in the given state to the fugacity of the same substance in the standard state*.

$$G = G^{o} + RT\,1n\,a$$

In the standard state, $G = G^{o}$ $\quad\therefore\quad RT\,1n\,a = 0$ or $a = 1$

*i.e.*, in the standard state the activity of a substance is equal to unity. In any other state the value of activity will depend upon the difference $(G - G^{o})$. The difference in free energy per mole caused on passing from one state in which the free energy is $G_1$ and the activity $a_1$ to another state in which these are $G_2$ and $a_2$ respectively, is given by the expression

$$\Delta G = G_2 - G_1 = (G^{o} + RT\,1n\,a_2) - (G^{o} + RT\,1n\,a_1)$$

or
$$\Delta G = RT\,1n\,\frac{a_2}{a_1}$$

The similarity between the above equation and equation

$$\Delta G = RT\,1n\,P_2/P_1$$

suggests that **activity is the thermodynamic counterpart of the gas pressure.**

For the standard state of any gas at the given temperature, the fugacity is taken as equal to unity, *viz*, $f^{o} = 1$ and on the basis of this definition the activity of any gas becomes equal to fugacity

$$a = \frac{f}{f^{o}} = \frac{f}{1} = f$$

The equation (*i*) can, therefore, be written as

$$G = G^{o} + RT\log_e f$$

For an *ideal gas* the fugacity is equal to pressure and $f/\mathrm{P} = 1$. For a *real gas*, the fugacity is not equal to $P$ and the ratio $f/P$ varies. It is observed, however, that on decreasing the pressure, the behaviour of the gas approaches that of an ideal gas. It may be stated, therefore, that $f$ approaches $P$ as $P$ approaches zero

*i.e.*,
$$\lim_{p \to 0} \frac{f}{P} = 1$$

or
$$\frac{f}{P} \to 1 \quad \text{as} \quad P \to 0$$

The ratio $f/P$ is called **activity coefficient** of a gas and is represented by the symbol $\gamma$. It gives a direct measure of the extent to which any gas deviates from ideal behaviour at any given pressure and temperature for the farther this ratio is from unity, the greater is the non-ideality of the gas.

## CHEMICAL POTENTIAL

### Partial Molar Properties

We have so far studied the thermodynamic systems in which there was a change in thermodynamic properties with the variation of one or more state variables. In such systems there was no transfer of mass taking place (closed systems). For studying the systems containing two or more phases or components G.N. Lewis introduced the concept of **partial molar properties** as in these cases both mass and composition vary (open systems). Consider any extensive thermodynamic property $X$ of such a system, the value of which is determined by the temperature, pressure and the amounts of various constituents present. Let the system consist of J constituents and let $n_1, n_2, n_3 \ldots. n_j$ be the number of moles of the various constituents present. Evidently $X$ must be a function of $P$, $T$ and the number of moles of various constituents present, *i.e.*

$$X = f(T, P, n_1, n_2, n_3 \ldots. n_j) \qquad ...(1)$$

If there is a small change in the temperature and pressure of the system as well as the amounts of its constituents, the change in the property $X$ is given by

$$dX = \left(\frac{\delta X}{\delta T}\right)_P \underset{n_1, n_2 .....n_j}{dT} + \left(\frac{\delta X}{\delta p}\right)_T \underset{n_1, n_2 .....n_j}{dp} + \left(\frac{dX}{\delta n}\right)_{T,P} \underset{n_2 .....n_j}{dn_1}$$

$$+ \left(\frac{\delta X}{\delta n_2}\right)_{T,P} \underset{n_1, n_3 .....n_j}{dn_2} + \left(\frac{\delta X}{\delta n_3}\right)_{T,P} \underset{n_1, n_2 .....n_j}{dn_3} + ..... +$$

$$\left(\frac{\delta X}{\delta n_j}\right)_{T,P} \underset{n_1, n_2 .....}{dn_j} \qquad ...(ii)$$

The quantity $\left(\frac{\delta X}{\delta n_1}\right)_{T,P,n_2 .....n_j}$ is called partial molar property for the constituent 1. It is represented by writing a bar over its symbol for the particular property i.e. $\overline{X}$ so that

$$\overline{X}_1 = \left(\frac{\delta X}{\delta n_1}\right)_{T,P,n_2 ....n_j} \quad ; \quad \overline{X}_2 = \left(\frac{\delta X}{\delta n_2}\right)_{T,P,n_1,n_3 ....n_j}$$

The equation (*ii*) may be written as :

$$dX = \left(\frac{\delta X}{\delta T}\right)_{P,} \underset{n_1,n_2 .....n_j}{dT} + \overline{X} = \left(\frac{\delta X}{\delta P}\right)_{T,} \underset{n_1,n_2 .....n_j}{dP}$$

$$+ \overline{X}_1 \, dn_1 + \overline{X}_2 \, dn_2 + \overline{X}_3 \, dn_3 + .....\overline{X}_j \, dn_j$$

If the temperature and the pressure of the system are kept constant $dT$ and $dP$ are zero so that

$$dX = \overline{X}_1 \, dn_1 + \overline{X}_2 \, dn_2 + .....\overline{X}_j \, dn_j \qquad ...(iii)$$

and this on integration for a system of definite composition represented by the number of moles $n_1$, $n_2$ ..... $n_j$ gives

$$X = n_1 \overline{X}_1 + n_2 \overline{X} + n_3 \overline{X}_3 + .....n_j \overline{X}_j \qquad ...(iv)$$

*i.e.*, the partial molal property $\overline{X}$ of any constituent may be regarded as the contribution of 1 mole of that constituent to the total value of the property of the system under specified conditions.

### Partial Molar Free Energy : Chemical Potential

If the extensive property under study is free energy ($G$), $\overline{G}$ will represent the partial molar free energy so that

$$\overline{G}_1 = \left(\frac{\delta G}{\delta n_1}\right)_{T,P,n_2 n_3 .....n_j} \quad \text{and } \overline{G}_j = \left(\frac{\delta G}{\delta n_j}\right)_{T,P,n_1 n_2 .....n_{j-1}}$$

This quantity is, for most purposes, identical with the function known as **chemical potential** represented by the symbol μ. Accordingly we have

$$\mu_1 = \overline{G}_1 = \left(\frac{\delta G}{\delta n_1}\right)_{T,P,n_2 .....n_j}$$

Thus, it is the partial derivative of the free energy with $n_i$ when all other variables are kept constant.

### Physical Significance of Chemical Potential

By definition the chemical potential of a given substance is the change in free energy of the system produced on addition of one mole of the substance at constant temperature and pressure to a large bulk of the mixture so that its composition does not undergo any change. It is an intensive property and it may be regarded as the force which drives the chemical system to equilibrium. At equilibrium the chemical potential of the substance in the system must have the same value through the system. In other words, the matter flows spontaneously from a region of high chemical potential to low chemical potential. The chemical potential may also be regarded as the escaping tendency of that system. Greater the chemical potential of a system greater will be its escaping tendency.

### Gibbs Duhem Equation

It has already been discussed that free energy $G$ is an intensive thermodynamic property. It can be determined by fixing the variables $T$, $P$ and number of moles of various constituents (composition of the mixture under study). Mathematically, we can write.

$$G = f\,(T, P, n_1, n_2 \,.....\, n_j) \qquad ...(i)$$

where $n_1, n_2 \,.......\, n_j$ are the number of moles of various constituents.

Differentiating equation (i), we get

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1, n_2 .....n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1, n_2 .....n_j} dP \ +$$

$$\left(\frac{\delta G}{\delta n_1}\right)_{T, P,\ n_2 .....n_j} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T, P,\ n_1 .....n_j} dn_2 + \left(\frac{\delta G}{\delta n_j}\right)_{T_1, P,\ n_1 .....n_{j-1}} dn_j$$

We know the chemical potential is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T, P, n_1, n_2 .....} = \bar{G}_1$$

Substituting in equation (*ii*) we get

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1, n_2 .....n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1, n_2 .....n_j} dP + \mu_1\, dn_1, + \mu_2\, dn_2, + .... + \mu_j\, dn_j \qquad ...(iii)$$

For a closed system there is no change in the composition and equation (*iii*) reduces to

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1, n_2 .....n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1, n_2 .....n_j} dP \qquad ...(iv)$$

But we know

$$dG = -\,SdT + VdP \qquad ...(v)$$

$$[\because \quad G = H - TS$$

$$H = E + PV$$

and $$G = dE + PdV + VdP - TdS - SdT]$$

comparing equation (*iv*) and (*v*)

$$\left(\frac{\delta G}{\delta T}\right)_{P, n_1 n_2 ....n_j} = -\,S$$

and $$\left(\frac{\delta G}{\delta T}\right)_{T, n_1 n_2 ....n_j} = -\,V$$

Putting these values in equation (*iii*) we get

$$dG = -\,SdT + VdP + \mu_1\, dn_1 + \mu_2\, dn_2 + \,.....\, \mu_j\, dn_j \qquad ...(vi)$$

At constant temperature and pressure equation (*vi*) reduces to

$$(dG)_{T.P} = \mu_1\, dn_1 + \mu_2\, dn_2 + \,.....\, \mu_j\, dn_j \qquad ...(vii)$$

Integrating equation (*vii*) we get the following for a system of definite composition

$$(G)_{T.P} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots\ldots \mu_j n_j \qquad \ldots(viii)$$

Differentiating equation (*viii*) we get

$$(dG)_{T.P} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots\ldots \mu_j dn_j + n_j d\mu_j \qquad \ldots(ix)$$

Comparing equation (*vii*) and (*ix*) we get

$$n_1 d\,\mu_1 + n_2 d\,\mu_2 + \ldots\ldots n_j d\,\mu_j = 0$$

or

$$\Sigma\, n_j d\,\mu_j = 0 \qquad \ldots(x)$$

Equation (*x*) is called Gibbs Duhem equation. It is applicable to a system at constant temperature and pressure.

## Variation of Chemical Potential with Temperature and Pressure

### (*a*) With Temperature

We know that chemical potential of a constituent *i* in a system is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1\ldots.n_j} = \bar{G}_i \qquad \ldots(i)$$

Differentiating equation (*i*) w.r.t. *T* at constant pressure *P*, we get

$$\left(\frac{\delta \mu_i}{\delta T}\right)_{P,n_1 n_2\ldots.n_j} = \frac{\delta^2 G}{\delta n_i \delta T} \qquad \ldots(ii)$$

We also know that

$$\left(\frac{\delta G}{\delta T}\right)_{P,n_1 n_2\ldots.n_j} = S \qquad \ldots(iii)$$

Differentiating equation (*iii*) w.r.t. $n_j$ at constant temperature and pressure.

$$-\left(\frac{\delta S}{\delta n_i}\right)_{T,P,n_1\ldots.n_j} = \frac{\delta^2 G}{\delta T \delta n_i} \qquad \ldots(iv)$$

Comparing equation (*ii*) and (*iv*), we have

$$\left(\frac{\delta \mu_i}{\delta T}\right)_{P,n_1 n_2\ldots.n_j} = \left(\frac{\delta S}{\delta n_i}\right)_{T,P,n_1\ldots.n_j} = \bar{S}_i$$

[By definition of Partial Molal Property]

Thus

$$\left(\frac{\delta \mu_i}{\delta T}\right)_{P,n_1 n_2\ldots.n_j} = \bar{S}_i = \text{Partial Molal Entropy}$$

This equation gives the variation of chemical potential of any constituent *i* with temperature.

### (*b*) With Pressure

By definition, chemical potential is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1\ldots.n_j} = \bar{G}_i \qquad \ldots(i)$$

Differentiating equation (*i*) w.r.t. pressure at constant temperature

$$\left(\frac{\delta \mu_i}{\delta P}\right)_{T,n_1 n_2\ldots.n_j} = \frac{\delta^2 G}{\delta n_i \delta P} \qquad \ldots(ii)$$

But we know that

$$\left(\frac{\delta G}{\delta P}\right)_{T, n_1 n_2 .... n_j} = V \qquad ...(iii)$$

Differentiating equation (*iii*) w.r.t. $n_i$ at constant $T$, $P$ and $n_j$

$$\left(\frac{\delta V}{\delta n_i}\right)_{T, P, n_1 n_2 .... n_j} = \frac{\delta^2 G}{\delta P\,\delta n_i} = \bar{V}_i \qquad ...(iv)$$

(By definition of Partial Molal Property)

Comparing equations (*ii*) and (*iv*)

$$\left(\frac{\delta \mu_i}{\delta P}\right)_{T, n_1 n_2 .... n_j} = \bar{V}_i = \text{Partial Molal Volume} \qquad ...(v)$$

Equation (*v*) gives the variation of Chemical potential of any constituent *i* with pressure. From this equation we can define the partial molar volume of a constituent *i* as the rate of change of chemical potential of a constituent *i* with pressure at constant temperature.

## TIME'S ARROW

The Second Law of Thermodynamics provides a definition of time's arrow. The law states that the entropy (usually) increases. And the increase occurs in time.

Imagine that we make a videotape of a "break" in a game of pool. We see 15 colored balls in a triangular configuration and a white ball coming in and breaking them up; the balls scatter in all directions.

If we run the videotape backwards we know immediately that this is (probably) not the correct direction for time.

If we reduce the number of billiard balls to, say, two, then a videotape of one ball colliding with another is just a possible as the tape running backwards. Here we see another manifestation of the fact that the determination of the direction of time from thermodynamics depends on having lots of objects in the system.

Another example is the relation between the scale of a physical system and the "correct" direction of time is milk swirling in water. A *RealMedia* video of this is available here. File size is 530k.

Thus the Second Law provides a definition of the direction of time. We know of two other definitions:

Expansion of the universe. Since the universe is expanding it is bigger today than it was yesterday.

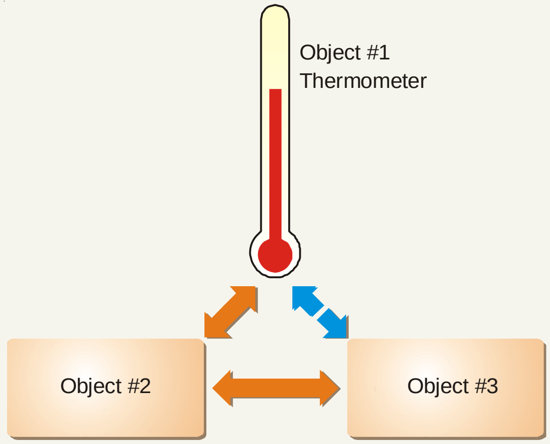
Consciousness. We remember yesterday but not tomorrow (at least in the usual case).

## ZEROTH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics is a generalized statement about bodies in contact at thermal equilibrium and is the basis for the concept of temperature. The most common definition of the zeroth law of thermodynamics is: **If two thermodynamic systems are in thermal equilibrium with a third,** they are also in thermal equilibrium with each other.

The term zeroth law was coined by Ralph H. Fowler. In many ways, the law is more fundamental than any of the others. However, the need to state it explicitly as a law was not perceived until the first third of the 20th century, long after the first three laws were already widely in use and named as such, hence the zero numbering. There is still some discussion about its status in relation to the other three laws.

## THERMODYNAMIC EQUILIBRIUM (ZEROTH LAW)



When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

Objects in thermodynamic equilibrium have the same temperature.

**A system in thermal equilibrium is a system whose macroscopic properties** (like pressure, temperature, volume, etc.) are not changing in time. A hot cup of coffee sitting on a kitchen table is not at equilibrium with its surroundings because it is cooling off and decreasing in temperature. Once its temperature stops decreasing, it will be at room temperature, and it will be in thermal equilibrium with its surroundings.

Two systems are said to be in thermal equilibrium when (*a*) both of the systems are in a state of equilibrium, and (*b*) they remain so when they are brought into contact, where 'contact' is meant to imply the possibility of exchanging heat, but not work or particles. And more generally, two systems can be in thermal equilibrium without thermal contact if one can be certain that *if they were* thermally connected, their properties would not change in time. Thus, thermal equilibrium is a relation between thermodynamical systems. Mathematically, the zeroth law expresses that this relation is an equivalence relation.

## EXAMINATION QUESTIONS

**1.** Define or explain the following terms :

| | | | |
|---|---|---|---|
| (*a*) | Entropy | (*b*) | Second law of thermodynamics |
| (*c*) | Carnot cycle | (*d*) | Third law of thermodynamics |
| (*e*) | Gibbs free energy | (*f*) | Gibbs Helmholtz equation |
| (*g*) | Spontaneous reactions | (*h*) | Clausius clapeyron equation |
| (*i*) | van't Hoff isotherm | | |

**2.** (*a*) Derive the concept of entropy from the Second law of Thermodynamics. Show that entropy is a state function.

(*b*) What is the change in entropy when 1 mole of helium gas is heated from 200 K to 400 K at constant pressure? (Given : $C_p$ for helium = 5.0 cal per degree per mole)

**Answer.** 3.466 cal/K

**3.** (*a*) Derive an expression for entropy change for ideal gas associated with temperature and pressure changes.

(*b*) Calculate the total entropy change when 5 grams of ice at 0°C is converted into steam at 100°C. (Latent heat of evaporation of water = 540 cals/g; $C_p$ for water = 18 cals/moles; Latent heat of water = 80 cal/mole)

**Answer.** (*b*) 10.265 cal/degree

**4.** Calculate the work performed when two gram of hydrogen gas is expanded isothermally and reversibly at 27°C from 10 to 100 litres. What is the amount of heat absorbed? What is the change in the internal energy?

**Answer.** 1372.81 cal; Zero

**5.** Two moles of an ideal gas undergo isothermal reversible expansion from 15 lit to 30 lit at 300 K. Calculate the work done and the change in entropy.

**Answer.** 826.5 cal; 2.755 cal $K^{-1}$

**6.** Water boils at 373 K at one atm pressure. At what temperature will it boil at a hill station where the atmospheric pressure is 500 mm Hg?

(Latent heat of vaporisation of water is 2.3 kJ $g^{-1}$ and $R = 8.314$ $JK^{-1}$ $mol^{-1}$)

**Answer.** 361.65 K

**7.** A Carnot's engine works between the temperature 27° and 127°C. Calculate the efficiency of the engine.

**Answer.** 25%

**8.** (*a*) Explain the term Thermodynamic efficiency.

(*b*) Calculate the work done on the system if one mole of an ideal gas at 300 K is compressed isothermally and reversibly to one-fifth of its original volume.

**Answer.** (*b*) $4014.98 \times 10^7$ ergs

**9.** What do you understand by the term enthalpy?

Calculate the work done in the expansion of 3 moles of hydrogen reversibly and isothermally at 27°C from 21.0 litres to 70.3 litres.

**Answer.** $9042.47 \times 10^7$ ergs

**10.** (*a*) "It is not profitable to carry out a process reversibly although maximum work can be obtained by doing so". Comment.

(*b*) Two moles of hydrogen are compressed adiabatically from NTP conditions to occupy a volume of 4.48 litres. Calculate the final pressure and temperature ($\gamma = 1.41$)

(*c*) Derive a relation between pressure and volume for an adiabatic reversible expansion of an ideal gas.

**Answer.** (*b*) 25.7 atm; 429.1°C

**11.** (*a*) Derive the Clapeyron-Clausius equation giving the temperature dependence of water pressure indicating clearly the assumption involved.

(*b*) An engine operates between 100°C and 0°C and another engine operates between 100°C and 0 K (absolute zero). Find the efficiencies in two cases.

**Answer.** (*b*) 26.8%; 100 %

**12.** (*a*) Explain giving reason "The net entropy of the universe tends to increase".

(*b*) For the reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(\ell)$$

the values of enthalpy change and free energy change are –68.32 and –56.69 kcal respectively at 25°C. Calculate the value of free energy change at 30°C.

(*c*) Write down the applications of Gibb's Helmholtz equation.

**Answer.** (*b*) –56.495 kcal

**13.** (*a*) Bring about clearly the criteria for reversibility and irreversibility in terms of *S*, *E*, *H* and *G*.

(*b*) 1.0 mole of steam is condensed at 100°C and water is cooled to 0°C and frozen to ice. Calculate the entropy change for the process. Latent heat of fusion of ice and evaporation of water are 80 and 540 cals/g respectively.

**Answer.** (*c*) 25.716 cal $deg^{-1}$ $mol^{-1}$

**14.** (*a*) Write a note on "Carnot's Cycle".

(*b*) How are work function and free energy related? Discuss the criteria of spontaneity of a chemical reaction.

(*c*) Calculate the entropy increase in the evaporation of a mole of water at 100°C (Heat of vaporization = 540 cal $g^{-1}$)

**15.** (*a*) Give the expression for Gibb's free energy change ($\Delta G$) for the reaction

$$nA + mB \rightleftharpoons pC + qD$$

(*b*) How is $\Delta G$ of a chemical reactions is related to $\Delta S$ and $\Delta H$?

(*c*) The enthalpy change for the transition of liquid water to steam is 40.8 kJ $mol^{-1}$ at 373 K. Calculate $\Delta G$ for the process.

**Answer.** (*b*) 109.38 3 $JK^{-1}$ $mol^{-1}$

**16.** Calculate $\Delta S$ when 28 gm of $N_2$ gas expands reversibly from 2 litres to 20 litres at 27°C.

**Answer.** 38.294 $JK^{-1}$

**17.** (*a*) Prove that Enthalpy remains constant when a real gas passes through a porous plug in adiabatic expansion.

(*b*) Explain the relationship between entropy and probability.

(*c*) Derive an expression for the efficiency of a Carnot's engine working between the two temperatures $T_1$ and $T_2$.

**18.** (*a*) Define standard heat of formation and standard entropy change of a reaction.

(*b*) Explain why in case of non-polar solvents, the $\Delta S$ is nearly equal to 88 $JK^{-1}$ $mol^{-1}$.

(*c*) Calculate the entropy change for the reaction :

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Given : $S°$ of $N_2$, $H_2$ and $NH_3$ as 191.5, 130.6 and 192.2 $JK^{-1}$ $mol^{-1}$ respectively.

**Answer.** –198.9 J $K^{-1}$ $mol^{-1}$ (*Delhi BSc, 2001*)

**19.** (*a*) Determine the entropy change for an ideal gas when temperature and volume are varied.

(*b*) Calculate the entropy change involved in isothermal expansion of 2 moles of the gas from a volume of 5 litres to a volume of 50 litres at 30°C.

**Answer.** 38.29 $JK^{-1}$ (*Guru Nanak Dev BSc, 2002*)

**20.** Calculate entropy change if 2 moles of water at 373 K are evaporated to vapours at 373 K. Give its units also. (Given molar heat of vaporisation of water is 9650 cal)

**Answer.** 216.49 $JK^{-1}$ (*Andhra BSc, 2002*)

**21.** 0.5 g of nitrogen is enclosed in a cylinder fitted with a piston at 25°C. Calculate the change in entropy, if the gas is expanded adiabatically to double its volume.

**Answer.** zero (*Guru Nanak Dev BSc, 2002*)

**22.** (*a*) Starting from appropriate definition of chemical potential of a component in an ideal gas solution, derive an expression for $\Delta G_{mixing}$ for the formation of ideal binary solution and show further that $\Delta H_{mixing}$=0 for the solution.

(*b*) A solution is prepared by mixing 2 moles of $CS_2$ and 3 moles of $CCl_4$ at 298 K and 1 atm pressure. Assuming ideal behaviour, calculate $\Delta G_{mixing}$ for the solution.

**Answer.** –3620.22 J (*Guru Nanak Dev BSc, 2002*)

**23.** Calculate entropy change for the fusion of one mole of a solid which melts at 300 K. The latent heat of fusion is 2.51 k J $mol^{-1}$.

**Answer.** 8.366 J (*Arunachal BSc, 2003*)

**24.** Calculate the change in entropy when 3 moles of an ideal gas is heated from 323 K to 423 K at a constant volume. ($C_v$ = 32.94 $JK^{-1}$ $mol^{-1}$)

**Answer.** 26.658 $JK^{-1}$ (*Nagpur BSc, 2003*)

**25.** Calculate the value of $dT/dP$ for water $\rightleftharpoons$ ice system at 273 K. $\Delta H_f$ for ice is 6007.8 J mol$^{-1}$; Molar Volume of water and ice are 0.018 dm$^3$ mol$^{-1}$ and 0.1963 dm$^3$ mol$^{-1}$ respectively.

(Given 1 J = $9.87 \times 10^3$ dm$^3$ atm)

**Answer.** 0.0100654 K atm$^{-1}$ (*Nagpur BSc, 2003*)

**26.** Calculate standard Gibb's Free energy change for the combustion of methane :

$$CH_4(g) + 2O_2(g) \rightarrow CO(g) + 2H_2O(g)$$

at 25°C. $\Delta H° = -191.8$ kcal and $\Delta S° = 1.2$ cal K$^{-1}$

**Answer.** –549.4 cal (*Sambalpur BSc, 2003*)

**27.** $\Delta G$ and $\Delta H$ values for a reaction at 300 K are : –66.944 kJ and –41.84 kJ respectively. Calculate the free energy change at 330 K, assuming that $\Delta H$ and $\Delta S$ remain constant over this temperature range.

**Answer.** –69.454 kJ (*Nagpur BSc, 2003*)

**28.** (*a*) Derive the integral Clausius-Clapeyron equation in the form

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303\,R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

for an ideal gas.

(*b*) At 373.6 K and 372.6 K the vapour pressure of $H_2O(\ell)$ are 1.018 and 0.982 atm respectively. What is the heat of vaporization of water? ($R$ = 1.987 cal)

**Answer.** (*b*) 41675.8 J (*Jamia Millia BSc, 2003*)

**29.** Explain the term fugacity. How is fugacity of a gas determined? (*Panjab BSc, 2003*)

**30.** (*a*) State Carnot's theorem and second law of thermodynamics.

(*b*) Define Chemical potential. Derive effect of temperature and pressure on chemical potential.

(*Indore BSc, 2004*)

**31.** Explain the following :

(*a*) Under what conditions can an isothermal expansion of a gas become a free expansion process.

(*b*) Increase in volume of a gas for a given decrease in pressure is less in an adiabatic expansion than in isothermal expansion.

(*c*) All spontaneous processes lead to increase the entropy of the universe.

(*d*) Free Energy of formation of an element at 1 atm and 298 K is assumed to be zero but entropy is not zero under the same conditions. (*Gulbarga BSc, 2004*)

**32.** (*a*) Describe Carnot's cycle for establishing the maximum convertibility of heat into work. How does it lead to the definition of Second Law of Thermodynamics?

(*b*) Heat supplied to a Carnot engine is 1897.86 kJ. How much useful work can be done by the engine which works between 0°C and 100°C?

**Answer.** (*b*) 508.80 kJ (*Madurai BSc, 2004*)

**33.** What do you understand by the term enthalpy?

Calculate the work done in the expansion of 3 moles of hydrogen reversibly and isothermally at 27°C from 21.0 litres to 70.3 litres.

**Answer.** $9042.47 \times 10^7$ ergs (*Kakatiya BSc, 2004*)

**34.** The heat of vaporisation, $\Delta H_{vap}$ of carbon tetrachloride, $CCl_4$, at 25 ºC is 43 kJ mol$^{-1}$. If 1 mole of liquid carbon tetrachloride at 25 ºC has an entropy of 214 JK$^{-1}$, what is the entropy of 1 mole of the vapour in equilibrium with the liquid at this temperature ?

**Answer.** 358 JK$^{-1}$ mol$^{-1}$ (*Kalyani BSc, 2005*)

**35.** Calculate the amount of the heat supplied to Carnot cycle working between 105 ºC and 20 ºC if the maximum work obtained is 200 cal ?

**Answer.** 889.4 cal (*Panjab BSc, 2005*)

**36.** The enthalpy change involved in oxidation of glucose is – 2880 kJ mol$^{-1}$. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance a person will be able to walk after eating 120 g of glucose ?

**Answer.** 4.8 km (*Delhi BSc, 2005*)

**37.** What is the entropy change for conversion of one mole of ice to water at 273 K and 1 atm pressure (Given $\Delta H$ of ice = 6.025 kJ mol$^{-1}$).

**Answer.** 22.069 J mol$^{-1}$ (*Bundelkhand BSc, 2005*)

**38.** Calculate the efficiency of steam engine operating between 100 ºC and 25 ºC. What would be the efficiency of the engine if the boiler temperature is raised to 150 ºC, the temperature of the sink remaining same ?

**Answer.** 22.1% ; 29.55% (*Agra BSc, 2006*)

**39.** At 373 K the entropy change for the transition of liquid water to steam is 109 JK$^{-1}$ mol$^{-1}$. Calculate the enthalpy change $\Delta H_{vap}$ for the process.

**Answer.** 40.657 kJ mol$^{-1}$ (*Madurai BSc, 2006*)

**40.** Ethanol boils at 78.4 ºC and standard enthalpy of vaporisation of ethanol is 42. kJ mol$^{-1}$. Calculate the entropy of vaporisation of ethanol.

**Answer.** 120.66 JK$^{-1}$ mol$^{-1}$ (*Barodra BSc, 2006*)

## MULTIPLE CHOICE QUESTIONS

**1.** A process which proceeds of its own accord, without any outside assistance, is called

(*a*) non-spontaneous process (*b*) spontaneous process
(*c*) reversible process (*d*) irreversible process

**Answer.** (*b*)

**2.** The tendency of a process to occur naturally is called

(*a*) momentum of the reaction (*b*) spontaneity of the reaction
(*c*) equilibrium of the reaction (*d*) equilibrium of the reaction

**Answer.** (*b*)

**3.** Which of the following is true about the criteria of spontaneity?

(*a*) a spontaneous change is unidirectional
(*b*) a spontaneous change to occur, time is no factor
(*c*) once a system is in equilibrium, a spontaneous change is inevitable
(*d*) all of the above

**Answer.** (*d*)

**4.** A spontaneous change is accompanied by _______ of internal energy or enthalpy.

(*a*) increase (*b*) decrease
(*c*) neither increase nor decrease (*d*) none of these

**Answer.** (*b*)

**5.** Mixing of two or more gases is a

(*a*) spontaneous process (*b*) non-spontaneous process
(*c*) reversible process (*d*) none of these

**Answer.** (*a*)

**6.** Entropy is a measure of _______ of the molecules of the system.

(*a*) concentration (*b*) velocity

(*c*) zig-zag motion (*d*) randomness or disorder

**Answer.** (*d*)

**7.** The second law of thermodynamics states that

(*a*) whenever a spontaneous process occurs, it is accompanied by an increase in the total energy of the universe

(*b*) the entropy of the system is constantly increasing

(*c*) neither of the above

(*d*) both (*a*) and (*b*)

**Answer.** (*d*)

**8.** The entropy of a pure crystal is zero at absolute zero. This is statement of

(*a*) first law of thermodynamics (*b*) second law of thermodynamics

(*c*) third law of thermodynamics (*d*) none of these

**Answer.** (*c*)

**9.** The entropy is measured in

(*a*) cal $K^{-1}$ $mol^{-1}$ (*b*) $JK^{-1}$ $mol^{-1}$

(*c*) entropy unit (*d*) all of these

**Answer.** (*d*)

**10.** The standard entropy, $S°$, of a substance is

(*a*) its entropy at 0°C and 1 atm pressure (*b*) its entropy at 0 K and 1 atm pressure

(*c*) its entropy at 25°C and 1 atm pressure (*d*) its entropy at 25 K and 1 atm pressure

**Answer.** (*c*)

**11.** The change in entropy of a reaction is given by

(*a*) $\Delta S = \Sigma S_{\text{Reactants}} + \Sigma S_{\text{Products}}$ (*b*) $\Delta S = \Sigma S_{\text{Products}} - \Sigma S_{\text{Reactants}}$

(*c*) $\Delta S = \Sigma S_{\text{Reactants}} - \Sigma S_{\text{Products}}$ (*d*) none of these

**Answer.** (*b*)

**12.** Which of the following is true for a cyclic process?

(*a*) $\Delta E = 0$ (*b*) $\Delta E = q - w$

(*c*) $q = w$ (*d*) all of these

**Answer.** (*d*)

**13.** A machine that can do work by using heat which flows out spontaneously from a high-temperature source to a low-temperature sink is called

(*a*) Carnot machine (*b*) cyclic machine

(*c*) heat machine (*d*) heat engine

**Answer.** (*d*)

**14.** The efficiency of a heat engine is the ratio of

(*a*) work obtained in a cyclic process ($w$) to the heat taken from the high temperature reservoir ($q$)

(*b*) heat taken from the high temperature reservoir ($q$) to the work obtained in a cyclic process

(*c*) work obtained in a cyclic process ($w$) to the heat taken from the low temperature sink ($q$)

(*d*) none of the above

**Answer.** (*a*)

**15.** The cycle of processes which occurs under reversible conditions is referred to as

(*a*) cyclic process (*b*) closed process (*c*) Carnot cycle (*d*) reversible cycle

**Answer.** (*c*)

**16.** The efficiency of a heat engine is given by

(*a*) $\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$ (*b*) $\frac{w}{q_2} = \frac{T_1 - T_2}{T_2}$

(*c*) $\frac{w}{q_2} = \frac{T_2 - T_1}{T_1}$ (*d*) $\frac{w}{q_2} = \frac{T_1 - T_2}{T_1}$

**Answer.** (*a*)

**17.** The second law of thermodynamics may be stated as

(*a*) it is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

(*b*) it is impossible to transfer heat from a body at a lower temperature to one at higher temperature

(*c*) the efficiency of heat engine is always less than 1

(*d*) all of the above

**Answer.** (*d*)

**18.** The efficiency of a heat operating between 400 K and 300 K is

(*a*) 1.0 (*b*) 0.75

(*c*) 0.50 (*d*) 0.25

**Answer.** (*d*)

**19.** The efficiency of heat engine operating between 1000 K and 300 K is _______ the engine operating between 1000 K and 500 K.

(*a*) greater than (*b*) lesser than

(*c*) is equal to (*d*) none of these

**Answer.** (*a*)

**20.** The entropy of the system increases in the order

(*a*) gas < liquid < solid (*b*) solid < liquid < gas

(*c*) gas < solid < liquid (*d*) none of these

**Answer.** (*b*)

**21.** The efficiency of an irreversible Carnot cycle is always _______ that of a reversible one operating between the same two temperatures

(*a*) less than (*b*) greater than

(*c*) equal to (*d*) none of these

**Answer.** (*a*)

**22.** The free energy function ($G$) is defined as

(*a*) $G = H + TS$ (*b*) $G = H - TS$

(*c*) $G = TS - H$ (*d*) none of these

**Answer.** (*b*)

**23.** The change in free energy is a measure of :

(*a*) net work done (*b*) net change is entropy

(*c*) net change in enthalpy (*d*) net change in internal energy

**Answer.** (*a*)

**24.** The work function (A) is defined as

(*a*) $A = E - TS$ (*b*) $A = E + TS$

(*c*) $A = TS - E$ (*d*) none of these

**Answer.** (*a*)

**25.** The change in free energy of a system is given by

(*a*) $\Delta G = \Delta A + P\,\Delta V$ (*b*) $\Delta G = \Delta H - T\,\Delta S$

(*c*) $\Delta G = \Delta E + P\,\Delta V - T\,\Delta S$ (*d*) all of these

**Answer.** (*d*)

**26.** Which out of the following is not a state function?

(*a*) free energy (*b*) work function

(*c*) entropy (*d*) work done

**Answer.** (*d*)

**27.** The variation of free energy with temperatures at constant pressure is given by the relation :

(*a*) $dG_P = -\,SdT_P$ (*b*) $\left(\frac{dG}{dT}\right)_P = -S$

(*c*) neither of these (*d*) both (*a*) and (*b*)

**Answer.** (*d*)

**28.** The variation of free energy with pressure at constant temperature is given by

(*a*) $(dG)_T = V\,d\,P_T$ (*b*) $dG_P = -\,SdT_P$

(*c*) $\left(\frac{dG}{dT}\right)_P = -S$ (*d*) none of these

**Answer.** (*a*)

**29.** The change in free energy in an isothermal process for *n* moles of the gas is given by

(*a*) $\Delta G = 2.303 \times n\,RT \log \frac{P_2}{P_1}$ (*b*) $\Delta G = 2.303 \times RT \log \frac{V_1}{V_2}$

(*c*) $\Delta G = 2.303 \times RT \log \frac{P_2}{V_1}$ (*d*) none of these

**Answer.** (*a*)

**30.** The Gibb's Helmholtz equation is applicable to

(*a*) all processes, chemical or physical

(*b*) all process, chemical or physical but in a closed system

(*c*) all chemical processes in a closed system

(*d*) all physical processes in a closed system

**Answer.** (*b*)

**31.** For a spontaneous process

(*a*) $\Delta G > 0$ (*b*) $\Delta G < 0$

(*c*) $\Delta G = 0$ (*d*) none of these

**Answer.** (*b*)

**32.** A process is in the equilibrium state when

(*a*) $\Delta G > 0$ (*b*) $\Delta G < 0$

(*c*) $\Delta G = 0$ (*d*) none of these

**Answer.** (*c*)

**33.** Which of the following equation is used to calculate the heats of reaction when $\Delta G$ at two temperature are given?

(*a*) Gibbs Helmholtz equation (*b*) Clapeyron equation

(*c*) Kirchoff's equation (*d*) none of these

**Answer.** (*a*)

**34.** The equation $\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)}$ is called

(*a*) Gibb's Helmholtz equation (*b*) Kirchoff's equation

(*c*) Clapeyron equation (*d*) Clausius Clapeyron equation

**Answer.** (*c*)

**35.** The Clausius Clapeyron equation helps to calculate

(*a*) latent heat of vaporization

(*b*) boiling point or freezing point

(*c*) vapour pressure at one temperature, if at another temperature is given

(*d*) all of the above

**Answer.** (*d*)

**36.** The decrease in the work function A in any process at constant temperature gives the ________ that can be obtained from the system during any change.

(*a*) minimum work (*b*) maximum work

(*c*) useful work (*d*) net work

**Answer.** (*b*)

**37.** The equation for van't Hoff isotherm is

(*a*) $-\Delta G = 2.303\, RT \log K_P$ (*b*) $\Delta G = 2.303\, RT \log K_P$

(*c*) $-\Delta G = 2.303\, RT^2 \log K_P$ (*d*) $\Delta G = 2.303\, RT^2 \log K_P$

**Answer.** (*a*)

**38.** The equation $\frac{\Delta H}{RT^2} = \frac{d\,(\ln K_P)}{dT}$ is known as

(*a*) van't Hoff equation (*b*) van't Hoff isochore

(*c*) Gibbs equation (*d*) Gibbs Duhem equation

**Answer.** (*b*)

**39.** Each substance in a given state has a tendency to escape from that state and this escaping tendency is called

(*a*) spontaneity (*b*) Gibbs free energy

(*c*) fugacity (*d*) activity

**Answer.** (*c*)

**40.** When water is cooled to ice, its entropy

(*a*) increases (*b*) decreases

(*c*) remains the same (*d*) becomes zero

**Answer.** (*b*)

**41.** Which of the following sets of conditions makes a process spontaneous at all temperatures?

(*a*) $\Delta H = 0; \Delta S > 0$ (*b*) $\Delta H = 0; \Delta S < 0$

(*c*) $\Delta H > 0; \Delta S > 0$ (*d*) $\Delta H < 0; \Delta S < 0$

**Answer.** (*c*)

**42.** The increase in entropy is maximum in

(*a*) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (*b*) $CO(g) + ½O_2(g) \rightarrow CO_2(g)$

(*c*) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (*d*) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

**Answer.** (*a*)

**43.** A spontaneous reaction proceeds with a decrease in

(*a*) entropy (*b*) enthalpy

(*c*) free energy
(*d*) internal energy

**Answer.** (*c*)

**44.** In a process $\Delta H = 100$ kJ and $\Delta S = 100$ JK$^{-1}$ at 400 K. The value of $\Delta G$ will be

(*a*) zero
(*b*) 100 kJ
(*c*) 50 kJ
(*d*) 60 kJ

**Answer.** (*d*)

**45.** A chemical reaction proceeds with decrease in both the enthalpy and entropy. This reaction will be spontaneous if

(*a*) $\Delta H = T\,\Delta S$
(*b*) $\Delta H < T\,\Delta S$
(*c*) $\Delta H > T\,\Delta S$
(*d*) none of these

**Answer.** (*b*)

**46.** Which is the correct unit for entropy?

(*a*) kJ mol
(*b*) JK$^{-1}$ mol
(*c*) JK$^{-1}$ mol$^{-1}$
(*d*) kJ mol

**Answer.** (*c*)

**47.** The efficiency of heat engine is maximum when

(*a*) temperatures of source and sink are maximum
(*b*) temperatures of source and sink are minimum
(*c*) temperature of source is minimum and that of sink is maximum
(*d*) temperature of source is maximum and that of sink is minimum

**Answer.** (*d*)

**48.** A reaction proceeds with increase in both the enthalpy and entropy. It will be spontaneous if

(*a*) $\Delta H = T\,\Delta S$
(*b*) $\Delta H > T\,\Delta S$
(*c*) $\Delta H < T\,\Delta S$
(*d*) none of these

**Answer.** (*c*)

**49.** A spontaneous reaction is not possible if

(*a*) $\Delta H$ and $T\,\Delta S$ are both negative
(*b*) $\Delta H$ and $T\,\Delta S$ are both positive
(*c*) $\Delta H$ is +ve and $T\,\Delta S$ is –ve
(*d*) $\Delta H$ is –ve and $T\,\Delta S$ is +ve

**Answer.** (*c*).

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