

1. Basic Terms

This lesson deals with heat changes accompanying physical and chemical processes.

1.1 System & Surroundings

Any specified portion of universe under investigation is called system and the rest of the universe is called surroundings.

1.2 Types of System

Open System

It is defined as a system, which can exchange matter as well as energy with the surroundings. For example, a liquid kept in an open flask.

Closed System

It is defined as a system which can exchange only energy with the surroundings.

For example: a liquid in a closed vessel.

Isolated System

It is defined as a system which can neither exchange matter nor energy with the surroundings. For example: a thermally insulated flask.

1.3 Thermodynamic Process

It is an operation by which a system undergoes a change from one state to another.

Isothermal Process

A process in which the temperature remains constant throughout its course is called isothermal process.

i.e. $\Delta T = 0$ and also $\Delta E = 0$.

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Adiabatic Process

A process during which no heat is exchanged between the system and the surroundings is called adiabatic process.

$$\text{i.e. } dq = 0.$$

Isochoric Process

A process during which volume of the system remains constant is called isochoric process.

$$\text{i.e. } \Delta V = 0.$$

Isobaric Process

A process during which pressure of the system remains constant is called isobaric process.

$$\text{i.e. } \Delta P = 0.$$

Cyclic Process

A process during which state of the system does not change is called cyclic process.

$$\text{i.e. } \Delta E = 0 \text{ and also } \Delta H = 0.$$

Reversible Process

A process in which the driving force is infinitesimally greater than the opposing force is called reversible process.

Irreversible Process

A process in which direction cannot be altered by small changes in variables like P, V, T etc. is called irreversible process.

1.4 Extensive & Intensive Properties

Properties which depend on the amount of matter are called extensive properties. e.g. mass, volume, energy, enthalpy, entropy etc.

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Properties which do not depend on the amount of matter are called intensive properties. e.g. Pressure, temperature, density, specific heat, specific volume, surface tension, viscosity, electromotive force etc.

1.5 State Functions or State Variables

Those fundamental properties which determine the state of a system are called state variables or state functions or thermodynamic parameters. The change in the state properties is dependent on the initial and final states of the system and not on the path followed.

State variables that are commonly used to describe the state of the thermodynamic system are

1. Pressure (P)
2. Volume (V)
3. Temperature (T)
4. Internal energy (E)
5. Enthalpy (H)
6. Entropy (S)
7. Free energy (G)
8. Number of moles (n)

1.6 Work & Types of Work

Work is defined as energy transfer to or from a system with reference to the surroundings.

If an object is displaced through a distance dx against a force F , then the amount of work done is defined as

$$w = F \times dx$$

Types of Work

(a) Gravitational work = mgh

Where, m = mass of body, g = acceleration due to gravity and h = height moved.

Work is an algebraic quantity. It is +ve if the mass is lifted (h is +ve), in which case it is said that work has been produced in the surroundings and

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it is –ve if the mass is lowered (h is –ve), in which case the work is said to be destroyed in the surroundings or has flowed from the surroundings.

(b) Electrical work = Charge \times potential = $q \times V$

(c) Mechanical work $\equiv P_{\text{ext}} (V_2 - V_1) \equiv P_{\text{ext}} \Delta V$

Where, P_{ext} = external pressure and ΔV = increase or decrease in volume.

Work done on a system increases the energy of the system and work done by the system decreases the energy of the system.

Work done on the system, $w = +ve$

Work done by the system, $w = -ve$.

1.7 Heat

It is defined as *the energy that flows across the boundary of a system during a change in its state by virtue of a difference in temperature between the system and its surroundings and flows from a point of higher to a point of lower temperature.*

Heat absorbed or evolved, $\Delta Q = m s \Delta t$

Where, m = mass of substance, s = specific heat and Δt = temperature difference.

- (i) If heat flows into the system, ΔQ or ΔH is +ve and the process is referred as endothermic.
- (ii) If heat flows out of the system, ΔQ or ΔH is –ve, and the process is referred as exothermic.

1.8 Units of Heat and Work

The unit of heat is calorie. *One calorie is defined as the quantity of heat required to raise the temperature of one gram of water by 1°C.*

Since heat and work are interrelated, SI unit of heat is Joule.

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$$1 \text{ cal} = 4.184 \text{ Joule}$$

$$1 \text{ litre atm} = 101.3 \text{ J} = 1.013 \times 10^9 \text{ erg} = 24.206 \text{ cal.}$$

1.9 Internal Energy

Every substance possesses a definite amount of energy which depends upon factors such as composition of the substance, temperature and pressure. This is called intrinsic or internal energy (E).

$$E = E_T + E_R + E_V + E_B + E_E \dots\dots\dots$$

Where, E_T = Translational energy, E_R = Rotational energy,

E_V = Vibrational energy,

E_B = Bonding energy and E_E = Electronic energy.

Internal energy of a system is state function and its absolute value cannot be calculated but its change can be determined. When the system undergoes a change in its state, the internal energy change is given by

$$\Delta E = E_2 - E_1$$

Where, E_1 = Internal energy in the initial state and E_2 = Internal energy in the final state.

In a chemical reaction, $\Delta E = E_P - E_R$

Where, E_P = Internal energy of products and E_R = Internal energy of reactants.

1.10 Enthalpy (H)

Heat content of a system at constant pressure is called enthalpy. It is related with internal energy by the equation,

$$H = E + PV$$

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Every substance has a definite value of enthalpy in a particular state. It is also a state function like internal energy. The change in enthalpy accompanying a process can be determined as

$$\Delta H = H_2 - H_1$$

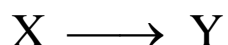
Where, H_1 = Enthalpy of a substance in the initial state and H_2 = Enthalpy of a substance in the final state.

In the case of a chemical reaction, $\Delta H = H_P - H_R$

Where, H_P = Enthalpy of products and H_R = Enthalpy of reactants.

1.11 Relation between ΔH and ΔE

Let us consider a chemical reaction,



Then at constant pressure (P), the enthalpy change would be given as

$$\Delta H = H_y - H_x$$

We know that, $H = E + PV$

Let E_x and V_x be the internal energy and volume of the reactants and E_y and V_y be the respective values of products. Then

$$H_x = E_x + PV_x \text{ \& } H_y = E_y + PV_y$$

$$\Delta H = (E_y + PV_y) - (E_x + PV_x)$$

$$\Delta H = (E_y - E_x) + P(V_y - V_x)$$

$$\Delta H = \Delta E + P\Delta V \quad \text{.....(i)}$$

2. First Law of Thermodynamics

The philosophical argument of Mayer and the experimental work of Joule, a pupil of John Dalton led Helmholtz to state “the conservation of energy” as a principle of universal validity. The first law of thermodynamics, states

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that “*energy can neither be created nor destroyed although it can be converted from one form into another.*”

2.1 Justification of First Law of Thermodynamics

The change in internal energy can be brought about in two ways.

- (i) Either by allowing the heat to be absorbed by the system or to evolve out of the system.
- (ii) By doing work on the system or the work is done by the system.

If a closed system having E_1 internal energy is supplied ‘q’ amount of heat, then the internal energy of the system becomes $(E_1 + q)$.

If work (w) is done on the system, then its internal energy further increases and becomes E_2 .

Thus

$$E_2 = E_1 + q + w$$

$$\text{or } E_2 - E_1 = q + w$$

$$\text{or } \Delta E = q + w. \quad \dots\dots(ii)$$

In case, q is the heat absorbed and w is the work done by the system, then

$$\Delta E = q + (-w) = q - w$$

Thus, first law of thermodynamics may also be stated as “*the net energy change of a closed system is equal to the heat absorbed plus the work done on the system or minus the work done by the system.*”

2.2 Conclusions Drawn From the 1st Law

- (i) For an ideal gas undergoing an isothermal change, the internal energy of the system does not change. i.e. $\Delta E = 0$, then

$$0 = q + w$$

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or $q = -w$

i.e. heat absorbed by the system is equal to the work done by the system.

or $w = -q$

heat evolved out of the system is equal to work done on the system.

- (ii) For an isochoric process no work is done, $w = 0$, then the first law is reduced to

$$\Delta E = q$$

i.e. increase in internal energy of the system is equal to the heat absorbed by the system or decrease in internal energy of the system is equal to the heat lost by the system.

- (iii) For adiabatic processes involving no exchange of heat between the system and the surroundings, $q = 0$. Thus,

$$\Delta E = w$$

i.e. if work is done on the system, its internal energy increases and the work done by the system decreases its internal energy.

- (iv) If a gas expands against constant external pressure, P and the corresponding change in volume is ΔV , then work done by the system

$$w = -P\Delta V$$

Thus, equation (ii) becomes

$$\Delta E = q - P\Delta V \quad \text{.....(iii)}$$

If the process is carried out at constant volume, then $\Delta V = 0$. Thus,

$$\Delta E = q_v$$

i.e. the change in internal energy is equal to the heat absorbed or evolved at constant volume.

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(v) We have, $q = \Delta E + P\Delta V$ (from equation (iii))

$$= (E_2 - E_1) + P(V_2 - V_1) = E_2 + PV_2 - (E_1 + PV_1) = H_2 - H_1$$

$$\text{or } q_p = \Delta H$$

i.e. the change in enthalpy is equal to the heat absorbed or evolved at constant pressure. This is important as most of the chemical reactions are carried out at constant pressure and temperature.

(vi) We know that, $\Delta H = \Delta E + P\Delta V = \Delta E + \Delta n_g RT$ ($\because P\Delta V = \Delta n_g RT$)

$$\text{or, } q_p = q_v + \Delta n_g RT \dots\dots\dots(\text{iv})$$

where, Δn_g = Difference between moles of gaseous products and gaseous reactants.

2.3 Heat Capacity

It is defined as the quantity of heat required to raise the temperature of the system by one degree.

$$\text{i.e. } C = \frac{dq}{dT}$$

where, C = Heat capacity, dq = Amount of heat absorbed by the system and dT = Rise in temperature.

Its unit is $J K^{-1}$ or $J / ^\circ C$.

Larger the sample, greater is its heat capacity. It is therefore, common to use specific heat capacity (specific heat) or molar heat capacity.

Specific Heat

The amount of heat required to raise the temperature of 1 gm of a substance by 1 degree is called specific heat.

$$\therefore \text{Specific heat} = \frac{\text{Heat capacity}}{\text{mass (in gm)}} = \frac{\text{Heat absorbed}}{\text{Rise in temperature} \times \text{mass (in gm)}}$$

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$$\text{Molar heat capacity} = \frac{\text{Heat capacity}}{\text{Molar mass}}$$

Units of specific heat & molar heat capacity are $\text{J K}^{-1} \text{g}^{-1}$ and $\text{J K}^{-1} \text{mol}^{-1}$ respectively.

Now, heat supplied = Mass \times specific heat \times rise in temperature.

$$\text{i.e. } q = m \times C_s \times \Delta T \quad \text{.....(v)}$$

The heat capacity of a system, especially in a gaseous system determined at constant volume is different from that at constant pressure.

At constant volume, $q_v = \Delta E$.

So, heat capacity at constant volume per mole,

$$C_V = \left(\frac{dE}{dT} \right)_V \quad \text{.....(vi)}$$

At constant pressure, $q_p = \Delta H$.

So, heat capacity at constant pressure per mole,

$$C_P = \left(\frac{dH}{dT} \right)_P \quad \text{.....(vii)}$$

Where, C_P & C_V are molar heat capacities at constant pressure & constant volume respectively. The heat capacity at constant pressure (C_P) is “generally” larger than that at constant volume (C_V) because at constant pressure, a part of heat added to the substance may be used in work of expanding whereas at constant volume all the added heat produces a rise in temperature. The term “generally” has been used because substances generally expand with increase of temperature at constant pressure, but in exceptional cases, there may be a contraction, e.g. water between 1° & 4°C .

3. Pressure – Volume Work

3.1 Isothermal Expansion

No heat flows out of or into the system in an isothermal expansion, so that temperature remains constant throughout the process of expansion. Since for an ideal gas, the internal energy (ΔE), depends only on temperature, the internal energy of the gas remains constant.

$$\text{i.e. } \Delta E = 0$$

From 1st law of thermodynamics,

$$\Delta E = q + w$$

For isothermal process, $\Delta E = 0$, hence

$$q = -w$$

In the case of isothermal expansion, work is done by the system at the cost of heat absorbed. The magnitude of 'q' or 'w' depends on the manner in which the process of expansion is carried out i.e. reversibly or irreversibly.

ΔH can be calculated as follows

$$\text{We know, } \Delta H = \Delta E + \Delta n_g RT$$

For isothermal process, $\Delta E = 0$ & $\Delta T = 0$ thus, $\Delta H = 0$.

Work–done in reversible isothermal expansion

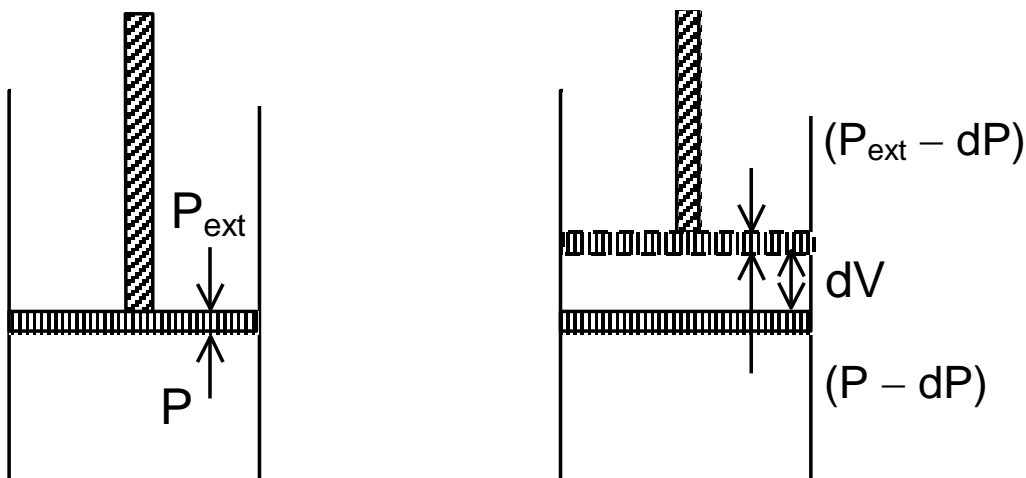
Let us consider a non-insulated cylinder fitted with a weightless and frictionless piston containing an ideal gas. Let P be the pressure of the gas which equals external pressure, P_{ext} .

$$P_{\text{ext}} = P$$

An infinitesimal expansion in volume, dV , results from an infinitesimal decrease in the external pressure, say dP . Consequently, the pressure of the

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gas inside the cylinder falls to $(P_{\text{ext}} - dP)$ i.e. it equals again to the external pressure and the piston come to rest again.



The workdone by the gas in each step of expansion is given as

$$dw = - (P_{\text{ext}} - dP) dV = - P_{\text{ext}} \cdot dV = - PdV$$

$dP \cdot dV$ is the product of two infinitesimal quantities and hence neglected.

The total amount of workdone during the isothermal reversible expansion of the gas from volume V_1 to V_2 is given by

$$\int_1^2 dw = - \int_{V_1}^{V_2} PdV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV \quad (\because PV = nRT).$$

$$\int_1^2 dw = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$w_{\text{rev}} = -2.303 nRT \log_{10} \frac{V_2}{V_1} \dots\dots(\text{viii})$$

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At constant temperature, $P_1V_1 = P_2V_2$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$\therefore w_{\text{rev}} = -2.303 nRT \log_{10} \frac{P_1}{P_2} \quad \dots\dots(\text{ix})$$

For isothermal compression, work done by an ideal gas is same as isothermal expansion but with positive sign. Thus equation (viii) & (ix) is the maximum work done in an expansion, or the minimum work needed to effect a compression. This equation tells us that the work required to compress a gas from 10 atm to 100 atm is just the same as that required to compress a gas from 1 atm to 10 atm.

Work Done In Irreversible Isothermal Expansion

Irreversible isothermal expansions observed are

- (i) Free expansion
- (ii) Intermediate expansion.

Since the external pressure is zero in free expansion, the work done is zero e.g. expansion of a gas in vacuum.

The external pressure is less than gas pressure in the case of intermediate expansion. Thus, the workdone when volume changes from V_1 to V_2 is

$$\begin{aligned} w_{\text{irrev}} &= - \int_{V_1}^{V_2} P_{\text{ext}} \times dV \\ &= - P_{\text{ext}}(V_2 - V_1) \end{aligned}$$

Since, P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than that during reversible isothermal expansion in which P_{ext} is almost equal to P .

3.2 Adiabatic Expansion

From first law of thermodynamics, $\Delta E = q + w$

In an adiabatic expansion, $q = 0$, $\therefore \Delta E = w$

The molar heat capacity at constant volume of an ideal gas is given by

$$C_v = \left(\frac{dE}{dT} \right)_v$$

or $dE = C_v \cdot dT$

and for finite changes, $\Delta E = C_v \times \Delta T = w$ (x)

The value of ΔT depends upon the nature of process (i.e. reversible or irreversible.)

Reversible Adiabatic Expansion

If P be the external pressure and ΔV be the increase in volume, then work done by the system is

$$w = -P\Delta V$$

If ΔT is the fall in temperature, then

$$C_v \Delta T = -P\Delta V$$

For very small change in a reversible process and for one mole of a gas,

$$C_v dT = -PdV = \frac{-RT}{V} \cdot dV$$

$$\text{or, } C_v \frac{dT}{T} = -R \cdot \frac{dV}{V}$$

For a process that takes the gas from a volume V_1 at a temperature T_1 to a new volume V_2 at a temperature T_2 , we have

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$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\log \frac{T_2}{T_1} = \frac{R}{C_V} \log \frac{V_1}{V_2} \quad \text{.....(xi)}$$

We know that $C_P - C_V = R$

Dividing it by C_V gives

$$\frac{C_P}{C_V} - 1 = \frac{R}{C_V}$$

$$\gamma - 1 = \frac{R}{C_V} \quad (\because \frac{C_P}{C_V} = \gamma)$$

Putting the value of R/C_V in equation (xi)

$$\log \frac{T_2}{T_1} = (\gamma - 1) \log \frac{V_1}{V_2} = \log \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \text{.....(xii)}$$

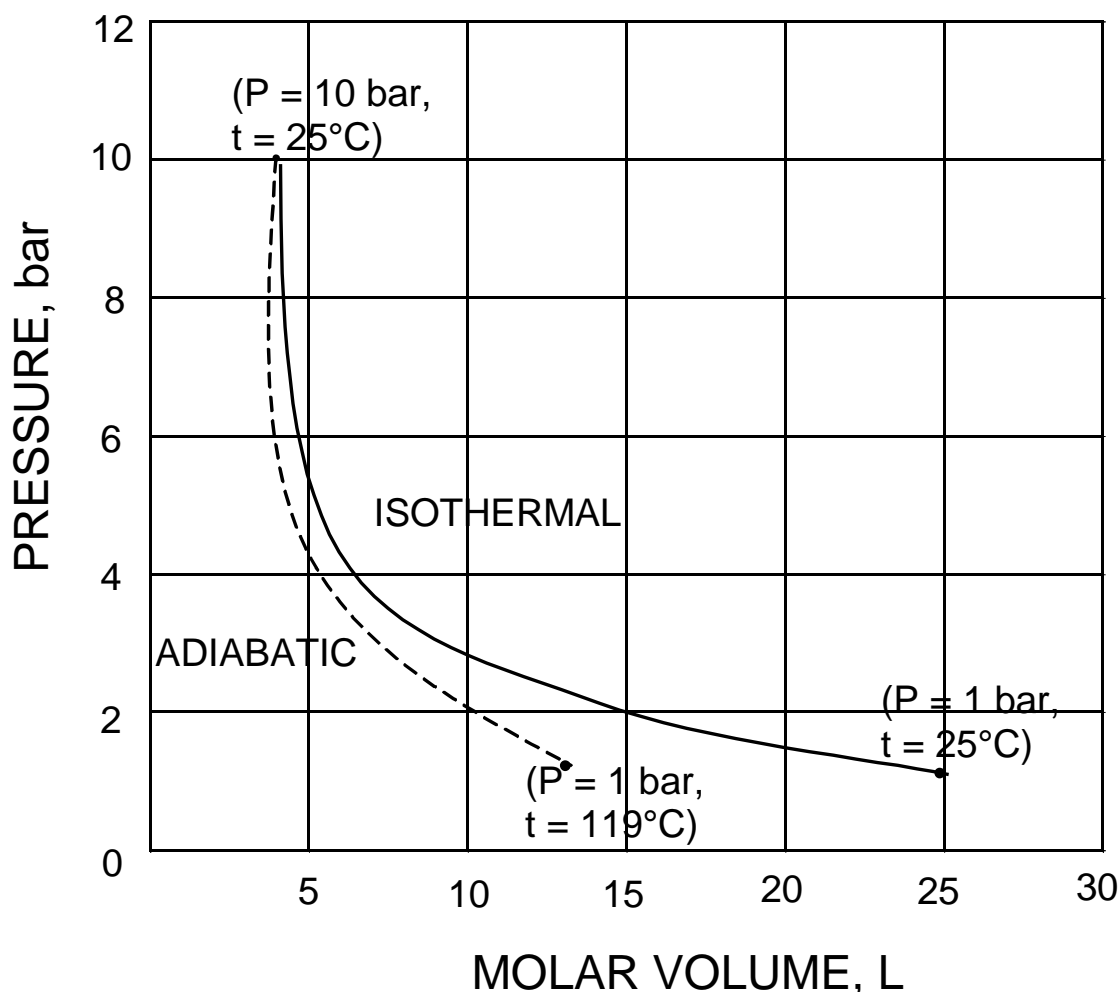
$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad \text{or} \quad \mathbf{TV^{\gamma-1} = constant}$$

$$\frac{P_1 V_1}{P_2 V_2} = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \text{or} \quad P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad \text{or} \quad \mathbf{PV^{\gamma} = constant}$$

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The above integration assumes that C_V is a constant and not a function of T . We know, for an isothermal expansion, $PV = \text{constant}$.

On plots of P versus V , curves for reversible adiabatic process are steeper than those for isothermal process as given below.



When a gas expands isothermally, thermal energy is supplied to make up for the energy delivered to the mechanical surroundings. For a balanced adiabatic expansion, work is done by the system on the surroundings ($-w$) i.e. the energy delivered to the surroundings must come from the internal of the gas. As a result, the temperature falls ($-\Delta E$) and the pressure change for a given expansion is greater than that in the corresponding isothermal expansion.

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From equation (xii),

$$\frac{T_1}{T_2} = \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{\gamma-1} \quad (\because V_1 = \frac{RT_1}{P_1})$$

$$\text{or} \quad \left(\frac{T_1}{T_2} \right)^{\gamma} = \left(\frac{P_2}{P_1} \right)^{1-\gamma} \quad \dots\dots(xiii)$$

$$\text{Now, work done} = C_V \times \Delta T = C_V (T_2 - T_1) = \frac{R}{\gamma - 1} (T_2 - T_1)$$

$$\text{For } n \text{ moles of a gas, work done} = \frac{nR}{\gamma - 1} (T_2 - T_1)$$

Irreversible Adiabatic Expansion

In free expansion, the external pressure is zero, i.e. work done is zero.

$$\therefore \Delta E = w = 0 \quad \& \quad \Delta T = 0 \quad \& \quad \Delta H = 0.$$

In intermediate expansion, suppose the pressure is suddenly released to 1 atm and the gas expands adiabatically against this constant pressure. Since this is not a reversible expansion equation (xii) cannot be used.

Since, $q = 0$, $\Delta E = w$

$$w = C_V (T_2 - T_1) \quad \dots\dots(xiv)$$

Let the volume changes from V_1 to V_2 against external pressure, P_{ext} .

$$w = -P_{\text{ext}} (V_2 - V_1) = -P_{\text{ext}} \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right)$$

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$$= -P_{\text{ext}} R \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right) \dots\dots(xv)$$

Equating equations (xiv) & (xv), we get

$$w = C_v(T_2 - T_1) = -R P_{\text{ext}} \left(\frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right) \dots\dots(xvi) \quad (\text{For one mole})$$

Illustration 1.

1 m³ of neon gas $\left(C_v = \frac{3}{2}R \right)$ at 273.2 K and 10 atm undergoes three different expansions to a final pressure of 1 atm. Calculate the final volume and the work done in three different expansions.

- (a) Isothermal reversible expansion
- (b) Adiabatic reversible expansion and
- (c) Irreversible adiabatic expansion.

Solution:

$$(a) \quad \text{Final volume, } V_2 = \frac{P_1 V_1}{P_2} = \frac{(1) (10)}{(1)} = 10 \text{ m}^3$$

The work done by the gas in expanding equals the heat absorbed by the gas from its surroundings.

$$\therefore -w = q = n R T \ln \frac{V_2}{V_1}$$

$$n = \frac{10 \times 10^3}{0.0821 \times 273.2} = 446.1 \text{ mol}$$

$$-w = (446.1) (8.314) (273.2) (2.303) \log_{10} 10 = 232.85 \text{ kJ}$$

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(b) For adiabatic reversible expansion,

$$V_2 = \left(\frac{P_1}{P_2} \right)^{\frac{1}{\gamma}} V_1$$

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{3}{2}R + R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\therefore V_2 = (10)^{3/5} (1) = \mathbf{3.981 \text{ m}^3}$$

The final temperature is obtained from

$$P_2 V_2 = nRT_2$$

$$T_2 = \frac{P_2 V_2}{nR} = \frac{(1) (3.981 \times 10^3)}{(446.1) 0.0821} = 108.8 \text{ K}$$

For an adiabatic process, $q = 0$ & $\Delta E = w$.

Also, since C_v is constant

$$\begin{aligned} w &= nC_v (T_2 - T_1) = \left(n \frac{3}{2} R \right) (T_2 - T_1) \\ &= (446.1) \left(\frac{3}{2} R \right) (108.8 - 273.2) = \mathbf{-914.1 \text{ kJ}} \end{aligned}$$

(c) For irreversible adiabatic expansion,

From equation (xvi), we have,

$$-C_v(T_2 - T_1) = nR P_2 \left(\frac{T_2}{P_2} - \frac{T_1}{P_1} \right)$$

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$$-\frac{3}{2}(T_2 - 273.2) = nR (1) \left(\frac{T_2}{1} - \frac{273.2}{10} \right)$$

$$\therefore T_2 = 174.8 \text{ K}$$

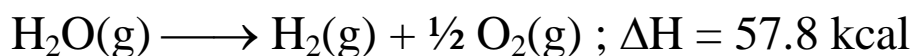
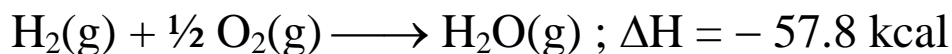
$$\therefore \Delta E = w = \frac{3}{2}nR (174.8 - 273.2) = -547.4 \text{ kJ}$$

Note that there is considerably less cooling of the gas and less work is done by the gas in the irreversible adiabatic expansion than in the reversible adiabatic expansion.

4. Thermochemistry

It is a branch of physical chemistry that deals with energy changes accompanying chemical transformations. It is also known as “Chemical Energetics”. It is based on the first law of thermodynamics.

Physicochemical changes are classified as endothermic, accompanied by absorption of heat and exothermic, accompanied by the evolution of heat. For example,



For exothermic reactions ($q < 0$)

At constant pressure, $\Delta H = (H_P - H_R) = -ve$ ($\because H_P < H_R$)

At constant volume, $\Delta E = (E_P - E_R) = -ve$ ($\because E_P < E_R$)

For endothermic reaction, ($q > 0$)

At constant pressure, $\Delta H = (H_P - H_R) = +ve$ ($\because H_P > H_R$)

At constant volume, $\Delta E = (E_P - E_R) = +ve$ ($\because E_P > E_R$)

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Like any other transfer of heat, the heat of a chemical reaction depends upon the conditions that hold during the process by which it is carried out.

Condition I:

If the volume of the system is kept constant, no work is done on the system and the first law of thermodynamics reduces to

$$\Delta E = q_v$$

This condition is excellently approximated when the reaction is carried out in a bomb calorimeter, where the volume remains constant.

Condition II:

During the course of an experiment under ordinary bench-top conditions, the pressure is kept constant. Many calorimeters operate at this constant atmospheric pressure. Then, we have

$$\Delta H = q_p$$

The heat of reaction measured at constant pressure is exactly equal to the change in enthalpy of the reaction system.

It is often necessary to use data obtained with bomb calorimeter which give ΔE in order to calculate ΔH .

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

If all the reactants and products are liquids or solids, the PV values change only slightly during the reaction, provided the pressure is low (say 1 atm).

In such cases, $q_p \cong q_v$.

For reactions in which gases are involved, the values of $\Delta(PV)$ depends on the change in the number of moles of gas as a result of reaction.

$$\therefore \Delta(PV) = \Delta n_g(RT)$$

$$\therefore \Delta H = \Delta E + \Delta n_g RT$$

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Constant pressure processes are much common in chemistry. Therefore, usually whenever we speak of heat of reaction, it implies enthalpy change at constant pressure.

4.1 Heat of Reaction

It is defined as the *amount of heat evolved or absorbed when the reacting species, as represented by a balanced chemical equation have completely reacted.*

Enthalpy or heat of reaction is given by $\Delta H = \sum H_P - \sum H_R$.

4.2 Standard States

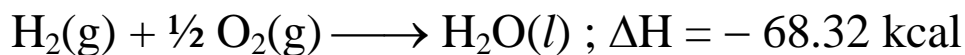
In the calculation of heat of reaction, it is a convention to assume that the heat of formation of elements in their standard state is zero. A pressure of 1 atm and a constant temperature is taken as standard state.

State	Standard state
Gas	Ideal gas at the given temperature & 1 atm.
Liquid	Pure liquid at the given temperature & 1 atm.
Solid	Stable crystalline form at given temperature and 1 atm pressure.

4.3 Factors Affecting Heat of Reaction

Physical State of Reactants And Products

Physical state always affects the heat of reaction as heat energy is involved in changing the physical state of a substance. For example,

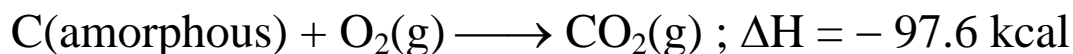


Difference in the value of ΔH is observed because heat is evolved when steam condenses.

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Allotropic Forms of the Element

The value of ΔH also depends on the allotropic form used in the reaction. For example,



The difference between the two values is equal to the heat absorbed when 12 g of diamond is converted into 12 g of amorphous carbon. This is called heat of transition.



Enthalpies of Solution

Enthalpies of solution differ depending on whether the substances react together in dry state or in solution. For example,



Temperature

Enthalpy of reaction also depends on temperature at which the reaction is carried out. This is due to variation in the heat capacity of the system with temperature.

Relation between ΔH or ΔE and temperature are given by Kirchoff's equation.

$$(\Delta H_2 - \Delta H_1) = \Delta C_P (T_2 - T_1)$$

$$(\Delta E_2 - \Delta E_1) = \Delta C_V (T_2 - T_1)$$

The above relations may be derived as follows:

For a reaction at constant pressure, $\Delta H = H_P - H_R$

Differentiating it w.r.t. T at constant P , we get

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$$\left(\frac{d\Delta H}{dT}\right)_P = \left(\frac{dH_P}{dT}\right)_P - \left(\frac{dH_R}{dT}\right)_P = (C_P)_P - (C_P)_R = \Delta C_P$$

or $d(\Delta H) = \Delta C_P dT$

Integrating this equation within appropriate limits, we get

$$\int_{T_1}^{T_2} d(\Delta H) = \Delta C_P \int_{T_1}^{T_2} dT$$

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_P (T_2 - T_1)$$

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{(T_2 - T_1)} = \Delta C_P \quad \text{.....(xvii)}$$

This equation is used to find heat of reaction at a temperature when it is known at another temperature.

Similarly, $\frac{\Delta E_{T_2} - \Delta E_{T_1}}{(T_2 - T_1)} = \Delta C_V \quad \text{.....(xviii)}$

In the limit as $(T_2 - T_1) \longrightarrow 0$, equation (xvii) yields the differential form

$$\frac{d(\Delta H)}{dT} = \Delta C_P$$

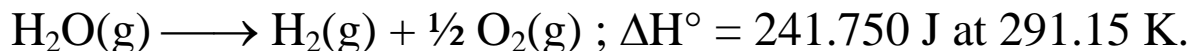
This shows that the rate of change of the enthalpy of a reaction is equal to the difference in heat capacities of products and reactants.

Since actually the heat capacities themselves vary with temperature, it is sufficiently accurate to use the average value of the heat capacity over the range of temperature considered.

Illustration 2.

Consider a reaction,

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What would be ΔH° at 298.15 K? Over the small temperature range, the effectively constant C_p values per mole are

$$C_p(\text{H}_2\text{O}) = 33.56, \quad C_p(\text{H}_2) = 28.83 ; \quad C_p(\text{O}_2) = 29.12 \text{ JK}^{-1} \text{ mol}^{-1}.$$

Solution:

$$(a) \quad \frac{\Delta H_{298.15}^\circ - \Delta H_{291.15}^\circ}{298.15 - 291.15} = \Delta C_p$$

$$\text{Now, } \Delta C_p = C_p(\text{H}_2) + \frac{1}{2} C_p(\text{O}_2) - C_p(\text{H}_2\text{O})$$

$$= 28.83 + \frac{29.12}{2} - 33.56 = 9.83 \text{ J K}^{-1}.$$

$$\therefore \Delta H_{298}^\circ = \mathbf{241.820 \text{ J}}$$

Illustration 3.

For Ag, \bar{c}_p ($\text{JK}^{-1} \text{ mol}^{-1}$) is given by $23.43 + 0.00628 T$. Calculate ΔH if 3 mol of silver are raised from 25°C to its melting point 961°C under 1 atm pressure.

Solution:

At constant P for 1 mole,

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} (23.43 + 0.00628 T) dT$$

$$\Delta H = 23.43 (T_2 - T_1) + \frac{1}{2} (0.00628 (T_2^2 - T_1^2)) \text{ Jmol}^{-1}.$$

Since, $T_1 = 273.15 + 25 = 298.15 \text{ K}$ and $T_2 = 273.15 + 961 = 1234.15 \text{ K}$.

$$(T_2 - T_1) = 936 \text{ K}$$

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$$\Delta H = 23.43(936) + \frac{1}{2} (0.00628) [(1234.15)^2 - (298.15)^2] = 21930 + 4500 \\ = 26430 \text{ J/mol.}$$

For 3 mol, $\Delta H = 3(26430) \text{ J} = \mathbf{79290 \text{ J}}$

4.4 Enthalpy or Heat of Formation

The amount of heat evolved or absorbed when one mole of a substance is formed from its constituent elements is called heat of formation.

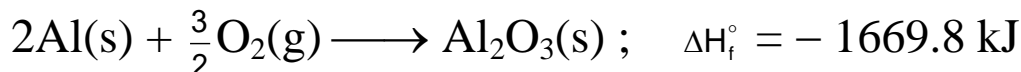
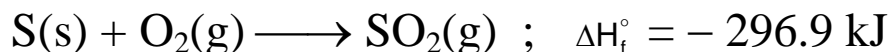


Thus, enthalpy of formation of HCl is -22 kcal .

The formation reaction of a compound has only one mole of the compound and nothing else on the product side. Only elements in their stable states of aggregation appear on the reactant side.

Standard Enthalpy of Formation (ΔH_f°)

It is enthalpy change of a reaction by which a compound is formed from its constituent elements, the reactants and products all being in a given, standard state (i.e. at 298 K and 1 atm pressure). For example,



Let us consider a reaction, $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) ; \Delta H_f^\circ = -393.5 \text{ kJ}$

$$\Delta H_f^\circ = H_P^\circ - H_R^\circ = -393.5 \text{ kJ}$$

Enthalpies of free elements in their standard states are assumed to be zero.

$$\text{so, } \Delta H_f^\circ = \Delta H_P^\circ = -393.5 \text{ kJ}$$

The compounds having positive enthalpies of formation are called endothermic compounds and are less stable than the reactants and those

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having negative enthalpies of formation are known as exothermic compounds and are more stable than the reactants.

If we know the standard heats of formation of various substances, we can calculate heat of reactions under standard conditions.

Thus,

$$\Delta H^\circ \text{ of a reaction} = \left[\text{Sum of the standard heats of formation of products} \right] - \left[\text{Sum of the standard heats of formation of reactants} \right]$$

$$\text{i.e. } \Delta H^\circ = \sum \Delta H_f^\circ (\text{Products}) - \sum \Delta H_f^\circ (\text{reactants})$$

The heats of formation of all the elements in their standard states are arbitrarily taken to be zero. For example, at 1 atm and 298 K, the stable state of aggregation of bromine is the liquid state. Hence liquid bromine, gaseous hydrogen, solid zinc, solid (rhombic) sulphur and solid (graphite) carbon, all have $H_{298}^\circ = 0$.

For elementary solids that exists in more than one crystalline form, the modification that is stable at 25°C and 1 atm is assigned $H^\circ = 0$. For example, zero assignment goes to rhombic sulphur rather than to monoclinic sulphur, to graphite rather than diamond. In cases in which more than one molecular species exists (e.g. O_2 and O_3), the zero enthalpy value goes to the most stable form at 25°C and 1 atm pressure i.e. for O_2 , $H_{298}^\circ(O_2, g) = 0$.

Once, the value of the standard enthalpy of the elements at 298 K has been assigned, the value at any other temperature can be calculated using Kirchoff's equation.

$$\int_{298}^T dH^\circ = \int_{298}^T C_P^\circ dT$$

$$H_T^\circ - H_{298}^\circ = \int_{298}^T C_P^\circ dT$$

$$H_T^\circ = H_{298}^\circ + \int_{298}^T C_P^\circ dT$$

This expression holds good for both elements as well as compounds. For elements, the first term on the right hand side is zero.

4.5 Enthalpy or Heat of Combustion

The amount of heat evolved or decrease in enthalpy when one mole of a substance is completely oxidised. Organic compounds containing only carbon, hydrogen and oxygen are burnt to gaseous carbon dioxide and liquid water. For example,



The measurements of the heat of combustion is used to determine the heats of formation of all organic compounds containing C, H, O, N etc.

Illustration 4.

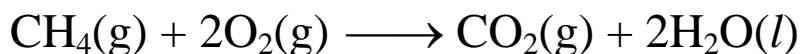
$$\Delta H_{\text{combustion}}^\circ(\text{CH}_4, \text{g}) = -890.36 \text{ kJ/mol} ;$$

$$H_f^\circ(\text{CO}_2, \text{g}) = -393.51 \text{ kJ/mol} ;$$

$$H_f^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ/mol} ;$$

$$H_f^\circ(\text{CH}_4, \text{g}) = ?$$

Solution:



$$\Delta H_{\text{combustion}}^\circ = H^\circ(\text{CO}_2, \text{g}) + 2H^\circ(\text{H}_2\text{O}, \text{l}) - H^\circ(\text{CH}_4, \text{g})$$

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$$\therefore H^\circ(\text{CH}_4, \text{g}) = H^\circ(\text{CO}_2, \text{g}) + 2H^\circ(\text{H}_2\text{O}, \text{l}) - \Delta H^\circ_{\text{combustion}}$$

$$= -393.51 + 2(-285.83) - (-890.36)$$

$$= -965.17 + 890.36 = -74.81 \text{ kJ/mol.}$$

4.6 Enthalpy or Heat of Solution

The amount of heat evolved or absorbed when one mole of solute is dissolved in excess of solvent so that further addition of solvent makes no heat change. For example,



Heat of an ideal solution is taken as zero.

4.7 Heat of Dilution

The amount of heat evolved or absorbed when solution containing one mole of solute is diluted from one concentration to another. For example,



If we subtract first equation from the second in the above set, we get



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This value of ΔH is the heat of dilution. The heat of dilution of a solution is dependent on the original concentration of the solution and on the amount of the solvent added.

Illustration 5.

The enthalpies of solution of anhydrous CuSO_4 and hydrated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are -66.5 and 11.7 kJ mol^{-1} respectively. Calculate the enthalpy of hydration of CuSO_4 to $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Solution:

Given that

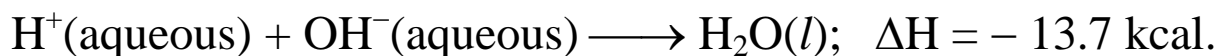
- (i) $\text{CuSO}_4(\text{s}) + \text{aqueous} \longrightarrow \text{CuSO}_4(\text{aqueous}) ; \Delta H_1 = -66.5 \text{ kJ/mol}$
- (ii) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) + \text{aqueous} \longrightarrow \text{CuSO}_4(\text{aqueous}) ; \Delta H_2 = 11.7 \text{ kJ/mol}$
- $\text{CuSO}_4(\text{s}) + 5\text{H}_2\text{O}(\text{l}) \longrightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}(\text{s}) ; \Delta H = ?$
- $\Delta H = \Delta H_1 - \Delta H_2 = -66.5 - 11.7 = -78.2 \text{ kJ}$

4.8 Enthalpy or Heat of Neutralisation

The amount of heat evolved when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base in dilute solution is called heat of neutralisation. For example,



Heat of neutralisation of a strong acid and a strong base is 13.7 kcal , or 57 kJ . The constant value is due to the fact that heat of neutralisation of strong acid and strong base is merely the heat of formation of H_2O from H^+ of an acid and OH^- of a base.



Determination of Heat of Neutralisation

It can be determined easily in the laboratory with the help of polythene or polystyrene bottle, fitted with a rubber cork and a stirrer as shown in the figure 1. 100 ml each of acid and alkali of equal normality are taken in separate bottles. The temperature of each solution is regularly recorded. When the constant temperature is attained, the alkali solution is added to the acid solution. The mixture is quickly stirred and the maximum temperature attained is noted.

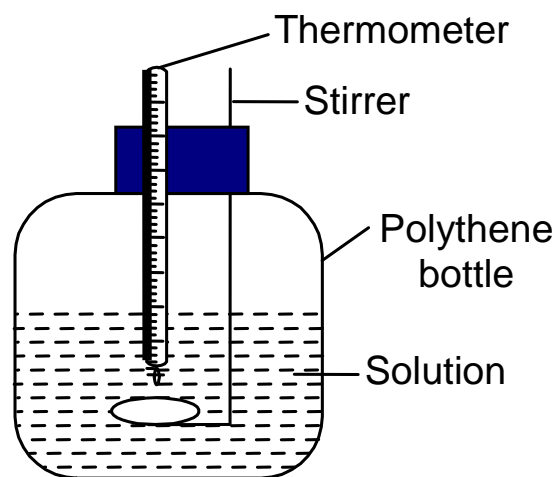


Figure 1

Let the initial temperature of acid & base be $T_1\text{K}$ and that after mixing be $T_2\text{K}$.

$$\therefore \text{Rise in temperature} = (T_2 - T_1)\text{K}.$$

Heat capacity of bottle is neglected as it is very small in comparison to that of solution. The specific heat capacity of the solution is assumed to be the same as that for water.

$$Q = m \times s \times (T_2 - T_1)$$

Where, Q = Heat change in the reaction, m = mass of solution and s = specific heat of solution.

$$\text{Thus, the enthalpy of neutralisation} = \frac{Q}{100} \times 1000 \times \frac{1}{N}$$

Where, N = normality of the acid or base.

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Illustration 6.

150 ml of 0.5 N nitric acid solution at 25.35°C was mixed with 150 ml of 0.5 N sodium hydroxide solution at the same temperature. The final temperature was recorded to be 28.77°C. Calculate the heat of neutralisation of nitric acid with sodium hydroxide.

Solution:

Total mass of solution = 150 + 150 = 300 gm

$$Q = 300 \times (28.77 - 25.35) = 300 \times 3.42 = 1026 \text{ cal}$$

$$\therefore \text{Heat of neutralisation} = \frac{Q}{150} \times 1000 \times \frac{1}{0.5} = \frac{1026}{150} \times 1000 \times \frac{1}{0.5} \\ = 13.68 \text{ kcal.}$$

Since, the enthalpy of neutralisation is always –ve, so, heat of neutralisation = – 13.68 kcal.

4.9 Enthalpies of Phase Transition

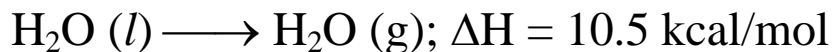
Enthalpy of Fusion

It is the enthalpy change involved in the conversion of one mole of a substance from solid state to liquid state at its melting point. This equals latent heat of fusion per gram multiplied by the molar mass. For example,



Enthalpy of Vapourisation

It is the enthalpy change involved in converting one mole of the substance from liquid state to gaseous state at its boiling point. For example,



Enthalpy of Sublimation

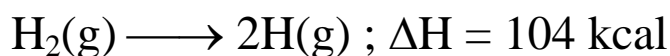
It is the enthalpy change involved in the conversion of one mole of a solid directly into its vapour at a given temperature below its melting point. For example,



$$\Delta H_{\text{sublimation}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vapourization}}$$

Heat of Atomisation

The amount of heat required for the formation of one mole of gaseous atoms from its elements is known as heat of atomization of that element.



In this case, heat of atomization of hydrogen is 52 kcal/mol.

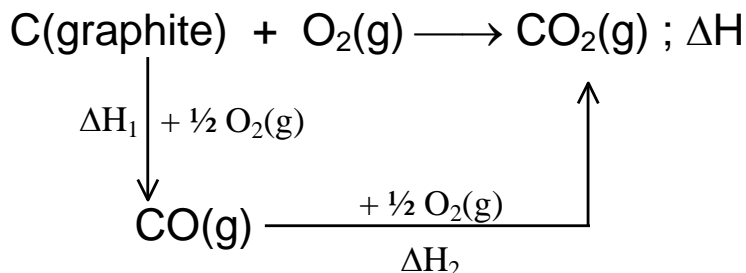
5. Hess's Law of Constant Heat Summation

The change in state of a system produced by a specified chemical reaction is definite. The corresponding enthalpy change is definite, since the enthalpy is a state function.

Thus, "if a specified set of reactants is transformed to a specified set of products by more than one sequence of reactions, the total enthalpy change must be the same for every sequence."

This rule, which is a consequence of the first law of thermodynamics, is known as *Hess's law*. More precisely, *"the enthalpy change in a chemical or physical process is the same whether the process is carried out in one step or in several steps"*. For example,

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$$\therefore \Delta\text{H} = \Delta\text{H}_1 + \Delta\text{H}_2$$

This property is due to the fact that the enthalpy change in a system is independent of the path followed.

5.1 Applications of Hess's Law

(i) Using Hess's law, enthalpy changes for the reactions, which are experimentally not possible, can be calculated.

e.g. for compounds such as C_2H_6 , C_6H_6 etc. whose direct synthesis from their constituent elements is not possible, the enthalpy of formation of such compounds can be calculated.

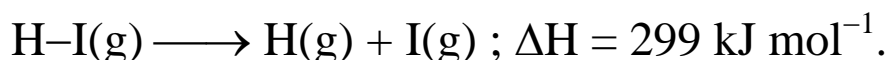
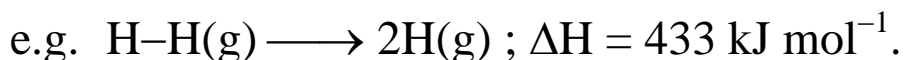
(ii) Calculation of Heat of Reaction

$$\Delta\text{H}_{\text{reaction}} = \sum \text{Heat of formation(Products)} - \sum \text{Heat of formation(Reactants)}$$

$$\Delta\text{H}_{\text{reaction}} = \sum \text{Heat of combustion(Reactants)} - \sum \text{Heat of combustion(Products)}$$

6. Bond Energies

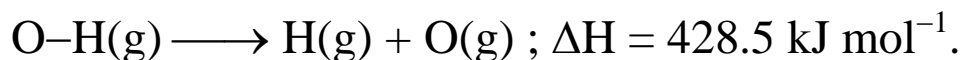
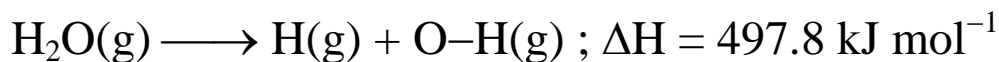
The amount of energy required to break one mole of a particular type of bond between the atoms in the gaseous state i.e. to separate the atoms in the gaseous state under one atmospheric pressure and the specified temperature is called bond dissociation energy.



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The bond dissociation energy of a diatomic molecule is also called bond energy. However, the bond dissociation energy depends on the nature of bonds and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. *This average bond dissociation energy required to break each bond in a compound is called bond energy which is also the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.*

Consider the dissociation of water molecule,



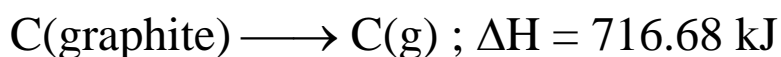
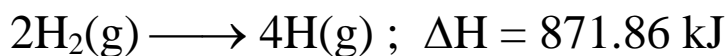
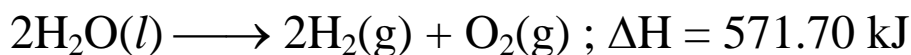
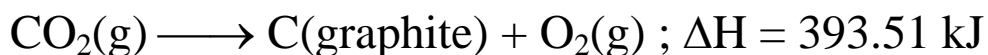
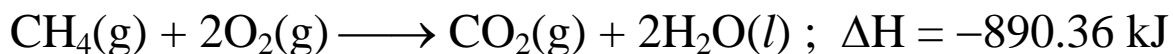
The average of these two bond dissociation energies gives the value of bond energy of O–H bond.

$$\therefore \text{B.E. of O-H bond} = \frac{497.8 + 428.5}{2} = 463.15 \text{ kJ mol}^{-1}.$$

Bond energies can be obtained from the data of heats of combustion and heats of dissociation.

Illustration 7.

Calculate bond energy of C–H bond from the following data.



Solution:

Adding all the equations, we get



$$\therefore \text{B.E of C-H bond} = \frac{1663.39}{4} = \mathbf{415.85 \text{ kJ mol}^{-1}}$$

6.1 Applications of Bond Energies

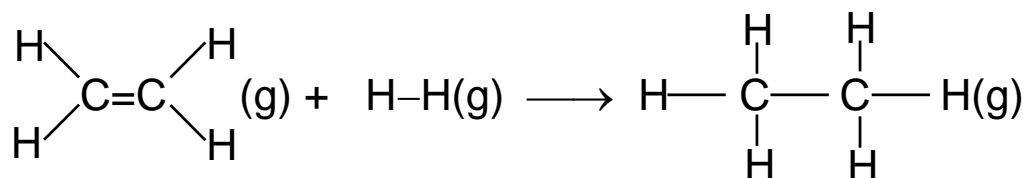
Determination of Heat Of Reactions

$\Delta H_{\text{reaction}}$ = Sum of bond energies of reactants – Sum of bond energies of products.

Illustration 8.

Given that the average bond energies of C–C, C=C, C–H and H–H bonds are 80.5, 145, 98.2 and 103 kcal mol^{–1} respectively; calculate the enthalpy of the reaction per mole.

Solution:



$$\Delta H_{\text{reaction}} = (\epsilon_{\text{H-H}} + \epsilon_{\text{C=H}}) - (2\epsilon_{\text{C-H}} + \epsilon_{\text{C-C}})$$

$$\Delta H_{\text{reaction}} = (103 + 145) - (196.4 + 80.5) = 248 - 276.9$$

$$\Delta H_{\text{reaction}} = \mathbf{-28.9 \text{ kcal/mol.}}$$

Determination of Resonance Energy

Resonance Energy

$$= (\text{Experimental/Actual heat of formation}) - (\text{Calculated heat of formation}).$$

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Illustration 9.

The standard molar enthalpies of formation of cyclohexane (*l*) and benzene (*l*) at 25°C are – 156 and 49 kJ mol⁻¹ respectively. The standard enthalpy of hydrogenation of cyclohexene (*l*) at 25°C is –119 kJ mol⁻¹. Use these data to estimate the magnitude of resonance energy of benzene.

Solution:



(This involves breaking up of one double bond and addition of one H₂ molecule).



(This involves breaking up of three double bonds and addition of three H₂ molecules).

Enthalpy change of equation (i) can be given as

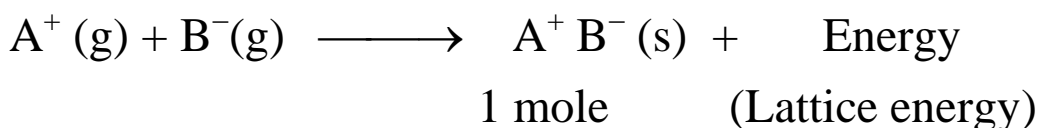
$$\Delta\text{H} = -357 = \Delta\text{H}_f(\text{C}_6\text{H}_{12}, \text{l}) - \Delta\text{H}_f(\text{C}_6\text{H}_6, \text{l})$$

$$\Delta\text{H}_f(\text{C}_6\text{H}_6, \text{l}) = -156 + 357 = 201 \text{ kJ}$$

$$\begin{aligned} \therefore \text{Resonance energy} &= \text{Observed } \Delta\text{H}_f - \text{calculated } \Delta\text{H}_f \text{ of } \text{C}_6\text{H}_6 \\ &= 49 - 201 = -152 \text{ kJ} \end{aligned}$$

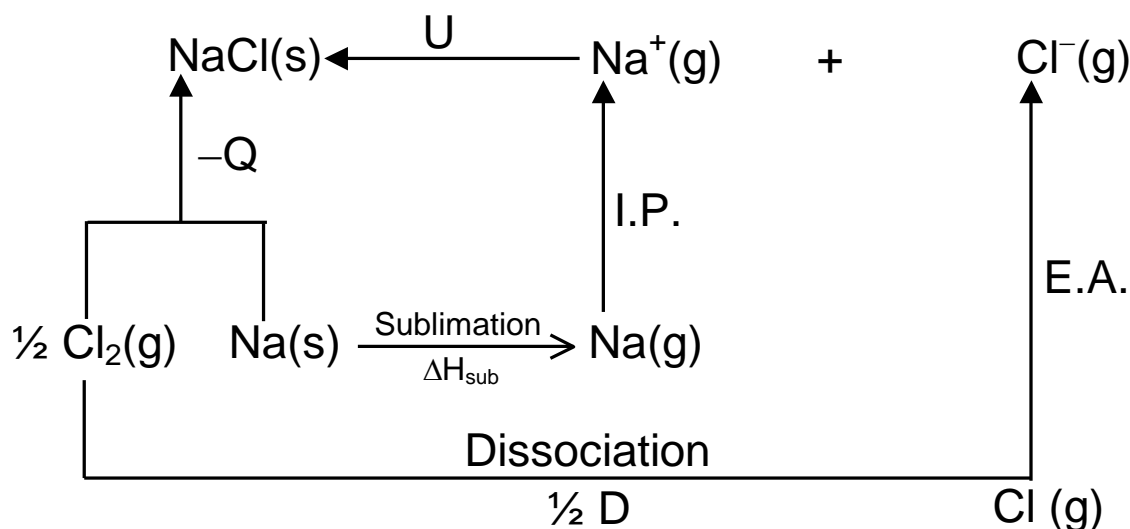
6.2 Determination of Lattice Energy (Born–Haber Cycle)

Lattice energy of an ionic compound is defined as the amount of energy released when one mole of the ionic compound is formed by the interaction of required number of constituent gaseous cations and gaseous anions.



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It is represented by the symbol, U . It is given negative sign as the energy is always released. Since, it is difficult to find the lattice energy by direct experiment, it is generally calculated by indirect method known as Born–Haber cycle, which is based on Hess’s law. The cycle can be easily explained by taking the example of the formation of sodium chloride (NaCl). The formation of sodium chloride can be schematically represented as:



The formation of sodium chloride can occur either by direct combination of sodium(s) and molecular chlorine(g) or in various steps.

Let the heat of formation of sodium chloride by direct combination be $-Q$.

The various steps in the formation of NaCl are the following. In each step, either energy is absorbed or released.

Steps involved	Energy change
(a) Solid sodium changes into gaseous sodium. Energy is absorbed. It is sublimation energy. $\text{Na(s)} + \text{sublimation energy} \longrightarrow \text{Na(g)}$	$+\Delta H_{\text{sub}}$
(b) Gaseous sodium atoms change into gaseous sodium ions. In this step, energy equivalent to ionisation potential is absorbed.	$+\text{I.P}$

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$\text{Na(g)} + \text{I.P.} \longrightarrow \text{Na}^+(\text{g}) + \text{e}^-$	
(c) Half mole of molecular chlorine dissociate into one mole of gaseous atomic chlorine. In this step, energy equivalent to one half of the dissociation energy is absorbed. $\frac{1}{2}\text{Cl}_2(\text{g}) + \frac{1}{2}D \longrightarrow \text{Cl}(\text{g})$	$+\frac{1}{2}D$
(d) Gaseous chlorine atoms change into chlorine ions by acceptance of electrons. In this process, energy equivalent to electron affinity is released. $\text{Cl}(\text{g}) + \text{e}^- \longrightarrow \text{Cl}^-(\text{g}) + \text{E.A.}$	$-\text{E.A.}$
(e) Sodium and chlorine ions are held together by electrostatic forces to form $\text{Na}^+ \text{Cl}^-(\text{s})$. The energy equivalent to lattice energy is released.	$-U$

Total energies involved in the above five steps is

$$= \Delta H_{\text{sub}} + \frac{1}{2}D + \text{I.P.} - \text{E.A.} - U$$

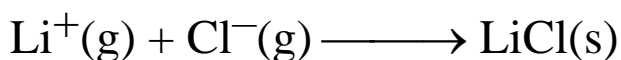
Thus, according to Hess's law

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2}D + \text{I.P.} - \text{E.A.} - U \quad \dots\dots\dots(\text{xix})$$

So, knowing all other quantities, U can be calculated.

Illustration 10.

Calculate the lattice energy for the reaction,



from the following data.

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$$\Delta H_{\text{sub}}(\text{Li}) = 160.67 \text{ kJ mol}^{-1};$$

$$\frac{1}{2}D(\text{Cl}_2) = 122.17 \text{ kJ mol}^{-1}; \text{I.P}(\text{Li}) = 520.07 \text{ kJ mol}^{-1};$$

$$\text{E.A}(\text{Cl}) = -365.26 \text{ kJ mol}^{-1} \text{ and } \Delta H_f^\circ(\text{LiCl}) = -401.66 \text{ kJ mol}^{-1}.$$

Solution:

Applying the equation (xix),

$$-Q = \Delta H_{\text{sub}} + \frac{1}{2}D + \text{I.P} - \text{E.A} - U$$

and substituting the respective values gives

$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 - U$$

$$U = 839.31 \text{ kJ mol}^{-1}$$

7. Experimental Determination of the Heat Of Reaction

The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called calorimeter. The principle of measurement is that heat given out is equal to heat taken, i.e.,

$$Q = (W + m) \times s \times (T_2 - T_1),$$

where Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of water in the calorimeter and s is its specific heat, T_2 is the final temperature and T_1 is the initial temperature of the system. Different types of calorimeters are used but two of the common types are

- (i) Water calorimeter and
- (ii) Bomb calorimeter

7.1 Water calorimeter

It is a simple form of calorimeter which can be conveniently used in the laboratory. It is shown in Figure 2.

It consists of a large vessel A in which a calorimeter B is held on corks. In between the calorimeter and the vessel, there is a packing of an insulating material such as cotton wool. Inside the calorimeter, there are holes through which a thermometer, a stirrer and the boiling tube containing reacting substances are fitted. A known amount of water is taken in the calorimeter and known amount of reacting substances are taken in the boiling tube.

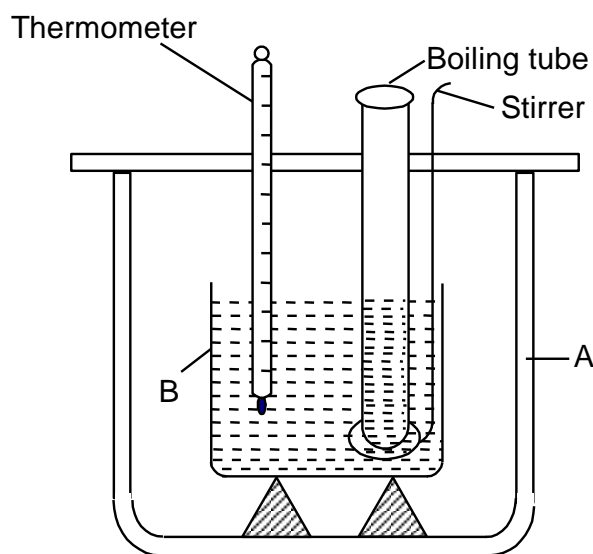


Figure 2

The heat evolved during the reaction will be absorbed by the water. The rise in temperature is recorded with the help of thermometer. The heat evolved is then calculated as

$$Q = (W + m) \times s \times (T_2 - T_1)$$

7.2 Bomb Calorimeter

This is commonly used to find the heat of combustion of organic substances. It consists of a sealed combustion chamber, called a bomb. A weighed quantity of the substance in a dish along with oxygen under about 20 atmospheric pressure is placed in the bomb, which is lowered in water contained in an insulated copper vessel. The vessel is fitted with a stirrer and a sensitive thermometer. The arrangement is shown in figure 3.

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The temperature of the water is noted and the substance is ignited by an electric current. After combustion, the rise in temperature of the system is noted. The heat of combustion can be calculated from the heat gained by water and calorimeter.

Since the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE .

$$\Delta E = \left(\frac{(W + m)(t_2 - t_1) \times s}{w_1} \times M \right) \text{ kcal}$$

where M is the molar mass of the substance

and w_1 is the mass of substance taken.

ΔH can be calculated from the relation,

$$\Delta H = \Delta E + \Delta n_g RT.$$

Illustration 11.

A sample of 0.16 g CH_4 was subjected to combustion at 27°C in a bomb calorimeter. The temperature of the calorimeter system (including water) was found to rise by 0.5°C . Calculate the heat of combustion of methane at (i) constant volume and (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K^{-1} and $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$.

Solution:

Heat of combustion at constant volume,

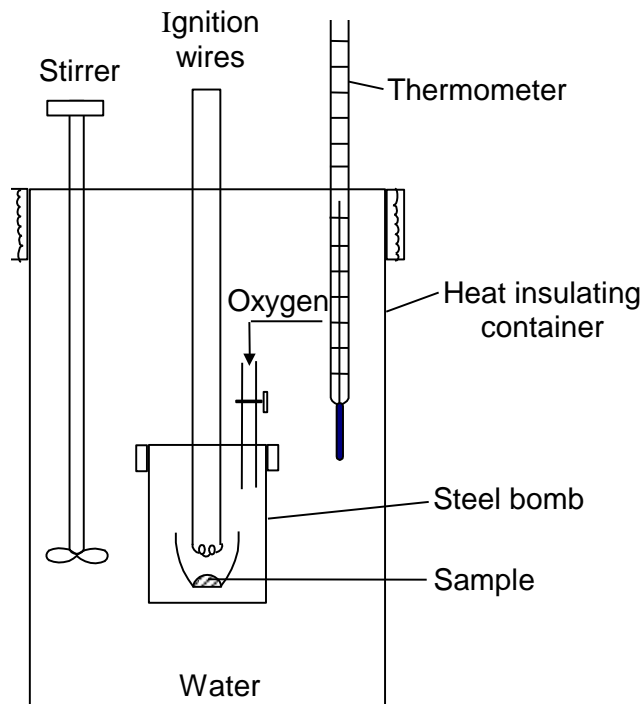


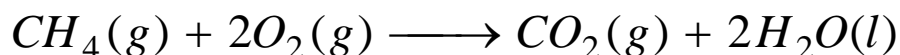
Figure 3

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$$\Delta E = \text{Heat capacity} \times \text{Rise in temperature} \times \frac{\text{Molar mass of compound}}{\text{Mass of compound}}$$

$$= 17.7 \times 0.5 \times \frac{16}{0.16} = 885$$

$$\text{i.e., } \Delta E = -885 \text{ kJ mol}^{-1}$$



$$\Delta n_g = 1 - 3 = -2, T = 300 \text{ K}, R = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\begin{aligned}\Delta H &= \Delta E + \Delta n_g RT = -885 + (-2) \times 8.314 \times 10^{-3} \times 300 \\ &= -885 - 4.988 = -889.988 \text{ kJ mol}^{-1}\end{aligned}$$

8. Second Law of Thermodynamics

8.1 Spontaneous Process

In any system, a spontaneous process is one which occurs on its own without the help of external energy. The natural changes that occur around us result from such processes.

For example, flow of heat from a hot body to a cold one, flow of water downhill, and the expansion of a gas from high pressure to low pressure. Besides being spontaneous, these processes are also unidirectional, i.e., they occur on their own in one direction only. A spontaneous process cannot be reversed without the aid of external work or energy. The work has to be done to move uphill or to compress a gas.

Many common chemical reactions are spontaneous and occur in one direction although finally a state of equilibrium is reached. Everything in nature has a tendency to move towards a state of lowest energy, at which point equilibrium exists. The heat energy which is given out during an

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exothermic reaction shows that there is a lowering in chemical energy on proceeding from the reactants to the products. From this, we may conclude that a reduction in enthalpy provides the necessary driving force for a reaction to occur. However, many endothermic reactions also proceed on their own and so it looks as though a negative enthalpy change is not a reliable criterion to judge the spontaneity of chemical reactions.

The first law of thermodynamics does not state whether a reaction is spontaneous or not and in which direction it will occur. For example, let us take a metal bar, which is heated at one end. Assuming no loss of heat from the bar, when heat passes from the hot end to the cold end, the decrease in thermal energy at the hot end is equal to the increase at the cold end. This satisfies the requirements of the I law. From experience, we know that heat will not flow, on its own from the cold end to the hot end. However, the Ist law does not exclude the occurrence of such non-spontaneous processes, but only tells us that an energy decrease in one part of the system is equal to an increase in another part.

8.2 Statement of the 2 Law

Second law of thermodynamics is concerned with the direction and spontaneity of processes. There are many ways of formulating the law based on our experience of the direction or manner in which natural processes occur. Clausius stated the law as **“The transference of heat from a cold to a hot body cannot be achieved without the performance of work”**.

Because natural or spontaneous processes occur over a period of time, they must be thermodynamically irreversible. Another way of formulating the second law is **‘Any process occurring on its own is thermodynamically irreversible’**.

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The basic concept of the second law of thermodynamics is that all spontaneous processes are unidirectional and thermodynamically irreversible.

8.3 Entropy

To decide whether a chemical reaction can take place or not, the first factor that has to be considered is whether there is enough energy available. If the reaction is exothermic, there is no reason why it should not take place spontaneously but if the reaction is endothermic then it would not. But in nature, we come across numerous examples of endothermic reactions, which are spontaneous (for example, evaporation of water). From this, we conclude that energy alone is not the deciding factor. This is where the concept of *entropy* becomes important.

Definition of Entropy

If any process is carried out reversibly, so that dq_{rev} is the heat absorbed by the system in the process at constant temperature (T), then the entropy change (dS) is given by

$$dS = \frac{dq_{rev}}{T}$$

For finite changes, $\Delta S = \frac{q_{rev}}{T}$

Meaning of Entropy

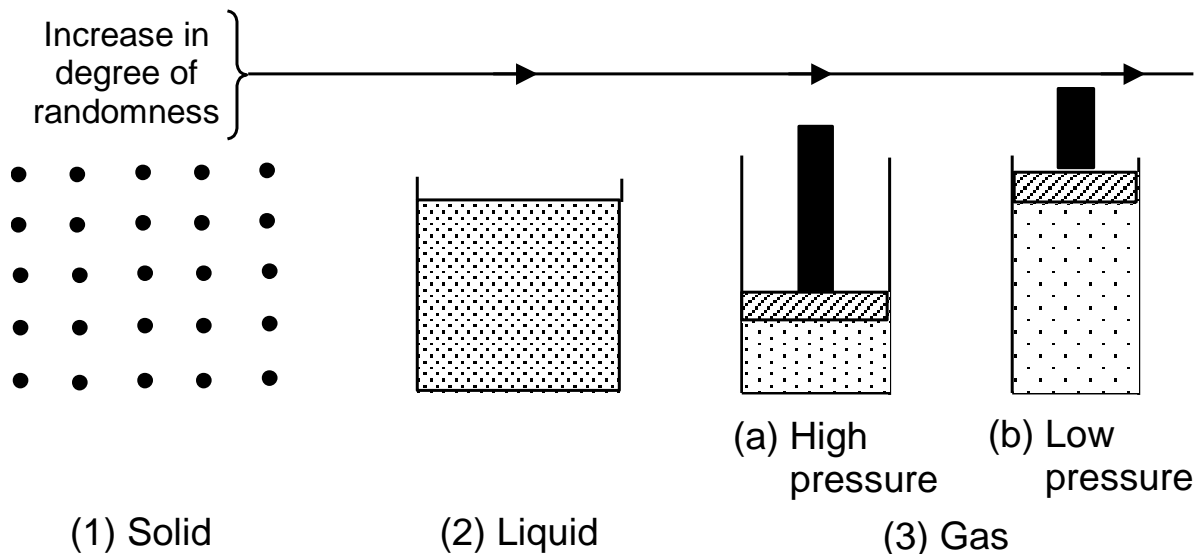
Although the concept of entropy was first applied to the performance of heat engines, pictorial representations of entropy can be obtained from two sources and lead to the following conclusions,

- (a) Entropy is the degree of disorder or randomness of a system.
- (b) Change in entropy is the capacity for spontaneous change in a system.

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Entropy is a measure of disorderness of a system.

To illustrate the meaning of disorder or randomness, consider a substance which changes state.



In the gaseous state and at low pressures, the molecules are free to move about unrestricted. If the pressure is increased, the same number of molecules now occupies a smaller volume. The chances of finding a molecule within a given volume are greater under these conditions than when it was at lower pressure. Hence, the molecules are more ordered (or less randomly distributed) at higher pressure. Added to this, the force of intermolecular attraction increases as the pressure increases and this too has a restricting effect on the molecules.

In the liquid state, the molecules are much closer together than in the gaseous state, because the volume containing the same number of molecules is much smaller. The molecules in the liquid state are more highly ordered than a gas at high pressure. Also in the liquid state, the forces of intermolecular attraction are greater, causing a still more highly ordered state.

In the solid state, the atoms, molecules or ions that form the crystal are usually held in fixed crystal lattices, which can only vibrate and rotate.

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Hence in a solid, the atoms, molecules or ions have little or no choice as to where they shall be i.e., they are highly ordered or have a very small freedom.

This gradual decrease in the measure of disorder of the molecules is identified with entropy changes, being high for a gas and low for a solid.

Entropy as the Capacity for Spontaneous Change

Let us consider the following examples of spontaneous change.

(i) Expansion of a gas from a region of high pressure to a region of low pressure

Suppose, there are two bulbs filled with a gas at different pressures. If the two bulbs are connected, the gas from the bulb at high pressure will flow into the bulb at low pressure till the pressures in the two bulbs become equal. The greater the pressure difference, the greater the flow of gas, the greater is the capacity of the system for spontaneous change and the greater is the entropy change.

(ii) Solute spreading from a region of high concentration to a region of low concentration.

If the concentration difference between two solutions is considerable, there is obviously a much greater flow of solute from the high concentration to the lower concentration region.

Degree of Randomness and Spontaneous Change

The two approaches are two ways of looking at the same problem and we inevitably come to the conclusion that **a system undergoing a spontaneous change is moving to a state of greater randomness.**

This is understood well by considering the two spontaneous processes cited above.

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(i) As a gas expands from a region of high pressure to a region of low pressure, the molecules move farther apart, so that the intermolecular attraction becomes less and the molecules are given a larger volume to move about in. Both these effects give the molecules more freedom and the system has moved to a **state of greater randomness during spontaneous expansion**.

(ii) When a solute spreads from a region of high concentration to a region of low concentration, the molecules move farther apart. Each molecule has more space to move about in and is therefore less restricted in position. Hence, the solute molecules are more randomly distributed throughout the solvent.

Entropy and Structure

The standard molar entropies of n-Octane; 2,2-Dimethyl hexane and 2,2,3,3-Tetramethylbutane (all of them are isomers) are 463.6, 431.4 and 394.6 J/l respectively. As the chain becomes more branched the top-like rotation of one carbon atom with respect to another becomes more hindered. Hence, we should expect n-octane to have a greater entropy than the branched chain isomers, The above values show this relationship between entropy and structure that helps in understanding why entropy changes are important in chemical reactions.

Entropy changes in chemical reactions can be easily identified. Larger complex molecules are more ordered and have less entropy. For example, in the formation of water from its elements



a more complex molecule is produced, the number of molecules decreases, and the system becomes more ordered.

The decomposition of phosphorus pentachloride



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is an endothermic process, which leads to the formation of twice as many molecules. This leads to increase in the distribution of matter and consequently results in increase in entropy of the system.

Now, let us consider the following reaction,



Normally, we would have expected no increase in the entropy of the system as the number of molecules of reactants and products are equal. However, we find that the entropy increases. The reason is heteronuclear diatomic molecules have higher entropy than homonuclear diatomic molecules because they possess a more random distribution of matter, i.e., they are more disordered.

Illustration 12.

For the reactions given below, predict the sign of ΔS as positive or negative?

- (a) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
- (b) $\text{Ni}(\text{s}) + 4\text{CO}(\text{g}) \longrightarrow \text{Ni}(\text{CO})_4(\text{g})$
- (c) $2\text{Ca}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow 2\text{CaO}(\text{s})$
- (d) $\text{H}_2(\text{g}) + \text{S}(\text{s}) \longrightarrow \text{H}_2\text{S}(\text{g})$

Solution:

- (a) Three gas molecules give rise to two gas molecules. Hence, disorderness decreases i.e., $\Delta S < 0$ (negative).
- (b) Four gas molecules are converted into a single gas molecule and hence, the disorderness decreases i.e., ΔS is < 0 (negative).
- (c) Three reacting units, of which two are solid and one gas are changed to two solid units. Disorderness decreases i.e. $\Delta S < 0$ (negative).

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- (d) Two reacting units, one of which is a solid, forms a gaseous molecule. Since a heteronuclear gas results, disorderness increases and ΔS is positive ($\Delta S > 0$).

Calculation of Entropy Change

The entropy change for a given process is given by

$$\Delta S = \int dS = \int \frac{dq_{rev}}{T}$$

If we replace dq by an expression for the heat absorbed for a particular process, we can calculate the entropy change.

(a) Heating of a solid

When only heat change is involved, as in the heating of a solid, the heat change is given by the expression

$$\text{Quantity of heat (q)} = m \times s \times \Delta t$$

(m = mass; s = specific heat; Δt = temperature rise)

OR

Quantity of heat (q) = number of moles \times molar heat \times temperature rise

For one mole, $dq = C_s \cdot dT$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_s \cdot dT}{T}$$

$$\Delta S = C_s \ln \frac{T_2}{T_1}$$

(b) Change of state

There are changes taking place at constant temperatures (i.e. isothermal) during which the two states are at equilibrium with one another provided

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the process is carried out reversibly. The heat absorbed will be **latent heat** (L) and the temperature will be melting or boiling point.

$$\Delta S = \frac{L}{T}.$$

Illustration 13.

The latent heat of fusion of water is 6016.6 J/mole at 0°C and 1 atm. Calculate the entropy change.

Solution:

$$\Delta S = \frac{L}{T} = \frac{6016.6}{273} = \mathbf{22.0 \text{ J/mole/deg}}$$

(c) Entropy change in ideal gas

For an ideal gas changing its state from (P₁, V₁, T₁) to (P₂, V₂, T₂)

$$\begin{aligned}\Delta S &= n C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \\ &= n C_p \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}\end{aligned}$$

1. For an isothermal process (T₂ = T₁)

$$\Delta S = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{P_2}{P_1}$$

2. For an isobaric process

$$\Delta S = n C_p \ln \frac{T_2}{T_1}$$

3. For an isochoric process

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$$\Delta S = n C_V \ln \frac{T_2}{T_1}$$

4. For an adiabatic process

Since $dq = 0$, $\Delta S = 0$

Such a process is called isoentropic process.

Illustration 14.

Calculate the entropy change per mole of substance in each of the following cases.

(i) The freezing of isobutane at -160°C .

$$\Delta H (\text{solid} \longrightarrow \text{liquid}) = 4540 \text{ J mol}^{-1}.$$

(ii) The vaporization of water at its boiling point, 100°C .

$$\Delta H (\text{liquid} \longrightarrow \text{vapour}) = 407 \text{ kJ mol}^{-1}.$$

(iii) Expansion reversibly and isothermally of an ideal gas from a volume of 2 dm^3 to 10 dm^3 at 27°C . Also calculate entropy change of surroundings due to the process.

(iv) Expansion irreversibly and isothermally of an ideal gas from volume 2 dm^3 to 10 dm^3 against a constant pressure of 1 atm , at 27°C . Also calculate entropy change of surroundings due to the process.

Solution:

(i) Freezing temperature of isobutane $= -160^\circ\text{C} = 113 \text{ K}$

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

$$\text{Here } q_{\text{rev}} = -4540 \text{ J mol}^{-1}$$

$$\therefore \Delta S = \frac{-4540}{113} = -40.2 \text{ JK}^{-1} \text{ mol}^{-1}$$

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Note that in freezing, the substance becomes more ordered. Hence, entropy is lost by the substance (ΔS is $-ve$).

(ii) For the reversible vaporisation of water at 100°C ,

$$\Delta S = \frac{q_{rev}}{T} = \frac{L}{T} = \frac{\Delta H_{vap}}{T} = \frac{407000}{373} = \mathbf{1091.2 \text{ JK}^{-1} \text{ mol}^{-1}}$$

(iii) For an isothermal process,

$$\Delta S = R \ln \frac{P_1}{P_2}$$

At constant temperature, $P_1 V_1 = P_2 V_2$

$$\therefore \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\therefore \Delta S = R \ln \frac{V_2}{V_1} = 8.314 \times 2.303 \log \frac{10}{2} = 13.4 \text{ J K}^{-1} \text{ mol}$$

If we treat system and surroundings as an isolated system, entropy change of surrounding = $-\Delta S = -13.4 \text{ J K}^{-1} \text{ mol}$. \therefore For a reversible process entropy of universe remains constant. Total entropy change for isolated system = $\Delta S - \Delta S = 0$.

(iv) Total entropy change of the system, has to be calculated assuming a reversible path,

$$\Delta S_{\text{system}} = \int \frac{dq_{rev}}{T} = R \ln \frac{V_2}{V_1} = 13.4 \text{ J K}^{-1} \text{ mol}^{-1}. \text{ [same as in (iii)]}$$

If we consider system & surroundings as an isolated system, entropy change of surrounding,

$$\Delta S_{\text{surrounding}} = \frac{\text{Heat exchanged by surrounding}}{T} = \frac{q}{T}.$$

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For the system,

$$\Delta E' = 0 = q + w \Rightarrow q = -w = P(V_2 - V_1).$$

For surrounding, $q = -P(V_2 - V_1)$.

$$\Rightarrow S_{\text{surrounding}} = \frac{-1(10-2) \text{ L atm}}{300 \text{ K}} = -\frac{8}{300} \times \frac{8.314}{0.0821} = -2.7 \text{ J/mol}^{-1} \text{ K}^{-1}.$$

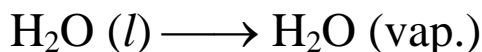
$$\begin{aligned} \text{Entropy change of isolated system} &= \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \\ &= 13.4 - 2.7 = 10.7 \text{ J/mol}^{-1} \text{ K}^{-1}. \end{aligned}$$

For an irreversible process, entropy of universe increases.

Illustration 15.

The enthalpy change for the transition of liquid water to steam is 41 kJ mol^{-1} at 100°C . Calculate the entropy change for the process.

Solution:



The equation for entropy change is

$$\Delta S = \frac{L}{T} = \frac{\Delta H_{\text{vap}}}{T} = \frac{41 \times 1000}{(273 + 100)} = \frac{41000}{373} = 110 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note that ΔS is greater than zero as there is an increase in the disorder (randomness) in the system.

Illustration 16.

3 moles of $\text{N}_2(\text{g})$ originally at 1 atm pressure are mixed isothermally with 5 moles of $\text{H}_2(\text{g})$ also at 1 atm pressure to yield a mixture whose total pressure is 1 atm. Assuming ideal behaviour, calculate entropy of mixing.

Solution:

Total pressure of mixture = 1 atm

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$$\text{Final pressure of N}_2 = \frac{3}{5+3}(1) = 0.375 \text{ atm}$$

$$\text{Final pressure of H}_2 = 1 - 0.375 = 0.625 \text{ atm}$$

For N₂, entropy change

$$\Delta S_{N_2} = -nR \ln \frac{P_2}{P_1} = -2.303 \times 3 \times 8.314 \times \log \left(\frac{0.325}{1} \right) = 28.03 \text{ J/K}$$

For H₂, entropy change

$$\Delta S_{H_2} = -nR \ln \frac{P_2}{P_1} = -5 \times 8.314 \times 2.303 \log \frac{0.675}{1} = 16.34 \text{ J/K.}$$

$$\text{Total entropy change due to mixing} = \Delta S_{N_2} + \Delta S_{H_2} = \mathbf{44.37 \text{ J/K.}}$$

Standard Molar Entropies of Elements and Compounds

Entropy can be defined very precisely and measured accurately. These are entropies per mole, at 1 atm in the units of Joules per Kelvin (J/K).

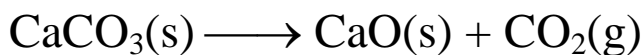
- (i) Standard molar entropies of substances are always positive quantities ($S^\circ > 0$).
- (ii) Elements as well as compounds are assigned standard entropies. This is in contrast to the heats of formation, when $H_f = 0$ for elements.
- (iii) Solids in general have lower entropies than liquids and in turn liquids have lower entropies than gases. For example,

	$S^\circ(\text{J/K})$
C(s)	5.7
H ₂ O(l)	69.9
CO ₂ (g)	213.6

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Illustration 17.

Calculate the standard entropy change for the reaction,



The standard entropy change $\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$

The entropies are $\text{CaO}(\text{s}) = 39.7 \text{ J/K mol}$, $\text{CO}_2(\text{g}) = 213.6 \text{ J/K mol}$, $\text{CaCO}_3(\text{s}) = 92.9 \text{ J/K mol}$.

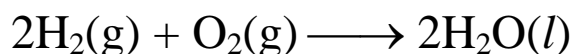
Solution:

$$\begin{aligned}\Delta S^\circ &= S^\circ_{\text{CaO}(\text{s})} + S^\circ_{\text{CO}_2(\text{g})} - S^\circ_{\text{CaCO}_3(\text{s})} = (39.7 + 213.6 - 92.9) \text{ J/K} \\ &= +160.4 \text{ J/K}\end{aligned}$$

Note that ΔS° for the decomposition of calcium carbonate is a positive quantity. This is to be expected as the gas formed CO_2 , has a much higher molar entropy than either of the solids, CaO or CaCO_3 .

Illustration 18.

Calculate the standard entropy change for the reaction,



Standard molar entropies are

$$\text{H}_2\text{O}(\text{l}) = 69.9 \text{ J/K}, \text{O}_2(\text{g}) = 205.0 \text{ J/K} \text{ and } \text{H}_2(\text{g}) = 130.6 \text{ J/K}.$$

Solution:

$$\begin{aligned}\Delta S^\circ &= 2S^\circ_{\text{H}_2\text{O}(\text{l})} - 2S^\circ_{\text{H}_2(\text{g})} - S^\circ_{\text{O}_2(\text{g})} = (139.8 - 261.2 - 205.0) \text{ J/K} \\ &= -326.4 \text{ J/K}\end{aligned}$$

Note that the entropy for the formation of water is a negative quantity.

Summarizing, we can say that a reaction, which results in the increase in the number of moles of gas, is accompanied by an increase in entropy.

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Conversely, if the number of moles of gas decreases, ΔS can be expected to be a negative quantity.

8.4 Free Energy Change (ΔG)

The two thermodynamic quantities, which affect the spontaneity of a reaction, are **enthalpy (H)** and **entropy (S)**. The next problem is how to arrange two quantities in such a way as to arrive at a single function, which can be used to determine whether a reaction is spontaneous, or not. J. Willard Gibbs introduced a new quantity called the Gibbs free energy and gave it the symbol G . The free energy of a substance, like its enthalpy or entropy is a characteristic property of the substance. In any reaction, the change in free energy, ΔG is the difference in free energies of products and reactants.

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

Gibbs showed that the sign of ΔG can be used to determine whether a reaction is spontaneous or not. For a reaction carried out at constant temperature and pressure,

- (1) If ΔG is negative, the forward reaction is spontaneous.
- (2) If ΔG is positive, the forward reaction is non-spontaneous. Instead, the reverse reaction will be spontaneous.
- (3) If ΔG is zero, the system is at equilibrium. There is no tendency for the net reaction to take place in either direction.

It can be inferred that ΔG is a measure of the driving force of a reaction. Reactions (at constant temperature and pressure) go in the direction in which there is a decrease of free energy. This implies that the direction in which a reaction takes place is determined by the relative free energies of products and reactants. If the products have a lower free energy than the reactants ($G_{\text{products}} < G_{\text{reactants}}$), the forward reaction will take place. If the reactants have a lower free energy than the products ($G_{\text{reactants}} < G_{\text{products}}$),

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the reverse reaction will take place. If $G_{\text{products}} = G_{\text{reactants}}$, the system is at equilibrium and there is no driving force to make the reaction go in either direction.

Relationship between ΔG , ΔH and ΔS

ΔG is made up of two terms; an energy term and an entropy term.

$$\Delta G = \underset{\substack{\text{energy} \\ \text{term}}}{\Delta H} - T \underset{\substack{\text{entropy} \\ \text{term}}}{\Delta S}$$

where, T is the temperature in Kelvin. This equation tells us that the driving force for a reaction, ΔG , represents two quantities. One of these is the enthalpy change due to the making and breaking of bonds, ΔH . The other is the product of the change in randomness, ΔS times the absolute temperature T .

Why does a reaction take place? The answer is that the reactants are unstable in the presence of each other and can exchange energy, so as to acquire a more stable state as products. In fact, all systems react so as to acquire a minimum energy irrespective of the fact that whether it is a mechanical, chemical or any other type of system.

The two factors which tend to make ΔG negative and hence gives rise to a spontaneous reaction are

(1) A negative value of ΔH

Exothermic reactions ($\Delta H < 0$) tend to be spontaneous because they contribute to a negative value of ΔG . Chemically, it means that there will be a tendency to form “strong” bonds at the expense of “weak” bonds.

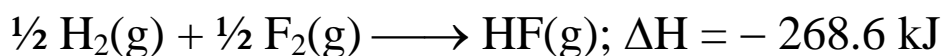
(2) A positive value of ΔS

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If the entropy change is positive, ($\Delta S > 0$) the term $-T\Delta S$ will make a negative contribution to ΔG . Hence, there will be a tendency for the reaction to be spontaneous provided the products are less ordered than the reactants.

In many physical processes, the increase in entropy is the major driving force. An example is the formation of a solution. When oxygen diffuses into nitrogen, or benzene is dissolved in toluene, the enthalpy change is practically zero, but ΔS is a positive quantity as the solution becomes less ordered than the pure substance. Another example is the spontaneous evaporation of water, although it is an endothermic reaction but liquid water, which is a more ordered arrangement, passes into water vapour, which is less ordered (ΔS increases).

In certain reactions, ΔS is nearly zero and ΔH is the chief and only component of the driving force of spontaneity. An example is the synthesis of hydrogen fluoride from its constituent elements,



In this reaction, ΔH has a large negative value. This is due to the fact that the bonds in HF are stronger than the bonds in H_2 and F_2 molecules.

In most cases, both ΔH and ΔS make significant contributions to ΔG . To determine the sign of ΔG , the values of ΔH and ΔS must be taken into consideration as well as the temperature.

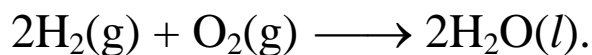
Standard Free Energy Change

Using the equation, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, it is possible to calculate the standard free energy change for the reaction, ΔG° . This is defined as the *free energy change when all the species involved in the reaction are at unit concentrations (for gases 1 atm and 1 M for ions or molecules in aqueous solution)*.

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Illustration 19.

Calculate the standard free energy change for the reaction at 25°C,



Given: ΔH° for the reaction is -571.0 kJ and ΔS° is -326.0 J/K .

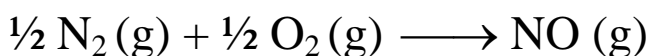
Solution:

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -571 - 298 \left(\frac{-326}{1000} \right) \\ &= -571 + 97.2 \text{ kJ} = -\mathbf{473.8 \text{ kJ}}\end{aligned}$$

This implies that the formation of $\text{H}_2\text{O}(\text{l})$ from $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ at 25°C is spontaneous.

Illustration 20.

For the following reaction,



$$\Delta H_{298}^\circ = 89.96 \text{ kJ}.$$

Standard molar entropies for $\text{NO}(\text{g})$, $\text{O}_2(\text{g})$ and $\text{N}_2(\text{g})$ are 210.67, 205.10 and 192.34 J/K respectively. Calculate ΔG° for the reaction.

Solution:

$$\Delta S^\circ = S_{\text{NO}}^\circ - \frac{1}{2}S_{\text{N}_2}^\circ - \frac{1}{2}S_{\text{O}_2}^\circ = 210.67 - 96.17 - 102.55 = 11.95 \text{ J/K}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= 89.96 - 298 \left(\frac{11.95}{1000} \right) = 89.96 - 3.56 = \mathbf{86.4 \text{ kJ/mole}}\end{aligned}$$

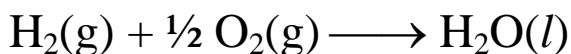
Thus at 25°C, the reaction does not occur spontaneously.

Illustration 21.

The heats of formation of $\text{H}_2\text{O} (l)$ is -285.8 kJ and standard molar entropies are $S^\circ_{\text{H}_2\text{O}(l)} = 69.9$, $S^\circ_{\text{H}_2(g)} = 130.6$, $S^\circ_{\text{O}_2(g)} = 205 \text{ J/K}$. Calculate the standard free energy of formation of liquid water at 25°C .

Solution:

ΔG_f° for H_2O is ΔG° for the reaction,



$$\Delta S^\circ = S^\circ_{\text{H}_2\text{O}(l)} - S^\circ_{\text{H}_2(g)} - \frac{1}{2} S^\circ_{\text{O}_2(g)} = 69.9 - 130.6 - 102.5 = -163.2 \text{ J/K}$$

$$\therefore \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta G^\circ = -285.8 - \left(298 \times \frac{-163.2}{1000} \right) = -285.8 + 48.6 = -237.2 \text{ kJ/mol}$$

8.5 Effect of Temperature Upon Spontaneity of a Reaction

When the temperature of a system is increased, the direction in which the reaction proceeds spontaneously may or may not change. Whether it changes or not depends upon the relative signs of ΔH and ΔS° . The four possibilities are given in table.

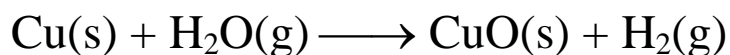
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Table: Effect of temperature on the spontaneity of a reaction at a given pressure

Case	ΔH	ΔS°	$\Delta G^\circ = \Delta H - T\Delta S^\circ$	Remarks
I	–	+	Always negative. For example, $C(s) + O_2(g) \rightarrow CO_2(g)$	Spontaneous at all temperatures; Reverse reaction always non-spontaneous.
II	+	–	Always positive. For example, $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$	Non-spontaneous at all temperatures; Reverse reaction takes place.
III	+	+	+ at low temperatures, – at high temperatures. For example, $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$	Non-spontaneous at low temperatures but becomes spontaneous at higher temperatures.
IV	–	–	– at low temperatures, + at high temperatures. For example, $PCl_3(g) + Cl_2(g) \rightarrow PCl_5(g)$	Spontaneous at low temperatures but at high temperatures reverse reaction becomes spontaneous.

Note:

(i) If ΔH and ΔS° have opposite sign (Case I and II), it is impossible to reverse the direction of spontaneity by temperature change alone. The two terms ΔH and $-T\Delta S$ strengthen one another. Therefore, ΔG° has the same sign at all temperatures. For the reaction,



ΔG° is positive at all temperatures. Hence the reaction cannot take place spontaneously at 1 atm whatever be the temperature.

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(ii) When ΔH and ΔS° have the same sign (Case III and IV,) the enthalpy and entropy factors oppose each other. ΔG° changes sign as temperature increases and the direction of spontaneity reverses. At low temperatures, ΔH predominates and the exothermic reaction is favoured. With increasing temperature, the factor $T\Delta S^\circ$ increases in magnitude and at a certain stage exceeds ΔH . At high temperatures, the reaction leading to an increase in entropy occurs. This explains why exothermic reactions are spontaneous at room temperature.

In the decomposition of calcium carbonate, it is found that ΔH and ΔS° have the same sign.

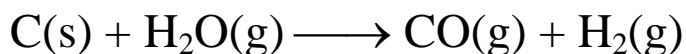


On calculation, $\Delta G = 178.0 \text{ kJ} - T (0.1604 \text{ kJ/K})$

- (a) Below 1100 K, ΔH predominates, i.e., ΔG° is positive and the reaction is not spontaneous at 1 atmosphere pressure.
- (b) Above 1100 K, $T\Delta S$ predominates and the reaction becomes spontaneous at 1 atmosphere pressure.
- (c) At about 1100 K, $\Delta H = T\Delta S^\circ$. Hence, $\Delta G^\circ = 0$ i.e. the system is at equilibrium at 1 atmosphere, which means if we put some solid CaCO_3 in a vessel and heat it to 1100 K, the pressure developed by CO_2 will be 1 atmosphere.

Illustration 22.

At what temperature will the reaction,



become spontaneous ($\Delta H^\circ = + 131.3 \text{ kJ/mole}$ and $\Delta S^\circ = + 0.1335 \text{ kJ/K}$)?

Solution:

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A reaction becomes spontaneous when its ΔG value becomes negative. Since ΔS is positive for this reaction, we should calculate the minimum temperature, i.e. the temperature at which $\Delta G = 0$, assuming that the value of ΔH and ΔS are constant over the range of temperature.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Substituting values,

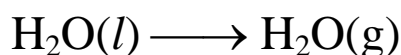
$$0 = 131.3 - T(0.1335)$$

$$T = \frac{131.3}{0.1335} = 983.5 \text{ K}$$

The reaction will be spontaneous at any temperature above 983.5 K.

Illustration 23.

For the vaporisation of water at 1 atmospheric pressure,



$\Delta H = + 44.3 \text{ kJ}$ and $\Delta S^\circ = + 118.8 \text{ J/K}$. Calculate the temperature at which liquid and vapour are at equilibrium at 1 atmosphere.

Solution:

At equilibrium, $\Delta G^\circ = 0$

$$\Delta G^\circ = \Delta H - T\Delta S^\circ$$

$$0 = \Delta H - T\Delta S^\circ$$

$$T\Delta S^\circ = \Delta H$$

$$T = \frac{\Delta H}{\Delta S^\circ} = \frac{44.3}{0.1188} = 373 \text{ K}$$

8.6 Standard Free Energy of Formation, G_f°

The standard free energy of formation, G_f° is defined as the *free energy change per mole when a compound is formed from the elements in their standard states*. Like the standard enthalpy of formation of an element, the standard free energy of formation of an element in its standard state is zero.

$$\Delta G^\circ = \Sigma G_f^\circ (\text{products}) - \Sigma G_f^\circ (\text{reactants})$$

(Sum of the standard Free energy of formation of products) (sum of the standard free energy of formation of reactants)

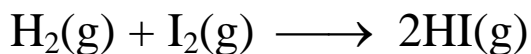
8.7 Standard Free Energy Change (ΔG°) and Equilibrium Constant (K_{eq})

The standard free energy change can be defined as the free energy change for a process at 298 K in which the reactants in their standard states are converted to the products in their standard states. It is denoted by the symbol ΔG° . Standard free energy change (ΔG°) is related to the equilibrium constant (K_{eq}) by the relation

$$\Delta G^\circ = -2.303 RT \log K_{eq}$$

Illustration 24.

Using G_f° (HI) = 1.3 kJ/mole, calculate the standard free energy change for the following reaction,



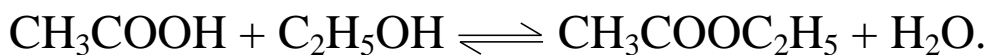
Solution:

$$\begin{aligned}\Delta G^\circ &= \Sigma G_f^\circ (\text{products}) - \Sigma G_f^\circ (\text{reactants}) = 2 \times (1.3) - (0 + 0) \\ &= 2.6 - 0 = \mathbf{2.6 \text{ kJ/mol}}\end{aligned}$$

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Illustration 25.

Calculate free energy change for the esterification reaction,



The equilibrium constant for the reaction at 25°C is 4.

Solution:

$$\begin{aligned}\Delta G^\circ &= -2.303 RT \log K = -2.303 \times 8.314 \times 298 \log 4 \\ &= -(2.303 \times 8.314 \times 298 \times 0.6021) = -3435.49 \text{ J/mol}\end{aligned}$$

Illustration 26:

Calculate the value of K_p at 25°C for an equilibrium reaction, if $\Delta G^\circ = -20 \text{ kJ/mole}$.

Solution:

$$\begin{aligned}\Delta G_p^\circ &= -2.303 RT \log K_p \\ -20 \times 1000 &= -2.303 \times 8.314 \times 298 \log K_p \\ \log K_p &= \frac{20 \times 1000}{2.303 \times 8.314 \times 298} = 3.464 \\ K_p &= \text{antilog}(3.505) = 2.91 \times 10^3\end{aligned}$$