9

CHAPTER

Second Law of Thermodynamics

The first law of thermodynamics states that one form of energy can change into another form but the total amount of energy remains the same. Once we specify a particular process or change, this law helps us to balance the internal energy, heat released and work done in the process. But the first law says nothing about whether the process of change we specify can, in fact, occur and if so in which direction. This question concerns the second law of thermodynamics. Before we can state the second law in a usable form, we must define some terms.

SPONTANEOUS PROCESSES

A process which proceeds of its own accord, without any outside assistance, is termed a spontaneous or natural process.

The reverse process which does not proceed on its own, is referred to as a nonspontaneous or unnatural process.

In general, the tendency of a process to occur naturally is called the spontaneity.
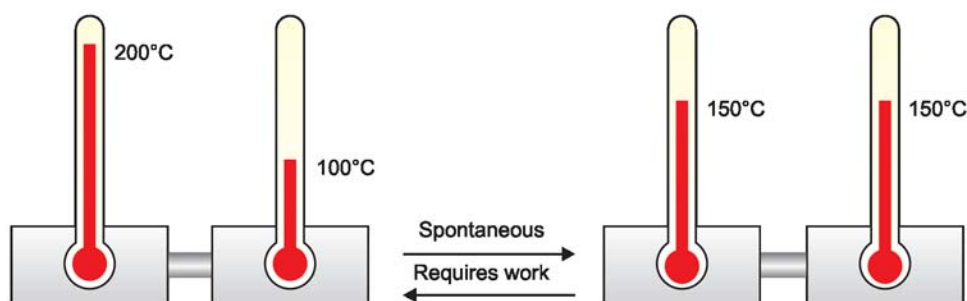
Examples of Spontaneous Processes

(1) **Cliff Jumping and Mountain Climbing.** Cliff jumping is a spontaneous process, whereas mountain climbing requires work.

(2) **Heat Flow.** When two balls of metal, one hot and one cold, are connected, heat flows spontaneously from the hot ball to the cold one, never from cold to hot. It requires work to transfer heat from one place to the other, say, by means of refrigerator pump.

(3) **Gas Flow.** When a vessel containing a gas is connected to another evacuated vessel, the gas spreads throughout spontaneously unless the pressure is the same in both the vessels. The reverse process of compressing the gas into the original vessel cannot occur unless work is done on it.

(a) Cliff Jumping and Mountain Climbing

Spontaneous   Requires work

(b) Heat Flow

200°C   100°C   150°C   150°C

Spontaneous
Requires work
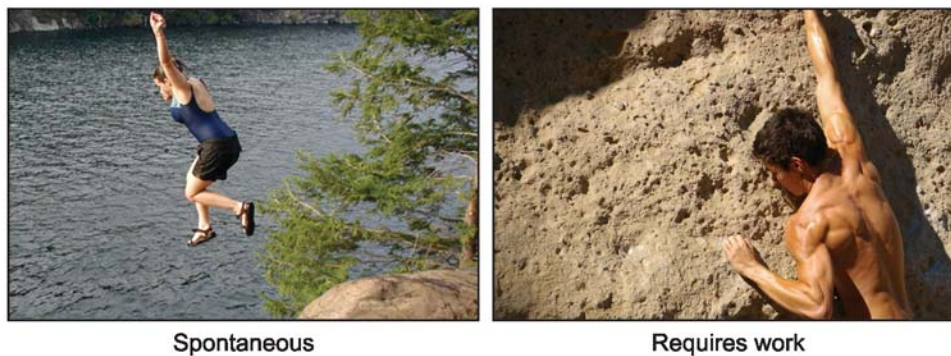
(c) Gas Flow

Spontaneous
Nonspontaneous
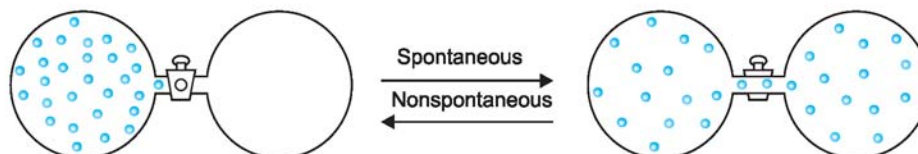
■ **Figure 9.1**
Spontaneous processes (Illustration).

CRITERIA OF SPONTANEITY

Some important criteria of spontaneous physical and chemical changes are listed below.

(1) **A spontaneous change is one-way or unidirectional.** For reverse change to occur, work has to be done.

(2) **For a spontaneous change to occur, time is no factor.** A spontaneous reaction may take

place rapidly or very slowly.

(3) **If the system is not in equilibrium state (unstable), a spontaneous change is inevitable.** The change will continue till the system attains the state of equilibrium.

(4) **Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed.** To take the system away from equilibrium, some external work must be done on the system.

(5) **A spontaneous change is accompanied by decrease of internal energy or enthalpy (ΔH).**

It implies that only such reactions will occur which are exothermic. But the melting of ice and evaporation of rain water are endothermic processes which proceed spontaneously. Clearly, there is some other factor in addition to ΔH which governs spontaneity. It is the second law of thermodynamics which introduces this new factor that is called *entropy*.
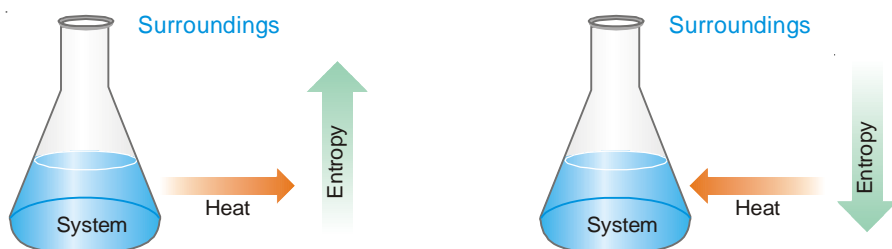
ENTROPY

For many years scientists believed that only exothermic changes resulting in a lowering of internal energy or enthalpy could occur spontaneously. But melting of ice is an endothermic process and yet occurs spontaneously. On a warm day, ice melts by itself. The evaporation of water is another example of a spontaneous endothermic process. Thus arose the need of inventing another driving force that affects the spontaneity. This was known as the entropy change, ΔS.

Melting of Ice is a classic example of 'Increasing Entropy'.

Spontaneity and Randomness

Careful examination shows that in each of the processes *viz.*, melting of ice and evaporation of water, there is an increase in randomness or disorder of the system. The water molecules in ice are arranged in a highly organised crystal pattern which permits little movement. As the ice melts, the water molecules become disorganised and can move more freely. The movement of molecules becomes freer still when the water evaporates into space as now they can roam about throughout the entire atmosphere. In other words, we can say that the randomness of the water molecules increases as ice melts into water or water evaporates into space.

Increase in Randomness Favours a Spontaneous Change

A change that brings about randomness is more likely to occur than one that brings about order. Let us suppose we have a suit of playing cards arranged numerically (Fig. 9.2 a). We can see that the sequence of cards is certainly highly organised. Now, if we throw the cards into the air, collect them and re-stack them, we will almost surely find that they have been placed at random. This is expected because when the cards are tossed, there are many ways for them to be disordered, while there is only one way for them to come together again in their original sequence. Thus on the basis of pure chance a disordered sequence is far more probable than the ordered one with which we started. The same law of chance applies to any physical or chemical process.

■ Figure 9.2
(*a*) **Cards are highly organised;** (*b*) **After they have been tossed,**
cards are placed at random.
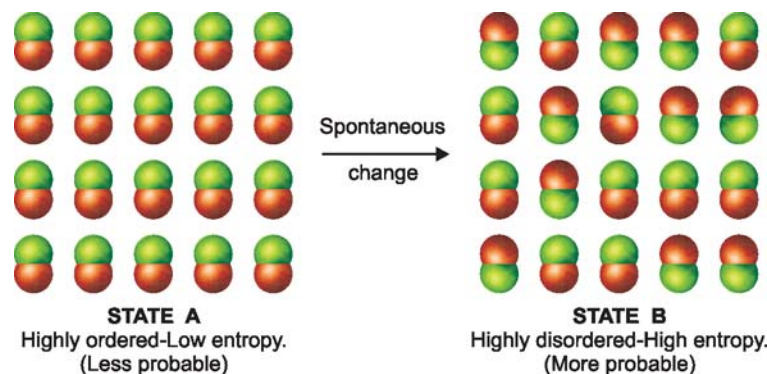
DEFINITION OF ENTROPY

Entropy is a thermodynamic state quantity that is a measure of the randomness or disorder of the molecules of the system.

The symbol of entropy is S, while the change in disorder accompanying a process from start to completion is represented by ΔS. The entropy of a system is a state function and depends only on the initial and final states of the system. The change in entropy, ΔS, for any process is given by the equation,

$$\Delta S = S_{final} - S_{initial}$$

When $S_{final} > S_{initial}$, ΔS is positive.

A process accompanied by an increase in entropy tends to be spontaneous. Let us consider a molecular system in states A and B (Fig. 9.3). In state A all the molecules are arranged and highly ordered, while in state B the molecules are present at random and it is highly disordered.

STATE A
Highly ordered-Low entropy.
(Less probable)

Spontaneous
change

STATE B
Highly disordered-High entropy.
(More probable)

■ Figure 9.3
(a) State A is highly ordered, low entropy and less probable;
(b) State B is highly disordered high entropy and more probable.

(1) By definition, the entropy of A is low and that of B high. Thus an increase of entropy occurs in the change from A to B.

(2) According to the law of chance (probability), A is less probable and B is more probable. Therefore, the change from A to B is spontaneous.

(3) From (1) and (2), it follows that the change from A to B which is accompanied by increase of entropy will tend to be spontaneous.

Hence we can say, in general, that a change in a system which is accompanied by an increase in entropy, tends to be spontaneous.
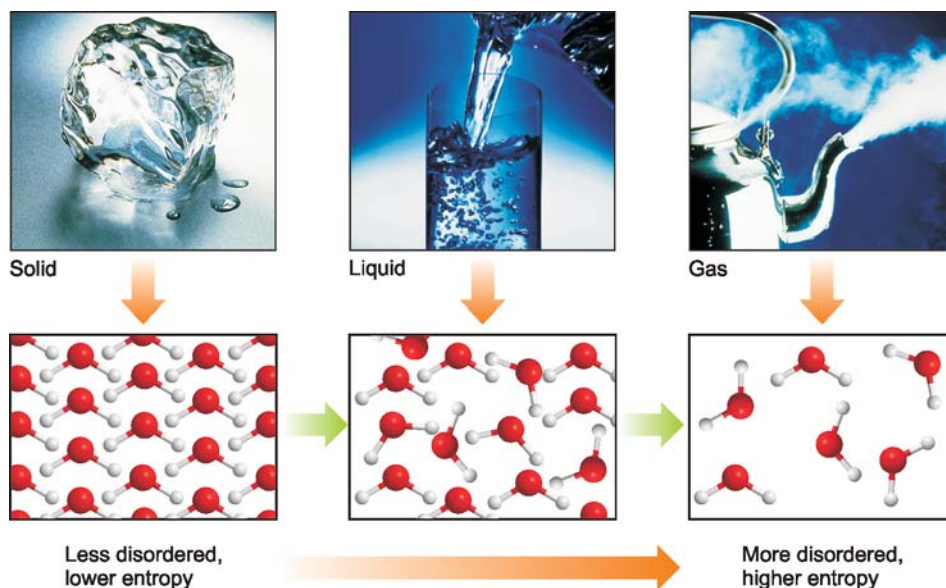
STATEMENT OF THE SECOND LAW

The second law of thermodynamics states that : **whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe.**

More specifically, we take the term 'universe' to mean the system and the surroundings. Thus,

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr}$$

The second law, as stated above, tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases. In other words $\Delta S_{univ} > 0$. When a reversible process occurs, the entropy of the system remains constant. $\Delta S_{univ} = 0$. Since the entire universe is undergoing spontaneous change, the second law can be most generally and concisely stated as : **the entropy of the system is constantly increasing.**

Solid   Liquid   Gas

Less disordered,   More disordered,
lower entropy   higher entropy

■ **Figure 9.4**
   Change of ice vapour to liquid and then to water vapour is accompanied by increase of entropy with increasing disorder.
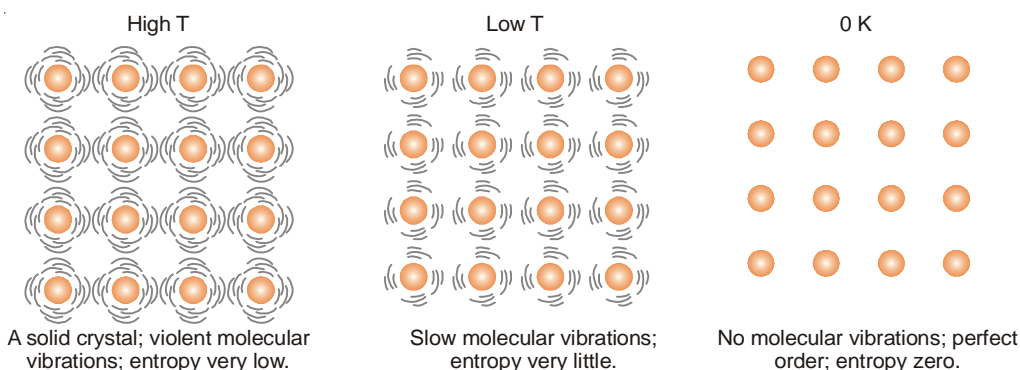
STATEMENT OF THE THIRD LAW

The entropy of a substance varies directly with temperature. The lower the temperature, the lower the entropy. For example, water above 100°C at one atmosphere exists as a gas and has higher entropy (higher disorder). The water molecules are free to roam about in the entire container. When the system

is cooled, the water vapour condenses to form a liquid. Now the water molecules are confined below the liquid level but still can move about somewhat freely. Thus the entropy of the system has decreased. On further cooling, water molecules join together to form ice crystal. The water molecules in the crystal are highly ordered and entropy of the system is very low.

If we cool the solid crystal still further, the vibration of molecules held in the crystal lattice gets slower and they have very little freedom of movement (very little disorder) and hence very small entropy. Finally, at absolute zero all molecular vibration ceases and water molecules are in perfect order. Now the entropy of the system will be zero.

This leads us to the statement of the third law of thermodynamics : **at absolute zero, the entropy of a pure crystal is also zero.** That is, $S = 0$ at $T = 0$ K.

High T	Low T	0 K
A solid crystal; violent molecular vibrations; entropy very low.	Slow molecular vibrations; entropy very little.	No molecular vibrations; perfect order; entropy zero.

■ **Figure 9.5**
Molecular states in a solid crystal (Illustration of the Third law).

NUMERICAL DEFINITION OF ENTROPY

We have discussed the physical definition of entropy. But classical thermodynamics does not require a physical explanation of the concept of entropy. All that we need is an operational definition so that we can calculate the entropy change of the system and the surroundings.

In 1850 Clausius introduced a numerical definition of entropy. According to him entropy of a system (not undergoing chemical or physical changes), is a constant quantity when there is no communication of heat. When heat (q) flows into a system, the entropy increases by q/T. Heat flowing out of a system produces a corresponding decrease. Thus entropy could be precisely defined as : **for a reversible change taking place at a fixed temperature (T), the change in entropy (ΔS) is equal to heat energy absorbed or evolved divided by the temperature (T).** That is,

$$\Delta S = \frac{q}{T}$$

If heat is absorbed, then ΔS is positive and there will be increase in entropy. If heat is evolved, ΔS is negative and there is a decrease in entropy.

UNITS OF ENTROPY

As stated above, entropy is equal to heat energy divided by absolute temperature. Therefore, it is measured in entropy units ('*eu*') which are calories per degree per mole *i.e.*, cal mol^{-1} K^{-1}.

In the SI system, the units are joules per mole per degree *i.e.*, J mol^{-1} K^{-1}. These are represented by *eu*.

$$1eu = 4.184$$

STANDARD ENTROPY

From the third law, we know that the entropy of a pure crystal is zero at absolute zero (K) Therefore, it is possible by measurement and calculation to find the actual amount of entropy that a substance possesses at any temperature above 0 K. It is often referred to as **absolute entropy.**

The absolute entropy of a substance at 25ºC (298 K) and one atmosphere pressure is called the standard entropy; S^o. The absolute entropy of elements is zero only at 0 K in a perfect crystal, and standard entropies of all substances at any temperature above 0 K always have positive values. The standard entropies of a number of elements and compounds are given in Table 9.1.

TABLE 9.1. STANDARD ENTROPIES OF SOME SUBSTANCES (25ºC, 1 ATM)

Substance	Entropy, S^o cal mol^{-1} K^{-1}	J mol^{-1} K^{-1}	Substance	Entropy, S^o cal mol^{-1} K^{-1}	J mol^{-1} K^{-1}
Ag (s)	41.32	172.9	$H_2(g)$	31.21	130.6
AgCl (s)	58.5	24.5	$H_2O(g)$	45.11	188.7
Al (s)	6.77	28.3	$H_2O(l)$	16.72	69.96
Al_2O_3 (s)	12.19	51.0	HCl (g)	44.62	186.7
C (s, graphite)	0.58	2.4	HNO_3 (l)	37.19	155.6
CO (g)	47.30	197.9	H_2SO_4 (l)	37.5	157.0
CO_2 (g)	51.06	213.6	Hg (l)	18.2	76.1
CH_4 (g)	44.50	186.2	K (s)	38.30	160.2
CH_3OH (l)	30.3	126.8	KCl (s)	57.24	239.5
$CO(NH_2)_2$ (s)	25.0	104.6	K_2SO_4 (s)	42.0	176.0
C_2H_2 (g)	48.0	200.8	N_2 (g)	45.77	191.5
C_2H_6 (g)	54.85	229.5	NH_3 (g)	46.01	192.5
Ca (s)	36.99	154.8	Na (s)	36.72	153.6
$CaCO_3$ (s)	22.2	92.9	NaCl (s)	17.30	72.88
Cl_2 (g)	53.29	223.0	O_2 (g)	49.0	205.0
Fe (s)	6.5	27.0	S (s)	7.62	31.9
Fe_2O_3 (s)	21.5	90.0	SO_2 (g)	59.40	248.5

Once we know the entropies of a variety of substances, we can calculate the standard entropy change, ΔS^o, for chemical reactions.

$$\Delta S^o = \Sigma S^o \text{ (products)} - \Sigma S^o \text{ (reactants)}$$

STANDARD ENTROPY OF FORMATION

It is the entropy of formation of 1 mole of a compound from the elements under standard conditions. It is denoted $\Delta S°_f$. We can calculate the value of entropy of a given compound from the values of $S°$ of elements.

$$S°_f = S° \text{ (compound)} - \Sigma S° \text{ (elements)}$$

SOLVED PROBLEM 1. Urea hydrolyses in the presence of water to produce ammonia and carbon dioxide.

$$CO(NH_2)_2 (aq) + H_2O (l) \longrightarrow CO_2(g) + 2NH_3(g)$$
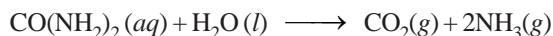
What is the standard entropy change for this reaction when 1 mole of urea reacts with water ? The standard entropies of reactants and products are listed below :

Substance	$S°$(cal/mole K)
$CO(NH_2)_2$	41.55
$H_2O (l)$	16.72
$CO_2 (g)$	51.06
$NH_3 (g)$	46.01

SOLUTION

We know that

$$\Delta S° = \Sigma S° \text{ (products)} - \Sigma S° \text{ (reactants)}$$

or

$$\Delta S° = \left(S°_{CO_2} + 2S°_{NH_3} \right) - \left(S°_{CO(NH_2)_2} + S°_{H_2O} \right)$$

$$= [51.06 + 2 \times 46.01] - [41.55 + 16.72] \text{ cal K}^{-1}$$

$$= \textbf{84.81 cal K}^{-1}$$

SOLVED PROBLEM 2. Calculate the standard entropy of formation, $\Delta S°_f$, of $CO_2(g)$. Given the standard entropies of $CO_2(g)$, $C(s)$, $O_2(g)$, which are 213.6, 5.740, and 205.0 JK^{-1} respectively.

SOLUTION

We know that

$$S°_f = S°_{compound} - \Sigma S°_{elements}$$

or

$$S°_f = S°_{CO_{2(g)}} - \left[S°_{C_{(s)}} + S°_{O_{2(g)}} \right]$$

Substituting the values

$$S°_f = 213.6 - [5.740 + 205.0] \text{ JK}^{-1}$$

$$= (213.6 - 210.74) \text{ JK}^{-1} = \textbf{2.86 JK}^{-1}$$

SOME USEFUL DEFINITIONS

(1) Cyclic Process

When a system undergoes a series of changes and in the end returns to its original state, it is said to have completed as cycle. The whole process comprising the various changes is termed a **cyclic process.**

Since the internal energy of a system depends upon its state, it stands to reason that in cyclic process the net change of energy is zero. Or, we can say that the work done by the system during all these changes should be equal to the heat absorbed by the system.

$$\Delta E = 0 = q - w \text{ or } q = w$$

(2) Heat Engines

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of a suitable device.

A machine which can do work by using heat that flows out spontaneously from a high-temperature source to a low-temperature sink, is called a heat engine.

A heat engine takes heat energy from a high-temperature reservoir and converts some of it into work, returning the unconverted heat to a low-temperature sink. A basic heat engine is illustrated in Fig. 9.6. A steam engine is a typical heat engine. It takes heat from the boiler (high-temperature source), converts some heat to work and returns the unused heat to the surroundings (low-temperature sink).

A heat engine running on a periodic cyclic process can yield work continuously.

(3) Efficiency of a Heat Engine

The ratio of the work obtained in a cyclic process (w) to the heat taken from the high-temperature reservoir (q) is referred to as the efficiency of a heat engine.

No heat engine, no matter how well constructed, can convert all the heat from the high-temperature reservoir into work. Such an engine would be 100% efficient. Sadi Carnot was the first scientist to realise this and deduce an expression showing the limitations of heat engines.

Figure 9.6
Principle of heat engine (illustration).

THE CARNOT CYCLE

In 1824 Sadi Carnot proposed a theoretical heat engine to show that the efficiency was based upon the temperatures between which it operated. Carnot's imaginary engine could perform a series of operations between temperatures T_1 and T_2, so that at the end of these operations the system was restored to the original state. **This cycle of processes which occurred under reversible conditions is referred to as the Carnot cycle.** The medium employed in operating Carnot's engine was one mole of an ideal gas which could be imagined to be contained in a cylinder fitted with a frictionless piston.

The Carnot cycle comprises four operations or processes.

(1) Isothermal reversible expansion
(2) Adiabatic reversible expansion
(3) Isothermal reversible compression
(4) Adiabatic reversible compression

The above four processes are shown in the indicator diagram of Carnot cycle (Fig. 9.7).

Figure 9.7
Indicator diagram of the Carnot cycle.

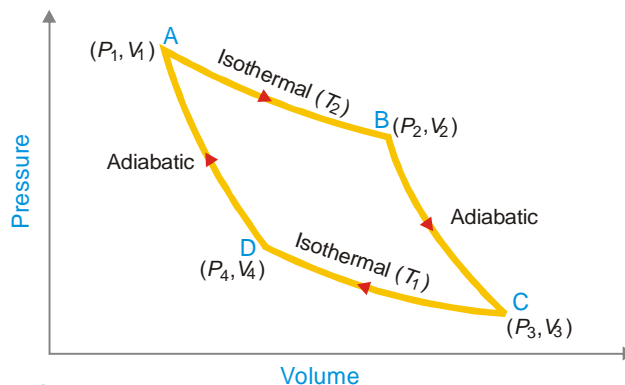### First Operation – Isothermal Reversible Expansion

Let T_2, P_1 and V_1 be the temperature, pressure and volume respectively of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temperature (T_2). Now the gas is allowed to expand isothermally and reversibly so that the volume increases from V_1 to V_2. AB represents the path of the process in the diagram.

Work done. Since the process in operation 1 is isothermal, $\Delta E = 0$. If q_2 be the heat absorbed by the system and w_1 the work done by it, according to the first law equation ($\Delta E = q - w$),

$$q_2 = w_1$$

But

$$w_1 = RT_2 \ln \frac{V_2}{V_1}$$

Therefore,

$$q_2 = RT_2 \ln \frac{V_2}{V_1} \qquad \qquad ...(1)$$

Second Operation – Adiabatic Reversible Expansion

The gas at B is at a temperature T_2 and has volume V_2 under the new pressure P_2. The gas is now allowed to expand reversibly from volume V_2 to V_3 when the temperature drops from T_2 to T_3 (along BC).

Work done. Since this step is adiabatic, $q = 0$. If w_2 be the work done, according to the first law equation ($\Delta E = q - w$),

$$\Delta E = -w_2$$

or

$$w_2 = -\Delta E$$

But

$$\Delta E = C_v (T_1 - T_2)$$

Therefore,

$$w_2 = C_v (T_2 - T_1) \qquad \qquad ...(2)$$

Third Operation – Isothermal Reversible Compression

Now the cylinder is placed in contact with a heat reservoir at a lower temperature, T_1. The volume of the gas is then compressed isothermally and reversibly from V_3 to V_4 (represented by CD in diagram).

Work done. During compression, the gas produces heat which is transferred to the low temperature reservoir. Since the process takes place isothermally, $\Delta E = 0$. If q_1 is the heat given to the reservoir and w_3 the work done on the gas, using proper signs for q and w, we have

$$-q_1 = -w_3 = RT_1 \ln \frac{V_4}{V_3} \qquad \qquad ...(3)$$

Fourth Operation – Adiabatic Reversible Compression

The gas with volume V_4 and temperature T_1 at D is compressed adiabatically (along DA) until it regains the original state. That is, the volume of the system becomes V_1 and its temperature T_2.

Work done. In this step work is done on the system and, therefore, bears the negative (–) sign. If it is denoted by w_4, we can write

$$-w_4 = -C_v (T_2 - T_1) \qquad \qquad ...(4)$$

Net Work Done in One Cycle

Adding up the work done (w) in all the four operations of the cycle as shown in equations (1), (2), (3) and (4), we have

$$w = w_1 + w_2 + (-w_3) + (-w_4)$$

$$= RT_2 \ln \frac{V_2}{V_1} + C_v (T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} - C_v (T_2 - T_1)$$

$$= RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

Net Heat Absorbed in One Cycle

If q is the net heat absorbed in the whole cycle.

$$q = q_2 - q_1$$

where q_2 is heat absorbed by the system in operation 1 and q_1 is the heat transferred to the sink reservoir.

From (1) and (3)

$$q = q_2 - q_1 = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

or

$$q = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_3}{V_4} \qquad ...(5)$$

According to the expression governing adiabatic changes,

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2} \right)^{\gamma - 1} \qquad \qquad \textit{...for adiabatic expansion}$$

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \qquad \qquad \textit{...for adiabatic compression}$$

or

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

or

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Therefore, substituting the value of V_3/V_4 in equation (5), the value of net heat may be given as

$$q = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$$

$$= R (T_2 - T_1) \ln \frac{V_2}{V_1} \qquad ...(6)$$

Calculation of Thermodynamic Efficiency

Since the total work done in a cycle is equal to net heat absorbed, from (6) we can write

$$w = R (T_2 - T_1) \ln \frac{V_2}{V_1} \qquad ...(7)$$

The heat absorbed, q_2, at higher temperature T_2 is given by equation (1),

$$q_2 = RT_2 \ln \frac{V_2}{V_1} \qquad ...(8)$$

Dividing (7) by (8)

$$\frac{w}{q_2} = \frac{R (T_2 - T_1) \ln V_2 / V_1}{RT_2 \ln V_2 / V_1} = \frac{T_2 - T_1}{T_2}$$

or

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} \qquad ...(9)$$

The factor w/q_2 is called **thermodynamical efficiency.** It is denoted by η and gives the fraction of the heat taken from the high-temperature reservoir which it is possible to convert into work by a heat

engine. Therefore, the efficiency of a Carnot engine, the most ideal of all engines, is limited by the operating temperatures of the engine. The larger the temperature difference $(T_2 - T_1)$ between the high and the low temperature reservoirs, the more the heat converted to work by the heat engine. For a given temperature of the high-temperature reservoir, the lower the temperature of the sink, the greater will be the efficiency of the machine. Similarly, for a given temperature of the sink, the efficiency will be increased by using a high temperature of the source reservoir.

Carnot Theorem

We have shown above that

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

This result deduced for a perfect gas depends upon the temperature limits between which the cycle operates. It is independent of all other factors. Thus Carnot stated an important relation known as the **Carnot theorem.** It states that : **every perfect engine working reversibly between the same temperature limits has the same efficiency, whatever be the working substance.**

MORE STATEMENTS OF THE SECOND LAW

From equation (9)

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = 1 - \frac{T_1}{T_2}$$

Evidently w/q_2 is less than 1, or q_2 is greater than w. This means that heat transferred by a spontaneous process is never completely converted into work (If so, w/q_2 would be 1). This leads to another statement of the Second law (Lord Kelvin).

It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

This statement recognises the fact that heat engines could never be 100% efficient, since some heat must be returned to a low-temperature reservoir. Another statement of the Second law was given by Clausius.

It is impossible for a cyclic process to transfer heat from a body at a lower temperature to one at higher temperature without at the same time converting some work to heat.

This statement recognises that heat flows spontaneously from hot objects to cold objects and to get it flow in the opposite direction, we have to expend some work.

SOLVED PROBLEM 1. An engine operating between 150°C and 25°C takes 500 J heat from a high temperature reservoir. Assuming that there are no frictional losses, calculate the work that can be done by this engine.

SOLUTION

From equation (9)

$$\text{Efficiency} = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

Here $\qquad T_2 = 423 \text{ K}; \ T_1 = 298 \text{ K}$

Substituting the values $\qquad \dfrac{w}{500} = \dfrac{423 - 298}{423}$

∴ $\qquad w = \mathbf{147.75 \ J}$

WONDERFUL ACHIEVEMENTS IN SCIENCE AND ENGINEERING

The Second Law of Thermodynamics

**"A spontaneous change is accompanied by an increase
in the total entropy of the system and its surroundings."**

$$\Delta S_{Sys} \quad + \quad \Delta S_{Surr} \quad > \quad 0$$

**ΔS_{Sys} is the entropy change of the system.
ΔS_{Surr} is the entropy change of the surroundings.**

Scientists responsible for the formulation and development of the Second Law Include Rudolph Clausius (1822-1888), Lord Kelvin (1824-1907), Josiah Willard Gibbs (1839-1903) and Ludwig Boltzmann (1844-1906). The Second Law explains why the rusting of Iron is inevitable, why car engines can never be 100% efficient and why batteries eventually run down. It governs the direction of all biochemical reactions including those responsible for glucose catabolism, DNA replication and protein synthesis - even life obeys the Second Law of Thermodynamics.

SOLVED PROBLEM 2. The boiling point of water at a pressure of 50 atmosphere is 265ºC. Compare the theoretical efficiencies of a steam engine operating between the boiling point of water at (*i*) 1 atmosphere (*ii*) 50 atmosphere, assuming the temperature of the sink to be 35ºC in each case.

SOLUTION

(*i*) *At 1 atmosphere :*

T_2 (boiling point of water) = 100ºC or 373 K

T_1 (temperature of sink) = 35ºC or 308 K

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{373 - 308}{373} = 0.174$$

(*ii*) *At 50 atmosphere :*

T_2 (boiling point of water) = 265ºC or 538 **K**

T_1 (temperature of sink) = 35ºC or 308 **K**

$$\text{Efficiency} = \frac{T_2 - T_1}{T_2} = \frac{538 - 308}{538} = \mathbf{0.428}$$

The possible increase of efficiency is very marked.

SOLVED PROBLEM 3. If a Carnot engine operating between two heat reservoirs at 227ºC and 27ºC absorbs 1000 calories from the 227ºC reservoir per cycle, how much heat is discharged into the 27ºC reservoir and how much work is done per cycle ? What is the efficiency of the cycle ?

SOLUTION

(*a*) We know that :

$$\text{Efficiency} = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

or
$$w = \frac{q_2\,(T_2 - T_1)}{T_2}$$

$$= \frac{1000\,(500 - 300)}{500}$$

$$= 400\,\text{cal}$$

∴   The work done per cycle is **400 cal**

(b) The heat from the high-temperature reservoir (q_2) minus the heat discharged into the low-temperature reservoir (q_1) is converted into work (w). Thus,

$$q_2 - q_1 = w$$

∴ $$1000 - q_1 = 400$$

or $$q_1 = 600\,\text{cal.}$$

(c) Efficiency :

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$= \frac{500 - 300}{500} = \frac{200}{500}$$

$$= 0.4$$

Therefore, efficiency of the engine is **0.4**

DERIVATION OF ENTROPY FROM CARNOT CYCLE

Because processes cannot be 100% efficient, a term to describe the energy available for doing useful work becomes necessary. Although we have discussed the concept of entropy already, its classical derivation deserves attention.

In a Carnot cycle, q_2 has a positive value and q_1 has a negative value, since former is *taken up* at a higher temperature and the latter is *given out* at the lower temperature. Thus thermodynamic efficiency may be expressed as

$$\eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}$$

or
$$1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

or
$$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

or
$$\frac{q_1}{T_1} = \frac{q_2}{T_2} \qquad\qquad ...(i)$$

using sign convention, heat absorbed (*i.e.*, q_2) is given the +ve sign and heat lost (*i.e.* q_1) is given the – ve sign. Equation (*i*) becomes

$$+\frac{q_2}{T_2} = -\frac{q_1}{T_1}$$

or
$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

or
$$\Sigma \frac{q}{T} = 0$$

Any reversible cycle may be regarded as made up of a number of Carnot cycles. Consider, for example, the cycle represented in Fig. 9.8 by the closed curve *ABA*. Imagine a series of isothermal
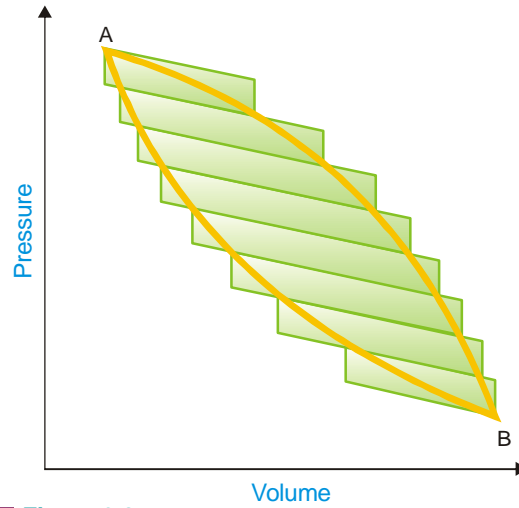
Figure 9.8
Carnot cycle.

and adiabatic curves drawn across the diagram so that a number of Carnot cycles are indicated. Starting at *A* and going through all the cycles successively from *A* to *B*, it can be shown that all paths inside the diagram cancel each other leaving only zigzag outer path. The larger the number of cycles taken in this manner, the closer will the resultant path correspond to *ABA* which represents the reversible cycle under consideration. The reversible cycle can, therefore, be regarded as being made up of an infinite number of Carnot cycles, for each of which the sum of the two *q*/*T* terms involved is zero *i.e.*,

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

For the reversible cycle *ABA* comprising a series of Carnot cycles, therefore, the above expression takes the form

$$\Sigma \frac{q}{T} = 0$$

and for an infinite number of Carnot cycles

$$\int \frac{dq}{T} = 0$$

Since the cycle is performed in two steps, *viz.*, from *A* to *B* and then back from *B* to *A*, we have:

$$\int \frac{dq}{T} = \int_A^B \frac{dq}{T} \text{ (Path I)} + \int_B^A \frac{dq}{T} \text{ (Path II)} = 0$$

$$\int_A^B \frac{dq}{T} \text{ (Path I)} = - \int_B^A \frac{dq}{T} \text{ (Path II)} = \int_A^B \frac{dq}{T} \text{ (Path II)}$$

It is evident, therefore, that both these integrals are independent of the path taken from *A* to *B*. Both depend upon the value of some function at *A* and the same function at *B*. This function is called **entropy** (*S*). Let S_B be the entropy at the state *B* and S_A in the state *A*. Then, the increase in entropy, ΔS, is given by the expression

$$\Delta S = S_B - S_A = \int_A^B \frac{dq}{T}$$

and for each infinitesimally small change

$$dS = \frac{dq}{T}$$

Like ΔE and ΔH, ΔS is dependent only on the state of the system and can be calculated if the substance can be brought reversibly from one state to the other. It is independent of the path taken.

SOLVED PROBLEM 1. Calculate the entropy change in the evaporation of 1 mole of water at 100°C. Latent heat of evaporation of water is 9,650 cals per mole.

SOLUTION

Entropy change on the evaporation of 1 mole of water is obtained by dividing the latent heat of evaporation of 1 mole of water by the absolute temperature

$$\therefore \qquad \Delta S = \frac{9,650}{373} = 25.87 \text{ cal K}^{-1} \text{ mol}^{-1}$$

SOLVED PROBLEM 2. Calculate the increase in entropy when one gram molecular weight of ice at 0°C melts to form water. Latent heat of fusion of ice = 80 calories.

SOLUTION

$$\Delta S = \frac{q}{T}$$

q for one mole of ice $= 80 \times 18$ calories

and $\qquad T = (0 + 273) = 273 \text{ K}$

$$\therefore \qquad \Delta S = \frac{80 \times 18}{273} = 5.274 \text{ cal K}^{-1} \text{ mol}^{-1}$$

ENTROPY CHANGE IN AN IRREVERSIBLE PROCESS

The efficiency of an irreversible Carnot cycle is always less than that of a reversible one operating between the same two temperatures.

$$\frac{q_2 - q_1}{q_2} < \frac{T_2 - T_1}{T_2}$$

where q_2 is the heat absorbed at temperature T_2 and q_1 is the heat returned at temperature T_1.

$$\frac{q_2}{T_2} - \frac{q_1}{T_1} < 0$$

In other words $\int \frac{dq}{T}$ for an irreversible cycle is always less than zero and the entropy of the final state is always greater than that of the initial state. **As most of the processes going on in nature are spontaneous and irreversible, it has been said that "the entropy of the universe always tends towards a maximum".**

PHYSICAL SIGNIFICANCE OF ENTROPY

Entropy is a measure of disorder or randomness of a system. The entropy of the system increases if it goes from less orderly state to more orderly state and vice–versa. This concept of entropy has led to the conclusion that *all substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy*. At this state, all motion ceases. In case of a perfect crystal the entropy is zero. This is **third law of Thermodynamics.**

ENTROPY CHANGE FOR AN IDEAL GAS

Entropy is a state function and its value depends on two of three variables T, P and V.

(a) T and V as Variables

Let us consider n moles of an ideal gas occupying volume V at pressure P and temperature T. If the system absorbs dq_{rev} heat reversibly then increase in entropy is given by

$$dS = \frac{dq_{rev}}{T} \qquad \qquad ...(i)$$

According to the first law of thermodynamics

$$dq_{rev} = dE + PdV$$

Putting in equation (i), we get

$$dS = \frac{dE + PdV}{T} \qquad \qquad ...(ii)$$

we know $\qquad \qquad PV = nRT$

or $\qquad \qquad P = \frac{n}{V}RT$

and $\qquad \qquad dE = n\,C_v\,dT \qquad \qquad \left[\because C_v = \frac{dE}{dT} \text{ for 1 mole} \right]$

where C_v is the molar heat at constant volume.

Substituting this value in equation (ii), we have

$$dS = \frac{n\,C_v\,dT + \left(\dfrac{n}{V}\,RT \right)dV}{T}$$

or $\qquad \qquad dS = n\,C_v\,\dfrac{dT}{T} + n\,R\,\dfrac{dV}{V}$

Integrating between the limits S_1, S_2 ; T_1, T_2 ; and V_1, V_2 we get

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} n\,C_v\,\frac{dT}{T} + \int_{V_1}^{V_2} n\,R\,\frac{dV}{V}$$

or $\qquad \qquad \Delta S = S_2 - S_1 = n\,C_v\,\ln\dfrac{T_2}{T_1} + n\,R\,\ln\dfrac{V_2}{V_1} \qquad \qquad ...(iii)$

or $\qquad \qquad \Delta S = 2.303\,n\,C_v\,\log\dfrac{T_2}{T_1} + 2.303\,R\,\log\dfrac{V_2}{V_1} \qquad \qquad ...(iv)$

For 1 mole of an ideal gas

$$\Delta S = 2.303\,C_v\,\log\frac{T_2}{T_1} + 2.303\,R\,\log\frac{V_2}{V_1}$$

(b) P and T as Variables

Let P_1 be the pressure in the initial state and P_2 in the final state then

$$\frac{P_1\,V_1}{T_1} = \frac{P_2\,V_2}{T_2}$$

or $\qquad \qquad \dfrac{V_2}{V_1} = \dfrac{P_1\,T_2}{P_2\,T_1}$

Substituting in equation (*iii*) we get

$$\Delta S = n\,C_v\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{P_1\,T_2}{P_2\,T_1}$$

$$= n\,C_v\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{P_1}{P_2}$$

$$= n\,(C_v + R)\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{P_1}{P_2}$$

$$= n C_P\,\ln\frac{T_2}{T_1} + n\,R\,\ln\frac{P_1}{P_2} \qquad\qquad [\because C_P = C_v + R]$$

or $$\Delta S = 2.303 \times n \times C_p \log\frac{T_2}{T_1} + 2.303 \times n \times R \log P_1/P_2 \qquad ...(v)$$

For 1 mole of an ideal gas

$$\Delta S = 2.303\,C_p \log\frac{T_2}{T_1} + 2.303\,R \log\frac{P_1}{P_2}$$

From this equation entropy change can be calculated.

Case 1. At constant temperature for an isothermal process
In this case $T_1 = T_2$, the equation (*iv*) and (*v*) reduce to

$$\Delta S_T = 2.303 \times n \times R \log\frac{V_2}{V_1}$$

and $$\Delta S_T = 2.303 \times n \times R \log\frac{P_1}{P_2}$$

In an isothermal expansion $V_2 > V_1$ or $P_1 > P_2$ hence ΔS_T is positive whereas in isothermal contraction $V_2 < V_1$ or $P_1 < P_2$, ΔS_T is negative

Case 2 : At constant pressure (Isobaric process)
In this case $P_1 = P_2$
The equation (*iv*) reduces to

$$\Delta S_P = 2.303\,n\,C_P \log\frac{T_2}{T_1}$$

Case 3 : At constant volume for an isobaric process
In this case $V_1 = V_2$
The equation (*iv*) reduces to

$$\Delta S_v = 2.303 \times n \times C_v \log\frac{T_2}{T_1}$$

SOLVED PROBLEM 1. Calculate the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 5 litres to a volume of 50 litres at 303 K.

SOLUTION. Here $n = 2$; $V_1 = 5$ litres; $V_2 = 50$ litres

using the relation $\Delta S_T = 2.303 \times n \times R \log\dfrac{V_2}{V_1}$

on substituting the values we get

$$\Delta S_T = 2.303 \times 2 \times 8.314 \times \log\frac{50}{5}$$

$$= \textbf{38.29 JK}^{-1}$$

SOLVED PROBLEM 2. Calculate the entropy change when 2 moles of an ideal gas are allowed to expand isothermally at 293 K from a pressure of 10 atmosphere to a pressure of 2 atmosphere.

SOLUTION. We know

$$\Delta S_T = 2.303 \times n \times R \times \log \frac{P_1}{P_2}$$

Here
$$n = 2; \ R = 8.314 \text{ J}$$
$$P_1 = 10 \text{ atm}; \ P_2 = 2 \text{ atm.}$$

Substituting the values we get

$$\Delta S_T = 2.303 \times 2 \times 8.314 \times \log \frac{10}{2}$$
$$= 2.303 \times 2 \times 8.314 \times 0.6990$$
$$= \textbf{26.76 JK}^{-1}$$

ENTROPY CHANGE ACCOMPANYING CHANGE OF PHASE

When there is a change of state from solid to liquid or liquid to vapours or solid to vapours (melting, evaporation and sublimation respectively), there is a change in entropy. This change may be carried out at constant temperature reversibly as two phases are in equilibrium during the change.

Let us consider the process of melting of 1 mole of the substance being carried out reversibly. It would absorb molar heat of fusion at temperature equal to its melting point. The entropy change is given by

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

where ΔH_f is the Molar heat of fusion at its melting point, T_f at constant pressure.

Similarly, when one mole of liquid is boiled reversibly it would absorb molar heat of vaporisation at a temperature equal to its boiling point. In this case entropy change is given by

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

where ΔH_v is Molar heat of vaporisation at its boiling point at constant pressure.

On similar lines we can calculate the change in entropy when one mole of a solid changes reversibly from one allotropic form to another at its transition temperature. We can write

$$\Delta S_t = \frac{\Delta H_t}{T_t}$$

Where ΔH_t is the Molar heat of transition at its transition temperature T_t.

SOLVED PROBLEM 1. Calculate the entropy change when 1 mole of ethanol is evaporated at 351 K. The molar heat of vaporisation of ethanol is 39.84 kJ mol^{-1}.

SOLUTION. We know

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Here
$$\Delta H_v = 39.84 \text{ kJ mol}^{-1}$$
$$= 39840 \text{ J mol}^{-1}$$
$$T_b = 351 \text{ K}$$

$\therefore$
$$\Delta S_v = \frac{39840}{351}$$
$$= \textbf{113.5 JK}^{-1}\textbf{ mol}^{-1}$$

SOLVED PROBLEM 2. 30 .4 kJ is required to melt one mole of sodium chloride. The entropy change during melting is 28.4 J mol^{-1} K^{-1}. Calculate the melting point of sodium chloride.

SOLUTION

We know

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Here $\Delta S_f = 28.4 \, \text{JK}^{-1} \, \text{mol}^{-1}$

and $\Delta H_f = 30.4 \, \text{kJ K}^{-1} \, \text{mol}^{-1}$

$= 30400 \, \text{JK}^{-1} \, \text{mol}^{-1}$

On substitution, we get

$$T_f = \frac{\Delta H_f}{\Delta S_f} = \frac{30400}{28.4}$$

$$= \textbf{1070.4 K}$$

Free Energy Function (G) and Work Function (A)

The free energy function (G) is defined as

$$G = H - TS$$

where H is the heat content or enthalpy of the system, T is its temperature and S its entropy. It is a single valued function of thermodynamic state of the system and is an extensive property.

Let us consider a system which undergoes a change of state from (1) to (2) at constant temperature.

We have

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

or $\Delta G = \Delta H - T \Delta S$

We know

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

$\therefore$ $\Delta G = \Delta E + P\Delta V - T\Delta S$

Also $\Delta A = \Delta E - T\Delta S$

$\therefore$ $\Delta G = \Delta A + P\Delta V$ (At constant P & T)

But $P\Delta V$ represents the work done due to expansion against a constant external pressure P. Therefore, it is clear that the decrease in free energy ($-\Delta G$) accompanying a process taking place at constant temperature and pressure is equal to the maximum work obtainable from the system other than the work of expansion. This quantity is referred to as the net work, so that

$$\text{Net work} = w - P\Delta V = -\Delta G$$

This quantity is of great importance in thermodynamics because the change in free energy is a measure of net work which may be electrical, chemical or surface work.

The work function (A) is defined as

$$A = E - TS$$

Where E is the energy content of the system, T its absolute temperature and S its entropy. Since E, T and S depend upon the thermodynamic state of the system only and not on its previous history, it is evident that the function A is also a single valued function of the state of the system.

Consider an isothermal change at temperature T from the initial state indicated by subscript (1) to the final state indicated by subscript (2) so that

$$A_1 = E_1 - TS_1 \qquad\qquad ...(i)$$

and $\qquad A_2 = E_2 - TS_2$ $\qquad$ ...(ii)

Subtracting (i) from (ii), we have

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$
$$\Delta A = \Delta E - T\Delta S \qquad ...(iii)$$

Where ΔA is the change in work function A, ΔE is the corresponding change in internal energy and ΔS as change in the entropy of the system.

Since $\Delta S = \dfrac{q_{rev}}{T}$ where q_{rev} is the heat taken up when the change is carried out in a reversible manner and constant temperature, we have

$$\Delta A = \Delta E - q_{rev} \qquad ...(iv)$$

According to first law of thermodynamics

$$dE = q_{rev} - w_{rev}$$

or $\qquad - w = \Delta E - q_{rev}$

substituting the value in equation (iv), we get

$$- \Delta A = w_{rev}$$

i.e., **decrease in the work function A in any process at constant temperature gives the maximum work that can be obtained from the system during any change.**

Variation of Free Energy with Temperature and Pressure

By definition

$$G = H - TS$$

and $\qquad H = E + PV$

$\therefore \qquad G = E + PV - TS$

Differentiating, we get

$$dG = dE + PdV + VdP - TdS - SdT \qquad ...(i)$$

For an infinitesimal stage of a reversible process

$$dq = dE + dw$$

and $\qquad dS = \dfrac{dq}{T}$

If the work done is restricted to work of expansion, then

$$dq = dE + PdV$$

and $\qquad dS = dE + PdV \qquad ...(ii)$

comparing equation (i) and (ii) we have

$$dG = dE + PdV + VdP - dE - PdV - SdT$$
$$= VdP - SdT$$

If the pressure remains constant

$$dG_p = - SdT_p$$

or $\qquad \left(\dfrac{dG}{dT}\right)_P = - S \qquad ...(iii)$

But at constant temperature $dT = 0$ and we have

$$(dG)_T = VdP$$

or $\qquad \left(\dfrac{dG}{dP}\right)_T = V \qquad ...(iv)$

Equations (iii) and (iv) give the variation of free energy with temperature and pressure respectively.

Isothermal change in Free Energy

By definition

$$G = H - TS$$

and

$$H = E + PV$$

$\therefore$

$$G = E + PV - TS$$

on differentiating we get

$$dG = dE + PdV + VdP - TdS - SdT \qquad ...(i)$$

and from first law of thermodynamics we have

$$dq = dE + PdV \qquad ...(ii)$$

From equation (i) and (ii) we get

$$dG = dq + VdP - TdS - SdT \qquad ...(iii)$$

For a reversible process

$$dS = \frac{dq}{T} \quad \text{or} \quad TdS = dq$$

Substituting this in equation (iii) we get

$$dG = TdS + VdP - TdS - SdT$$

$$= VdP - SdT \qquad ...(iv)$$

Since the process is isothermal (there is no change in temperature) $dT = 0$, the equation (iv) reduces to

$$dG = VdP$$

Integrating with in the limits G_1 and G_2; P_1 and P_2, we get

$$\Delta G = G_2 - G_1 = \int_{P_1}^{P_2} VdP$$

For 1 mole of the gas $PV = RT$

or

$$V = \frac{RT}{P}$$

On substitution we get

$$dG = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$= RT \ln \frac{P_2}{P_1} \qquad ...(v)$$

For n moles of the gas we have

$$\Delta G = nRT \ln \frac{P_2}{P_1} \qquad ...(vi)$$

We know that $P_1 V_1 = P_2 V_2$

or

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

From equation (v) we get

$$\Delta G = RT \ln \frac{V_1}{V_2}$$

and from equation (*vi*) we get

$$\Delta G = n\ RT\ \ln \frac{V_1}{V_2}$$

Changing to natural logarithms, we get

$$\Delta G = 2.303 \times nRT\ \log \frac{P_2}{P_1}$$

or $$\Delta G = 2.303 \times nRT\ \log \frac{V_1}{V_2}$$

With the help of these equations we can calculate the change in free energy in isothermal process having an ideal gas.

SOLVED PROBLEM 1. Four moles of an ideal gas expand isothermally from 1 litre to 10 litres at 300 K. Calculate the change in free energy of the gas. ($R = 8.314\ \mathrm{JK^{-1}\ mol^{-1}}$)

SOLUTION

For an isothermal process

$$\Delta G = 2.303 \times nRT\ \log \frac{V_1}{V_2}$$

Here
$$V_1 = 1\ \text{litre}\ ; V_2 = 10\ \text{litres}$$
$$T = 300\ \mathrm{K}; R = 8.314\ \mathrm{JK^{-1}\ mol^{-1}}$$
$$n = 4$$

Substituting the values in the formula we get

$$\Delta G = 2.303 \times 300 \times 4 \times 8.314 \times \log \frac{1}{10}$$
$$= 22976.5 \times [-1.0]$$
$$= -22976.5\ \mathrm{J}$$
$$= -\ \textbf{22.9765 kJ}$$

SOLVED PROBLEM 2. Two moles of an ideal gas are allowed to expand reversibly and isothermally at 300 K from a pressure of 1 atm to a pressure of 0.1 atm. What is the change in Gibbs free energy ?

SOLUTION. We know for an isothermal process

$$\Delta G = 2.303 \times nRT\ \log \frac{P_2}{P_1}$$

Here
$$P_1 = 1.0\ \text{atm}; P_2 = 0.1\ \text{atm}.$$
$$n = 2\ \text{moles}\ R = 8.314\ \mathrm{JK^{-1}\ mol^{-1}}$$
$$T = 300\ \mathrm{K}$$

On substitution we get

$$\Delta G = 2.303 \times 2 \times 8.314 \times 300 \times \log \frac{0.1}{1}$$
$$= 11488.2 \times [-1.0]$$
$$= -11488.2\ \mathrm{J}$$
$$= -\ \textbf{11.4882 kJ}$$

GIBB'S HELMHOLTZ EQUATIONS

These are two equations derived by J.W. Gibbs and H.Von Helmholtz and are known as Gibbs Helmholtz equations. One equation can be expressed in terms of changes in free energy (ΔG) and enthalpy (ΔH), while the other can be expressed in terms of changes in internal energy (ΔE) and work function (ΔA). The former is generally employed and is applicable to all processes, chemical or physical, but in a closed system.

(a) In Terms of Free Energy and Enthalpy

We know that

$$dG = VdP - SdT$$

At constant pressure $dP = 0$, then

$$dG = -SdT$$

Let G_1 be the initial free energy at temperature T, $G_1 + dG_1$, be the free energy at temperature $T + dT$. Then

$$dG_1 = -S_1\, dT \qquad \text{...(i)}$$

Where S_1 is the entropy of the system in the initial state. Now suppose the free energy of the system in the final state is G_2 at temperature T, and $G_2 + dG_2$ is the free energy at temperature $T + dT$ in the final state.

Then

$$dG_2 = -S_2\, dT \qquad \text{...(ii)}$$

where S_2 is the entropy of the system in the final state.

Subtracting (i) from (ii) we get

$$dG_2 - dG_1 = -(S_2 - S_1)\, dT$$

or

$$d\,(\Delta G) = -\Delta S\, dT$$

At constant pressure

$$d\left(\frac{\Delta G}{dT}\right)_{\text{p}} = -\Delta S \qquad \text{...(iii)}$$

We know

$$\Delta G = \Delta H - T\,\Delta S$$

or

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

Comparing equations (iii) and (iv)

$$\frac{\Delta G - \Delta H}{T} = d\left(\frac{\Delta G}{dT}\right)_{\text{p}}$$

or

$$\Delta G = \Delta H + Td\left(\frac{\Delta G}{dT}\right)_{\text{p}}$$

This equation is called Gibb's Helmholtz equation in terms of free energy and enthalpy change at constant pressure.

(b) In terms of Internal Energy and Work Function

By definition the work function

$$A = E - TS \qquad \text{...(i)}$$

or

$$\Delta A = \Delta E - T\Delta S$$

or

$$-\Delta S = \frac{\Delta A - \Delta E}{T} \qquad \text{...(ii)}$$

Differentiating equation (*i*) we get

$$dA = dE - TdS - SdT \qquad \qquad ...(iii)$$

From the first law of thermodynamics

$$dq = dE + PdV$$

and at constant volume $dV = 0$

$$\therefore \qquad dq = dE$$

For a reversible change

$$dS = \frac{dq}{T}$$

or

$$dq = TdS - dE \qquad \qquad ...(iv)$$

Comparing equations (*iii*) and (*iv*) we get

$$dA = -SdT$$

Let A_1 be the work function in its initial state at temperature T and $A_1 + dA_1$ be the work function in its initial state at $T + dT$. And A_2 be the work function in its final state at temperature T and $A_2 + dA_2$ be the work function in its final state at $T + dT$. Then

$$dA_1 = -S_1 \, dT \qquad \qquad ...(v)$$

and

$$dA_2 = -S_2 \, dT \qquad \qquad ...(vi)$$

where S_1 and S_2 are the entropies of the system in initial and final states of the system respectively. Subtracting equation (*v*) from equation (*vi*) we get

$$dA_2 - dA_1 = -(S_2 - S_1) \, dT$$

or

$$d(\Delta A) = -\Delta S \, dT$$

At constant volume

$$d\left(\frac{\Delta A}{dT}\right)_v = -\Delta S$$

From equation (*ii*) we have

$$\frac{\Delta A - \Delta E}{T} = -\Delta S$$

On comparison we have

$$\frac{\Delta A - \Delta E}{T} = d\left(\frac{\Delta A}{dT}\right)_v$$

or

$$\Delta A = \Delta E + T \, d\left(\frac{\Delta A}{dT}\right)_v$$

This equation is called Gibbs Helmholtz equation in terms of internal energy and work function at constant volume.

Importance of Gibb's Helmholtz Equations

Gibb's Helmholtz equations are used to calculate the heats of reaction (ΔH or ΔE) when ΔG or ΔA at two temperatures are given. This point is made clear in the following examples.

SOLVED PROBLEM 1. For the reaction

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l)$$
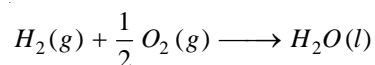
The values of enthalpy change and free energy change are – 68.32 and – 56.69 kcals respectively. Calculate the value of free energy change at 25°C.

SOLUTION. Using the Gibb's Helmholtz equation

$$\Delta G = \Delta H + T d\left(\frac{\Delta G}{dT}\right)_p$$

Here

$$\Delta G = -56.69 \text{ Kcal}$$
$$\Delta H = -68.32 \text{ kcals}$$

and

$$T = 273 + 25 = 298 \text{ K}$$

On substitution we get

$$-56.69 = -68.32 + 298 \left[d\left(\frac{\Delta G}{dT}\right)_p\right]$$

or

$$d\left(\frac{\Delta G}{dT}\right)_p = \frac{-56.69 + 68.32}{298}$$

$$= 0.0390 \text{ kcal}$$

Assuming that $d\left(\frac{\Delta G}{dT}\right)_p$ remains constant over this temperature range. At 30°C we can write

$$\Delta G = 68.32 + 303 \times 0.039$$

$$= -68.32 + 11.817$$

$$= -\textbf{56.503 kcals}$$

SOLVED PROBLEM 2. For the following reaction

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$
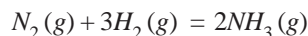
The free energy changes at 25°C and 35°C are – 33.089 and – 28.018 kJ respectively. Calculate the heat of reaction.

SOLUTION. We know

$$\Delta G = \Delta H + T d\left(\frac{\Delta G}{dT}\right)_p$$

Here

$$G_1 = -33.089 \text{ kJ} \quad T_1 = 273 + 25 = 298 \text{ K}$$
$$G_2 = -28.018 \text{ kJ} \quad T_2 = 273 + 35 = 308 \text{ K}$$

∴

$$d\left(\frac{\Delta G}{dT}\right)_p = \frac{-28.018 - (-33.089)}{308 - 298}$$

$$= 0.507 \text{ kJ}$$

At 35°C

$$\Delta G = -28.018 \text{ kJ}$$
$$T = 273 + 35 = 308 \text{ K}$$

∴

$$\Delta G = \Delta H + T d\left(\frac{\Delta G}{dT}\right)_p$$

$$-28.018 = \Delta H + 308 \times 0.507$$

or

$$\Delta H = 28.018 + 156.156$$

$$= \textbf{184.174 kJ}$$

Conditions of Equilibrium and Criterion for a Spontaneous Process

(a) In Terms of Entropy Change

The entropy of a system remains unchanged in a reversible change while it increases in an irreversible change *i.e.*

$\Sigma \, dS = 0$ For Reversible change

and $\Sigma \, dS > 0$ For Irreversible change

For a system with its surroundings we can write

$$dS_{\text{system}} + dS_{\text{surroundings}} = 0$$

and $\quad dS_{\text{system}} + dS_{\text{surroundings}} > 0$

combining the two relations, we have

$$dS_{\text{system}} + dS_{\text{surroundings}} \geq 0 \qquad\qquad\qquad ...(i)$$

If we assume the change in surroundings as reversible and surroundings evolve dq heat reversibly, then

$$dS_{\text{surrounding}} = -\frac{dq}{T}$$

From the first law of Thermodynamics

we know

$$dS = -\frac{dq}{T} = \frac{dE + dw}{T}$$

where dE is the increase in internal energy of the system and dw be the work done by the system.

From equation (i) we get

$$dS_{\text{system}} - \frac{dE + dw}{T} \geq 0$$

or $\qquad TdS_{\text{system}} - dE - dw \geq 0$

or $\qquad TdS_{\text{system}} - dE - PdV \geq 0 \qquad\qquad\qquad ...(ii)$

$$[\because \; dw = PdV]$$

Case I. When E and V are constant

In this case $dE = 0$ and $dV = 0$ the equation (i) reduces to

$$dS_{E.V} \geq 0$$

or $\qquad\qquad\qquad dS_{E.V} > 0$ for an irreversible change (spontaneous)

and $\qquad\qquad\qquad dS_{E.V} = 0$ for a reversible change (equilibrium)

Case II. When S and V are constant

Here $\qquad\qquad\qquad dS = 0$ and $dV = 0$

The equation (i) reduces to $- dE \geq 0$

or $\qquad\qquad\qquad - dE > 0$ for an irreversible change (spontaneous)

and $\qquad\qquad\qquad - dE = 0$ for a reversible change (equilibrium)

(b) In Terms of Enthalpy Change

We know

$$H = E + PV$$

on differentiating

$$dH = dE + PdV + VdP$$

or $\qquad\qquad - dE - PdV = - dH + VdP$

Putting in equation (ii)

$$TdS - dH + VdP \geq 0$$

or $\qquad dH - VdP - TdS \leq 0$

At constant S and P

Here $\qquad\qquad dS = 0$ and $dP = 0$

$\therefore$　we have $dH \leq 0$

or $\qquad\qquad dH < 0$ for an irreversible change (spontaneous)

and $\qquad\qquad dH = 0$ for a reversible change (equilibrium)

(c) In Terms of Free Energy Change

We know

$$G = H + TS$$

or $\qquad\qquad G = E + PV + TS \qquad\qquad\qquad\qquad [\because\ H = E + PV]$

on differentiating we get

$$dG = dE + PdV + VdP + TdS + SdT$$

$$TdS - dE - PdV = -dG + VdP - SdT$$

Substituting in equations (*ii*) we get

$$-dG + VdP - SdT \geq 0$$

or $\qquad\qquad dG - VdP + SdT \leq 0$

At constant pressure in an isothermal process (T is also constant) this equation reduces to

$$dG \leq 0$$

or $\qquad\qquad dG < 0$ for an irreversible change (spontaneous)

and $\qquad\qquad dG = 0$ for a reversible change (equilibrium)

Thus the conditions for spontaneity and equilibrium may be summed up in the Table 9.2.

TABLE 9.2. CONDITIONS FOR SPONTANEITY AND EQUILIBRIUM		
Conditions	**Irreversible Process (Spontaneous)**	**Reversible Process (Equilibrium)**
At Constant E, V	$dS > 0$	$dS = 0$
At Constant S, V	$-dE > 0$	$-dE = 0$
At Constant S, P	$dH < 0$	$dH = 0$
At Constant P, T	$dG < 0$	$dG = 0$

THE CLAPEYRON EQUATION

A useful thermodynamic relation which gives us important information about a system consisting of any two phases of a single substance in chemical equilibrium is the Clapeyron equation. It is derived from the Gibbs-Helmholtz equation mentioned above.

Let the system studied be
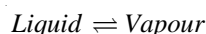
$$Liquid \rightleftharpoons Vapour$$

Consider one gram mole of a liquid confined in a cylinder by a frictionless piston. Let the volume of the liquid be V_1 and its vapour pressure equal to p. Now allow the liquid to evaporate reversibly at a constant temperature T and when the whole of it has vaporised, let the volume of the vapour be V_2.

$\therefore$　Work done during evaporation $w = p\,(V_2 - V_1)$ $\qquad\qquad\qquad\qquad\qquad$ ...(*i*)

Differentiating equation (*i*) with respect to temperature at constant $(V_2 - V_1)$, we get,

$$\frac{dw}{dT} = (V_2 - V_1)\,\frac{dp}{dT} \qquad\qquad ...(ii)$$

Heat absorbed from the surroundings is the latent heat of vaporisation L which on substitution in the first law equation gives us

$$\Delta E = w - L \qquad\qquad ...(iii)$$

On substitution of expressions (*ii*) and (*iii*) in the Gibbs-Helmholtz equation, we have

$$w + \Delta E = T\,\frac{dw}{dT}$$

$$w + (L - w) = T\,(V_2 - V_1)\,\frac{dp}{dT}$$

or

$$L = T\,\frac{dp}{dT}\,(V_2 - V_1)$$

or

$$\frac{dp}{dT} = \frac{L}{T\,(V_2 - V_1)}$$

This is the Clapeyron equation which in its general form may be written as

$$\frac{dp}{dT} = \frac{\Delta H}{T\,(V_2 - V_1)} \qquad\qquad ...(1)$$

where ΔH is the heat of transition when a volume V_1 of a definite weight of one form changes to a volume V_2 of the same weight of other form at the temperature T.

CLAUSIUS–CLAPEYRON EQUATION

The above equation can be simplified by neglecting the small volume of the liquid in comparison with the volume of the vapour. Equation (1) given above in such a case becomes

$$\frac{dp}{dT} = \frac{\Delta H}{TV}$$

Supposing the vapour obeys the ideal gas laws

$$V_2 = \frac{RT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta H\;p}{RT^2}$$

or

$$\frac{1}{p} \times \frac{dp}{dT} = \frac{\Delta H}{RT^2}$$

But

$$\frac{1}{p} \times \frac{dp}{dT} = \frac{d\,\log_e p}{dT}$$

$\therefore$

$$d\,\log_e \frac{p}{dT} = \frac{\Delta H}{RT^2} \qquad\qquad ...(2)$$

Equation (2) above is known as the **Clausius-Clapeyron equation** and though approximate is of very great value.

If ΔH is regarded as constant, we may integrate the above equation

$$d\,\log_e P = \Delta H\,\frac{dT}{RT^2}$$

$$\int d\,\log_e p = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

or
$$\log_e p = \frac{-\Delta H}{RT} + \text{Constant}$$

$$\log_{10} p = \frac{-\Delta H}{2.303\ RT} + C$$

If p_1 is the vapour pressure at T_1 and p_2 the vapour pressure at T_2 we have

$$\log_{10} p_1 = \frac{-\Delta H}{2.303\ RT_1} + C \qquad \text{...(i)}$$

and
$$\log_{10} p_2 = \frac{-\Delta H}{2.303\ RT_2} + C \qquad \text{...(ii)}$$

Subtracting (i) from (ii)

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H}{2.303\ R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad \text{...(3)}$$

APPLICATIONS OF CLAPEYRON-CLAUSIUS EQUATION

(1) Calculation of Latent Heat of Vaporisation

If the vapour pressure of a liquid at two temperatures T_1 and T_2 be p_1 and p_2 respectively, the molar heat of vaporisation ΔH_v can be calculated by substituting these values in Clapeyron-Clausius equation.

SOLVED PROBLEM. If the vapour pressures of water at 95°C and 100°C are 634 and 760 mm respectively, calculate the latent heat of vaporisation per mole.

SOLUTION

The Clapeyron Clausius equation states that

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_v}{2.303\ R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

In this case, we have :

$$p_1 = 634\,\text{mm}$$
$$p_2 = 760\,\text{mm}$$
$$T_1 = 273 + 95 = 368\,\text{K}$$
$$T_2 = 273 + 100 = 373\,\text{K}$$
$$R = 1.987\,\text{cal}$$
$$\Delta H_v = ?$$

Substituting the above values in the Clapeyron-Clausius equation, we have :

$$\log \frac{760}{634} = \frac{\Delta H_v}{2.303\ R} \left[\frac{1}{368} - \frac{1}{373} \right]$$

$\therefore$ $$\Delta H_v = \textbf{9886 cal mol}^{-1}$$

In a similar manner, if the vapour pressures at two different temperatures of a solid in equilibrium with its liquid phase are known, the **latent heat of fusion** can be calculated.

(2) Calculation of Boiling Point or Freezing Point

If the freezing point or the boiling point of a liquid at one pressure is known, it is possible to calculate it at another pressure by the use of the Clapeyron-Clausius equation.

SOLVED PROBLEM. At what temperature will water boil under a pressure of 787 mm? The latent heat of vaporisation is 536 cals per gram.

SOLUTION

The data is follows

$$p_1 = 760 \text{ mm} \qquad T_1 = 373 \text{ K}$$
$$p_2 = 787 \text{ mm} \qquad T_2 = ?$$
$$\Delta H_v = 536 \times 18 \text{ cal mol}^{-1}$$

According to Clapeyron-Clausius equation, we have :

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_v}{4.576} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Substituting the above values, we have :

$$\log_{10} \frac{787}{760} = \frac{536 \times 18}{4.576} \left[\frac{T_2 - 373}{373 \, T_2} \right]$$

$$T_2 = \textbf{374 K}$$

$\therefore$ Water will boil at 101°C under a pressure of 787 mm.

(3) Calculation of Vapour Pressure at Another Temperature

If the mean heat of vaporisation is available, it is possible to calculate the vapour pressure of a liquid at given temperature if the vapour pressure at another temperature is known.

SOLVED PROBLEM. Calculate the vapour pressure of water at 90.0°C if its value at 100.0°C is 76.0cm. The mean heat of vaporisation of water in the temperature range 90° and 100°C is 542 calories per gram.

SOLUTION

In this problem, we have :

$$\Delta H_v = 542 \times 18 \text{ cal per mole}$$
$$p_2 = ?$$
$$p_1 = 76.0 \text{ cm}$$
$$T_2 = 90 + 273 = 363 \text{ K}$$
$$T_1 = 100 + 273 = 373 \text{ K}$$

Using the Clapeyron-Clausius equation we have :

$$\log_{10} \frac{p_2}{p_1} = \frac{\Delta H_v}{4.576} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

or

$$\log_{10} \frac{p_2}{76} = \frac{542 \times 18}{4.576} \left[\frac{363 - 373}{363 \times 373} \right]$$

$\therefore$

$$p_2 = \textbf{52.88 cm} \text{ or } \textbf{528.8 mm}$$

(4) Calculation of Molal Elevation Constant

The molal elevation constant (K_b) of a solvent is defined **as the elevation in boiling point which may theoretically be produced when one mole of any solute is dissolved in 1000 g of the solvent.** Accordingly, if w g of a solute of molecular weight M is dissolved in 1000 g of the solvent and ΔT is the elevation produced, the molal elevation K_b is given by the equation

$$K_b = \frac{M \ \Delta T}{w}$$

Let the boiling point of the pure solvent be T and that of the solvent $(T + \Delta T)$ when the atmospheric pressure is p_1. While p_1 is the vapour pressure of the solution at $(T + \Delta T)$ and is also the vapour pressure of the solvent at T, p_2 the vapour pressure of the solvent at $(T + \Delta T)$ can be calculated by the application of Clapeyron-Clausius equation.

$$\log_e \frac{p_2}{p_1} = \frac{L}{R}\left[\frac{1}{T} - \frac{1}{(T + \Delta T)}\right]$$

$$= \frac{L}{R}\left[\frac{\Delta T}{T\ (T + \Delta T)}\right]$$

$$= \frac{L}{R} \times \frac{\Delta T}{T^2} \quad \text{when } \Delta T \text{ is very small.}$$

Now $\log_e \dfrac{p_2}{p_1} = \log_e\left(1 + \dfrac{p_2 - p_1}{p_1}\right) = \dfrac{p_2 - p_1}{p_1}$ since $(p_2 - p_1)$ is very small and the remainder of the terms can be neglected.

According to Raoult's law, the relative lowering of vapour pressure in a dilute solute is equal to the molar fraction of the solute in solution

$$\therefore \qquad\qquad \frac{p_2 - p_1}{p_2} = \frac{n}{N}$$

When the difference between p_2 and p_1 is very small as has just been supposed, $\dfrac{p_2 - p_1}{p_2}$ may be taken equal to $\dfrac{p_2 - p_1}{p_1}$.

$$\therefore \qquad\qquad \frac{p_2 - p_1}{p_2} = \frac{n}{N} = \frac{L\ \Delta T}{RT^2}$$

or $$\Delta T = \frac{RT^2}{L} \times \frac{n}{N}$$

But $$n = \frac{w}{m} \quad \text{and} \quad N = \frac{W}{M}$$

$$\therefore \qquad\qquad \Delta T = \frac{RT^2}{L} \times \frac{wM}{mW}$$

If 1 mole of the solute is dissolved in 1000 g of the solvent, the above equation becomes :

$$\Delta T = \frac{RT^2}{L \times 1000}$$

But $$K_b = \frac{M\ \Delta T}{w}$$

$$\therefore \qquad\qquad K_b = \frac{M\ RT^2}{L \times 1000}$$

But $$\frac{L}{M} = l, \text{ the latent heat of vaporisation per gram of the solvent.}$$

$\therefore$ $K_b = \dfrac{RT^2}{1000\,l}$

Putting $R = 2$ gm cals, we have

$$K_b = \dfrac{0.002\,T^2}{l}$$

SOLVED PROBLEM. The heat of vaporisation of 1 g of carbon disulphide is 86.72 calories and the boiling point is 46ºC. Calculate the molal elevation constant.

SOLUTION

The molal elevation constant of a solvent is given by the expression

$$K_b = \dfrac{0.002\,T^2}{l}$$

Here $T = 273 + 46 = 319\,K$

               $l = 86.72\,cal$

$\therefore$ $K_b = \dfrac{0.002 \times 319 \times 319}{86.72}$

               $= \textbf{2.34º per 1000}\,g$ **of carbon disulphide**

(5) Calculation of Molal Depression Constant

By an exactly similar reasoning, we can calculate the molal depression constant of a solvent as

$$K_f = \dfrac{RT^2}{1000\,l_f}$$

where l_f is the latent heat of fusion per gram of the solvent,

or $K_f = \dfrac{0.002\,T^2}{l_f}$

SOLVED PROBLEM. The latent heat of fusion of ice per gram is 80 calories and the freezing point of water is 0ºC. Calculate the molal depression constant of water.

SOLUTION

The molal depression constant of a solvent is given by the expression

$$K_f = \dfrac{0.002\,T^2}{l_f}$$

In this problem :

               $T = 0 + 273 = 273\,K$

               $l_f = 80\,cal$

$\therefore$ $K_f = \dfrac{0.002 \times 273 \times 273}{80}$

               $= \textbf{1.86º}$

FREE ENERGY AND WORK FUNCTIONS

Besides heat content (H), internal energy (E) and entropy (S), there are two other thermodynamic functions depending upon the state of the system which utilize E, H or S in their derivation and are

more convenient for use. These are **Work** and **Free energy functions** represented by A and G respectively.

The Work Function

The work function (A) is defined by

$$A = E - TS$$

where E is the energy content of the system, T is its absolute temperature and S its entropy. Since E, T and S depend upon the thermodynamic state of the system only and not on its previous history, it is evident that the function A is also a single valued function of the state of the system.

Consider an isothermal change at temperature T from the initial state indicated by subscript 1 to the final state indicated by subscript 2, so that

$$A_1 = E_1 - TS_1 \qquad \qquad ...(1)$$

and
$$A_2 = E_2 - TS_2 \qquad \qquad ...(2)$$

Subtracting (1) from (2), we have :

$$A_2 - A_1 = (E_2 - E_1) - T(S_2 - S_1)$$

or
$$\Delta A = \Delta E - T\Delta S \qquad \qquad ...(3)$$

where ΔA is the increase in function A, ΔE is the corresponding increase in internal energy and ΔS is the increase in the entropy of the system.

Since $\Delta S = q_{rev}/T$ where q_{rev} is the heat taken up when the change is carried out in a reversible manner at a constant temperature, we have :

$$\Delta A = \Delta E - q_{rev} \qquad \qquad ...(4)$$

According to the first law of thermodynamics, $\Delta E = (q_{rev} - w_{rev})$

or
$$-w_{rev} = \Delta E - q_{rev} \qquad \qquad ...(5)$$

Substituting this value in equation (4), we get

$$-\Delta A = w_{rev}$$

i.e., **decrease in the work function A in any process at constant temperature gives the maximum work that can be obtained from the system during any change.**

VAN'T HOFF ISOTHERM

The van't Hoff isotherm gives the net work that can be obtained from a gaseous reactant at constant temperature when both the reactants and the products are at suitable arbitrary pressures. It can be derived by using the "equilibrium box" which is a theoretical device with the supposition that of its four walls, one is permeable to A, the second to B, the third to C and the fourth to D when the gaseous reaction to be considered is

$$A + B \rightleftharpoons C + D$$
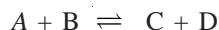
Let the initial pressures of A and B be p_a and p_b and the final pressure of C and D be p_c and p_d respectively and let the equilibrium pressure of the four be P_A, P_B, P_C and P_D respectively.

The following theoretical operations may be performed :

(*i*) Change the pressure on A from the initial pressure p_a to the equilibrium pressure P_A.

$$\therefore \qquad \text{Work done by the gas} = RT \ln \frac{p_a}{P_A}$$

(*ii*) Change the pressure on B from p_b to P_B.

$$\therefore \qquad \text{Work done by the gas} = RT \ln \frac{p_b}{P_B}$$

■ Figure 9.9
van't Hoff equilibrium box.

(*iii*) Introduce 1 gm mole of A and 1 gm mole of the gas B through their respective semipermeable membranes into the equilibrium box which contains the reactants and the products at the equilibrium pressure. This will not involve any work as the partial pressures of A and B inside the box are equal to the pressure of the gases coming in. A and B react to form 1 gm mole of C and 1 gm mole of D.
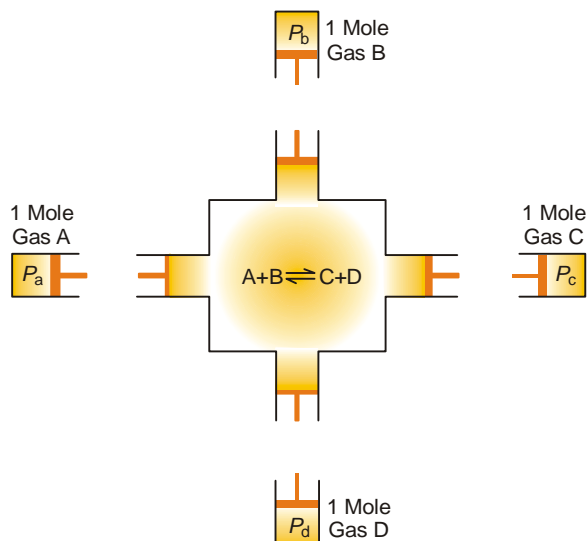
(*iv*) Withdraw 1 gm mole of C and 1 gm mole of D from the equilibrium box through their respective semipermeable walls. No work is done in this process as the gases come out at the equilibrium pressure P_C and P_D.

(*v*) Now alter the pressure on the gas from the equilibrium pressure P_C and P_D to the final pressure p_c and p_d.

$$\text{Work done by the gas } C = RT \ln \frac{P_C}{p_c}$$

$$\text{Work done by the gas } D = RT \ln \frac{P_D}{p_d}$$

As the change in free energy is equal to the total work done by the gases :

$$- \Delta G = RT \ln \frac{P_C \times P_D}{P_A \times P_B} - RT \ln \frac{p_c \times p_d}{p_a \times p_b}$$

$$= RT \ln K_p - RT \ln \frac{p_c \times p_d}{p_a \times p_b}$$

If the reaction is started with reactants at a partial pressure of 1 atmosphere and the resulting products are also at 1 atmosphere pressure we have,

$$- \Delta G = RT \ln K_p - RT \ln 1$$

or
$$- \Delta G = RT \ln K_p$$

i.e., the net work of the reaction is equal to the decrease in free energy of the system and is given by the expression, **RT 1n K_p** or **2.303 RT log K_p.**

It will be observed that ΔG is + ve when K_p is less than unity. It is – ve when K_p is greater than one and is zero when $K_p = 1$.

VAN'T HOFF ISOCHORE

The van't Hoff Isochore is obtained by combining the van't Hoff Isotherm with the Gibbs Helmholtz equation.

$$\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT} \right]_p$$

or

$$-\Delta H = T \left[\frac{d(\Delta G)}{dT} \right]_p - \Delta G$$

Dividing both sides by T^2 gives

$$-\frac{\Delta H}{T^2} = \frac{T \left[d\left(\frac{\Delta G}{dT}\right) \right]_p - \Delta G}{T^2}$$

The right-hand side of the above expression is obtained by differentiating $\Delta G/T$ w.r.t. T at constant pressure

i.e.,

$$\left[\frac{d(\Delta G/T)}{dT} \right]_p = -\frac{T \left[\frac{d(\Delta G)}{dT} \right]_p}{T^2} - \Delta G$$

$$\therefore \qquad -\frac{\Delta H}{T^2} = \left[\frac{d(\Delta G/T)}{dT} \right]_p \qquad \qquad ...(i)$$

According to van't Hoff isotherm,

$$-\Delta G = RT \ln K_p \qquad \qquad ...(ii)$$

combining this with equation (i), we have

$$\frac{\Delta H}{T^2} = \frac{Rd(\ln K_p)}{dT}$$

$$\frac{\Delta H}{RT^2} = \frac{d(\ln K_p)}{dT}$$

The above equation is known as van't Hoff Isochore.

For applying the Isochore to any particular reaction, it is essential to integrate it. If ΔH remains constant over a range of temperature, we have on integration

$$\ln K_p = \int \frac{\Delta H}{RT^2} \, dT$$

$$= \frac{-\Delta H}{RT} + Constant$$

Applying the limits T_1 and T_2 at which the equilibrium constants are K_{p_1} and K_{p_2} respectively, we have

$$\ln K_{p_2} - \ln K_{p_1} = -\frac{\Delta H}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln K_{p_2} - \ln K_{p_1} = \frac{\Delta H}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\ln \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

or
$$\log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Knowing the equilibrium constant at two different temperatures it is possible, therefore, to calculate the change in heat content.

> **SOLVED PROBLEM.** The equilibrium constant K_p for a reaction
>
> $A + B \rightleftharpoons C + D$ is 10^{-12} at 327°C and 10^{-7} at 427°C. Calculate the enthalpy of the reaction.
>
> $$(R = 8.314 \text{ JK}^- \text{mol}^-)$$
>
> **SOLUTION**
>
> Applying van't Hoff's equation
>
> $$\log \frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$
>
> Here
> $$K_{P_2} = 10^{-7}; T_2 = 427 + 273 = 700 \text{ K}$$
> $$K_{P_1} = 10^{-12}; T_1 = 327 + 273 = 600 \text{ K}$$
> $$R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$$
>
> On substitution we get
> $$\log \frac{10^{-7}}{10^{-12}} = \frac{\Delta H}{2.303 \times 8.314} \left[\frac{700 - 600}{700 \times 600} \right]$$
> $$\Delta H = \log 10^5 \times \frac{2.303 \times 8.314 \times 700 \times 600}{100}$$
> $$= 402089.98 \text{ J}$$
> $$= \textbf{402.08998 kJ}$$

FUGACITY AND ACTIVITY

It has already been pointed out that equation $\Delta G = RT \log_e P_2/P_1$ is applicable only to ideal gases. When applied to real gases, particularly at higher pressures, it is found that this expression does not reproduce the change in free energy, the reason being that under these conditions V is not equal to nRT/P. In order to apply this equation to non-ideal systems, Lewis introduced two new thermodynamic quantities, **fugacity** and **activity.**

Consider a system composed of liquid water and its vapour. Liquid water has a tendency to escape into the vapour phase while the vapour tends to escape the gaseous state and come into the liquid phase by condensation. When the system is in equilibrium, these two escaping tendencies become equal and we observe a constant vapour pressure at a constant temperature. In general, **it may be stated that each substance in a given state has a tendency to escape from that state and this escaping tendency denoted by f is called fugacity.** It is related to the free energy content (G) by the expression

$$G = RT \ln f + B$$

where B is a constant depending upon the temperature and the nature of the substance. It is not possible to evaluate B since the absolute values of the free energy are not known. To circumvent this difficulty, all free energy measurements for any given substance are referred to as standard reference point. If we represent by $G^°$ the free energy per mole and $f^°$ the fugacity in this standard state, then $G^°$ is given by

$$G^° = RT \ln f^° + B$$

If G is the free energy of the substance in any state, then the free energy difference between this state and the standard state is given by

$$G - G° = RT \ln f/f°$$

or $$G = G° + RT \ln f/f° \qquad ...(i)$$

The ratio $f/f°$ is called **activity** and is denoted by the symbol a. The activity of any substance may therefore, be defined as the *ratio of fugacity of the substance in the given state to the fugacity of the same substance in the standard state*.

$$G = G° + RT \ln a$$

In the standard state, $G = G°$ $\therefore$ $RT \ln a = 0$ or $a = 1$

i.e., in the standard state the activity of a substance is equal to unity. In any other state the value of activity will depend upon the difference $(G - G°)$. The difference in free energy per mole caused on passing from one state in which the free energy is G_1 and the activity a_1 to another state in which these are G_2 and a_2 respectively, is given by the expression

$$\Delta G = G_2 - G_1 = (G° + RT \ln a_2) - (G° + RT \ln a_1)$$

or $$\Delta G = RT \ln \frac{a_2}{a_1}$$

The similarity between the above equation and equation

$$\Delta G = RT \ln P_2/P_1$$

suggests that **activity is the thermodynamic counterpart of the gas pressure.**

For the standard state of any gas at the given temperature, the fugacity is taken as equal to unity, *viz*, $f° = 1$ and on the basis of this definition the activity of any gas becomes equal to fugacity

$$a = \frac{f}{f°} = \frac{f}{1} = f$$

The equation (i) can, therefore, be written as

$$G = G° + RT \log_e f$$

For an *ideal gas* the fugacity is equal to pressure and $f/P = 1$. For a *real gas*, the fugacity is not equal to P and the ratio f/P varies. It is observed, however, that on decreasing the pressure, the behaviour of the gas approaches that of an ideal gas. It may be stated, therefore, that f approaches P as P approaches zero

i.e., $$\lim_{p \to 0} \frac{f}{P} = 1$$

or $$\frac{f}{P} \to 1 \quad \text{as} \quad P \to 0$$

The ratio f/P is called **activity coefficient** of a gas and is represented by the symbol γ. It gives a direct measure of the extent to which any gas deviates from ideal behaviour at any given pressure and temperature for the farther this ratio is from unity, the greater is the non-ideality of the gas.

CHEMICAL POTENTIAL

Partial Molar Properties

We have so far studied the thermodynamic systems in which there was a change in thermodynamic properties with the variation of one or more state variables. In such systems there was no transfer of mass taking place (closed systems). For studying the systems containing two or more phases or components G.N. Lewis introduced the concept of **partial molar properties** as in these cases both mass and composition vary (open systems). Consider any extensive thermodynamic property X of such a system, the value of which is determined by the temperature, pressure and the amounts of various constituents present. Let the system consist of J constituents and let n_1, n_2, n_3 .... n_j be the number of moles of the various constituents present. Evidently X must be a function of P, T and the number of moles of various constituents present, *i.e.*

$$X = f(T, P, n_1, n_2, n_3 .... n_j) \qquad ...(1)$$

If there is a small change in the temperature and pressure of the system as well as the amounts of its constituents, the change in the property X is given by

$$dX = \left(\frac{\delta X}{\delta T}\right)_{P,\ n_1,n_2.....n_j} dT + \left(\frac{\delta X}{\delta p}\right)_{T,\ n_1,n_2.....n_j} dp + \left(\frac{dX}{\delta n}\right)_{T,P,\ n_2.....n_j} dn_1$$

$$+ \left(\frac{\delta X}{\delta n_2}\right)_{T,P,\ n_1,n_3.....n_j} dn_2 + \left(\frac{\delta X}{\delta n_3}\right)_{T,P,\ n_1,n_2.....n_j} dn_3 + ... +$$

$$\left(\frac{\delta X}{\delta n_j}\right)_{T,P,\ n_1,n_2.....} dn_j \qquad\qquad ...(ii)$$

The quantity $\left(\dfrac{\delta X}{\delta n_1}\right)_{T,P,n_2.....n_j}$ is called partial molar property for the constituent 1. It is represented by writing a bar over its symbol for the particular property i.e. $\overline{X}$ so that

$$\overline{X}_1 = \left(\frac{\delta X}{\delta n_1}\right)_{T,P,n_2...n_j} \; ; \; \overline{X}_2 = \left(\frac{\delta X}{\delta n_2}\right)_{T,P,n_1,n_3....n_j}$$

The equation (ii) may be written as :

$$dX = \left(\frac{\delta X}{\delta T}\right)_{P,\ n_1,n_2.....n_j} dT + \overline{X} = \left(\frac{\delta X}{\delta P}\right)_{T,\ n_1,n_2.....n_j} dP$$

$$+ \overline{X}_1 \, dn_1 + \overline{X}_2 \, dn_2 + \overline{X}_3 \, dn_3 + ...\overline{X}_j \, dn_j$$

If the temperature and the pressure of the system are kept constant dT and dP are zero so that

$$dX = \overline{X}_1 \, dn_1 + \overline{X}_2 \, dn_2 + ...\overline{X}_j \, dn_j \qquad\qquad ...(iii)$$

and this on integration for a system of definite composition represented by the number of moles n_1, n_2 ..... n_j gives

$$X = n_1\overline{X}_1 + n_2\overline{X} + n_3\overline{X}_3 + ...n_j\overline{X}_j \qquad\qquad ...(iv)$$

i.e., the partial molal property $\overline{X}$ of any constituent may be regarded as the contribution of 1 mole of that constituent to the total value of the property of the system under specified conditions.

Partial Molar Free Energy : Chemical Potential

If the extensive property under study is free energy (G), $\overline{G}$ will represent the partial molar free energy so that

$$\overline{G}_1 = \left(\frac{\delta G}{\delta n_1}\right)_{T,P,n_2\,n_3.....n_j} \quad \text{and} \quad \overline{G}_j = \left(\frac{\delta G}{\delta n_j}\right)_{T,P,n_1\,n_2.....n_{j-1}}$$

This quantity is, for most purposes, identical with the function known as **chemical potential** represented by the symbol μ. Accordingly we have

$$\mu_1 = \overline{G}_1 = \left(\frac{\delta G}{\delta n_1}\right)_{T,P,n_2.....n_j}$$

Thus, it is the partial derivative of the free energy with n_i when all other variables are kept constant.

Physical Significance of Chemical Potential

By definition the chemical potential of a given substance is the change in free energy of the system produced on addition of one mole of the substance at constant temperature and pressure to a

large bulk of the mixture so that its composition does not undergo any change. It is an intensive property and it may be regarded as the force which drives the chemical system to equilibrium. At equilibrium the chemical potential of the substance in the system must have the same value through the system. In other words, the matter flows spontaneously from a region of high chemical potential to low chemical potential. The chemical potential may also be regarded as the escaping tendency of that system. Greater the chemical potential of a system greater will be its escaping tendency.

Gibbs Duhem Equation

It has already been discussed that free energy G is an intensive thermodynamic property. It can be determined by fixing the variables T, P and number of moles of various constituents (composition of the mixture under study). Mathematically, we can write.

$$G = f\,(T, P, n_1, n_2 ..... n_j) \qquad ...(i)$$

where $n_1, n_2 .... n_j$ are the number of moles of various constituents.

Differentiating equation (i), we get

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,n_2.....n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,n_2.....n_j} dP +$$

$$\left(\frac{\delta G}{\delta n_1}\right)_{T,P,\ n_2.....n_j} dn_1 + \left(\frac{\delta G}{\delta n_2}\right)_{T,P,\ n_1.....n_j} dn_2 + \left(\frac{\delta G}{\delta n_j}\right)_{T_1,P,\ n_1.....n_{j-1}} dn_j$$

We know the chemical potential is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1,n_2.....} = \overline{G}_1$$

Substituting in equation (ii) we get

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,n_2.....n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,n_2.....n_j} dP + \mu_1\,dn_1, + \mu_2\,dn_2, + ... + \mu_j\,dn_j \qquad ...(iii)$$

For a closed system there is no change in the composition and equation (iii) reduces to

$$dG = \left(\frac{\delta G}{\delta T}\right)_{P,\ n_1,n_2.....n_j} dT + \left(\frac{\delta G}{\delta P}\right)_{T,\ n_1,n_2.....n_j} dP \qquad ...(iv)$$

But we know

$$dG = -\,SdT + VdP \qquad ...(v)$$

$$[\because\ G = H - TS$$

$$H = E + PV$$

and $$G = dE + PdV + VdP - TdS - SdT]$$

comparing equation (iv) and (v)

$$\left(\frac{\delta G}{\delta T}\right)_{P,n_1\,n_2....n_j} = -\,S$$

and $$\left(\frac{\delta G}{\delta T}\right)_{T,n_1\,n_2....n_j} = -\,V$$

Putting these values in equation (iii) we get

$$dG = -\,SdT + VdP + \mu_1\,dn_1 + \mu_2\,dn_2 + ... \mu_j\,dn_j \qquad ...(vi)$$

At constant temperature and pressure equation (vi) reduces to

$$(dG)_{T,P} = \mu_1\,dn_1 + \mu_2\,dn_2 + ... \mu_j\,dn_j \qquad ...(vii)$$

Integrating equation (*vii*) we get the following for a system of definite composition

$$(G)_{T.P} = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \ldots \mu_j n_j \qquad \ldots(viii)$$

Differentiating equation (*viii*) we get

$$(dG)_{T.P} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 + \ldots \mu_j dn_j + n_j d\mu_j \qquad \ldots(ix)$$

Comparing equation (*vii*) and (*ix*) we get

$$n_1 d\mu_1 + n_2 d\mu_2 + \ldots n_j d\mu_j = 0$$

or $\qquad\qquad\qquad\qquad \Sigma\, n_j d\mu_j = 0 \qquad\qquad\qquad\qquad \ldots(x)$

Equation (*x*) is called Gibbs Duhem equation. It is applicable to a system at constant temperature and pressure.

Variation of Chemical Potential with Temperature and Pressure

(*a*) With Temperature

We know that chemical potential of a constituent *i* in a system is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1 \ldots n_j} = \bar{G}_i \qquad \ldots(i)$$

Differentiating equation (*i*) w.r.t. *T* at constant pressure *P*, we get

$$\left(\frac{\delta\mu_i}{\delta T}\right)_{P,n_1 n_2 \ldots n_j} = \frac{\delta^2 G}{\delta n_i \delta T} \qquad \ldots(ii)$$

We also know that

$$\left(\frac{\delta G}{\delta T}\right)_{P,n_1 n_2 \ldots n_j} = S \qquad \ldots(iii)$$

Differentiating equation (*iii*) w.r.t. n_j at constant temperature and pressure.

$$-\left(\frac{\delta S}{\delta n_i}\right)_{T,P,n_1 \ldots n_j} = \frac{\delta^2 G}{\delta T \delta n_i} \qquad \ldots(iv)$$

Comparing equation (*ii*) and (*iv*), we have

$$\left(\frac{\delta\mu_i}{\delta T}\right)_{P,n_1 n_2 \ldots n_j} = \left(\frac{\delta S}{\delta n_i}\right)_{T,P,n_1 \ldots n_j} = \bar{S}_i$$

[By definition of Partial Molal Property]

Thus

$$\left(\frac{\delta\mu_i}{\delta T}\right)_{P,n_1 n_2 \ldots n_j} = \bar{S}_i = \text{Partial Molal Entropy}$$

This equation gives the variation of chemical potential of any constituent *i* with temperature.

(*b*) With Pressure

By definition, chemical potential is given by

$$\mu_i = \left(\frac{\delta G}{\delta n_i}\right)_{T,P,n_1 \ldots n_j} = \bar{G}_i \qquad \ldots(i)$$

Differentiating equation (*i*) w.r.t. pressure at constant temperature

$$\left(\frac{\delta\mu_i}{\delta P}\right)_{T,n_1 n_2 \ldots n_j} = \frac{\delta^2 G}{\delta n_i \delta P} \qquad \ldots(ii)$$

But we know that

$$\left(\frac{\delta G}{\delta P}\right)_{T,n_1 n_2....n_j} = V \qquad\qquad ...(iii)$$

Differentiating equation (*iii*) w.r.t. n_i at constant T, P and n_j

$$\left(\frac{\delta V}{\delta n_i}\right)_{T,P,n_1 n_2....n_j} = \frac{\delta^2 G}{\delta P\,\delta n_i} = \bar{V}_i \qquad\qquad ...(iv)$$

(By definition of Partial Molal Property)

Comparing equations (*ii*) and (*iv*)

$$\left(\frac{\delta \mu_i}{\delta P}\right)_{T,n_1 n_2....n_j} = \bar{V}_i = \text{Partial Molal Volume} \qquad\qquad ...(v)$$

Equation (*v*) gives the variation of Chemical potential of any constituent *i* with pressure. From this equation we can define the partial molar volume of a constituent *i* as the rate of change of chemical potential of a constituent *i* with pressure at constant temperature.

TIME'S ARROW

The Second Law of Thermodynamics provides a definition of time's arrow. The law states that the entropy (usually) increases. And the increase occurs in time.

Imagine that we make a videotape of a "break" in a game of pool. We see 15 colored balls in a triangular configuration and a white ball coming in and breaking them up; the balls scatter in all directions.

If we run the videotape backwards we know immediately that this is (probably) not the correct direction for time.

If we reduce the number of billiard balls to, say, two, then a videotape of one ball colliding with another is just a possible as the tape running backwards. Here we see another manifestation of the fact that the determination of the direction of time from thermodynamics depends on having lots of objects in the system.

Another example is the relation between the scale of a physical system and the "correct" direction of time is milk swirling in water. A *RealMedia* video of this is available <u>here</u>. File size is 530k.

Thus the Second Law provides a definition of the direction of time. We know of two other definitions:

Expansion of the universe. Since the universe is expanding it is bigger today than it was yesterday.

Consciousness. We remember yesterday but not tomorrow (at least in the usual case).

ZEROTH LAW OF THERMODYNAMICS

The zeroth law of thermodynamics is a generalized statement about bodies in contact at thermal equilibrium and is the basis for the concept of temperature. The most common definition of the zeroth law of thermodynamics is: **If two thermodynamic systems are in thermal equilibrium with a third,** they are also in thermal equilibrium with each other.

The term zeroth law was coined by Ralph H. Fowler. In many ways, the law is more fundamental than any of the others. However, the need to state it explicitly as a law was not perceived until the first third of the 20th century, long after the first three laws were already widely in use and named as such, hence the zero numbering. There is still some discussion about its status in relation to the other three laws.

THERMODYNAMIC EQUILIBRIUM (ZEROTH LAW)
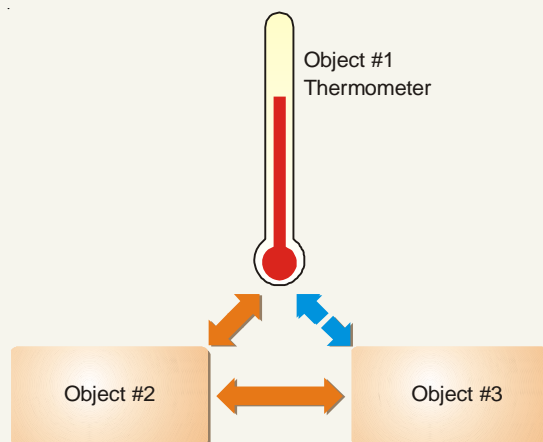
When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

Objects in thermodynamic equilibrium have the same temperature.

A system in thermal equilibrium is a system whose macroscopic properties (like pressure, temperature, volume, etc.) are not changing in time. A hot cup of coffee sitting on a kitchen table is not at equilibrium with its surroundings because it is cooling off and decreasing in temperature. Once its temperature stops decreasing, it will be at room temperature, and it will be in thermal equilibrium with its surroundings.

Two systems are said to be in thermal equilibrium when (*a*) both of the systems are in a state of equilibrium, and (*b*) they remain so when they are brought into contact, where 'contact' is meant to imply the possibility of exchanging heat, but not work or particles. And more generally, two systems can be in thermal equilibrium without thermal contact if one can be certain that *if they were* thermally connected, their properties would not change in time. Thus, thermal equilibrium is a relation between thermodynamical systems. Mathematically, the zeroth law expresses that this relation is an equivalence relation.

EXAMINATION QUESTIONS

1. Define or explain the following terms :
   - (*a*) Entropy
   - (*b*) Second law of thermodynamics
   - (*c*) Carnot cycle
   - (*d*) Third law of thermodynamics
   - (*e*) Gibbs free energy
   - (*f*) Gibbs Helmholtz equation
   - (*g*) Spontaneous reactions
   - (*h*) Clausius clapeyron equation
   - (*i*) van't Hoff isotherm
2. (*a*) Derive the concept of entropy from the Second law of Thermodynamics. Show that entropy is a state function.
   (*b*) What is the change in entropy when 1 mole of helium gas is heated from 200 K to 400 K at constant pressure? (Given : C_P for helium = 5.0 cal per degree per mole)
   Answer. 3.466 cal/K

3. (*a*) Derive an expression for entropy change for ideal gas associated with temperature and pressure changes.

   (*b*) Calculate the total entropy change when 5 grams of ice at 0°C is converted into steam at 100°C. (Latent heat of evaporation of water = 540 cals/g; C_p for water = 18 cals/moles; Latent heat of water = 80 cal/mole)

   Answer. (*b*) 10.265 cal/degree

4. Calculate the work performed when two gram of hydrogen gas is expanded isothermally and reversibly at 27°C from 10 to 100 litres. What is the amount of heat absorbed? What is the change in the internal energy?

   Answer. 1372.81 cal; Zero

5. Two moles of an ideal gas undergo isothermal reversible expansion from 15 lit to 30 lit at 300 K. Calculate the work done and the change in entropy.

   Answer. 826.5 cal; 2.755 cal K^{-1}

6. Water boils at 373 K at one atm pressure. At what temperature will it boil at a hill station where the atmospheric pressure is 500 mm Hg?

   (Latent heat of vaporisation of water is 2.3 kJ g^{-1} and $R = 8.314$ JK^{-1} mol^{-1})

   Answer. 361.65 K

7. A Carnot's engine works between the temperature 27° and 127°C. Calculate the efficiency of the engine.

   Answer. 25%

8. (*a*) Explain the term Thermodynamic efficiency.

   (*b*) Calculate the work done on the system if one mole of an ideal gas at 300 K is compressed isothermally and reversibly to one-fifth of its original volume.

   Answer. (*b*) 4014.98 × 10^7 ergs

9. What do you understand by the term enthalpy?

   Calculate the work done in the expansion of 3 moles of hydrogen reversibly and isothermally at 27°C from 21.0 litres to 70.3 litres.

   Answer. 9042.47 × 10^7 ergs

10. (*a*) "It is not profitable to carry out a process reversibly although maximum work can be obtained by doing so". Comment.

    (*b*) Two moles of hydrogen are compressed adiabatically from NTP conditions to occupy a volume of 4.48 litres. Calculate the final pressure and temperature ($\gamma = 1.41$)

    (*c*) Derive a relation between pressure and volume for an adiabatic reversible expansion of an ideal gas.

    Answer. (*b*) 25.7 atm; 429.1°C

11. (*a*) Derive the Clapeyron-Clausius equation giving the temperature dependence of water pressure indicating clearly the assumption involved.

    (*b*) An engine operates between 100°C and 0°C and another engine operates between 100°C and 0 K (absolute zero). Find the efficiencies in two cases.

    Answer. (*b*) 26.8%; 100 %

12. (*a*) Explain giving reason "The net entropy of the universe tends to increase".

    (*b*) For the reaction

   $$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(\ell)$$
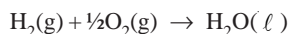
   the values of enthalpy change and free energy change are –68.32 and –56.69 kcal respectively at 25°C. Calculate the value of free energy change at 30°C.

    (*c*) Write down the applications of Gibb's Helmholtz equation.

    Answer. (*b*) –56.495 kcal

13. (*a*) Bring about clearly the criteria for reversibility and irreversibility in terms of *S*, *E*, *H* and *G*.

    (*b*) 1.0 mole of steam is condensed at 100°C and water is cooled to 0°C and frozen to ice. Calculate the

entropy change for the process. Latent heat of fusion of ice and evaporation of water are 80 and 540 cals/g respectively.

Answer. (c) 25.716 cal deg^{-1} mol^{-1}

14. (a) Write a note on "Carnot's Cycle".
    (b) How are work function and free energy related? Discuss the criteria of spontaneity of a chemical reaction.
    (c) Calculate the entropy increase in the evaporation of a mole of water at 100°C (Heat of vaporization = 540 cal g^{-1})

15. (a) Give the expression for Gibb's free energy change (ΔG) for the reaction
$$nA + mB \rightleftharpoons pC + qD$$
    (b) How is ΔG of a chemical reactions is related to ΔS and ΔH?
    (c) The enthalpy change for the transition of liquid water to steam is 40.8 kJ mol^{-1} at 373 K. Calculate ΔG for the process.

    Answer. (b) 109.38 3 JK^{-1} mol^{-1}

16. Calculate ΔS when 28 gm of N$_2$ gas expands reversibly from 2 litres to 20 litres at 27°C.

    Answer. 38.294 JK^{-1}

17. (a) Prove that Enthalpy remains constant when a real gas passes through a porous plug in adiabatic expansion.
    (b) Explain the relationship between entropy and probability.
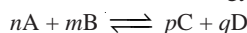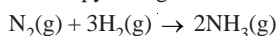   (c) Derive an expression for the efficiency of a Carnot's engine working between the two temperatures T_1 and T_2.

18. (a) Define standard heat of formation and standard entropy change of a reaction.
    (b) Explain why in case of non-polar solvents, the ΔS is nearly equal to 88 JK^{-1} mol^{-1}.
    (c) Calculate the entropy change for the reaction :
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
    Given : $S°$ of N$_2$, H$_2$ and NH$_3$ as 191.5, 130.6 and 192.2 JK^{-1} mol^{-1} respectively.

    Answer. –198.9 J K^{-1} mol^{-1} (*Delhi BSc, 2001*)

19. (a) Determine the entropy change for an ideal gas when temperature and volume are varied.
    (b) Calculate the entropy change involved in isothermal expansion of 2 moles of the gas from a volume of 5 litres to a volume of 50 litres at 30°C.

    Answer. 38.29 JK^{-1} (*Guru Nanak Dev BSc, 2002*)

20. Calculate entropy change if 2 moles of water at 373 K are evaporated to vapours at 373 K. Give its units also. (Given molar heat of vaporisation of water is 9650 cal)

    Answer. 216.49 JK^{-1} (*Andhra BSc, 2002*)

21. 0.5 g of nitrogen is enclosed in a cylinder fitted with a piston at 25°C. Calculate the change in entropy, if the gas is expanded adiabatically to double its volume.

    Answer. zero   (*Guru Nanak Dev BSc, 2002*)

22. (a) Starting from appropriate definition of chemical potential of a component in an ideal gas solution, derive an expression for ΔG_{mixing} for the formation of ideal binary solution and show further that ΔH_{mixing}=0 for the solution.
    (b) A solution is prepared by mixing 2 moles of CS$_2$ and 3 moles of CCl$_4$ at 298 K and 1 atm pressure. Assuming ideal behaviour, calculate ΔG_{mixing} for the solution.

    Answer. –3620.22 J   (*Guru Nanak Dev BSc, 2002*)

23. Calculate entropy change for the fusion of one mole of a solid which melts at 300 K. The latent heat of fusion is 2.51 k J mol^{-1}.

    Answer. 8.366 J   (*Arunachal BSc, 2003*)

24. Calculate the change in entropy when 3 moles of an ideal gas is heated from 323 K to 423 K at a constant volume. (C_v = 32.94 JK^{-1} mol^{-1})

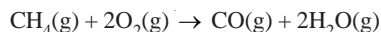   **Answer.** 26.658 JK^{-1} (*Nagpur BSc, 2003*)

25. Calculate the value of dT/dP for water $\rightleftharpoons$ ice system at 273 K. ΔH_f for ice is 6007.8 J mol^{-1}; Molar Volume of water and ice are 0.018 dm^3 mol^{-1} and 0.1963 dm^3 mol^{-1} respectively.

(Given 1 J = 9.87×10^3 dm^3 atm)

Answer. 0.0100654 K atm^{-1} (*Nagpur BSc, 2003*)

26. Calculate standard Gibb's Free energy change for the combustion of methane :

$$CH_4(g) + 2O_2(g) \rightarrow CO(g) + 2H_2O(g)$$

at 25°C. $\Delta H° = -191.8$ kcal and $\Delta S° = 1.2$ cal K^{-1}

Answer. –549.4 cal   (*Sambalpur BSc, 2003*)

27. ΔG and ΔH values for a reaction at 300 K are : –66.944 kJ and –41.84 kJ respectively. Calculate the free energy change at 330 K, assuming that ΔH and ΔS remain constant over this temperature range.

Answer. –69.454 kJ   (*Nagpur BSc, 2003*)

28. (*a*) Derive the integral Clausius-Clapeyron equation in the form

$$\log \frac{P_2}{P_1} = \frac{\Delta H}{2.303\ R}\left[\frac{T_2 - T_1}{T_1\ T_2}\right]$$

for an ideal gas.

(*b*) At 373.6 K and 372.6 K the vapour pressure of $H_2O(\ell)$ are 1.018 and 0.982 atm respectively. What is the heat of vaporization of water? (R = 1.987 cal)

Answer. (*b*) 41675.8 J   (*Jamia Millia BSc, 2003*)

29. Explain the term fugacity. How is fugacity of a gas determined?   (*Panjab BSc, 2003*)

30. (*a*) State Carnot's theorem and second law of thermodynamics.

(*b*) Define Chemical potential. Derive effect of temperature and pressure on chemical potential.

(*Indore BSc, 2004*)

31. Explain the following :

(*a*) Under what conditions can an isothermal expansion of a gas become a free expansion process.

(*b*) Increase in volume of a gas for a given decrease in pressure is less in an adiabatic expansion than in isothermal expansion.

(*c*) All spontaneous processes lead to increase the entropy of the universe.

(*d*) Free Energy of formation of an element at 1 atm and 298 K is assumed to be zero but entropy is not zero under the same conditions.   (*Gulbarga BSc, 2004*)

32. (*a*) Describe Carnot's cycle for establishing the maximum convertibility of heat into work. How does it lead to the definition of Second Law of Thermodynamics?

(*b*) Heat supplied to a Carnot engine is 1897.86 kJ. How much useful work can be done by the engine which works between 0°C and 100°C?

Answer. (*b*) 508.80 kJ   (*Madurai BSc, 2004*)

33. What do you understand by the term enthalpy?

Calculate the work done in the expansion of 3 moles of hydrogen reversibly and isothermally at 27°C from 21.0 litres to 70.3 litres.

Answer. 9042.47×10^7 ergs   (*Kakatiya BSc, 2004*)

34. The heat of vaporisation, ΔH_{vap} of carbon tetrachloride, CCl_4, at 25 °C is 43 kJ mol^{-1}. If 1 mole of liquid carbon tetrachloride at 25 °C has an entropy of 214 JK^{-1}, what is the entropy of 1 mole of the vapour in equilibrium with the liquid at this temperature ?

Answer. 358 JK^{-1} mol^{-1} (*Kalyani BSc, 2005*)

35. Calculate the amount of the heat supplied to Carnot cycle working between 105 °C and 20 °C if the maximum work obtained is 200 cal ?

Answer. 889.4 cal   (*Panjab BSc, 2005*)

36. The enthalpy change involved in oxidation of glucose is – 2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance a person will be able to walk after eating 120 g of glucose ?

    Answer. 4.8 km   (*Delhi BSc, 2005*)

37. What is the entropy change for conversion of one mole of ice to water at 273 K and 1 atm pressure (Given ΔH of ice = 6.025 kJ mol^{-1}).

    Answer. 22.069 J mol^{-1} (*Bundelkhand BSc, 2005*)

38. Calculate the efficiency of steam engine operating between 100 °C and 25 °C. What would be the efficiency of the engine if the boiler temperature is raised to 150 °C, the temperature of the sink remaining same ?

    Answer. 22.1% ; 29.55%   (*Agra BSc, 2006*)

39. At 373 K the entropy change for the transition of liquid water to steam is 109 JK^{-1} mol^{-1}. Calculate the enthalpy change ΔH_{vap} for the process.

    Answer. 40.657 kJ mol^{-1} (*Madurai BSc, 2006*)

40. Ethanol boils at 78.4 °C and standard enthalpy of vaporisation of ethanol is 42. kJ mol^{-1}. Calculate the entropy of vaporisation of ethanol.

    Answer. 120.66 JK^{-1} mol^{-1} (*Barodra BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. A process which proceeds of its own accord, without any outside assistance, is called
   (*a*) non-spontaneous process   (*b*) spontaneous process
   (*c*) reversible process   (*d*) irreversible process
   Answer. (*b*)

2. The tendency of a process to occur naturally is called
   (*a*) momentum of the reaction   (*b*) spontaneity of the reaction
   (*c*) equilibrium of the reaction   (*d*) equilibrium of the reaction
   Answer. (*b*)

3. Which of the following is true about the criteria of spontaneity?
   (*a*) a spontaneous change is unidirectional
   (*b*) a spontaneous change to occur, time is no factor
   (*c*) once a system is in equilibrium, a spontaneous change is inevitable
   (*d*) all of the above
   Answer. (*d*)

4. A spontaneous change is accompanied by _____ of internal energy or enthalpy.
   (*a*) increase   (*b*) decrease
   (*c*) neither increase nor decrease   (*d*) none of these
   Answer. (*b*)

5. Mixing of two or more gases is a
   (*a*) spontaneous process   (*b*) non-spontaneous process
   (*c*) reversible process   (*d*) none of these
   Answer. (*a*)

6. Entropy is a measure of _____ of the molecules of the system.
   (a) concentration
   (b) velocity
   (c) zig-zag motion
   (d) randomness or disorder
   Answer. (d)

7. The second law of thermodynamics states that
   (a) whenever a spontaneous process occurs, it is accompanied by an increase in the total energy of the universe
   (b) the entropy of the system is constantly increasing
   (c) neither of the above
   (d) both (a) and (b)
   Answer. (d)

8. The entropy of a pure crystal is zero at absolute zero. This is statement of
   (a) first law of thermodynamics
   (b) second law of thermodynamics
   (c) third law of thermodynamics
   (d) none of these
   Answer. (c)

9. The entropy is measured in
   (a) $cal\,K^{-1}\,mol^{-1}$
   (b) $JK^{-1}\,mol^{-1}$
   (c) entropy unit
   (d) all of these
   Answer. (d)

10. The standard entropy, $S°$, of a substance is
    (a) its entropy at 0°C and 1 atm pressure
    (b) its entropy at 0 K and 1 atm pressure
    (c) its entropy at 25°C and 1 atm pressure
    (d) its entropy at 25 K and 1 atm pressure
    Answer. (c)

11. The change in entropy of a reaction is given by
    (a) $\Delta S = \Sigma S_{Reactants} + \Sigma S_{Products}$
    (b) $\Delta S = \Sigma S_{Products} - \Sigma S_{Reactants}$
    (c) $\Delta S = \Sigma S_{Reactants} - \Sigma S_{Products}$
    (d) none of these
    Answer. (b)

12. Which of the following is true for a cyclic process?
    (a) $\Delta E = 0$
    (b) $\Delta E = q - w$
    (c) $q = w$
    (d) all of these
    Answer. (d)

13. A machine that can do work by using heat which flows out spontaneously from a high-temperature source to a low-temperature sink is called
    (a) Carnot machine
    (b) cyclic machine
    (c) heat machine
    (d) heat engine
    Answer. (d)

14. The efficiency of a heat engine is the ratio of
    (a) work obtained in a cyclic process (w) to the heat taken from the high temperature reservoir (q)
    (b) heat taken from the high temperature reservoir (q) to the work obtained in a cyclic process
    (c) work obtained in a cyclic process (w) to the heat taken from the low temperature sink (q)
    (d) none of the above
    Answer. (a)

15. The cycle of processes which occurs under reversible conditions is referred to as
    (a) cyclic process
    (b) closed process

(c) Carnot cycle   (d) reversible cycle

Answer. (c)

16. The efficiency of a heat engine is given by

(a) $\dfrac{w}{q_2} = \dfrac{T_2 - T_1}{T_2}$

(b) $\dfrac{w}{q_2} = \dfrac{T_1 - T_2}{T_2}$

(c) $\dfrac{w}{q_2} = \dfrac{T_2 - T_1}{T_1}$

(d) $\dfrac{w}{q_2} = \dfrac{T_1 - T_2}{T_1}$

Answer. (a)

17. The second law of thermodynamics may be stated as

(a) it is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

(b) it is impossible to transfer heat from a body at a lower temperature to one at higher temperature

(c) the efficiency of heat engine is always less than 1

(d) all of the above

Answer. (d)

18. The efficiency of a heat operating between 400 K and 300 K is

(a) 1.0   (b) 0.75

(c) 0.50   (d) 0.25

Answer. (d)

19. The efficiency of heat engine operating between 1000 K and 300 K is _____ the engine operating between 1000 K and 500 K.

(a) greater than   (b) lesser than

(c) is equal to   (d) none of these

Answer. (a)

20. The entropy of the system increases in the order

(a) gas < liquid < solid   (b) solid < liquid < gas

(c) gas < solid < liquid   (d) none of these

Answer. (b)

21. The efficiency of an irreversible Carnot cycle is always _____ that of a reversible one operating between the same two temperatures

(a) less than   (b) greater than

(c) equal to   (d) none of these

Answer. (a)

22. The free energy function (G) is defined as

(a) $G = H + T S$ (b) $G = H - T S$

(c) $G = T S - H$ (d) none of these

Answer. (b)

23. The change in free energy is a measure of :

(a) net work done   (b) net change is entropy

(c) net change in enthalpy   (d) net change in internal energy

Answer. (a)

24. The work function (A) is defined as

(a) $A = E - T S$ (b) $A = E + T S$

(c) $A = T S - E$ (d) none of these

Answer. (a)

25. The change in free energy of a system is given by

(a) $\Delta G = \Delta A + P \Delta V$ (b) $\Delta G = \Delta H - T \Delta S$

(c) $\Delta G = \Delta E + P \Delta V - T \Delta S$ (d) all of these

Answer. (d)

26. Which out of the following is not a state function?

(a) free energy   (b) work function

(c) entropy   (d) work done

Answer. (d)

27. The variation of free energy with temperatures at constant pressure is given by the relation :

(a) $dG_P = - SdT_P$ (b) $\left(\dfrac{dG}{dT}\right)_P = -S$

(c) neither of these   (d) both (a) and (b)

Answer. (d)

28. The variation of free energy with pressure at constant temperature is given by

(a) $(dG)_T = V d P_T$ (b) $dG_P = - SdT_P$

(c) $\left(\dfrac{dG}{dT}\right)_P = -S$ (d) none of these

Answer. (a)

29. The change in free energy in an isothermal process for n moles of the gas is given by

(a) $\Delta G = 2.303 \times n\, RT \log \dfrac{P_2}{P_1}$ (b) $\Delta G = 2.303 \times RT \log \dfrac{V_1}{V_2}$

(c) $\Delta G = 2.303 \times RT \log \dfrac{P_2}{V_1}$ (d) none of these

Answer. (a)

30. The Gibb's Helmholtz equation is applicable to

(a) all processes, chemical or physical

(b) all process, chemical or physical but in a closed system

(c) all chemical processes in a closed system

(d) all physical processes in a closed system

Answer. (b)

31. For a spontaneous process

(a) $\Delta G > 0$ (b) $\Delta G < 0$

(c) $\Delta G = 0$ (d) none of these

Answer. (b)

32. A process is in the equilibrium state when

(a) $\Delta G > 0$ (b) $\Delta G < 0$

(c) $\Delta G = 0$ (d) none of these

Answer. (c)

33. Which of the following equation is used to calculate the heats of reaction when ΔG at two temperature are given?

(a) Gibbs Helmholtz equation   (b) Clapeyron equation

(c) Kirchoff's equation   (d) none of these

Answer. (a)

34. The equation $\dfrac{dP}{dT} = \dfrac{\Delta H}{T(V_2 - V_1)}$ is called

    (a) Gibb's Helmholtz equation   (b) Kirchoff's equation

    (c) Clapeyron equation   (d) Clausius Clapeyron equation

    Answer. (c)

35. The Clausius Clapeyron equation helps to calculate

    (a) latent heat of vaporization

    (b) boiling point or freezing point

    (c) vapour pressure at one temperature, if at another temperature is given

    (d) all of the above

    Answer. (d)

36. The decrease in the work function A in any process at constant temperature gives the _____ that can be obtained from the system during any change.

    (a) minimum work   (b) maximum work

    (c) useful work   (d) net work

    Answer. (b)

37. The equation for van't Hoff isotherm is

    (a) $-\Delta G = 2.303\, RT \log K_P$ (b) $\Delta G = 2.303\, RT \log K_P$

    (c) $-\Delta G = 2.303\, RT^2 \log K_P$ (d) $\Delta G = 2.303\, RT^2 \log K_P$

    Answer. (a)

38. The equation $\dfrac{\Delta H}{RT^2} = \dfrac{d\,(\ln K_P)}{dT}$ is known as

    (a) van't Hoff equation   (b) van't Hoff isochore

    (c) Gibbs equation   (d) Gibbs Duhem equation

    Answer. (b)

39. Each substance in a given state has a tendency to escape from that state and this escaping tendency is called

    (a) spontaneity   (b) Gibbs free energy

    (c) fugacity   (d) activity

    Answer. (c)

40. When water is cooled to ice, its entropy

    (a) increases   (b) decreases

    (c) remains the same   (d) becomes zero

    Answer. (b)

41. Which of the following sets of conditions makes a process spontaneous at all temperatures?

    (a) $\Delta H = 0;\ \Delta S > 0$ (b) $\Delta H = 0;\ \Delta S < 0$

    (c) $\Delta H > 0;\ \Delta S > 0$ (d) $\Delta H < 0;\ \Delta S < 0$

    Answer. (c)

42. The increase in entropy is maximum in

    (a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ (b) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

    (c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (d) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

    Answer. (a)

43. A spontaneous reaction proceeds with a decrease in

    (a) entropy   (b) enthalpy

(*c*) free energy   (*d*) internal energy

Answer. (*c*)

44. In a process $\Delta H = 100$ kJ and $\Delta S = 100$ JK^{-1} at 400 K. The value of ΔG will be

(*a*) zero   (*b*) 100 kJ

(*c*) 50 kJ   (*d*) 60 kJ

Answer. (*d*)

45. A chemical reaction proceeds with decrease in both the enthalpy and entropy. This reaction will be spontaneous if

(*a*) $\Delta H = T \Delta S$ (*b*) $\Delta H < T \Delta S$

(*c*) $\Delta H > T \Delta S$ (*d*) none of these

Answer. (*b*)

46. Which is the correct unit for entropy?

(*a*) kJ mol   (*b*) JK^{-1} mol

(*c*) JK^{-1} mol^{-1} (*d*) kJ mol

Answer. (*c*)

47. The efficiency of heat engine is maximum when

(*a*) temperatures of source and sink are maximum

(*b*) temperatures of source and sink are minimum

(*c*) temperature of source is minimum and that of sink is maximum

(*d*) temperature of source is maximum and that of sink is minimum

Answer. (*d*)

48. A reaction proceeds with increase in both the enthalpy and entropy. It will be spontaneous if

(*a*) $\Delta H = T \Delta S$ (*b*) $\Delta H > T \Delta S$

(*c*) $\Delta H < T \Delta S$ (*d*) none of these

Answer. (*c*)

49. A spontaneous reaction is not possible if

(*a*) ΔH and $T \Delta S$ are both negative   (*b*) ΔH and $T \Delta S$ are both positive

(*c*) ΔH is +ve and $T \Delta S$ is –ve   (*d*) ΔH is –ve and $T \Delta S$ is +ve

Answer. (*c*).

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