4. CHEMICAL THERMODYNAMICS

Can you recall ?

1. How do you define energy?
2. What are the different forms of energy?

4.1 Introduction : You know transformation of liquid water into vapour, solid ice into liquid water or burning of carbon forming carbon dioxide, CO_2, are accompanied by a change in energy. In dry cell, the chemical energy is converted into electrical energy. On the other hand, in electroplating of metals electrical energy is converted into chemical energy. Thus it may be realized that the energy can be transformed from one form into another.

Do you know ?

At the top of dam, water is stored in a reservoir. It has certain potential energy due to its height from ground level and its kinetic energy is negligible as it is not in motion. As the water starts to fall down through an outlet its potential energy decreases and kinetic energy increases due to the downward velocity. It means that potential energy of falling water is converted into kinetic energy.

Thermodynamics is concerned with the energy changes in physical and chemical transformations. Thermodynamics, however gives no information on the rates of physical or chemical processes or underlying mechanisms involved in these.

4.2 Terms used in thermodynamics

4.2.1 System and surrounding :

Consider a gas enclosed in a cylinder equipped with a movable piston as shown in Fig. 4.1. Suppose we undertake study of change in volume of a gas and the amount of energy released or gained by a gas when the pressure is varied by putting certain mass on the piston. In this case, a gas under study is called the system.

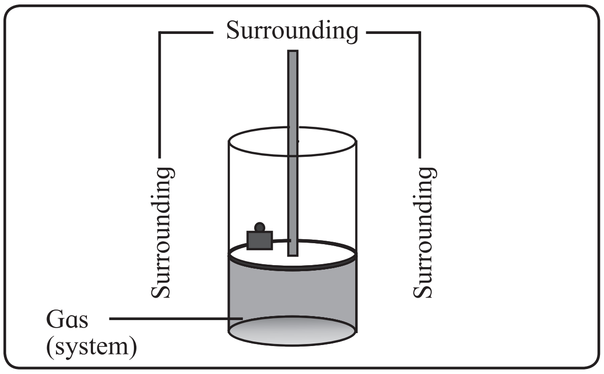


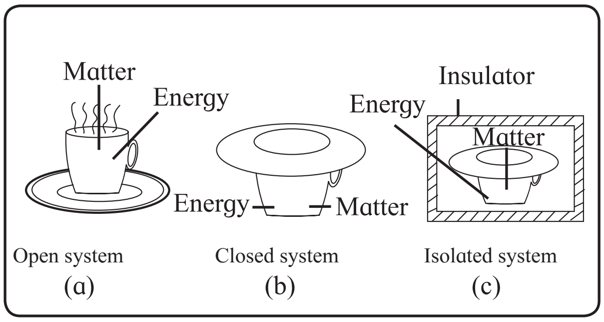
Fig. 4.1 : System and surroundings

A part of the universe under thermodynamic investigation is called the system.All other parts of the universe outside the system such as cylinder, room and others, are surroundings. The universe is made of system plus surroundings.

4.2.2 Types of system :

Observe and discuss...

Observe Fig. 4.2 and discuss with reference to transaction of energy and matter.



Open system (a)
Closed system (b)
Isolated system (c)

Fig. 4.2 : Kinds of systems

Three types of systems are shown in Fig. 4.2.

i. Open system : Fig. 4.2(a) shows an open cup containing hot coffee placed in a room. You observe coffee cools down releasing heat to the surroundings. The water vapour from coffee simultaneously passes into surroundings. Such a system (coffee) which exchanges both energy and matter with the surroundings is called an open system.

ii. Closed system : In Fig. 4.2(b), a cup containing hot coffee is covered with a saucer. Coffee cools down by giving away heat to the surroundings. The water vapour from coffee now does not pass into surroundings. Such a system that exchanges energy and not the matter with the surroundings is called a closed system.

iii. Isolated system : As you see in Fig. 4.2(c), a cup containing hot coffee covered with a saucer is insulated from the surroundings. Coffee does not cool down. Moreover, there is no escape of water vapour into the surroundings. Such a system that does not allow exchange of either energy or matter with the surroundings is an isolated system.

4.2.3 Properties of system

i. Extensive property :

A property which depends on the amount of matter present in a system is called an extensive property.

Examples : Mass, volume, internal energy, heat capacity, number of moles.

ii. Intensive property :

A property which is independent of the amount of matter in a system is called intensive property.

Examples : Pressure, temperature, surface tension, viscosity, melting point, boiling point, specific heat.

4.2.4 State functions : As shown in Fig. 4.1, certain amount of a gas is enclosed in a cylinder fitted with a movable piston. Suppose the pressure of the gas is 1 bar (P_1), volume is 1 dm^3 (V_1) and temperature is 300 K (T_1) in the beginning. This initial state of the system is fully defined by specifying the values of these properties. Such properties defining the state of a system, are **state functions**.

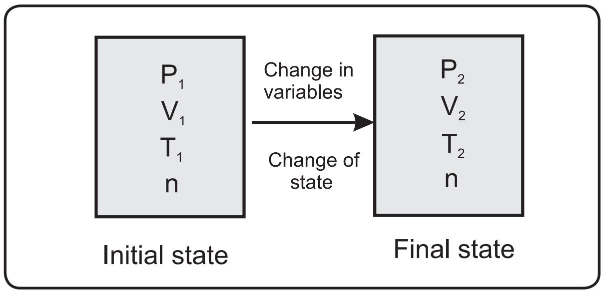


Fig. 4.3 : Change of state

Suppose the pressure of the system is increased to 2 bar, (P_2) volume changes to 0.5 dm^3 (V_2) and the temperature is maintained at 300 K (T_1). This is the final state of the system which is different from the initial state. A change in state functions of the system brings forth a change of its state. This is shown in Fig. 4.3.

The final state of the system in Fig. 4.3. is described by pressure 2 bar (P_2), volume 0.5 dm^3(V_2) and temperature 300 K(T_1). A system continues to be in such state as long as the state functions are unchanged. How the pressure 2 bar is attained whether by increasing from 1 bar to 2 bar or decreasing from 5 bar to 2 bar, would not matter.

The property which depends on the state of a system and independent of a path followed to attain it, is called the **state function.**

The term process means a physical or chemical change in a system on going from one state to another. This can be achieved by a number of paths by some operation. A path here refers to a sequence of situations the system undergoes during the accomplishment of the change. In other words the process in general may not necessarily determine the change in unique way. Only isothermal and adiabatic reversible processes follow the unique path to bring about the change of state of the system.

4.2.5 Path Functions : The properties which depend on the path are called path functions. For example, work (W) and heat (Q).

4.2.6 Thermodynamic equilibrium :

Consider a gas enclosed in a cylinder fitted with a movable piston shown in Fig. 4.1. The gas has temperature T_1, pressure P_1 and volume V_1. These state functions continue to be constant as long as piston is motionless, and no heat exchange takes place. This is an equilibrium state.

Now move the piston in upward direction so that the gas expands. It passes through states for which pressure, volume and temperature are not specified and vary continuously during the movement of the piston. The gas would then be in nonequilibrium state.

Stop the movement of the piston. Suppose at this stage the pressure and volume of the gas are respectively P_2 and V_2 and the temperature is constant at T_1. The state functions are constant since the piston is motionless. The gas is then in another equilibrium state.

A system is said to be in thermodynamic equilibrium when its state functions do not vary with time. Thermodynamics considered here is limited to equilibrium states.

4.2.7 Process and its types :

A transition from one equilibrium state to another is called a process. They are of different types.

i. Isothermal process : It is the process in which temperature of the system remains constant throughout the transformation.

In such process heat flows from the system to surroundings and vice versa so as to keep the temperature constant. For a given temperature the internal energy *(U)* of the system remains constant. Thus, $\Delta T = 0$ and $\Delta U = 0$.

ii. Isobaric process : In isobaric process the pressure remains constant during the transformation. In the laboratory chemical reactions are carried out in open containers at constant atmospheric pressure or $\Delta P = 0$

iii. Isochoric process : It is a process during which volume of the system remains constant during the transformation. A chemical reaction carried out in a closed container is isochoric. For isochoric process $\Delta V = 0$.

iv. Adiabatic process : A process in which there is no exchange of heat between system and surroundings is an adiabatic process. ($Q = 0$). In adiabatic process the system is completely insulated from the surroundings. For an exothermic process the heat is released which rises temperature of the system. If the process is endothermic the temperature falls. This results in either increase or decrease of internal energy.

v. Reversible process : Consider a gas enclosed in a cylinder fitted with a movable piston. Let the external pressure be P_{ext} on the outer surface of the piston be set equal to pressure P of the gas. Neither expansion nor compression of the gas occurs. A system is then said to be in mechanical equilibrium with surroundings.

Consider P_{ext} is reduced by an infinitesimal amount. Now it the P_{ext} is infinitesimally smaller than P the piston moves out slowly allowing gas to expand.

If P_{ext} is slightly increased so that it becomes infinitesimally greater than P, the piston moves inward with a compression of the gas.

For the system in mechanical equilibrium with its surroundings, infinitesimal change may cause the process to occur in the reverse direction. The process is then said to be thermodynamically reversible. A process conducted in such a way so that at every stage the driving force due to pressure *(P)* is infinitesimally greater than the opposing force due to external pressure (P_{ext}) and which can be reversed by a slight change of the opposing force is reversible process.

Features of reversible process

i. The driving and opposing forces differ by an infinitesimal amount.

ii. The process can be reversed by an infinitesimal change in conditions.

iii. A reversible process proceeds infinitely slowly and takes place in infinite number of steps.

iv. At the end of every step of the process, the system attains mechanical equilibrium with the surroundings.

4.3 Nature of heat and work

4.3.1 Nature of work *(W)* : In mechanics the work is defined as the energy by which body is displaced through a distance d with an application of force. Thus,

$$W = f \times d$$

In thermodynamics the type of work involved is pressure-volume or *PV* work, that is, work is done when the system (gas) expands or contracts against the external opposing force.

It may be realized that the product of pressure and volume is equal to work. Pressure is defined as force per unit area. If *d* is the distance, area $A = d^2$ and volume $V = d^3$. Then

$$PV = \frac{f}{A} \times V = \frac{f}{d^2} \times d^3 = f\,d = W$$

Now let us explore the *PV* work with two chemical reactions in a cylinder equipped with frictionless movable piston attached with a certain mass on its outer surface.

i. Decomposition of H_2O_2

Consider $2\ H_2O_2(l) \longrightarrow 2\ H_2O(l) + O_2(g)$

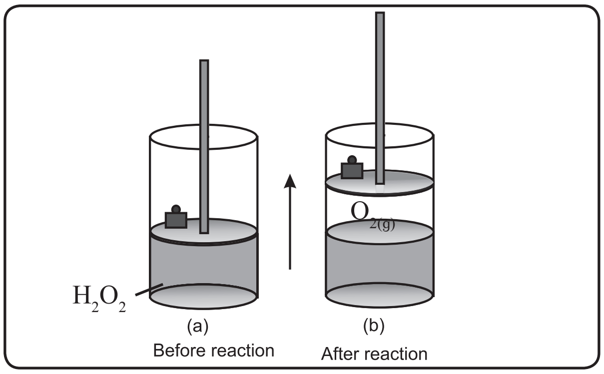


Fig. 4.4 : Decomposition of H_2O_2

The gas produced in above reaction pushes the piston upwards so that the mass in the surroundings is raised as shown in Fig. 4.4. In lifting the mass the system loses energy to the surroundings or it performs work on the surroundings. With no heat being transferred a loss of energy by the system is equal to work done by the system on the surroundings. This is *PV* expansion.

ii. Reaction between NH_3 gas and HCl gas

Now, consider

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

As the reaction progresses the gases are consumed resulting in a decrease of volume. The piston moves down. A decrease in the height of the mass is shown in Fig. 4.5.

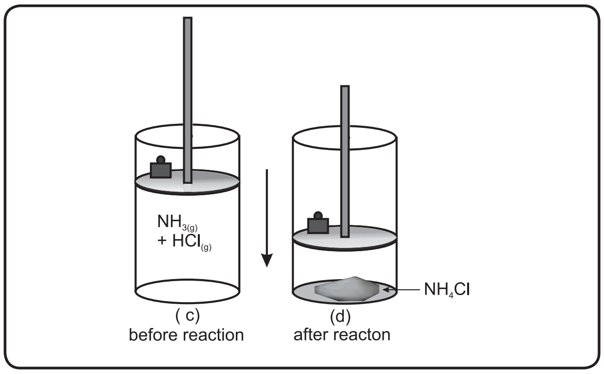


Fig. 4.5 : Reaction between NH_3(g) and HCl(g)

In the process the surroundings lose energy to the system and perform work on the system. If no heat transfer occurs work done by the surroundings is equal to gain in energy by the system. This is *PV* work.

Thus the work refers to a way by which a system exchanges energy with surroundings.

4.3.2 Nature of heat *(Q)* : Like heat is a form of energy by which the system exchanges energy with its surroundings. When the system and its surroundings are at different temperatures heat either flows in or let out of the system.

4.3.3 Sign conventions of *W* and *Q* : The energy changes for the system are considered hereafter.

The energy entering the system from the surroundings has positive value. While the energy leaving the system and flowing into the surroundings is negative. This is shown in Fig. 4.6.

$+Q$: Heat is absorbed by the system from the surroundings.

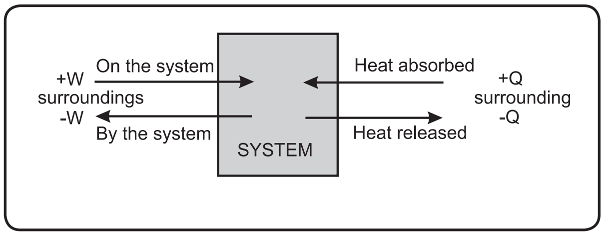


Fig. 4.6 : Sign conventions

$-Q$: Heat is released by the system to the surroundings.

$+W$: Work is done on the system by the surroundings.

$-W$: Work is done by the system on the surroundings.

Note W and Q are path functions.

4.4 Expression for pressure-volume *(PV)* work : Consider a certain amount of gas at constant pressure P is enclosed in a cylinder fitted with frictionless, rigid movable piston of area A. This is shown in Fig. 4.7.

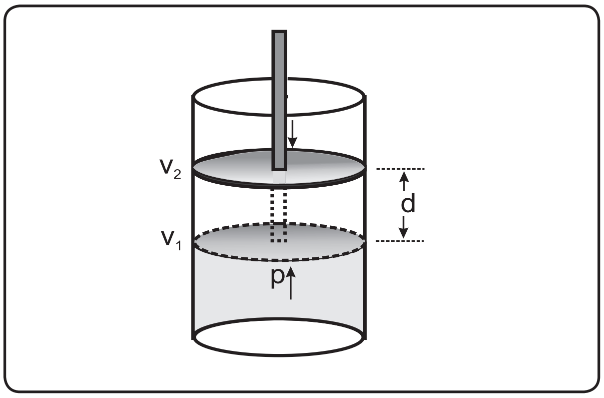


Fig. 4.7 : Pressure-volume work

Let volume of the gas be V_1 at temperature T.

On expansion the force exerted by a gas is equal to area of the piston multiplied by pressure with which the gas pushes against piston. This pressure is equal in magnitude and opposite in sign to the external atmospheric pressure that opposes the movement and has its value $-P_{ext}$. Thus,

$$f = -P_{ext} \times A \qquad \text{.......} (4.1)$$

where P_{ext} is the external atmospheric pressure.

If the piston moves out a distance d, then the amount of work done is equal to the force multiplied by distance.

$$W = f \times d \qquad \text{.......} (4.2)$$

Substitution from Eq. (4.1) gives

$$W = -P_{ext} \times A \times d \qquad \text{.......} (4.3)$$

The product of area of the piston and distance it moves is the volume change (ΔV) in the system.

$$\Delta V = A \times d \qquad \text{.......} (4.4)$$

Combining equations (4.3) and (4.4) we write

$$W = -P_{ex} \Delta V \qquad \text{.......} (4.5)$$

$$W = -P_{ex}(V_2 - V_1)$$

where V_2 is final volume of the gas.

When the gas expands, work is done by the system on the surroundings. Since $V_2 > V_1$, W is negative. When the gas is compressed, work is done on the system by surroundings. In this case $V_1 < V_2$, and $-P_{ext} \Delta V$ or W is positive.

Eq. (4.5) shows the external pressure determines the work during expansion (or compression) of the gas. A volume change does no work unless the system is linked to the surroundings by external pressure.

Remember...

Remember during expansion of a gas, work is done by the system on the surroundings and during compression work is done on the system by the surroundings.

4.4.1 Free expansion : A free expansion means expansion against zero opposing force. Such expansion occurs in vacuum. The work done by a system during such expansion is given by Eq. (4.5), W = $-P_{ext} \Delta V$. When the gas expands in vacuum, there is no opposing force that is P_{ext} and hence, $W = 0$. In other words no work is done when the gas expands freely in vacuum.

4.4.2 Units of energy and work

$$1\ \text{J} = 1\ \text{kg m}^2\ \text{s}^{-2} = 1\ \text{Pa m}^3$$

$$1\ \text{Pa} = 1\ \text{kg m}^{-1}\ \text{s}^{-2}$$

From to Eq. (4.5), $W = -P_{ext}\,\Delta V$, if pressure is expressed in bar and ΔV in dm³, then the work has the units of bar dm³.

$$1\ \text{bar} = 10^5\ \text{Pa} = 10^5\ \text{kg m}^{-1}\ \text{s}^{-2}$$

$$1\ \text{dm}^3\ \text{bar} = \text{dm}^3 \times 10^5\ \text{kg m}^{-1}\ \text{s}^{-2}$$

$$= \text{m}^3 \times 10^{-3} \times 10^5\ \text{kg m}^{-1}\ \text{s}^{-2}$$

$$= 100\ \text{kg m}^2\ \text{s}^{-2} = 100\ \text{J}$$

Problem 4.1 : Three moles of an ideal gas are expanded isothermally from 15 dm³ to 20 dm³ at constant external pressure of 1.2 bar. Estimate the amount of work in dm³ bar and J.

Solution :

$W = -P_{ext}\,\Delta V = -P_{ext}\,(V_2 - V_1)$

$P_{ext} = 1.2$ bar, $V_1 = 15$ dm³, $V_2 = 20$ dm³

Substitution of these quantities into the equation gives

$$W = -1.2\ \text{bar}\ (20\ \text{dm}^3 - 15\ \text{dm}^3)$$

$$= -1.2\ \text{bar} \times 5\text{dm}^3 = -6\ \text{dm}^3\ \text{bar}$$

$$1\ \text{dm}^3\ \text{bar} = 100\ \text{J}$$

Hence, $W = -6\ \text{dm}^3\ \text{bar} \times 100\ \text{J/dm}^3$

bar $= -600$ J

Problem 4.2 : Calculate the constant external pressure required to compress 2 moles of an ideal gas from volume of 25 dm³ to 13 dm³ when the work obtained is 4862.4 J.

Solution :

$W = -P_{ext}\,\Delta V = -P_{ext}\,(V_2 - V_1)$

$V_1 = 25$ dm³, $V_2 = 13$ dm³, $W = 4862.4$ J

$$W = 4862.4\ \text{J} \times \frac{\text{dm}^3\ \text{bar}}{100\ \text{J}} = 48.62\ \text{dm}^3\ \text{bar}$$

Substitution of these into the equation gives

$$48.62\ \text{dm}^3\ \text{bar} = -P_{ext}\,(13\ \text{dm}^3 - 25\ \text{dm}^3)$$

$$= -P_{ext} \times 12\ \text{dm}^3$$

Hence, $P_{ext} = \dfrac{48.62\ \text{dm}^3\ \text{bar}}{12\ \text{dm}^3} = 4.052$ bar

Problem 4.3 : 200 mL ethylene gas and 150 mL of HCl gas were allowed to react at 1 bar pressure according to the reaction

$$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g)$$

Calculate the PV work in joules.

Solution :

$W = -P_{ext}\,\Delta V = -P_{ext}\,(V_2 - V_1)$

According to the equation of reaction 1 mole of C_2H_4 reacts with 1 mole of HCl to produce 1 mole of C_2H_5Cl. Hence, 150 mL of HCl would react with only 150 mL of C_2H_4 to produce 150 mL of C_2H_5Cl.

$V_1 = 150\ \text{mL} + 150\ \text{mL} = 300\ \text{mL} = 0.3\ \text{dm}^3$

$V_2 = 150\ \text{mL} = 0.15\ \text{L}$, $P_{ext} = 1$ bar

Substitution of these quantities in above

$$W = -1\ \text{bar}\ (0.15\ \text{dm}^3 - 0.3\ \text{dm}^3)$$

$$= 0.15\ \text{dm}^3\ \text{bar}$$

$$= 0.15\ \text{dm}^3\ \text{bar} \times 100\ \frac{\text{J}}{\text{dm}^3\ \text{bar}}$$

$$= 15.0\ \text{J}$$

4.5 Concept of maximum work : Eq. (4.5) shows the amount of work performed by a system is governed by the opposing force (P_{ext}). Larger the opposing force more work is done by the system to overcome it.

If the opposing force is zero no work is involved. With an increase of the opposing force from zero, more work will be needed by the system. When the opposing force reaches its maximum the system performs maximum work. With an opposing force being greatest more effort would be needed to overcome it.

Thus when the opposing force (P_{ext}) becomes greater than the driving force (P) the process gets reversed. Since the opposing force cannot be greater than the driving force it should be the maximum.

If the pressure P of the gas differs from P_{ext} by a quantity ΔP then $P - P_{ext} = \Delta P$ and $P_{ext} = P - \Delta P$. The eq. (4.5) then becomes

$$W = -(P - \Delta P)\,\Delta V$$

The work *(W)* would be maximum when ΔP is smallest. This means the opposing force (P_{ex}) must be infinitesimally smaller than the driving force *(P)* for the work to be maximum. This is required for the process to be reversible. The maximum work is obtained from the change which is thermodynamically reversible.

4.5.1 Expression for the maximum work :

Consider n moles of an ideal gas enclosed in a cylinder fitted with frictionless movable rigid piston. It expands isothermally and reversibly from the initial volume V_1 to final volume V_2 at temperature *T*. The expansion takes place in a number of steps illustrated in Fig. 4.8.

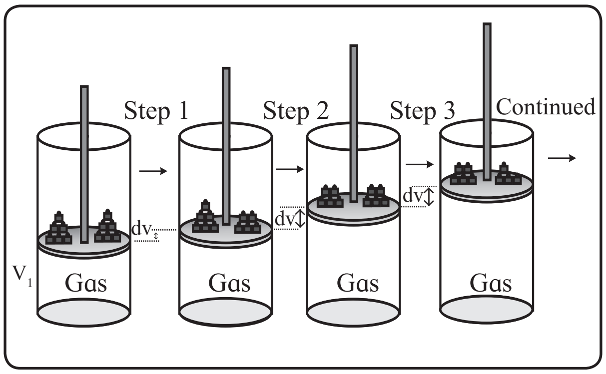


Fig. 4.8 : Reversible expansion

During each step the external pressure P_{ext} is made infinitesimally smaller than the pressure P of the gas, with a gradual removal of masses from the piston. The gas expands slowly and its pressure *P* would decrease. The expansion continues until the pressure of the gas falls to P_{ext}. Beyond this no further expansion occurs and the system attains mechanical equilibrium with its surroundings. The volume of a gas is increased by an infinitesimal quantity dv in each single step.

The process is repeated in such a way that every time P_{ext} is lowered infinitesimally the gas undergoes a series of infinitesimal increments in volume until the volume V_2 is attained.

When the volume of a gas increases by an infinitesimal amount *dV* in a single step, the small quantity of work done

$$dW = -P_{ext}\,dV \qquad \text{.......} (4.6)$$

As the expansion is reversible, *P* is greater by a very small quantity dp than p_{ex}. Thus,

$$P - P_{ext} = dP \text{ or } P_{ext} = P - dP \qquad \text{......} (4.7)$$

Combining equations (4.6) and (4.7),

$$dW = -(P - dP)dV = -PdV + dP\,dV$$

Neglecting the product *dpdV* which is very small, we get

$$dW = -PdV \qquad \text{.......} (4.8)$$

The total amount of work done during entire expansion from volume V_1 to V_2 would be the sum of infinitesimal contributions of all the steps. The total work is obtained by integration of Eq. (4.8) between the limits of initial and final states. This is the maximum work, the expansion being reversible. Thus,

$$\int_{\text{initial}}^{\text{final}} dW = -\int_{V_1}^{V_2} PdV$$

Hence $$W_{max} = -\int_{V_1}^{V_2} PdV \qquad \text{.......} (4.9)$$

Using the ideal gas law

$$PV = nRT$$

$$W_{max} = -\int_{V_1}^{V_2} nRT\frac{dV}{V}$$

$$= -nRT\int_{V_1}^{V_2}\frac{dV}{V} \quad \text{because } T \text{ is constant.}$$

$$= -nRT\ln(V)_{V_1}^{V_2}$$

$$= -nRT(\ln V_2 - \ln V_1)$$

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

$$= -2.303\ \text{nRT}\log_{10}\frac{V_2}{V_1} \qquad \text{.......} (4.10)$$

At constant temperature, $P_1V_1 = P_2V_2$ or

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

Replacing V_2/V_1 in Eq. (4.10) by P_1/P_2, We have

$$W_{max} = -2.303\, nRT \log \frac{P_1}{P_2} \quad ....(4.11)$$

Problem 4.4 : 2 moles of an ideal gas are expanded isothermally and reversibly from 20 L to 30 L at 300 K. Calculate the work done (R= 8.314 J K^{-1} mol^{-1})

Solution : $W_{max} = -2.303\, nRT \log_{10}\frac{V_2}{V_1}$

$n = 2$ mol, $T = 300$ K, $V_1 = 20$ L, $V_2 = 30$ L, $R = 8.314$ J/K mol

Substitution of these quantities into the equation gives

$$W_{max} = -2.303 \times 2 \text{ mol} \times 8.314 \text{ J/K mol} \times 300\text{K} \times \log_{10}\frac{30 \text{ L}}{20 \text{ L}}$$

$$= -2.303 \times 2 \times 8.314 \text{ J}\times 300 \times \log_{10} 1.5$$

$$= -2.303 \times 2 \times 8.314 \text{ J}\times 300 \times 0.1761$$

$$= -2023 \text{ J} = -2.023 \text{ kJ}$$

Problem 4.5 : 22 g of CO_2 are compressed isothermally and reversibly at 298 K from initial pressure of 100 kPa when the work obtained is 1.2 kJ. Find the final pressure.

Solution :

$$W = -2.303\, nRT \log_{10}\frac{P_1}{P_2}$$

$n = \frac{22 \text{ g}}{44 \text{ g mol}^{-1}}$ =0.5 mol, $T = 298$ K,

P_1= 100 kPa, $W = 1.2$ kJ = 1200 J

Hence, 1200 J = -2.303 × 0.5 mol ×8.314 J K^{-1} mol^{-1} × 298K × $\log_{10}\frac{100 \text{ kPa}}{P_2}$

or $\log_{10}\frac{100 \text{ kPa}}{P_2} =$

$$\frac{-1200}{2.303 \times 0.5 \times 8.314 \times 298}$$

$$= -0.4206$$

$$\frac{100 \text{ kPa}}{P_2} = \text{antilog } (-0.4206) = 0.3797$$

Therefore, $P_2 = \frac{100 \text{ kPa}}{0.3797} = 263.4$ kPa

Problem 4.6 : 300 mmol of an ideal gas occupies 13.7 dm^3 at 300 K. Calculate the work done when the gas is expanded until its volume has increased by 2.3 dm^3 (a) isothermally against a constant external pressure of 0.3 bar (b) isothermally and reversibly (c) into vacuum.

Solution :

a. $W = -P_{ex}\,\Delta V$

$P_{ext} = 0.3$ bar, $\Delta V = 2.3$ dm^3

$W = -0.3$ bar × 2.3 dm^3

$= -0.69$ dm^3 bar

$= -0.69 \text{ dm}^3 \text{ bar} \times \frac{100 \text{ J}}{\text{dm}^3 \text{ bar}}$

$= -\,69$ J

b. $W_{max} = -\,2.303\, nRT \log_{10}\frac{V_2}{V_1}$

$n = 300$ mmol $= 300 \times 10^{-3}$ mol $= 0.3$ mol, $T = 300$ K

$$W_{max} = -\,2.303 \times 0.3 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 300\text{K} \times \log_{10}\frac{16}{13.7}$$

$$= -2.303 \times 0.3 \times 8.314 \text{ J} \times 300 \times 0.0674$$

$$= -\,116.1 \text{ J}$$

c. $W = -\,P_{ex}\,\Delta V$

When gas is expanded to vaccum, $P_{ext} = 0$ and W = 0

4.6 Internal energy (U) : Every substance is associated with a definite amount of energy. This energy stored in a substance is internal energy denoted by U.

The internal energy of a system is made up of kinetic and potential energies of individual particles of the system.

$$\Delta U = U_2 - U_1$$

where U_1 and U_2 are internal energies of initial and final states, respectively. U is a state function and extensive property.

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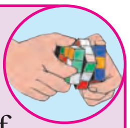


25 kJ of work is done on the system and it releases 10 kJ of heat. What is ΔU?

A transfer of energy (as heat or work) from the system would change its internal energy. To know ΔU the energy supplied to or removed from the system need to be monitored.

i. The energy transferred to the system by heating it or performing work on it is added to the system.

ii. The energy transferred from the system by cooling or by performing work on the surroundings is removed from the system.

The following examples illustrate how to determine ΔU.

i. 30 kJ of heat supplied to the system. It would be added to internal energy of the system and $\Delta U = +30$ kJ.

ii. If 20 kJ of work is done on the system, it is added to internal energy of the system. Consequently, $\Delta U = +\ 20$ kJ.

iii. Suppose a system releases 10 kJ of heat and performs 15 kJ of work on the surroundings. These quantities are removed from internal energy of the system and $\Delta U = -\ 25$ kJ

4.7 First law of thermodynamics : First law of thermodynamics is simply the conservation of energy. According to this law the total energy of a system and surroundings remains constant when the system changes from an initial state to final state. The law is stated in different ways as follows.

i. Energy of the universe remains constant

ii. The total internal energy of an isolated system is constant

iii. Energy is neither created nor destroyed and can only be converted from one form to another.

All above statements are equivalent.

4.7.1 Formulation of first law of thermodynamics : A system exchange energy with its surroundings either by transfer of heat or by doing work. An energy supplied to the system increases its internal energy. On the other hand, removal of heat or work from the system decreases its internal energy.

Suppose (Q) is heat supplied to the system and W work done on the system by the surroundings. The internal energy of the system would increase.

Increase in internal energy of the system is equal to sum of the quantity of heat supplied to the system and amount of work done on the system or

$$\Delta U = Q + W \qquad \text{.......} (4.12)$$

where ΔU is an increase in internal energy of the system. Eq. (4.12) is the first law of thermodynamics. For infinitesimal changes.

$$dU = dQ + dW \qquad \text{.......} (4.13)$$

4.7.2 First law of thermodynamics for various processes

i. Isothermal process : Temperature is constant in such process, internal energy is constant. Hence, $\Delta U = 0$
For isothermal process

$$0 = Q + W \text{ or } W = -Q \qquad \text{.......}(4.14)$$

The above equation implies that heat absorbed by the system is entirely used for doing work on the surroundings. When work is done on the system by the surroundings it results in release of heat.

ii. Adiabatic process : In adiabatic process, there is no exchange of heat between system and its surroundings that is, $Q = 0$. then

$$-\Delta U = -W \qquad \text{.......} (4.15)$$

Thus an increase in internal energy of the system is the work done on it. If the work is done by the system on the surroundings at the expense of its internal energy, the internal energy accompanying the adiabatic process would decrease.

iii. Isochoric process : Substitution of

$W = -P_{ext}\,\Delta V$ into Eq. (4.12)

$$\Delta U = Q - P_{ext}\,\Delta V \qquad \text{.......} \ (4.16)$$

As the reaction is carried out in a closed container, volume of the system is constant or $\Delta V = 0$ and

$$\Delta U = Q_v \qquad \text{.......} \ (4.17)$$

Equation (4.17) shows a change in internal energy of the system is due to heat transfer at constant volume. The subscript 'V' indicates that heat is transferred at the constant volume. Further U being a state function, Q_v is also a state function.

iv. Isobaric process : Usually chemical reactions are carried out in the open containers under constant atmospheric pressure. In such reactions, $\Delta V \neq 0$

Replacing Q by Q_p and ΔU by $Q_p - P_{ext}\,\Delta V$ in equation (4.16) gives

$$Q_p = \Delta U + P_{ext}\,\Delta V \qquad \text{.......} \ (4.18)$$

The reactions carried out in open containers under constant atmospheric pressure are common in chemistry, a special symbol ΔH, the enthalpy change, is given to indicate heat changes occurring at constant pressure.

> **Remember...**
> q is not a state function.
> Whereas Q_v and Q_p are state functions.

4.8 Enthalpy (H) : Enthalpy of a system is sum of internal energy of a system and the energy equivalent to PV work.

$$H = U + PV \qquad \text{.......} \ (4.19)$$

Change in enthalpy, ΔH, is also state function given by

$$\Delta H = H_2 - H_1 \qquad \text{.......} \ (4.20)$$

where H_1 and H_2 are the enthalpies of initial and final states, respectively.

From Eq. (4.19), we write

$$H_1 = U_1 + P_1V_1 \text{ and } H_2 = U_2 + P_2V_2$$

With these

$$\Delta H = U_2 + P_2V_2 - U_1 + P_1V_1$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$= \Delta U + \Delta(PV) \qquad \text{.......} (4.21)$$

For constant pressure, $P_1 = P_2 = P$ and

$$\Delta H = \Delta U + P\Delta V \qquad \text{.......} \ (4.22)$$

If the pressure inside and outside is the same or $P_{ext} = P$, Eq. (4.18) gives

$$Q_p = \Delta U + P\,\Delta V \qquad \text{.......} \ (4.23)$$

From equations (4.22) and (4.23)

$$\Delta H = Q_p \qquad \text{.......} (4.24)$$

Thus change in enthalpy of a system is equal to heat transferred from it at the constant pressure. H and Q_p are state functions.

4.8.1 Relationship between ΔH and ΔU for chemical reactions : At constant pressure, ΔH and ΔU are related as

$\Delta H = \Delta U + P\Delta V$

i. For reactions involving solids and liquids, ΔV usually is very small (solids or liquids do not show volume change with change of pressure) and $\Delta H = \Delta U$

ii. For reactions involving gases, ΔV cannot be neglected and

$$\Delta H = \Delta U + P\Delta V$$

$$= \Delta U + P(V_2 - V_1)$$

$$\Delta H = \Delta U + PV_2 - PV_1 \qquad \text{.......}(4.25)$$

where V_1 is the volume of gas phase reactants and V_2 that of the gaseous products.

We assume reactant and product behave ideally. Applying ideal gas equation $PV = nRT$. When n_1 moles of gaseous reactants produce n_2 moles of gaseous products. The ideal gas equation give,

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT \qquad \text{.......} (4.26)$$

Substitution of Eq. (4.26) into Eq. (4.25) yields

$$\Delta H = \Delta U + n_2RT - n_1RT$$
$$= \Delta U + (n_2 - n_1)\,RT$$
$$= \Delta U + \Delta n_g RT \qquad \text{....... (4.27)}$$

where Δn_g is difference between the number of moles of products and those of reactants.

Problem 4.7 : ΔH for the reaction,

$2C(s) + 3H_2(g) \longrightarrow C_2H_6(g)$ is -84.4 kJ at 25 ^{0}C. Calculate ΔU for the reaction at 25 ^{0}C. (R = 8.314 J K^{-1} mol^{-1})

Solution :

$$\Delta H = \Delta U + \Delta n_g RT$$

Δn_g = (moles of product gases) - (moles of reactant gases)

$$\Delta n_g = 1 - 3 = -2 \text{ mol}$$

ΔH = -84.4 kJ, R = 8.314 J K^{-1} mol^{-1}

= 8.314 × 10^{-3} kJ K^{-1} mol^{-1}

Substitution of these in above

-84.4 kJ = ΔU + 8.314 × 10^{-3} kJ K^{-1} mol^{-1} × 298 K × (-2 mol)

= ΔU - 4.96 kJ

Hence, ΔU = -84.4 kJ + 4.96 kJ = - 79.44 kJ

Under what conditions $\Delta H = \Delta U$?

Problem 4.8 : In a particular reaction 2 kJ of heat is released by the system and 6 kJ of work is done on the system. Determine of ΔH and ΔU?

Solution : According to the first law of thermodynamics

$$\Delta U = Q + W$$

$$Q = -2 \text{ kJ}, \qquad W = +6 \text{ kJ}$$

$$\Delta U = -2 \text{ kJ} + 6 \text{ kJ} = +4 \text{ kJ}$$

$Q_p = \Delta H$ = - 2kJ

Problem 4.9 : Calculate the work done in oxidation of 4 moles of SO_2 at 25^{0}C if

$2\ SO_2(g) + O_2(g) \longrightarrow 2\ SO_3(g)$

R = 8.314 J $K^{-1}mol^{-1}$

State whether work is done on the system or by the system.

Solution :

For oxidation of 4 moles of SO_2, the reaction is

$4\ SO_2(g) + 2\ O_2(g) \longrightarrow 4\ SO_3(g)$

$$W = -\Delta n_g RT$$

Δn_g = 4 - 6 = - 2 mol, T = 298 K

Hence,

W = -2 mol × -8.314 J K^{-1} mol^{-1} × 298 K

= 4955 J = 4.955 J

Work is done on the system (since $W > 0$).

4.8.2 Work done in chemical reaction :

The work done by a system at constant temperature and pressure is given by

$W = P_{ext}\,\Delta V$. Assuming $P_{ext} = P$,

$$W = -P\Delta V$$
$$= -P\,(V_2 - V_1)$$
$$= -PV_2 + PV_1$$

If the gases were ideal, using Eq. (4.26)

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

At constant temperature and pressure.

$$W = -n_2RT + n_1RT$$
$$= -(n_2 - n_1)\,RT$$
$$= -\Delta n_g RT \qquad \text{....... (4.28)}$$

The above equation gives the work done by the system in chemical reactions. The sign of W depends on ΔV. We consider the following cases:

i. If $n_2 > n_1$, Δn_g is positive and $W < 0$ or work is done by the system.

ii. If $n_1 > n_2$, Δn_g is negative and $W > 0$ or work is done on the system.

iii. If $n_1 = n_2$, $\Delta n_g = 0$ and $W = 0$, or

No PV work is done when number of moles of reactants and products are equal.

4.9 Enthalpies of physical transformations

4.9.1 Enthalpy of phase transition : In phase transition, one phase of a substance is converted into another at constant temperature and pressure without change in chemical composition.

i. Enthalpy of fusion ($\Delta_{fus}H$) : Enthalpy change that occurs when one mole of a solid is converted into liquid without change in temperature at constant pressure is enthalpy of fusion. For example,

$$H_2O\,(s) \longrightarrow H_2O\,(l)$$

$\Delta_{fus}H = +6.01$ kJ mol^{-1} at 0 ^{0}C

When 1 mole of solid ice melts at 0 ^{0}C and 1 atm pressure, change in enthalpy is 6.01 kJ. The same amount of heat is absorbed by ice during the melting. A reverse of fusion is freezing of solid.

$$H_2O\,(l) \longrightarrow H_2O\,(s),\ \Delta_{freez}H = -6.01 \text{ kJ mol}^{-1} \quad \text{at } 0\ ^0C$$

Thus, when one mole of liquid water freezes at 0 ^{0}C, heat is evolved.

ii. Enthalpy of vaporization ($\Delta_{vap}H$) : It is the enthalpy change accompanying the vaporization of one mole of liquid without changing its temperature at constant pressure.

For example,

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta_{vap}H = +40 \text{ kJ mol}^{-1} \quad \text{at } 100\ ^0C$$

$$H_2O(l) \longrightarrow H_2O(g) \quad \Delta_{vap}H = +44 \text{ kJ mol}^{-1} \quad \text{at } 25\ ^0C$$

Thus, when one mole of water is vaporised at 1 atm presure, the enthalpy change is + 40 kJ at 100 ^{0}C and +44 kJ at 25 ^{0}C.

On the other hand, the condensation to vapour is accompanied with a release of heat.

$$H_2O(g) \longrightarrow H_2O(l),\ \Delta_{con}H = -40.7 \text{ kJ mol}^{-1} \quad \text{at } 100\ ^0C$$

iii. Enthalpy of sublimation ($\Delta_{sub}H$) : It is the enthalpy change for the conversion of one mole of solid directly into vapour at constant temperature and pressure. Consider

$$H_2O(s) \longrightarrow H_2O(g),\ \Delta_{sub}H = 51.08 \text{ kJ mol}^{-1}, \quad \text{at } 0\ ^0C$$

The conversion of solid to vapour occurs in one or two steps, first melting of solid into liquid and second its vaporization; the enthalpy change is the same since enthalpy is the state function. At 0 ^{0}C

$$\begin{array}{lll} H_2O(s) \longrightarrow H_2O(l) & \Delta_{fus}H = 6.01 \text{ kJ mol}^{-1} \\ H_2O(l) \longrightarrow H_2O(g) & \Delta_{vap}H = 45.07 \text{ kJ mol}^{-1} \\ \hline H_2O(s) \longrightarrow H_2O(g) & \Delta_{sub}H = 51.08 \text{ kJ mol}^{-1} \end{array}$$

It follows that

$$\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H. \text{ (See Fig. 4.9)}$$

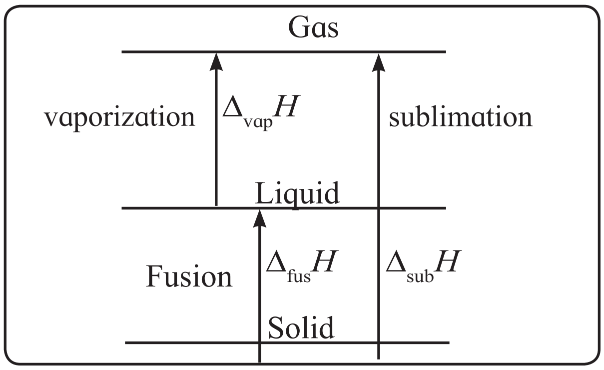


Fig. 4.10 Representing $\Delta_{fus}H$, $\Delta_{vap}H$ and $\Delta_{sub}H$

4.9.2 Enthalpy for the atomic / molecular change

i. Enthalpy of ionization ($\Delta_{ion}H$) : It is the enthalpy change accompanying the removal of an electron from one mole of gaseous atom. For example,

$$Na(g) \longrightarrow Na^{\oplus}(g) + e^{\ominus}\ \Delta_{ion}H = 494 \text{ kJ mol}^{-1}$$

The equation signifies when one mole of gas-phase atomic sodium is ionized to gas phase $Na^{\oplus}$ ions, the enthalpy change is 494 kJ. The same amount of heat would be required to ionize one mole of Na atoms.

The electron gain enthalpy on the other hand, gives the enthalpy change when one mole of gas-phase atoms of an element accept electron to form gaseous anion.

For example,

$Cl(g) + e^{\ominus} \longrightarrow Cl^{\ominus}(g)\ \Delta_{eg}H = -349\ kJ\ mol^{-1}$

Electron gain enthalpy of Cl is -349 kJmol^{-1}

ii. Enthalpy of atomization ($\Delta_{atom}H$) : The enthalpy change accompanying the dissociation of one mole of gaseous substance into atoms is the enthalpy of atomization. Consider,

$Cl_2(g) \longrightarrow Cl(g) + Cl(g);\ \Delta_{atom}H = 242\ kJ\ mol^{-1}$

$CH_4(g) \longrightarrow C(g) + 4H(g);\ \Delta_{atom}H = 1660\ kJ\ mol^{-1}$

iii. Enthalpy of solution ($\Delta_{soln}H$) : Enthalpy of solution is the enthalpy change in a process when one mole of a substance is dissolved in specified amount of solvent.

$NaCl(s) + aq \rightleftharpoons NaCl(aq)\ \Delta_{soln}H = 4\ kJ\ mol^{-1}$

Enthalpy of solution at infinite dilution is the enthalpy change when one mole of substance is dissolved in infinite amount of solvent.

An ionic compound dissolves in water in two steps:

1. The ions are separated from the molecule

$MX(s) \longrightarrow M^{\oplus}(g) + X^{\ominus}(g)$

Enthalpy change for this step is crystal lattice enthalpy, $\Delta_L H$ which is always positive.

2. The ions are hydrated with water molecules surrounding them.

$M^{\oplus}(g) + x\ H_2O \longrightarrow [M(H_2O)_x]^{\oplus}$

$X^{\ominus}(g) + y\ H_2O \longrightarrow [\ X(H_2O)_y]^{\ominus}$

The enthalpy change for this step is always negative and called enthalpy of hydration, $\Delta_{hyd}H$.

The enthalpy of solution is the sum of crystal lattice enthalpy and enthalpy of hydration.

$$\Delta_{soln}H = \Delta_L H + \Delta_{hyd}H$$

For NaCl, $\Delta_L H$ = +790 kJ/mol and

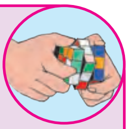
$\Delta_{hyd}H$ = -786 kJ/mol^{-1}

The enthalpy of solution of NaCl is

$\Delta_{soln}H$ (NaCl) = (+790 - 786) kJ/mol^{-1}

= +4 kJ/mol^{-1}

Try this...



For KCl, $\Delta_L H$ = 699 kJ/mol^{-1} and $\Delta_{hyd}H$ = -681.8 kJ/mol^{-1}. What will be its enthalpy of solution?

4.10 Thermochemistry : Thermochemistry deals with enthalpy changes in chemical reactions

4.10.1 Enthalpy of chemical reaction ($\Delta_r H$)

Consider, $aA + bB \longrightarrow cC + dD$

The enthalpy change for the reaction is

$$\Delta_r H = (cH_C + d\ H_D) - (a\ H_A + bH_B)$$

where H_A, H_B, H_C and H_D are molar enthalpies of A, B, C and D, respectively. We write

$$\Delta_r H = \sum H_{products} - \sum H_{reactants} \quad \text{.......} (4.29)$$

Thus, **enthalpy of a chemical reaction is the difference between the sum of enthalpies of products and that of reactants with each substance in definite physical state and their amounts (moles) being represented by the coefficients in the balanced equation of the reaction.**

4.10.2 Exothermic and endothermic reactions : The enthalpy of a reaction can be positive or negative depending on $\sum H_{products}$ and $\sum H_{reactants}$.

Thus $\sum H_{products} > \sum H_{reactants}$, $\Delta_r H$ is positive signifies the reaction is endothermic.

On the other hand, if

$$\sum H_{products} < \sum H_{reactants},\ \Delta_r H \text{ is negative}$$

which means that heat is released and the reaction is exothermic.

For example,

$N_2(g) + 2\ O_2(g) \longrightarrow 2\ NO_2(g)$,

$\Delta_r H = 66.4$ kJ (endothermic)

$2\ KClO_3(s) \longrightarrow 2\ KCl(s) + 3O_2(g)$,

$\Delta_r H = -78$ kJ (exothermic)

4.10.3 Standard enthalpy of reaction($\Delta_r H^0$)

To compare enthalpy changes of different reactions they have to be reported under similar set of conditions.

Thermodynamic standard state : The standard state of a substance is the form in which the substance is most stable at a pressure of 1 bar and at temperature 298 K. If the reaction involves species in solution its standard state refers to 1 M concentration.

Standard states of certain elements and compounds are $H_2(g)$, $Hg(l)$, $Na(s)$ or C(graphite), $C_2H_5OH(l)$, $CaCO_3(s)$, $CO_2(g)$ $C_2H_5OH(l)$, $H_2O(l)$, $CaCO_3(s)$, $CO_2(g)$ refer to 1 bar and 25 ^{0}C.

The standard enthalpy ($\Delta_r H^0$) of reaction is the enthalpy change accompanying the reaction when the reactants and products involved are in their standard states.

4.10.4 Thermochemical equation : It is the balanced chemical equation in which the enthalpy change, physical states and the number of moles of reactants and products, have been specified. Here follow the guidelines for writing thermochemical equations :

i. Consider the balanced equation for reactants and products.

ii. The value and appropriate sign of enthalpy change is given on the right hand side. This value is $\Delta_r H^0$.

iii. The physical states of reactants and products are specified by letter, s (solid), l (liquid), g (gas) and aq (aqueous). $\Delta_r H^0$ value refers to physical states of substances those appear in the equation.

iv. The given value of $\Delta_r H^0$ assumes that the reaction occurs in a given direction. $\Delta_r H^0$ for the reverse reaction equals in magnitude and opposite in the sign to that of the forward reaction. An exothermic reaction on reversal becomes endothermic and vice versa.

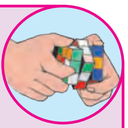
v. When the coefficients indicating the number of moles of all substances in thermochemical equation are multiplied or divided by a certain numerical factor, the corresponding $\Delta_r H^0$ need to be multiplied or divided by the same.

Example of thermochemical equation

$$CH_4(g) + 2\ O_2(g) \longrightarrow CO_2(g) + 2H_2O(l),\quad \Delta_r H^0 = -890 \text{ kJ}$$

The equation signifies that when 1 mole of gaseous CH_4 and 2 moles of O_2 in their standard states produce 1 mole of CO_2 gas and 2 moles of liquid water also in their standard states the enthalpy change would be -890 kJ.

Try this...



Given the thermochemical equation,

$$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2CO_2(g) + H_2O(l),\quad \Delta_r H^0 = -1300 \text{ kJ}$$

Write thermochemical equations when

i. Coefficients of substances are multiplied by 2.

ii. equation is reversed.

4.10.5 Standard enthalpy of formation ($\Delta_f H^0$)

Consider

$$H_2(g) + \frac{1}{2}\ O_2(g) \longrightarrow H_2O(l),\ \Delta_r H^0 = -286 \text{ kJ}$$

For the reaction where one mole of liquid water in standard state is formed from H_2 and O_2 gases in their standard states, the enthalpy changes for the reaction would be the standard enthalpy of formation of water. $\Delta_f H$ of water is -286 $kJmol^{-1.}$

The standard enthalpy of formation of a compound is the enthalpy change that accompanies a reaction in which one mole of pure compound in its standard state is formed from its elements in their standard states.

The formation of one mole of CH_4 in its standard state from the elements carbon and hydrogen in their standard states is represented by

$$C_{(graphite)} + 2H_2(g) \longrightarrow CH_4(g),\ \Delta_r H^0 = -74.8 \text{ kJ}$$

or $\Delta_f H^0\ (CH_4) = -74.8 \text{ kJ mol}^{-1}$

Do you know ?

The reaction to form a substance from its constituent elements is hypothetical. It is not possible to combine C and H_2 in the laboratory to prepare CH_4. The enthalpy of reaction for the formation of CH_4 can be obtained indirectly by knowing the standard enthalpy change for system. The value -74.8 kJ mol^{-1} corresponds to the hypothetical reaction.

4.10.6 Standard enthalpy of reaction from standard enthalpies of formation

The standard enthalpies of formation of compounds are used to determine standard enthalpies of reactions.

Calculations of $\Delta_r H^0$ from $\Delta_f H^0$ of compounds are based on the following.

i. Standard enthalpies of formation of an element is zero.

$$\Delta_f H^0(H_2) = \Delta_f H^0(Cl_2) = \Delta_f H^0(C) = 0$$

ii. Standard enthalpy of formation of a compound is equal to its standard enthalpy

$$\Delta_f H^0(\text{compound}) = H^0(\text{compound})$$

Consider the reaction

$$aA + bB \longrightarrow cC + dD$$

Standard enthalpy of the reaction is given by

$$\Delta_f H^0 = (cH^0_C + dH^0_D) - (aH^0_A + bH^0_B)$$

$$= [c\ \Delta_f H^0(C) + d\ \Delta_f H^0(D)] - [a\ \Delta_f H^0(A) + b\ \Delta_f H^0(B)]$$

$$= \sum \Delta_f H^0\ (\text{products}) - \sum \Delta_f H^0\ (\text{reactants}) \quad \text{.......}\ (4.30)$$

Problem 4.10

Calculate standard enthalpy of reaction,

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4\ CO_2(g) + 6\ H_2O(l)$$

Given that

$\Delta_f H^0\ (CO_2) = -393.5 \text{ kJ mol}^{-1}$,

$\Delta_f H^0\ (H_2O) = -285.8 \text{ kJ mol}^{-1}$ and

$\Delta_f H^0(C_2H_6) = -84.9 \text{ kJ mol}^{-1}$

Solution -

$$\Delta_r H^0 = \sum \Delta_f H^0(\text{products}) - \sum \Delta_f H^0(\text{reactants})$$

$$= [4\ \Delta_f H^0(CO_2) + 6\ \Delta_f H^0(H_2O)] - [2\ \Delta_f H^0(C_2H_6) + 7\ \Delta_f H^0(O_2)]$$

$$= [4 \text{ mol} \times (-393.5 \text{ kJ mol}^{-1}) + 6 \text{ mol} \times (-285.8 \text{ kJ mol}^{-1})] - [2 \text{ mol} \times (-84.9 \text{ kJ mol}^{-1}) + 0]$$

$$= -1574 \text{ kJ} - 1714.8 \text{ kJ} + 169.8 \text{ kJ}$$

$$= -3119 \text{ kJ}$$

4.10.7 Standard enthalpy of combustion ($\Delta_c H^0$)

Consider the reaction

$$C_2H_2(g) + \frac{5}{2}\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(l),\quad \Delta_r H^0 = -1300 \text{ kJ}$$

In the above reaction, the standard enthalpy change of the oxidation reaction, -1300 kJ is the standard enthalpy of combustion of $C_2H_2(g)$.

The standard enthalpy of combustion of a substnce is the standard enthalpy change accompanying a reaction in which one mole of the substance in its standard state is completely oxidised.

Try this...

Write thermochemical equation for complete oxidation of one mole of $H_2(g)$. Standard enthalpy change of the reaction is -286 kJ.

Is the value -286 kJ, enthalpy of formation or enthalpy of combustion or both? Explain.

Problem 4.11: Estimate the standard enthalpy of combustion of $CH_4(g)$ if $\Delta_f H^0(CH_4)$ = -74.8 kJ mol^{-1}, $\Delta_f H^0(CO_2)$ = -393.5 kJ mol^{-1} and $\Delta_f H^0(H_2O)$ = -285.8 kJ mol^{-1}

Solution : The equation for the combustion of CH_4 is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l), \quad \Delta_r H^0 = ?$$

$$\Delta_r H^0 = [\Delta_f H^0 (CO_2) + 2\,\Delta_f H^0(H_2O)] - [\Delta_f H^0(CH_4) + 2\,\Delta_f H^0(O_2)]$$

$$= [1 \times (-393.5) + 2 \times (-285.8)] - [1 \times (-74.8) + 2 \times 0]$$

$$\Delta_c H^0(CH_4) = -890.3 \text{ kJ}$$

4.10.8 Bond enthalpy

Consider the reaction

$$H_2(g) \longrightarrow H(g) + H(g), \ \Delta_r H^0 = 436.4 \text{ kJ}$$

It shows that H-H bond in one mole of $H_2(g)$ is decomposed producing gaseous H atoms. The enthalpy change of the reaction, 436.4 kJ is bond enthalpy of the H-H bond. **The enthalpy change required to break particular covalent bond in one mole of gaseous molecule to produce gaseous atoms and/or radicals, is called bond enthalpy.**

Try this...

Write equation for bond enthalpy of Cl-Cl bond in Cl_2 molecule $\Delta_r H^0$ for dissociation of Cl_2 molecule is 242.7 kJ

Remember...

For diatomic molecules the bond enthalpy is the same as enthalpy of atomization.

HCl molecule dissociates as

$$HCl(g) \longrightarrow H(g) + Cl(g), \ \Delta_r H^0 = 431.9 \text{ kJ}$$

$$\Delta H^0 \text{ (H-Cl bond)} = 431.9 \text{ kJ mol}^{-1}$$

Average bond enthalpy in polyatomic molecules : Each covalent bond in polyatomic molecules is associated with its own specific bond enthalpy. The thermochemical equation for dissociation of H_2O molecules is

$$H_2O(g) \longrightarrow 2\,H(g) + O(g), \ \Delta_r H^0 = 927 \text{ kJ}$$

The above equation implies that the enthalpy change for breaking of two O-H bonds in one mole of gaseous H_2O molecules is 927 kJ. Two O-H bonds in H_2O are identical the energies needed to break individual O-H bonds are different.

The bonds in H_2O are broken in successive steps as shown

i. $H_2O(g) \longrightarrow OH(g) + H(g) \quad \Delta_r H^0 = 499$ kJ

ii. $OH(g) \longrightarrow O(g) + H(g) \quad \Delta_r H^0 = 428$ kJ

$$H_2O(g) \longrightarrow 2\,H(g) + O(g) \quad \Delta_r H^0 = 927 \text{ kJ}$$

The total enthalpy change, 927 kJ, not twice as large of the O-H bond enthalpy. What is the enthalpy of O-H bond in H_2O molecule?

For polyatomic molecules the average bond enthalpy of a particular bond would be considered. Thus, the average bond enthalpy of the O-H bond = 927 2 = 463.5 kJ or ΔH^0 (O-H) = 463.5 kJ mol^{-1}

Do you know ?

In CH_4 molecule there are four identical C-H bonds. The bond enthalpy of all the 4 C-H bonds are different. The breaking of C-H bonds in CH_4 occurs in four steps as follows:

$CH_4(g) \rightarrow CH_3(g) + H(g), \ \Delta_r H^0 = 427 \text{ kJ}$

$CH_3(g) \rightarrow CH_2(g) + H(g), \ \Delta_r H^0 = 439 \text{ kJ}$

$CH_2(g) \rightarrow CH(g) + H(g), \ \Delta_r H^0 = 452 \text{ kJ}$

$CH(g) \rightarrow C(g) + H(g), \ \Delta_r H^0 = 347 \text{ kJ}$

$CH_4(g) \rightarrow C(g) + 4 H(g), \Delta_r H^0 = 1665 \text{ kJ}$

Average C-H bond enthalpy

$= 1665 \text{ kJ}/4 = 416 \text{ kJ}$

Hence, $\Delta_r H^0(\text{C-H}) = 416 \text{ kJ mol}^{-1}$

Reaction and bond enthalpies : In a chemical reaction bonds are broken and formed. The enthalpies of reactions involving substances having covalent bonds are calculated by knowing the bond enthalpies of reactants and those in products. The calculations assume all the bonds of a given type are identical.

Enthalpy change of a reaction

$$\Delta_r H^0 = \sum \Delta H^0 (\text{reactant}) - \sum \Delta H^0 (\text{product}) \quad \text{....... (4.31)}$$

Consider the reaction

$H_2(g) + I_2(g) \longrightarrow 2 HI(g)$

The enthalpy is given by

$\Delta_r H^0 = [\Delta H^0 (\text{H-H}) + \Delta H^0 (\text{I-I})] - [2\Delta H^0 (\text{H-I})]$

Remember...

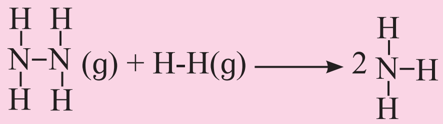
If reactants and products are diatomic molecules the Eq. (4.31) gives accurate results. The bond enthalpies are known accurately. For reactions involving polyatomic molecules the reaction enthalpies calculated via. Eq. (4.31) would be approximate and refer to averag bond enthalpies.

Examples 4.12 : Calculate the standard enthalpy of :

$N_2H_4(g) + H_2(g) \longrightarrow 2 NH_3(g)$

if $\Delta H^0(\text{N-H}) = 389 \text{ kJ mol}^{-1}$, $\Delta H^0(\text{H-H}) = 435 \text{ kJ mol}^{-1}$, $\Delta H^0 (\text{N-N}) = 159 \text{ kJ mol}^{-1}$

Solution :



$$\underset{\substack{| \quad | \\ H \quad H}}{\overset{\substack{H \quad H \\ | \quad |}}{N-N}} (g) + \text{H-H}(g) \longrightarrow 2 \ \underset{\substack{| \\ H}}{\overset{\substack{H \\ |}}{N}}\text{-H}$$

$\Delta_r H^0 = \sum \Delta H^0 (\text{reactant}) -$

$\sum \Delta H^0 (\text{product})$

$= [4\Delta H^0(\text{N-H}) + \Delta H^0(\text{N-N}) + \Delta H^0(\text{H-H})] - [6 \Delta H^0(\text{N-H})]$

$= \Delta H^0 (\text{N-N}) + \Delta H^0(\text{H-H}) - 2 \Delta H^0(\text{N-H})$

$= 1 \times 159 + 1 \text{ mol} \times 435 - 2 \times 389$

$= -184 \text{ kJ}$

Example 4.13 : The enthalpy change of the following reaction

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$, $\Delta_r H^0 = -104$ kJ. Calculate C-Cl bond enthalpy. The bond enthalpies are

Bond	C-H	Cl-Cl	H-Cl
$\Delta H^0/\text{kJ mol}^{-1}$	414	243	431

Solution

$\Delta_r H^0 = \sum \Delta H^0 (\text{reactant}) - \sum \Delta H^0 (\text{product})$

$= [4\Delta H^0(\text{C-H}) + \Delta H^0(\text{Cl-Cl})] - [3\Delta H^0(\text{C-H}) + \Delta H^0(\text{C-Cl}) + \Delta H^0(\text{H-Cl})]$

$= \Delta H^0(\text{C-H}) + \Delta H^0(\text{Cl-Cl}) - \Delta H^0(\text{C-Cl}) - \Delta H^0(\text{H-Cl})$

$-104 \text{ kJ} = 1 \times 414 + 1\times 243 - 1 \times \Delta H^0(\text{C-Cl}) - 1 \times 431$

$= 226 - 1 \times \Delta H^0(\text{C-Cl})$

$1 \times \Delta H^0(\text{C-Cl}) = 226 + 104$

$\Delta H^0(\text{C-Cl}) = 330 \text{ kJ mol}^{-1}$

4.10.9 Hess's law of constant heat summation

The law states that, "**Overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction**".

The enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs. Hess's law is a direct consequence of the fact that enthalpy is state function. The enthalpy change of a reaction depends only on the initial and final states and not on the path by which the reaction occurs.

To determine the overall equation of reaction, reactants and products in the individual steps are added or subtracted like algebraic entities.

Consider the synthesis of NH_3

i. $2H_2(g) + N_2(g) \longrightarrow N_2H_4(g)$, $\quad \Delta_r H_1^0 = + 95.4$ kJ

ii. $N_2H_4(g) + H_2(g) \longrightarrow 2\ NH_3(g)$, $\quad \Delta_r H_2^0 = -187.6$ kJ

$3\ H_2(g) + N_2(g) \longrightarrow 2\ NH_3(g)$, $\quad \Delta_r H^0 = -92.2$ kJ

The sum of the enthalpy changes for steps (i) and (ii) is equal to enthalpy change for the overall reaction.

Application of Hess's law

The Hess's law has been useful to calculate the enthalpy changes for the reactions with their enthalpies being not known experimentally.

Example 4.14 : Calculate the standard enthalpy of the reaction,

$$2Fe(s) + 3/2\ O_2(g) \longrightarrow Fe_2O_3(s)$$

Given :

i. $2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$, $\quad \Delta_r H^0 = -847.6$ kJ

ii. $2\ Al(s) + 3/2\ O_2(g) \longrightarrow Al_2O_3(s)$, $\quad \Delta_r H^0 = -1670$ kJ

Solution :

Reverse Eq.(i) and then add to Eq. (ii)

$2Fe(s) + Al_2O_3(s) \longrightarrow 2\ Al(s) + Fe_2O_3(s)$, $\quad \Delta_r H^0 = +847.6$ kJ

$2\ Al(s) + 3/2\ O_2(g) \longrightarrow Al_2O_3(s)$, $\quad \Delta_r H^0 = -1670$ kJ

$2Fe(s) + 3/2\ O_2(g) \longrightarrow Fe_2O_3(s)$, $\quad \Delta_r H^0 = -822.4$ kJ

Example 4.15 : Calculate the standard enthalpy of the reaction,

$SiO_2(s) + 3C(graphite) \longrightarrow SiC(s) + 2\ CO(g)$

from the following reactions,

i. $Si(s) + O_2(g) \longrightarrow SiO_2(s)$, $\quad \Delta_r H^0 = -911$ kJ

ii. $2\ C(graphite) + O_2(g) \longrightarrow 2CO(g)$, $\quad \Delta_r H^0 = -221$ kJ

iii. $Si(s) + C(graphite) \longrightarrow SiC(s)$, $\quad \Delta_r H^0 = -65.3$kJ

Solution : Reverse the Eq. (i)

iv. $SiO_2(s) \longrightarrow Si(s) + O_2(g)$, $\quad \Delta_r H^0 = -911$ kJ

Add equations (ii), (iii) and (iv)

ii. $2\ C(graphite) + O_2(g) \longrightarrow 2\ CO(g)$, $\quad \Delta_r H^0 = -221$ kJ

iii. $Si(s) + C(graphite) \longrightarrow SiC(s)$, $\quad \Delta_r H^0 = -65.3$ kJ

iv. $SiO_2(s) \longrightarrow Si(s) + O_2(g)$, $\quad \Delta_r H^0 = +911$ kJ

$SiO_2(s)+3\ C(graphite) \longrightarrow SiC(s) +2\ CO(g)$, $\quad \Delta_r H^0 = +624$ kJ

4.11 Spontaneous (irreversible) process :

Spontaneous processes have a natural tendency to occur and do not require any external influence for their occurrence.

Do you know ?

i. The aqueous NaOH and HCl solutions mixed together. NaOH immediately combines with HCl to form NaCl and water.

$$NaOH(aq) + HCl(aq) \longrightarrow NaCl(aq) + H_2O(l), \quad \Delta_r H^0 = -57 \text{ kJ}$$

No external force or energy is required for the reaction to occur. This is spontaneous. The process stops when HCl or NaOH is consumed.

NaCl is dissolved in water, it does not react with water to produce NaOH and HCl.

ii. Water flows from higher level to lower level. It is not necessary to apply external force. It is a spontaneous process. The flow ceases when two levels become equal or when the equilibrium is reached.

iii. Ice melts spontaneously above 0 °C.

iv. Hot coffee in a cup placed in a room cools down releasing heat to the surroundings. This is spontaneous.

Key points of spontaneous process

i. It occurs of its own and does not require any external agency to occur.

ii. It proceeds in one direction and cannot take place in the opposite direction unless the external stimulant is present.

iii. The spontaneous processes can be rapid or slow or spontaneity is not concerned with the rate of the reaction.

iv. The process continues till equilibrium is reached. **The spontaneous (natural) processes tend to occur in a direction that leads to equilibrium.**

4.11.1 Energy and spontaneity :

The spontaneous reaction takes place in a direction in which energy of the system is lowered. It is accompanied by release of energy. The reaction between NaOH and HCl is exothermic ($\Delta_r H°$ = -57 kJ) and is spontaneous.

On the other hand :

i. Ice melts spontaneously above 0 °C by absorbing heat from the surroundings. It is endothermic.

ii. Likewise, NaCl dissolves spontaneously in water with the absorption of heat from the surroundings.

$$NaCl(s) + aq \longrightarrow Na^{\oplus}(aq) + Cl^{\ominus}(aq) \quad \Delta H^0 = +3.9 \text{ kJ mol}^{-1}$$

These are endothermic and spontaneous. It is therefore, clear that the exothermicity is not the sufficient criterion for deciding of spontaneity. There needs to be an another factor to describe spontaneity.

4.11.2 Entropy :

To know what is entropy consider the following processes:

i. In solid state water molecules in ice are arranged in a definite order.

ii. When ice melts, this highly crystalline arrangements of water molecules collapse. The molecules become free in liquid state. An ordered state thus tends to become more disordered.

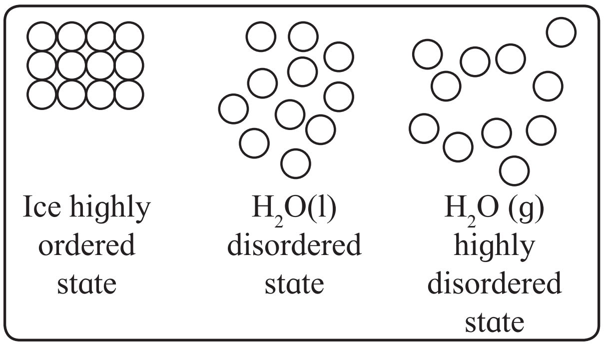


Fig. 4.10 Increasing disorder

iii. When liquid water vaporises, gaseous water molecules move freely and randomly in the available space. A less disordered state becomes highly disordered as shown in Fig. 4.10.

During melting of ice or the vaporisation of liquid water the disorder or randomness increases. The disorder or randomness is measured by **entropy,** denoted by S. Greater the disorder of a system larger is its entropy. The melting of ice and vaporisation of liquid water show that disorder and hence, entropy of substance increases as it passes from solid to liquid to gas.

In both processes entropy change $\Delta S > 0$. Look at the following processes :

i. Dissolution of solid I_2 in water :

$I_2(s) + aq. \longrightarrow I_2(aq)$ (ΔS is positive)

ordered state disordered state

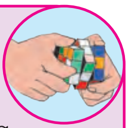
When solid iodine dissolves in water I_2 molecules move randomly. Thus disorder and hence, entropy of the system increases or ΔS is positive for the dissolution process.

ii. Dissociation of H_2 molecule into atoms

$H_2(g) \longrightarrow 2H(g)$ (ΔS is positive)

One mole of H_2 gas is converted into two H atoms. Larger disorder is associated with separated H atoms than with H_2 molecule. Thus, disorder and hence entropy increases or ΔS is positive.

Try this...



State whether ΔS is positive, negative or zero for the following reactions.

i. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

ii. $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

Quantitative definition of entropy

Entropy is a measure of molecular disorder or randomness. An entropy change of a system is equal to the amount of heat transferred (Q_{rev}) to it in a reversible manner divided by the temperature in kelvin T at which the transfer takes place. Thus

$$\Delta S = \frac{Q_{rev}}{T} \qquad \text{....... (4.32)}$$

the ΔS is thus expressed in J K^{-1}.

Entropy or its change ΔS is a state function and depends on the initial and final states of the system and not on the path connecting two states.

i. When heat is added to a system the molecular motions increase owing to increase of their kinetic energies. This results in increased molecular disorder and thus entropy of the system. ΔS is proportional to Q_{rev}.

ii. The effectiveness of the addition of heat to increase randomness depends on temperature.

If a certain amount of heat is added to system at the higher temperature then the disorder caused is lesser than that caused by adding the same amount of heat is added to system at the lower temperature Thus, ΔS relates reciprocally to temperature at which the of heat is added.

4.11.3 Entropy and spontaneity (Second law of Thermodynamics)

Look at the following examples :

i. The entropy increases when ice melts above 0 °C and water vaporizes at 100 °C. Both are spontaneous.

ii. Consider the spontaneous reaction at room temperature

$2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g),$

$\Delta S = +126$ J K^{-1}

Entropy increases due to the formation of O_2 gas.

From above examples, it is clear that the entropy of the system increases in the spontaneous processes. Consider the reaction.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l), \quad \Delta S = -327 \text{ J K}^{-1}.$$

The entropy of the system decreases. Note the reaction is spontaneous.

4.11.4 Second law of thermodynamics :

The second law of thermodynamics states that total entropy of a system and its surroundings increases in a spontaneous process. For the process to be spontaneous

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0 \qquad (4.33)$$

Consider

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

ΔS = -327 J K^{-1}, and ΔH = -572 kJ (both at 298 K)

To find ΔS_{total}, we need to know ΔS_{surr}. ΔH for the reaction is -572 kJ. When 2 moles of H_2 and 1 mole of O_2 gas combine to form 2 moles of liquid water, 527 kJ of heat is released which is received by surroundings at constant pressure (and 298 K). The entropy change of surroundings is

$$\Delta S_{surr} = \frac{Q_{rev}}{T} = \frac{572 \times 10^3 \text{ J}}{298 \text{ K}} = 1919 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= -327 \text{ J K}^{-1} + 1919 \text{ J K}^{-1}$$

$$= +\,1592 \text{ J K}^{-1}$$

$$\Delta S_{total} > 0.$$

The reaction is thus spontaneous. It follows that to decide spontaneity of reactions, we need to consider the entropy of system and its surroundings.

The total entropy increases during a spontaneous process that finally reaches equilibrium. The equilibrium corresponds to maximum total entropy. The total entropy change, ΔS_{total} must be zero for a process at equilibrium.

From above,

i. $\Delta S_{total} > 0$, the process is spontaneous

ii. $\Delta S_{total} < 0$, the process is nonspontaneous

iii. $\Delta S_{total} = 0$, the process is at equilibrium

4.11.5 Gibbs energy

As pointed out in the preceding section, it is necessary to determine, ΔS_{sys} and ΔS_{surr}, for predicting the spontaneity of a reaction. We are more interested in the system (reaction mixture) . It. is, therefore convenient to consider the criterion of spontaneity in terms of the thermodynamic properties of a system. This problem was solved by American theoretician J. W. Gibbs. He introduced a new thermodynamic property called Gibbs energy usually denoted by G.

The Gibbs energy is defined as

$$G = H - TS \qquad \text{....... (4.34)}$$

where H is enthalpy and S entropy of the system. Since H, T and S are state functions, G is state function. A change in Gibbs energy depends on initial and final states of the system and not on a path connecting the two states.

The change in Gibbs energy at constant temperature and constant pressure is given by

$$\Delta G = \Delta H - T\,\Delta S \qquad \text{....... (4.35)}$$

4.11.6 Gibbs energy and spontaneity

The total entropy change that accompanies a process is given by

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= \Delta S + \Delta S_{surr} \qquad \text{....... (4.36)}$$

The subscript sys that refers to the system is dropped hereafter.

Relation between ΔG and ΔS_{total}

According to second law of thermodynamics for a process to be spontaneous, $\Delta S_{total} > 0$

If ΔH is the enthalpy change accompanying a reaction (system) the enthalpy change of the surroundings is $-\Delta H$. With

$$\Delta S_{surr} = - \frac{\Delta H}{T} \qquad \text{.......} \quad (4.37)$$

Substituting above into Eq. (4.36),

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T} \qquad \text{.......} \quad (4.38)$$

Thus ΔS_{total} is expressed in terms of the properties of the system only. Rearranging

$$T\,\Delta S_{total} = \Delta H - T\,\Delta S \qquad \text{.......} \quad (4.39)$$

Substituting in Eq. (4.35)

$$\Delta G = -\,T\,\Delta S_{total} \qquad \text{.......} \quad (4.40)$$

For a spontaneous reaction $S_{total} > 0$ and hence, $\Delta G < 0$. At constant temperature and pressure Gibbs energy of the system decreases in a spontaneous process.

The second law leads to the conditions of spontaneity which are summarised here.

i. $\Delta S_{total} > 0$ and $\Delta G < 0$, the process is spontaneous.

ii. $\Delta S_{total} < 0$ and $\Delta G > 0$, the process is nonspontaneous.

iii. $\Delta S_{total} = 0$ and $\Delta G = 0$, the process is at equilibrium.

4.11.7 Sponaneity and ΔH or ΔS

From $\Delta G = \Delta H - T\,\Delta S$ (at constant T and P).

The temperature term determines relative contributions of ΔH and ΔS to ΔG.

1. ΔH and ΔS are both negative then ΔG will be negative only when ΔH is more negative than $T\Delta S$. This is possible at **low temperatures** only**.**

2. ΔH amd ΔS both positive ΔG will be negative only if $T\Delta S > \Delta H$. This is possible only at high temperatures.

3. For ΔH negative and ΔS is positive it follows that ΔG is negative regardless of temperature.

4. For ΔH positive and ΔS is negative then

ΔG is positive regardless of temperature. Such reactions are nonspontaneous at all temperatures.

4.11.8 Temperature of equilibrium

For equilibrium

$$\Delta G = \Delta H - T\Delta S \text{ gives}$$

$$\therefore\ T = \frac{\Delta H}{\Delta S} \qquad \text{.......} \quad (4.41)$$

T is the temperature at which the change over from spontaneous to nonspontaneous behavior occurs. ΔH and ΔS are assumed to be independent of temperature in Eq. (4.41). Introducing of temperature dependence of ΔH or ΔS would not cause significant error for the moderate temperature range.

4.11.9 Gibbs function and equilibrium constant : Gibbs energy change for a chemical reaction is given by

$$\Delta G = \Delta G^0 + RT \ln Q \qquad \text{.......} \quad (4.42)$$

where ΔG^0 is standard Gibbs energy change that is, the Gibbs energy change when the reactants and products in a reaction are in their standard states. Q is called reaction quotient Q is analogus to that of the equilibrium constant. and involves nonequilibrium concentrations or partial pressures in case of gaseous reaction.

Consider

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G = \Delta G^0 + RT \ln Q_c$$

$$= \Delta G^0 + RT \ln \frac{[C]^c[D]^d}{[A]^a\,[B]^b} \qquad \text{.......} (4.43)$$

or $$\Delta G = \Delta G^0 + RT \ln Q_p$$

$$= \Delta G^0 + RT \ln \frac{P_C^{\,c} \times P_D^{\,d}}{P_A^{\,a} \times P_B^{\,b}} \qquad \text{.......} (4.44)$$

When the reaction reaches equilibrium, $\Delta G^0 = 0$ and Q_c and Q_p become K_c and K_p, respectively. Thus,

$$0 = \Delta G^0 + RT \ln K_c \text{ and } 0 = \Delta G^0 + RT \ln K_p$$

or

$$\Delta G^0 = -RT \ln K_c \text{ and } \Delta G^0 = -RT \ln K_p \quad \ldots\ldots(4.45)$$

or $\Delta G^0 = -2.303\ RT \log_{10} K_c$

and

$$\Delta G^0 = -2.303\ RT \log_{10} K_p \quad \ldots\ldots\ (4.46)$$

Problem 4.16 : State whether following reactions are spontaneous or not. Further state whether they are exothermic or endothermic.

a. $\Delta H = -110$ kJ and $\Delta S = +40$ JK^{-1} at 400 K

b. $\Delta H = +50$ kJ and $\Delta S = -130$ JK^{-1} at 250 K

Solution :

a. $\Delta G = \Delta H - T\Delta S$

$\Delta H = -110$ kJ, $\Delta S = +40$ J K^{-1}

$= +40 \times 10^{-3}$ kJ K^{-1}, T = 400 K

Therefore, $\Delta G = -110$ kJ -400 K $\times 40 \times 10^{-3}$ kJ K^{-1}

$= -110$ kJ $- 16$ kJ $= -126$ kJ

Since ΔG is negative, the reaction is spontaneous. It is exothermic since ΔH is negative

b. $\Delta H = +50$ kJ, $\Delta S = -130 \times$J K^{-1}

$= -130 \times 10^{-3}$ kJ K^{-1} $T = 250$ K

$\Delta G = +50$ kJ $- 250$ K $\times(-130 \times 10^{-3}$ kJ $K^{-1})$

$= 50$ kJ $+ 32.5$ kJ $= +82.5$ kJ

As ΔG is positive, the reaction is nonspontaneous. It is endothermic since ΔH is positive.

Problem 4.17

For a certain reaction ΔH^0 is -224 kJ and ΔS^0 is -153 J K^{-1}. At what temperature the change over from spontaneous to nonspontaneous will occur?

Solution -

$$T = \frac{\Delta H^0}{\Delta S^0}$$

$\Delta H^0 = -224$ kJ, $\Delta S^0 = -153$ $JK^{-1} = -0.153$ kJ K^{-1}

Therefore, $T = \dfrac{-224 \text{ kJ}}{-0.153 \text{ J K}^{-1}} = +1464$ K

Since ΔH^0 and ΔS^0 are both negative, the reaction is spontaneous at low temperatures. A change over will occur at 1464 K. The reaction is spontaneous below 1464 K .

Problem 4.18

For the reaction,

$CH_4(g) + H_2(g) \longrightarrow C_2H_6(g)$,

$K_p = 3.356 \times 10^{17}$

Calculate ΔG^0 for the reaction at 25 ^{0}C.

Solution :

$\Delta G^0 = -2.303\ RT \log_{10} K_p$

$R = 8.314$ J $K^{-1}mol^{-1}$, $T = 298$ K,

$K_p = 3.356 \times 10^{17}$

$\Delta G^0 = -2.303 \times 8.314 \times 298 \times \log_{10}(3.356 \times 10^{17})$

$= -2.303 \times 8.314$ J $mol^{-1} \times 298 \times 17.526$

$= -100{,}000$ J mol^{-1}

$= -100$ kJ mol^{-1}

Problem 4.19 : Calculate ΔS_{total} and state whether the reaction is spontaneous or nonspontaneous at 25 ^{0}C.

$HgS(s) + O_2(g) \longrightarrow Hg(l) + SO_2(g)$,

$\Delta H^0 = -238.6$ kJ, $\Delta S^0 = +36.7$ J K^{-1}

Solution :

$$\Delta S_{surr} = -\frac{\Delta H^0}{T}$$

$$= \frac{(-238.6 \text{ kJ})}{298 \text{ K}}$$

$$= +0.8007 \text{ kJ K}^{-1} = +800.7 \text{ J K}^{-1}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$$

$$= +36.7 \text{ JK}^{-1} + 800.7 \text{ JK}^{-1}$$

$$= +837.4 \text{ J K}^{-1}$$

$\Delta S_{total} > 0$, the reaction is spontaneous at 25 ^{0}C.

Problem 4.20 : Calculate ΔG for the reaction at 25 ^{0}C

$CO(g) + 2\,H_2(g) \longrightarrow CH_3OH(g)$, $\Delta G^0 = -24.8$ kJ mol^{-1} The partial pressures of gases are $P_{CO} = 4$ bar, $P_{H_2} = 2$ bar and $P_{CH_3OH} = 2$ bar

Solution : $\Delta G = \Delta G^0 + RT \ln Q_p$

$$= \Delta G^0 + 2.303\, RT \log_{10} \frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}$$

$\Delta G^0 = -24.8$ kJ mol^{-1}, $R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}, $T = 298$ K

Calculate Q_p,

$$Q_p = \frac{P_{CH_3OH}}{P_{Co} \times P^2_{H_2}} = \frac{2}{4 \times 4} = \frac{1}{8} = 0.125$$

$\Delta G = -24.8$ kJ mol^{-1} $+2.303 \times 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1} $\times$ 298 K $\times \log_{10} 0.125$

$= -24.8$ kJ mol^{-1} $+ 5.706 \times (-0.903)$ kJ mol^{-1}

$= -24.8$ kJ mol^{-1} $- 5.153$ kJ mol^{-1}

$= -29.953$ kJ mol^{-1}

Exercises

1. Select the most aprropriate option.

i. The correct thermodynamic conditions for the spontaneous reaction at all temperatures are

a. $\Delta H < 0$ and $\Delta S > 0$

b. $\Delta H > 0$ and $\Delta S < 0$

c. $\Delta H < 0$ and $\Delta S < 0$

d. $\Delta H < 0$ and $\Delta S = 0$

ii. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 bar from an initial volume of 2.5 L to a final volume of 4.5 L. The change in internal energy, ΔU of the gas will be

a. -500 J b. + 500 J

c. -1013 J d. + 1013 J

iii. In which of the following, entropy of the system decreases?

a. Crystallization of liquid into solid

b. Temperature of crystalline solid is increased from 0 K to 115 K

c. $H_2(g) \longrightarrow 2H(g)$

d. $2\,NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$

iv. The enthalpy of formation for all elements in their standard states is

a. unity

b. zero

c. less than zero

d. different elements

v. Which of the following reactions is exothermic?

a. $H_2(g) \longrightarrow 2H(g)$

b. $C(s) \longrightarrow C(g)$

c. $2\,Cl(g) \longrightarrow Cl_2(g)$

d. $H_2O(s) \longrightarrow H_2O(l)$

vi. 6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat. Enthalpy of vaporization of ethanol will be

a. 43.4 kJ mol^{-1}

b. 60.2 kJ mol^{-1}

c. 38.9 kJ mol^{-1}

d. 20.4 kJ mol^{-1}

vii. If the standard enthalpy of formation of methanol is -238.9 kJ mol^{-1} then entropy change of the surroundings will be

a. -801.7 J K^{-1} b. 801.7 J K^{-1}

c. 0.8017 J K^{-1} d. -0.8017 J K^{-1}

viii. Which of the following are not state functions?

1. $Q + W$ 2. Q 3. W 4. $H\text{-}TS$

a. 1,2 and 3 b. 2 and 3

c. 1 and 4 d. 2,3 and 4

ix. For vaporization of water at 1 bar,

$\Delta H = 40.63$ kJ mol^{-1} and $\Delta S = 108.8$ J K^{-1} mol^{-1}. At what temperature, $\Delta G = 0$?

a. 273.4 K b. 393.4 K

c. 373.4 K d. 293.4 K

x. Bond enthalpies of H-H, Cl-Cl and H-Cl bonds are 434 kJ mol^{-1}, 242 kJ mol^{-1} and 431 kJ mol^{-1}, respectively. Enthalpy of formation of HCl is

a. 245 kJ mol^{-1} b. -93 kJmol^{-1}

c. -245 kJ mol^{-1} d. 93 kJ mol^{-1}

2. Answer the following in one or two sentences.

i. Comment on the statement: no work is involved in an expansion of gas in vacuum.

ii. State the first law of thermodynamics.

iii. What is enthalpy of fusion?

iv. What is standard state of a substance?

v. State whether ΔS is positive, negative or zero for the reaction $2H(g) \longrightarrow H_2(g)$. Explain.

vi. State second law of thermodynamics in terms of entropy.

vii. If the enthalpy change of a reaction is ΔH how will you calculate entropy of surroundings?

viii. Comment on spontaneity of reactions for which ΔH is positive and ΔS is negative.

3. Answer in brief.

i. Obtain the relationship between ΔG^0 of a reaction and the equilibrium constant.

ii. What is entropy? Give its units.

iii. How will you calculate reaction enthalpy from data on bond enthalpies?

iv. What is the standard enthalpy of combustion ? Give an example.

v. What is the enthalpy of atomization? Give an example.

vi. Obtain the expression for work done in chemical reaction.

vii. Derive the expression for *PV* work

viii. What are intensive properties? Explain why density is intensive property.

ix. How much heat is evolved when 12 g of CO reacts with NO_2 ? The reaction is :

$$4\ CO(g) + 2\ NO_2(g) \longrightarrow 4\ CO_2(g) + N_2(g),\ \Delta_r H^0 = -1200\ kJ$$

4. Answer the following questions.

i. Derive the expression for the maximum work.

ii. Obtain the relatioship between ΔH and ΔU for gas phase reactions.

iii. State Hess's law of constant heat summation. Illustrate with an example. State its applications.

iv. Although ΔS for the formation of two moles of water from H_2 and O_2 is $-327 JK^{-1}$, it is spontaneous. Explain. (Given ΔH for the reaction is -572 kJ).

v. Obtain the relation between ΔG and ΔS_{total} Comment on spontaneity of the reaction.

vi. One mole of an ideal gas is compressed from 500 cm^3 against a constant external pressure of 1.2×10^5 Pa. The work involved in the process is 36.0 J. Calculate the final volume. (200 cm^3)

vii. Calculate the maximum work when 24 g of O_2 are expanded isothermally and reversibly from the pressure of 1.6 bar to 1 bar at 298 K.

Ans. : (-873.4 J)

viii. Calculate the work done in the decomposition of 132 g of NH_4NO_3 at 100 ^{0}C.

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2\ H_2O(g)$$

State whether work is done on the system or by the system.

Ans. : (-18.6 kJ)

ix. Calculate standard enthalpy of reaction,

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2\ Fe(s) + 3CO_2(g)$, from the following data.

$\Delta_f H^0(Fe_2O_3) = -824$ kJ/mol,

$\Delta_f H^0(CO) = -110$ kJ/mol,

$\Delta_f H^0(CO_2) = -393$ kJ/mol

Ans. : (-25 kJ)

x. For a certain reaction ΔH^0 =219 kJ and ΔS^0 = -21 J/K. Determine whether the reaction is spontaneous or nonspontaneous.

xi. Determine whether the following reaction is spontaneous under standard state conditions.

$$2\ H_2O(l) + O_2(g) \longrightarrow 2H_2O_2(l)$$

if $\Delta H^0 = 196$ kJ, $\Delta S^0 = -126$ J/K

Does it have a cross-over temperature?

(Nonspontaneous, No)

xii. Calculate ΔU at 298 K for the reaction,

$$C_2H_4(g) + HCl(g) \longrightarrow C_2H_5Cl(g),\quad \Delta H = -72.3\ kJ$$

How much PV work is done?

Ans. : (-69.8 kJ, 2.48 kJ)

xiii. Calculate the work done during synthesis of NH_3 in which volume changes from 8.0 dm^3 to 4.0 dm^3 at a constant external pressure of 43 bar. In what direction the work energy flows?

Ans. : (17.2 kJ, work energy flows into system)

xiv. Calculate the amount of work done in the (a) oxidation of 1 mole HCl(g) at 200 ^{0}C according to reaction.

$$4HCl(g) + O_2(g) \longrightarrow 2\ Cl_2(g) + 2\ H_2O(g)$$

(b) decomposition of one mole of NO at 300 ^{0}C for the reaction

$$2\ NO(g) \longrightarrow N_2(g) + O_2$$

Ans. : (a = + 983 kJ ; b = 0 kJ)

xv. When 6.0 g of O_2 reacts with CIF as per

$$2Cl\,F(g) + O_2(g) \longrightarrow Cl_2O(g) + OF_2(g)$$

The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction ?

($\Delta_r H^0 = 205.6$ kJ)

xvi. Calculate the standard enthalpy of formation of $CH_3OH(l)$ from the following data

i. $CH_3OH(l) + \frac{3}{2}\,O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$,

$\Delta H^0 = -726$ kJ mol^{-1}

ii. $C\,(\text{Graphite}) + O_2(g) \longrightarrow CO_2(g)$,

$\Delta_c H^0 = -393$ kJ mol^{-1}

iii. $H_2(g) + \frac{1}{2}\,O_2(g) \longrightarrow H_2O(l)$,

$\Delta_f H^0 = -286$ kJ mol^{-1}

Ans. : (- 239 kJ mol^{-1})

xvii. Calculate ΔH^0 for the following reaction at 298 K

$$H_2B_4O_7(s) + H_2O(l) \longrightarrow 4HBO_2\,(aq)$$

i. $2H_3BO_3(aq) \longrightarrow B_2O_3(s) + 3H_2O(l)$,

$\Delta H^0 = 14.4$ kJ mol^{-1}

ii. $H_3BO_3(aq) \longrightarrow HBO_2(aq) + H_2O,(l)$

$\Delta H^0 = -0.02$ kJ mol^{-1}

iii. $H_2B_4O_7(s) \longrightarrow 2P_2O_3(s) + H_2O(l)$,

$\Delta H^0 = 17.3$ kJ mol^{-1}

Ans. : (- 11.58 kJ)

xviii. Calculate the total heat required (a) to melt 180 g of ice at 0 ^{0}C, (b) heat it to 100 ^{0}C and then (c) vapourise it at that temperature. Given $\Delta_{fus}H^0$(ice) = 6.01 kJ mol^{-1} at 0 ^{0}C, $\Delta_{vap}H^0(H_2O)$ = 40.7 kJ mol^{-1} at 100 ^{0}C specific heat of water is 4.18 J g^{-1} K^{-1}

Ans. : (542.3 kJ)

xix. The enthalpy change for the reaction,

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

is -620 J when 100 ml of ethylene and 100 mL of H_2 react at 1 bar pressure. Calculate the pressure volume type of work and ΔU for the reaction.

Ans.: (W = +10.13 J; ΔU = -609.9 J)

xx. Calculate the work done and comment on whether work is done on or by the system for the decomposition of 2 moles of NH_4NO_3 at 100 ^{0}C

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$$

Ans. (-18.61 kJ, work is done by the system)

Activity :

Following are some processes occurrring in nature.

- **River originates in a mountain and flows towards sea.**
- **After proper incubations for 21 days a chicken egg hatches and baby chick comes out.**
- **List out some more processes you come across in nature.**
- **Identify the processes that are in accordance with the second law of thermodynamics and those which are against it.**