

# 4.

# THERMODYNAMICS AND THERMOCHEMISTRY

## 1. INTRODUCTION

Thermodynamics, as the word suggests, is the heat in motion. The systems related to usage of heat for doing work. Every system was observed and accordingly laws were framed for categorising many such processes. In this Chapter, we would be learning about these laws and the systems governed by them.

### 1.1 Definition of Thermodynamics

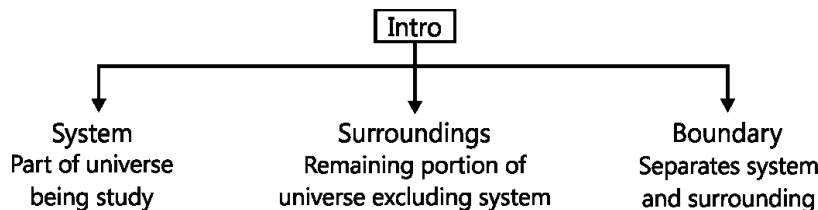
Thermodynamics is a Greek word which means flow of heat in physical and chemical reactions. Thermodynamics is a branch of science dealing with study of different forms of energy and their inter conversions.

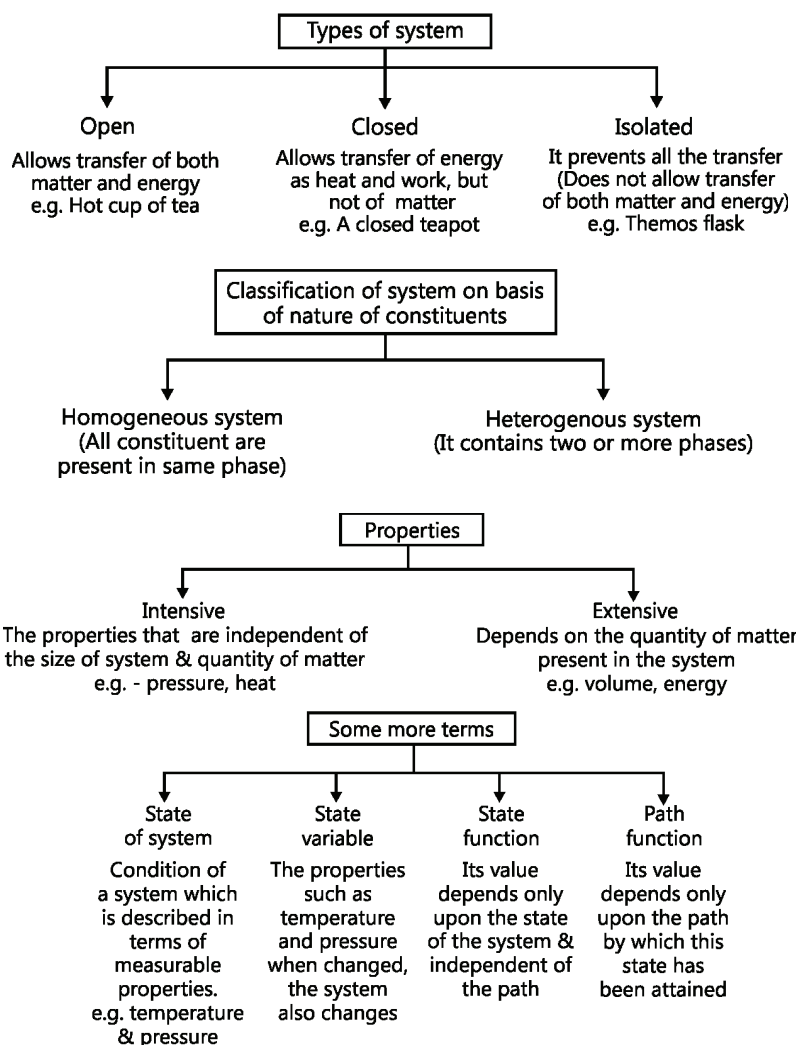
### 1.2 Importance of Thermodynamics

- (a) Useful to predict whether any chemical reaction can occur under specified conditions.
- (b) Used to predict the extent of chemical reaction before equilibrium is reached.
- (c) Used to derive important laws like law of equilibrium.

## 2. TERMS USED IN THERMODYNAMICS

**Example:** The fixed potential energy of a person standing on the top of a lighthouse stands as a state function, since it is not dependent on the path taken by the person. Whereas the work done by the legs of the person stands as a path function.





Flowchart 4.1: Terminology used in Thermodynamics

## 2.1 Mathematics of State Function

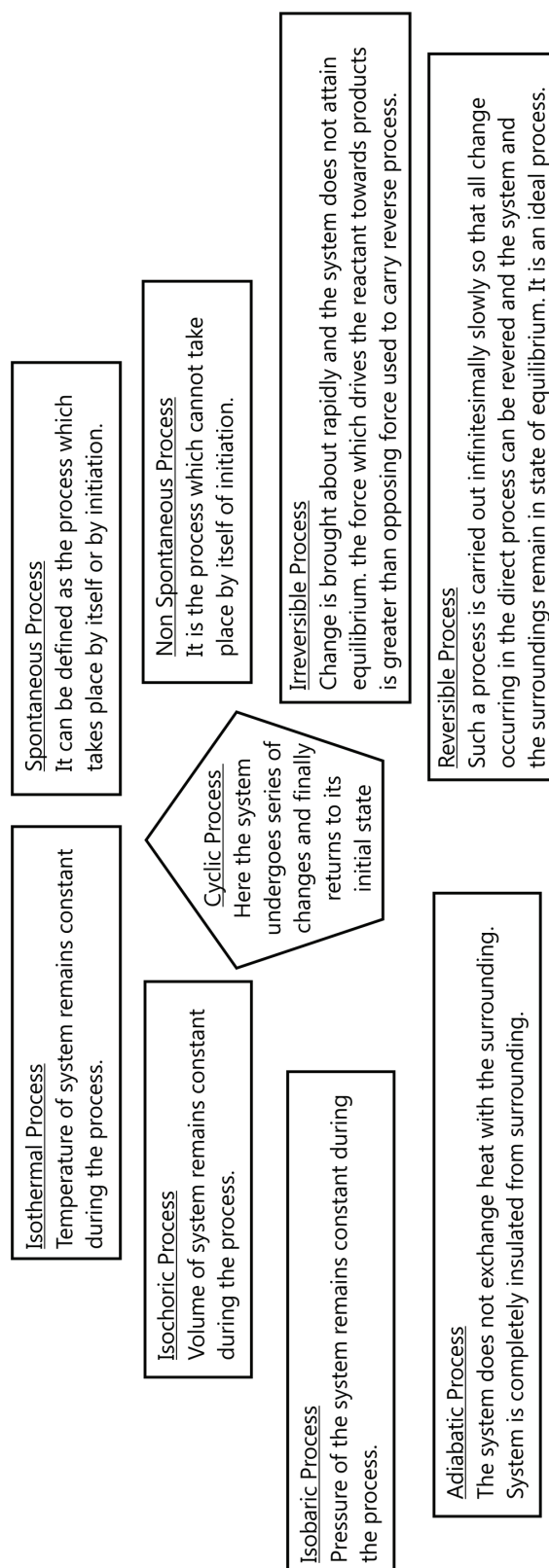
State functions can be thought of as integrals depending on three things: the function, the lower limit and the upper limit. Similarly, they depend on three more things: the property, the initial value, and the final value.

For example,  $\int_{t_0}^{t_1} H(t)dt = H(t_1) - H(t_0)$ ;  $t_0$  gives the initial case and  $t_1$  gives the final case. Thus,  $\Delta H = H_{\text{final}} - H_{\text{initial}}$

Table 4.1: Difference between state and path functions

State Function	Path Function
Independent of path taken to establish property or value	Dependent on path taken to establish property or value
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple steps result in different value.
Based on established state of systems (temperature, pressure, amount and identity of systems)	Based on how state of system was established.
Normally represented by an uppercase letter.	Normally represented by lowercase letter.

### 3. INTRODUCTION TO VARIOUS PROCESSES



**Figure 4.1: (a)** Various processes

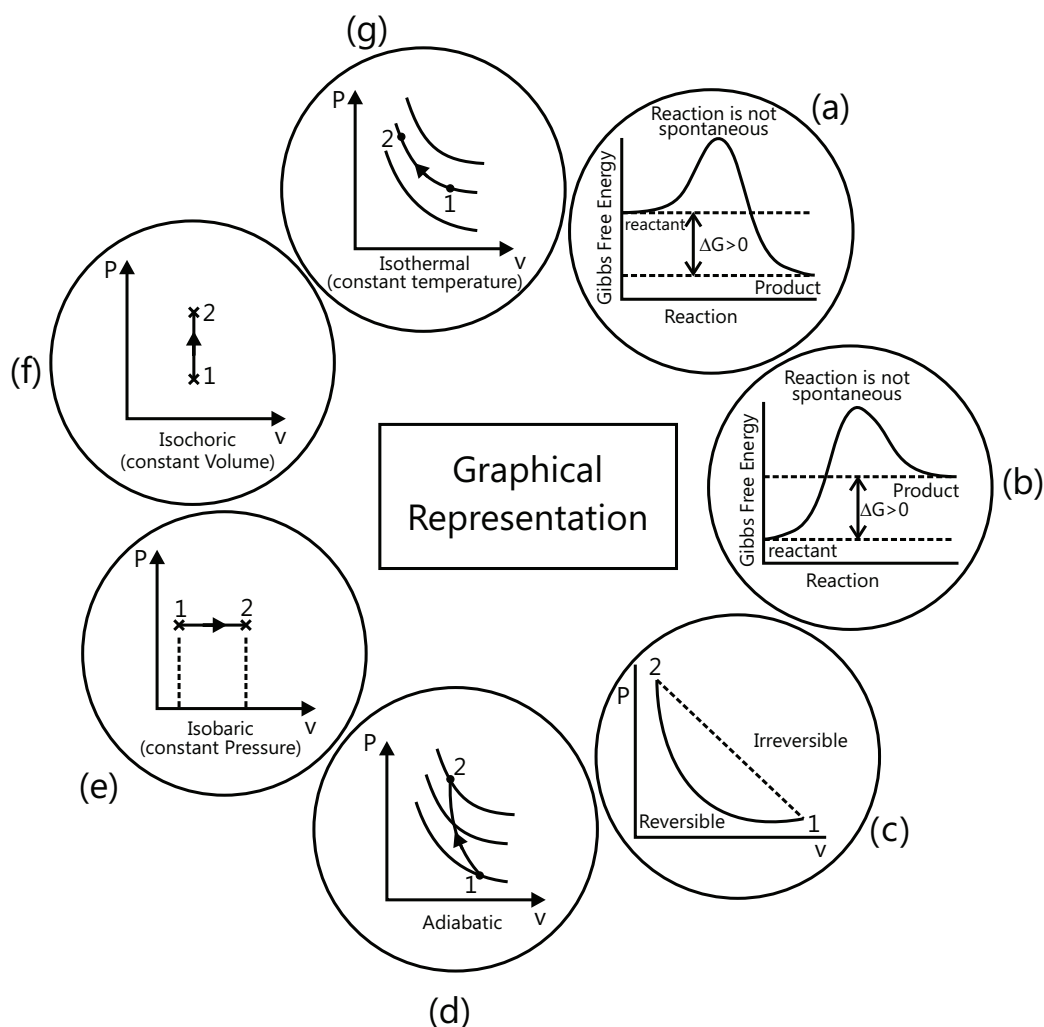


Figure 4.2 a to g: (b) Representation for the above processes

**Illustration 1:** Can you tell whether density is an intensive or extensive quantity?

**(JEE MAIN)**

**Sol:** Intensive properties are those which does not depend on the amount of matter that is present whereas extensive properties vary with amount of matter present. Density is an intensive property. This is due to the fact that it does not depend on the amount of matter that is present. Different weights of the same matter will have the same density.

### PLANCESS CONCEPTS

How to check whether a quantity is intensive or extensive?

Suppose to measure a quantity  $q(S)$  relative to a system  $S$ . Now reproduce a copy of  $S$  and measure the same quantity for the system  $S+S$  composed of the two identical systems considered as a single system. If  $q(S+S) = q(S)$ , then  $q$  is an intensive quantity.

If, for two different systems  $S$  and  $T$ ,  $q(S+T) = q(S) + q(T)$ , then  $q$  is an extensive quantity.

**Nikhil Khandelwal (JEE 2009 AIR 94)**

## 4. MAJOR THERMODYNAMIC PARAMETERS: WORK, HEAT AND INTERNAL ENERGY

### 4.1 Work

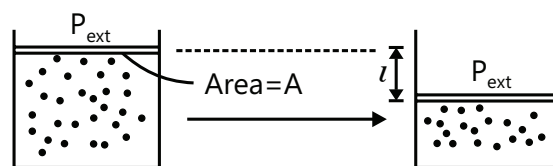
Work is defined as a movement against force. It is a mode of energy transfer to or from a system with reference to surroundings.

Work:  $W = F \cdot l$

Applied Force  $\nearrow$  Distance

**Mathematical Expression:** If an object is displaced through a distance  $l$  against a force  $F$ , then the amount of work done is defined as **expansion work**.

Work associated with change in volume of a system against external pressure is called **mechanical work**.



$$\text{Mechanical Work (} = W) = P_{\text{ext}}(V_2 - V_1) = P_{\text{ext}} \Delta V$$

Where  $P_{\text{ext}}$  = External pressure,  $\Delta V$  = increase or decrease in volume.

#### 4.1.1 Convention

'-' Sign	$W > 0$ Positive work	$\Delta V < 0$	Work is done ON the system BY the surroundings
'+' Sign	$W < 0$ Negative work	$\Delta V > 0$	Work is done BY the system ON the surroundings

If  $P_{\text{ext}}$  is not constant, then we have to look at infinitesimal changes.

$$dw = -P_{\text{ext}} dV \quad (\text{d means this is not an exact differential})$$

$$\text{Integral } w = -\int_1^2 P_{\text{ext}} dV \quad (\text{depends on the path})$$

#### Path dependence of W:

**Example: Type of Process:** Reversible process

**Condition:**  $P_{\text{ext}} = P$

**Type of Work Done:** Compression (by 2 paths)

$V_1 > V_2$  and  $P_1 < P_2$

**Table 4.2:** To show path dependence of work

First Path	Second Path
$V_1 \rightarrow V_2$ at $P = P_1$ Then $P_1 \rightarrow P_2$ at $V = V_2$	$P_1 \rightarrow P_2$ at $V = V_1$ Then $V_1 \rightarrow V_2$ at $P = P_2$
$W_{(1)} = -\int_{V_1}^{V_2} P_{\text{ext}} dV - \int_{V_1}^{V_2} P_{\text{ext}} dV$ $= -\int_{V_1}^{V_2} P_1 dV$ $= -P_1(V_2 - V_1)$ <div style="border: 1px solid black; padding: 2px; display: inline-block;"><math>W_{(1)} = P_1(V_1 - V_2)</math></div>	$W_{(2)} = -\int_{V_1}^{V_2} P_{\text{ext}} dV - \int_{V_1}^{V_2} P_{\text{ext}} dV$ $= -\int_{V_1}^{V_2} P_2 dV$ $= -P_2(V_2 - V_1)$ <div style="border: 1px solid black; padding: 2px; display: inline-block;"><math>W_{(2)} = P_2(V_1 - V_2)</math></div>

$W > 0 \Rightarrow$  Work is done ON the system. It is compressed.

$$W_{(1)} \neq W_{(2)}$$

**Illustration 2:** Calculate the work done by 1 mole of an ideal gas in a piston fitted cylinder at the initial pressure of 24.83 atm pressure and 300 K to expand its volume to 10 litre if

- External pressure is reduced to 1 atm in single step.
- External pressure is reduced to 5 atm in 1<sup>st</sup> operation and then 1 atm in next step.
- Gas is allowed to expand into an evacuated space of 10 litre.

(JEE MAIN)

**Sol:** By using ideal gas equation calculate the volume term and then calculate work done by the system by using pressure volume relationship.

$$P \times V_1 = nRT$$

$$V_1 = \frac{1 \times 0.0821 \times 300}{24.63} = 1 \text{ liter}$$

$$(a) \quad W = P \Delta V = -1 \times (10 - 1) = -9 \text{ L-atm}$$

or  $W_{\text{system}} = -9 \text{ L-atm}$  and  $W_{\text{surr}} = +9 \text{ L-atm}$

$$(b) \quad [\because P_1 V_1 = P_2 V_2; 24.63 \times 1 = 5 \times V_2; \therefore V_2 = 4.926]$$

$$W = W_1 + W_2 = -5 \times (V_2 - V_1) + [-1 \times (10 - V_2)]$$

$$= -5 \times (4.926 - 1) + [-1 \times (10 - 4.926)]$$

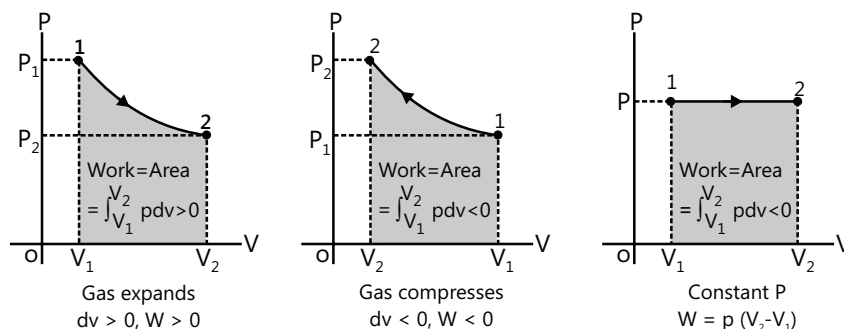
$$= -19.630 - 5.074$$

$$= -24.704 \text{ L-atm}$$

$$\therefore W_{\text{sys}} = -24.704 \text{ L-atm}; W_{\text{surr}} = +24.704 \text{ L-atm}$$

$$(c) \quad W = -P \times \Delta V = -0 \times (10 - 1) = 0 \text{ L-atm}$$

**Work plots:** In the following figures, observe how the sign of work changes on changing the volume.



### PLANCESS CONCEPTS

Work done is equal to the area under the P-V graph. But be careful about the sign. In case of expansion, the sign is negative while in compression, it is positive.

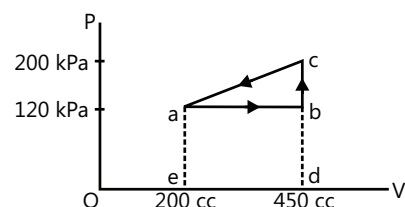
Neeraj Toshniwal (JEE 2009 AIR 21)

**Illustration 3:** Calculate the work done by a gas as it is taken from the state a to b, b to c and c to a as shown in figure. **(JEE MAIN)**

**Sol:** By using ideal gas equation calculate the volume term and then calculate work done by the system by using pressure volume relationship.

The work done by the gas in the process a to b is the area of abde

$$W_{ab} = (120 \text{ kPa}) (250 \text{ cc}) \\ = 120 \times 10^3 \times 250 \times 10^{-6} \text{ J} = 30 \text{ J}.$$



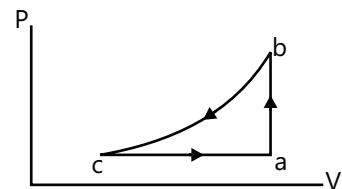
In the process b to c the volume remains constant and the work done is zero.

In the process c to a, the gas is Compressed. The volume is decreased and the work done by the gas is negative.

The magnitude is equal to the area of caed. This area is  $\text{cab} + \text{baed} = \frac{1}{2}(80 \text{ kPa})(250 \text{ cc}) + 30 \text{ J} = 10 \text{ J} + 30 \text{ J} = 40 \text{ J}$ .

Thus, the work done in the process c to a is -40 J.

**Illustration 4:** A sample of an ideal gas is taken through the cyclic process abca. It absorbs 50 J of heat during the part ab, no heat during bc and rejects 70 J of heat during ca. 40 J of work is done on the gas during the part bc. (a) Find the internal energy of the gas at b and c if it is 1500 J at a (b) Calculate the work done by the gas during the part ca. **(JEE ADVANCED)**



**Sol:** By using the following equation find out the missing terms

$$\Delta Q = \Delta U + \Delta W.$$

- (a) In the part ab, the volume remains constant. Thus, the work done by the gas is zero. The heat absorbed by the gas is 50 J. The increase in internal energy from a to b is  $\Delta U = \Delta Q = 50 \text{ J}$

As the internal energy is 1500 J at a, it will be 1550 J at b, in the part bc, the work done by the gas is

$\Delta W = -40 \text{ J}$  and no heat is given to the system. The increase in internal energy from b to c is

$$\Delta U = -\Delta W = 40 \text{ J}$$

As the internal energy is 1550 J at b, it will be 1590 J at c.

- (b) The change in internal energy from c to a is  $\Delta U = 1500 \text{ J} - 1590 \text{ J} = -90 \text{ J}$

The heat given to the system is  $\Delta Q = \Delta U + \Delta W$ .

$$\Delta W = \Delta Q - \Delta U = -70 \text{ J} + 90 \text{ J} = 20 \text{ J}$$

## 4.2 Heat and Internal Energy

The flow or exchange of energy between the system and the surroundings which can induce a change in the temperature of the system and/or the surroundings. Heat always flows from high temperature to low temperature.

It is expressed as q. Heat absorbed or evolved,  $q = ms\Delta t$

m=Mass of substance, s=Specific heat and  $\Delta t$  =Temperature difference.

Heat is absorbed by the system	q= +ve
Heat is released by the system	q= -ve

**Type of function:** Path Function

**Unit:** Calories (1 cal = heat needed to raise the temperature of 1 g  $\text{H}_2\text{O}$  by  $1^\circ\text{C}$ ).

Also expressed as Joule (1 cal = 4.184J)

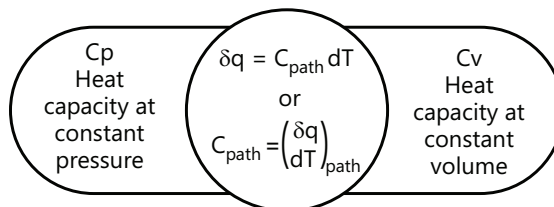
### 4.2.1 Heat Capacity

It is the amount of heat required to raise the temperature by one degree (usually expressed in Celsius or Kelvin). It is expressed in units of thermal energy per degree temperature.

It is expressed as C.

Let  $dq$  be the amount of heat given to a system and the temperature of the system rises by  $dT$ .

$$\text{Heat capacity} = \frac{dq}{dT}$$



### 4.2.2 Relation of Work and Heat with Internal Energy

Temperature of water can be raised by-

Heating	Doing work
<p>(a) With only heat</p> <p><math>T_1 \rightarrow T_2</math></p> <p><b>Figure 4.2:</b> (a) Heating to raise temperature</p>	<p>(b) With only work (Weight falls &amp; churns propeller)</p> <p><math>T_1 \rightarrow T_2</math></p> <p><b>Figure 4.2:</b> (b) Doing work to raise temperature</p>

$$\text{But, } \oint (dw + dq) = 0$$

$\Rightarrow (w + q)$  is independent of path

$\Rightarrow$  This implies that there exist a state function whose differential is  $dw + dq$ , known as **internal energy** or just energy. It is expressed as 'U'.

$$\therefore dU = dw + dq$$

Internal energy can be given as:

$$U = U_{\text{Kinetics}} + U_{\text{Potential}} + U_{\text{Electronic}} + U_{\text{nuclear}} + \dots$$

**Illustration 5:** A steam boiler made up of steel weighs 900kg. The boiler contains 400kg of water. Assuming 70% of the heat is delivered to boiler and water, how much heat is required to raise the temperature of the whole from  $10^\circ\text{C}$  to  $100^\circ\text{C}$ ? Heat capacity of steel is  $0.11 \text{ kcal/kg}\cdot\text{K}$  and heat capacity of water is  $1 \text{ kcal/kg}\cdot\text{K}$  **(JEE MAIN)**

$$\text{Sol: } \Delta q = (m\Delta T)_{\text{Boiler}} + (m\Delta T)_{\text{Water}}$$

By using the above equation, first find out the  $\Delta H$  required for complete heating and then by using the value of  $\Delta H$  calculate the actual heat required when 70% is transferred to the system.

$$\begin{aligned} \Delta q &= (m\Delta T)_{\text{Boiler}} + (m\Delta T)_{\text{Water}} \\ &= 900 \times 0.11 \times 90 + 400 \times 1 \times 90 = 44910 \text{ kcal} \end{aligned}$$

Since, only 70% of heat given is used upto do so.

$$\text{Thus, actual heat required} = \frac{44910 \times 100}{70} = 64157 \text{ Kcal.}$$

**Illustration 6:** Assume an ideal gas obeys  $\frac{P}{V} = \text{constant}$ . This gas confined in piston fitted cylinder having initial volume and pressure 2 litre and 1 atm is allowed to expand to occupy finally 6 litres. Calculate the work done by the system. **(JEE ADVANCED)**



**Sol:** From the given data calculate work done in terms of volume pressure relationship. i.e  $W = -\int_{V_1}^{V_2} P \Delta V$

Given,  $\frac{P}{V} = K \therefore K = \frac{1}{2} \text{ atm L}^{-1}$  (initial condition)

$$W = -\int_{V_1}^{V_2} P \Delta V = -\int_{V_1}^{V_2} KV \Delta V = -K \int_{V_1}^{V_2} \frac{V^2}{2} = -K \left[ \frac{V_2^2}{2} - \frac{V_1^2}{2} \right] = -\frac{1}{2} \left[ \frac{36}{2} - \frac{4}{2} \right] = -8 \text{ L-atm}$$

### PLANCESS CONCEPTS

Always remember that the sign convention for work in physics and chemistry are both opposite. In physics the work done by the system is considered to be positive while in chemistry the work done on the system is considered to be positive. Hence in physics work =  $\int P dV$  while in chemistry work =  $-\int P dV$

Heat given to the system is considered to be positive while the heat extracted from the system is considered to be negative. This is same for both physics and chemistry.

**Nikhil Khandelwal (JEE 2009 AIR 94)**

## 5. ZEROth LAW OF THERMODYNAMICS

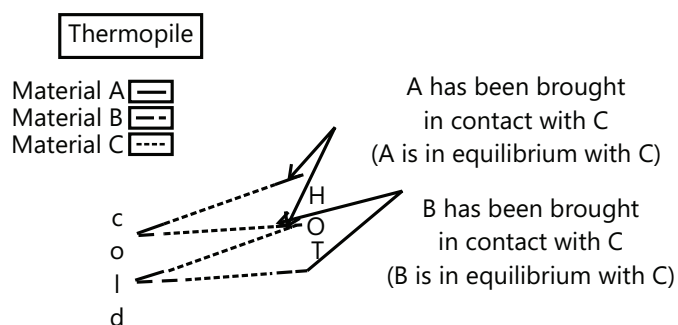
It was introduced after the 1<sup>st</sup> and 2<sup>nd</sup> law and thus got its name.

The law states: If two systems are in equilibrium with a third system, they are also in thermal equilibrium with each other. If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

**Thermometers:** Thermometers are common temperature measuring devices that are based on the zeroth law of thermodynamics.

### Thermopile:

- Conversion of thermal energy into electrical energy can be done with the help of a thermopile, which is a device made up of multiple thermocouples connected in series.
- In accordance to the temperature increase in the thermocouples, proportional electrical output is received.



**Figure 4.3:** Thermopile

## 6. FIRST LAW OF THERMODYNAMICS

The increase in the internal energy of a thermodynamic system is equal to the amount of heat energy added to the system minus the work done by the system on the surroundings. When a system is changed from initial state to the final state it undergoes a change in the internal energy from  $E_i$  to  $E_f$ . Thus,  $\Delta E$  can be written as:  $\Delta E = E_f - E_i$

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

- Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).
- By doing work on the system or the work done by the system.

Therefore,  $E_f - E_i = q + w$  or  $\Delta E = q + w$

Therefore, we can state that the change in internal energy of the system is equal to heat absorbed plus work done on the system

OR

The change in internal energy of the system is equal to heat absorbed minus work done by the system

OR

Energy is conserved; it can be neither created nor destroyed.

Therefore, it can be summarized as:  $dU = dq + dw$

Or Mathematical statement:  $\Delta U = q + w$  or  $-\oint dq = \oint dw$

$$\Delta U_{\text{system}} = q + w;$$

$$\Delta U_{\text{surroundings}} = -q - w$$

$$\Rightarrow \Delta U_{\text{universe}} = \Delta U_{\text{system}} + \Delta U_{\text{surroundings}} = 0$$

**Clausius statement of 1<sup>st</sup> law:** The energy of the universe is conserved.

## 6.1 Enthalpy

Considering a system at constant pressure, the amount of heat which is released or absorbed is termed as **Enthalpy**. The change in enthalpy for a specific process is actually the change in internal energy associated with the changing volume.

$$H = U + PV$$

Enthalpy is a state function and an extensive property

Let a system at state-I be transformed to state – II at constant pressure condition  $H = U + PV$

**Table 4.2:** Parameters for the given system

Parameters	State – I	State -II
Enthalpy	$H_1$	$H_2$
Internal energy	$E_1$	$E_2$
Pressure	$P$	$P$
Volume	$V_1$	$V_2$
	$H_1 = E_1 + PV_1$	$H_2 = E_2 + PV_2$
$H_2 - H_1 = \Delta H = (E_2 + PV_2) - (E_1 + PV_1)$ $= (E_2 - E_1) + P(V_2 - V_1)$ $\Delta H = \Delta E + P\Delta V$		

$$\text{Also for an ideal gas } PV = nRT \Rightarrow PV_1 = n_1RT \text{ and } PV_2 = n_2RT \Rightarrow P(V_2 - V_1) = \Delta n_g RT$$

$$\text{When } \Delta n_g = 0 \Rightarrow \Delta H = \Delta E$$

$$\text{When } \Delta n_g > 0 \Rightarrow \Delta H > \Delta E$$

$$\text{When } \Delta n_g < 0 \Rightarrow \Delta H < \Delta E$$

$$\text{Also } \Delta E = q_p - P\Delta V \quad q_p = \Delta E + P\Delta V$$

And  $\Delta H = q_p$  (i.e. Enthalpy change = heat exchange at constant pressure condition)

$$\text{Also } \Delta E = q_v, \Delta H = \Delta E + P\Delta V, q_p = q_v + P\Delta V$$

For a given system,  $H = f(T, P)$ ;

$$dH = \left( \frac{\partial H}{\partial T} \right)_P dT + \left( \frac{\partial H}{\partial P} \right)_T dP$$

## 6.2 Degree of Freedom

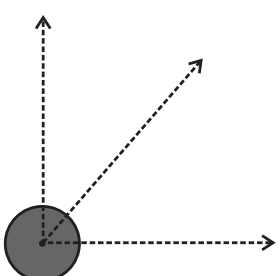
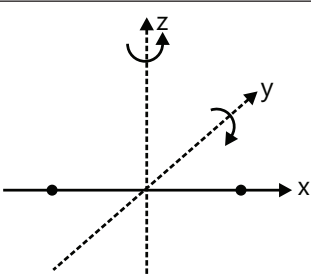
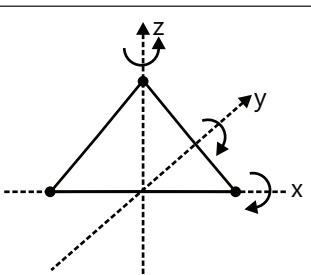
### Degree of freedom of gas molecules

A gas molecule can have following types of energies:

- (a) Translational kinetic energy
- (b) Rotational kinetic energy
- (c) Vibrational energy (potential + kinetic)

**Vibrational energy:** The forces between different atoms of a gas molecule may be visualized by imagining every atom as being connected to its neighbours by springs. Each atom can vibrate along the line joining the atoms. Energy associated with this is called vibrational energy.

**Table 4.4:** Degree of Freedom

Degree of freedom	Explanation	Value of f	Diagram
<b>Degree of freedom of monoatomic gas</b>	1. A monoatomic gas molecule (like He) consists of a single atom. 2. Translational motion seen in any direction	3-all translational; due to its small moment of inertia, rotational kinetic energy is neglected	
<b>Degree of freedom of a diatomic and linear polyatomic gas</b>	Can not only move bodily but also rotate about any one of the three co-ordinate axes	$f = 5$ (3 translational + 2 rotational) at room temperatures and $f = 7$ (3 translational + 2 rotational + 2 vibrational) at high temperatures.	
<b>Degree of freedom of nonlinear polyatomic gas</b>	Can rotate about any of three co-ordinate axes	$f = 6$ (3 translational + 3 rotational) at room temperatures. and $f = 8$ (3 translational + 3 rotational + 2 vibrational) at high temperatures.	

**PLANCESS CONCEPTS**

Degree of freedom of a diatomic and polyatomic gas depends on temperature since there is no clear cut demarcation line above which vibrational energy becomes significant. Moreover, this temperature varies from gas to gas. On the other hand for a monoatomic gas there is no such confusion. Degree of freedom here is 3 at all temperatures. Unless and until stated in the question, you can take  $f = 3$  for monoatomic gas,  $f = 5$  for a diatomic gas and  $f = 6$  for a non-linear polyatomic gas.

**Nikhil Khandelwal (JEE 2009 AIR 94)**

**6.3 Law of Equipartition of Energy**

An ideal gas is the one which distributes internal energy equally in all degrees of freedom.

In each degree of freedom, energy of one mole of an ideal gas is  $\frac{1}{2}RT$ , where  $T$  is the absolute temperature of the gas. Thus, if  $f$  be the number of degrees of freedom, the internal energy of 1 mole of the gas will be  $\frac{f}{2}RT$  or internal energy of  $n$  moles of the gas will be  $\frac{n}{2}fRT$ .

Thus,  $U = \frac{n}{2}fRT$ .

For a monoatomic gas,  $f = 3$

Therefore,  $U = \frac{3}{2}RT$ . (For 1 mole of a monoatomic gas.)

For a di and linear polyatomic gas at low temperatures,  $f = 5$ , so,  $U = \frac{5}{2}RT$  (For 1 mole)

and for non-linear polyatomic gas at low temperatures,  $f = 6$ , so,  $U = \frac{6}{2}RT$  (For 1 mole)

**6.4 Specific Heats of Gases**

The specific heats of gases are generally expressed as molar specific heats.

The expression for the internal energy is

$$U = nN_A KE_{avg} = nN_A \frac{3}{2}kT = \frac{3}{2}nRT$$

Two specific heats are defined for gases, one for constant volume ( $C_v$ ) and one for constant pressure ( $C_p$ ).

For a constant volume process with a monoatomic ideal gas, the first law of thermodynamics gives:

$$Q = C_v n\Delta T \quad Q = \Delta U + P\Delta V = \Delta U$$

$$C_v = \frac{1\Delta U}{n\Delta T} = \frac{3}{2}R$$

Further application of the ideal gas law and first law gives the relationship  $C_p = C_v + R$

Using first law of thermodynamics for a constant pressure process,  $\Delta U + P\Delta V = nC_p\Delta T$

From the ideal gas law ( $PV = nRT$ ) under constant pressure condition it can be seen that,

$$P\Delta V = nR\Delta T \text{ so that } \frac{\Delta U}{\Delta T} + nR = nC_p$$

Since the constant volume specific heat is  $c_v = \frac{1}{n} \frac{\Delta U}{\Delta T}$ ;

Thus,  $C_p = C_v + R$

Ratio of heat capacity  $\gamma = \frac{C_p}{C_v}$  depends on atomicity of gas.

## 6.5 Expansion of Ideal Gases

### 6.5.1 Isothermal Expansion

**Isothermal Gas Expansion:** In an isothermal gas expansion the temperature of the system remains constant throughout the process. Since, Internal energy depends on temperature, it follows that at constant temperature the total internal energy of the system remains constant. i.e.  $\Delta E = 0$

According to first law thermodynamics,

$$\Delta U_{\text{system}} = q + w; \text{ Since for isothermal expansion } \Delta U = 0; q = -w$$

Also  $\Delta H = \Delta U + \Delta(nRT)$  since  $\Delta U$  and  $\Delta T$  are zero, Hence  $\Delta H = 0$

$$\text{Gas } (p_1, v_1, T) \Rightarrow \text{gas } (p_2, v_2, T) \quad (\Delta T = 0)$$

Work done in reversible isothermal expansion:

The work done by the gas in each step of expansion can be given as

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

Total amount of work done by the isothermal reversible expansion ideal gas from volume  $V_1$  to volume  $V_2$  is,

$$W_{\text{rev}} = \int_{V_1}^{V_2} PdV$$

For an ideal gas,  $P = \frac{nRT}{V}$

$$\text{So, } w = -nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{Integrating, } w = -nRT \log_e \frac{V_2}{V_1} = -2.303nRT \log \frac{V_2}{V_1}$$

At constant temperature, according to Boyle's Law,  $w = -2.303nRT \log \frac{P_1}{P_2}$

**Work done for Isothermal Compression:** It has exactly same value as that of isothermal expansion but with opposite sign.

$$w = 2.303nRT \log \frac{V_1}{V_2} = 2.303nRT \log \frac{P_2}{P_1}$$

**Work done for Irreversible Isothermal Expansion:**

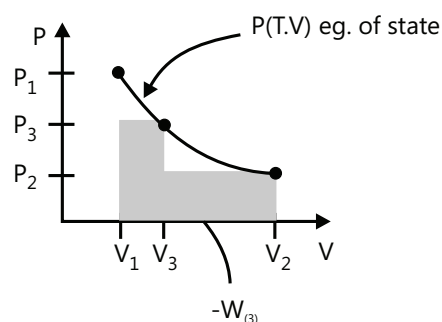
(a) **Free expansion:** In free expansion external work is zero thus work done is zero.

(b) **Intermediate expansion:**

$$w = \int_{V_1}^{V_2} P_{\text{ext}} \times dV = -P_{\text{ext}}(V_2 - V_1)$$

**Maximum Work:** Maximum work delivered to surroundings for isothermal gas expansion is obtained using a reversible path

$$\text{For ideal gas: } W_{\text{rev}} = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \ln \frac{P_2}{P_1}$$



**Figure 4.4:** More work done to the surroundings of the

## 6.5.2 Adiabatic Expansion

### Reversible adiabatic Expansion (or compression) of an Ideal Gas

1 mole gas ( $V_1, T_1$ ) = 1 mole gas ( $V_2, T_2$ )

Adiabatic  $\Rightarrow dq = 0$

Reversible  $\Rightarrow dw = -PdV \Rightarrow$  Ideal gas

From 1<sup>st</sup> law  $dU = -PdV \Rightarrow C_v dT = -PdV$  (along path)

$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow C_v \frac{dT}{T} = -R \frac{dV}{V} \quad \left(\text{using } P = \frac{RT}{V}\right)$$

Integrating on both the sides

$$\log \frac{T_2}{T_1} = \frac{-R}{C_v} \log_e \frac{V_2}{V_1} = \frac{R}{C_v} \log \frac{V_1}{V_2}$$

$$C_p - C_v = R; \frac{C_p}{C_v} - 1 = \frac{R}{C_v}; (\gamma - 1) = \frac{R}{C_v}$$

Putting the value in above equation we get,  $\log \frac{T_2}{T_1} = \frac{R}{C_v} \log_e \frac{V_1}{V_2}$ ;  $\log \frac{T_2}{T_1} = \log \left( \frac{V_1}{V_2} \right)^{\gamma-1}$ ;  $\left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$

For monoatomic ideal gas :  $\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} \quad (> 1 \text{ generally})$

In an adiabatic expansion ( $V_2 > V_1$ ), the gas cools ( $T_2 < T_1$ ) and in an adiabatic compression ( $V_2 < V_1$ ), the gas heats up.

For an ideal gas (one mole),  $T = \frac{PV}{R}$

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

$\Rightarrow PV^{\gamma}$  is constant in an adiabatic process

For an isothermal process ( $T = \text{constant}$ )

$\Rightarrow PV = \text{constant}$ .

Note that  $V_2^{\text{adiabatic}} < V_2^{\text{isothermal}}$  because the gas cools during reversible adiabatic expansion

$$\text{Work done} = C_v \cdot \Delta T = C_v (T_2 - T_1) = -\frac{R}{\gamma - 1} (T_2 - T_1)$$

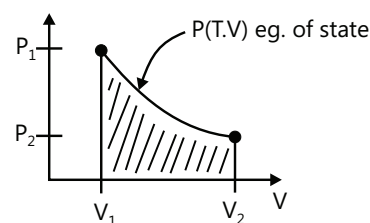
$$\text{For } n \text{ moles, } W = \frac{nR}{(\gamma - 1)} (T_1 - T_2)$$

### Irreversible Adiabatic Expansion of an ideal gas against a constant external pressure

In free expansion, the external pressure is zero i.e. work done is zero. Accordingly  $\Delta E$  which is equal to  $w$  is also zero. If  $\Delta E = 0$ ,  $\Delta T$  should be zero. Thus in free expansion  $\Delta T = 0$ ,  $\Delta E = 0$ ,  $w = 0$  and  $\Delta H = 0$

In intermediate expansion, the volume changes from  $V_1$  to  $V_2$  against external pressure  $P_{\text{ext}}$ .

$$w = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left( \frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right) = -P_{\text{ext}} \left( \frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right) \times R$$



**Figure 4.5:** Comparison plots for different gases

$$\text{or } w = C_v(T_2 - T_1) = -RP_{\text{ext}} \left( \frac{T_2 P_1 - T_1 P_2}{P_1 P_2} \right)$$

### 6.5.3 Isobaric Process

In an Isobaric process,  $P = \text{constant}$

$$\Delta U = Q - W, W = \int P dV = \int_1^2 P dV = P(V_2 - V_1)$$

$$Q = \Delta U + P(V_2 - V_1) = (U_2 - U_1) + P(V_2 - V_1) = (U_2 + PV_2) - (U_1 + PV_1) = H_2 - H_1 = \Delta H$$

### 6.5.4 Isochoric Process

Isochoric process is a Constant volume process, This implies,  $V = \text{constant}$

$$Q - W = \Delta U, W = \int P dV = 0, \text{ no work done}$$

$$Q = \Delta U = m\Delta u = m \int C_v dT$$

### 6.5.5 Polytropic Process

Polytropic Process: Its P-V relation can be expressed as  $PV^n = \text{Constant}$ , where  $n$  is a constant for a specific process

(a) Isothermal,  $T = \text{Constant}$ , if the gas is an ideal gas then  $PV = RT = \text{constant}$ ,  $n = 1$

(b) Constant-volume,  $V = \text{constant}$ ,  $V = \text{constant}(P)^{(1/n)}$ ,  $n = \infty$  (For all substances)

(c) Adiabatic process,  $n = k$  for an ideal gas

$$P_1 V_1^n = P_2 V_2^n = PV^n$$

$$W = \int_1^2 P dV = \int_1^2 (P_1 V_1^n) V^{-n} dV$$

$$= (P_1 V_1^n) \int_1^2 V^{-n} dV = \frac{(P_1 V_1^n)}{1-n} (V_2^{1-n} - V_1^{1-n}) = \frac{P_2 V_2 - P_1 V_1}{1-n}$$

## 6.6 Joule-Thomson Effect

A **Joule-Thomson effect** or a **process** is the change in temperature which was observed when a liquid or a gas was forced (or expands) through a small opening i.e. valve or a porous plug. This whole process being carried out in an isolated chamber prevented any heat exchange. Founded by Sir James Prescott Joule and Sir William Thomson, this was seen for almost a decent number of gases. But hydrogen, helium and neon seemed to behave differently. They heated up instead of cooling down. This instance was explained by the Inversion temperature i.e. a unique temperature possessed by every gas, below which it cools down on expansion.

**Example** - Diesel engines are used to power large trucks and other heavy equipment. In the cylinders of a diesel engine, air is compressed to very small volumes, raising the temperature to the point where fuel ignites spontaneously when injected into it.

## 6.7 Free Expansion

### Adiabatic free expansion

(a) Expansion of gas in vacuum i.e. at zero external pressure, the system will give zero work.

(b) Thus,  $W_{\text{irr}} = 0$

$$W_{\text{irr}} = 0$$

$$Q = 0$$

$$\Delta E = -W_{\text{irr}} = nC_v(T_2 - T_1)$$

$$\Delta H = nC_p(T_2 - T_1) = 0$$

$$T_1 = T_2$$

Considering an ideal gas, the above case is true. But, the final states of reversible and irreversible adiabatic transformations will be different. Thus,  $\Delta E$  and  $\Delta H$  will be different.

## 6.8 Limitations of First Law of Thermodynamics

Though the first law of thermodynamics gives us the exact equivalence of heat and work, whenever there is a change of heat into work or vice versa, it suffers from the following two limitations:

- (a) No indication is available about the direction in which the change will proceed.
- (b) This law can easily explain the heating of bullet when it strikes a block due to the conversion of kinetic energy into heat, but it fails to explain as to why heat in the block cannot be changed into kinetic energy of bullet and make it fly back from inside of the block.
- (c) Practically it is not possible to convert the heat energy into an equivalent amount of work.

**Illustration 7:** One mole of a monatomic ideal gas is confined in to piston fitted cylinder occupying 10 litre at 300K. On heating the gas up to 400 K the gas also shows expansion and finally occupies 20 litres. Calculate  
(JEE ADVANCED)

- (a) Change in internal energy in L-atm
- (b) Change in heat enthalpy in L-atm

**Sol:** Using ideal gas equation to solve this problem to find out the pressure. Internal energy can be found out using heat content. Now we have calculated pressure and internal energy from these two terms, calculate the heat Enthalpy by the following equation.

$$\Delta H = \Delta U + \Delta(PV)$$

$$P_1 = P_{\text{initial}} = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 300}{10} = 2.463 \text{ atm}$$

$$P_1 - P_{\text{final}} = \frac{nRT}{V} = \frac{1 \times 0.0821 \times 400}{20} = 1.642 \text{ atm} ; \quad \Delta U = nC_v \cdot \Delta T$$

$$\Delta U = 1 \times \frac{3R}{2} \times 100 = 300 \text{ cal}$$

$$\begin{aligned} \therefore \Delta H &= \Delta U + \Delta(PV) \\ &= 12.39 + P_1(V_2 - V_1) + V_2(P_2 - P_1) \\ &= 12.39 + 2.463 \times (20 - 10) + 20(1.642 - 2.463) \\ &= 12.39 + 24.63 - 16.42 = 20.6 \text{ L-atm} \end{aligned}$$

**Illustration 8:** A mole of a monoatomic ideal gas at 1 atm and 273 K is allowed to expand adiabatically against a constant pressure of 0.395 bar until equilibrium is reached.

- (a) What is the final temperature?
- (b) What is the final volume?
- (c) How much work is done by the gas?



(d) What is the change in internal energy?

(JEE MAIN)

**Sol:** Let the initial and final volumes of the gas be  $V_1$  and  $V_2$  m<sup>3</sup> respectively. Given that the initial pressure ( $p_1$ ) is  $1 \times 10^5$  Pa, final pressure ( $p_2$ ) is  $0.395 \times 10^5$  Pa and the initial temperature is 273 K. Let the final Temperature be  $T_2$ .

We have,

$$p_1 V_1 = n_1 R T_1$$

$$V_1 = \frac{1 \times 8.314 \times 273}{1 \times 10^5} = 0.022697 \text{ m}^3$$

For an adiabatic expansion of 1 mole of monoatomic ideal gas against a constant external pressure ( $p_2$ ), work done is given as

$$W = -p_2 (V_2 - V_1) = C_v (T_2 - T_1) = \frac{3R}{2} (T_2 - T_1)$$

$$\text{Or } -0.395 \times 10^5 (V_2 - 0.022697) = (3 \times 8.314) / 2 (T_2 - 273) \quad \dots (i)$$

$$\begin{aligned} \text{Again, } p_2 V_2 &= n R T_2 \\ 0.395 \times 10^5 \times V_2 &= 1 \times 8.314 \times T_2 \quad \dots (ii) \end{aligned}$$

Solving eqns. (i) and (ii) we get,

(a) The final temperature,  $T_2 = 207$  K

(b) The final volume,  $V_2 = 0.043578$  m

**Illustration 9:** A quantity of air is kept in a container having walls which are slightly conducting. The initial temperature and volume are 27° C (equal to the temperature of the surrounding) and 800 cm<sup>3</sup> respectively. Find the rise in the temperature if the gas is compressed to 200 cm<sup>3</sup> (a) in short time (b) in a long time. Take  $\gamma = 1.4$

(JEE MAIN)

**Sol:** By using the following equation calculate the missing terms

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

(a) Since compression of the gas takes place in a short time, the process is adiabatic.

$$\text{Thus, } T_2 V_2^{(\gamma-1)} = T_1 V_1^{\gamma-1} \quad \text{or} \quad T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\gamma-1} = (300 \text{ K}) \times \left[ \frac{800}{200} \right]^{0.4} = 522 \text{ K}$$

$$\text{Rise in temperature} = T_2 - T_1 = 222 \text{ K.}$$

(b) Since compression of the gas takes place for a long time, the process is isothermal.

Thus, the temperature remains equal to the temperature of the surrounding that is 27° C.

The rise in temperature = 0.

**Illustration 10:** A gas undergoes a process such that  $P \propto \frac{1}{T}$ . If the molar heat capacity for this process is  $C = 33.25$  mol-K, find the degree of freedom of the molecules of the gas.

(JEE ADVANCED)

$$\text{Sol: As } P \propto \frac{1}{T} \quad \text{or} \quad PT = \text{constant} \quad \dots (i)$$

We have for one mole of an ideal gas  $PV = RT$

...(ii) From Eq. (i) and (ii)

$$P^2V = \text{constant} \text{ or } PV^{1/2} = K \text{ (say)} \quad \dots \text{ (iii)}$$

From first law of thermodynamics,

$$\Delta Q = \Delta U + \Delta W \quad \text{Or} \quad C\Delta T = C_v\Delta T + \Delta W \quad \text{Or} \quad C = C_v + \frac{\Delta W}{\Delta T} \quad \dots \text{ (iv)}$$

$$\text{Here, } \Delta W = \int P dV = K \int_{V_i}^{V_f} V^{-1/2} dV = \frac{P_f V_f - P_i V_i}{1 - 1/2} = \frac{R(T_f - T_i)}{1/2} = \frac{R\Delta T}{1/2}$$

$$\therefore \frac{\Delta W}{\Delta T} = 2R$$

$$\text{Substituting in Eq. (iv), we have } C = C_v + 2R = \frac{R}{\gamma - 1} + 2R$$

$$\text{Substituting the values, } 33.25 = R \left( \frac{1}{\gamma - 1} + 2 \right) = 8.31 \left( \frac{1}{\gamma - 1} + 2 \right)$$

Solving this we get  $\gamma = 1.5$

$$\text{Now, } \gamma = 1 + \frac{2}{f}$$

$$\text{Or degree of freedom } f = f + \frac{2}{\gamma - 1} = \frac{2}{1.5 - 1} = 4$$

**Illustration 11:** 0.40 mole of a monoatomic gas fills a  $1\text{ dm}^3$  container to a pressure  $1.013 \times 10^6 \text{ Pa}$ . It is expanded reversibly and adiabatically until a pressure of  $1.013 \times 10^5 \text{ Pa}$  is reached. Calculate:

- What is final volume of gas?
- Initial and final temperature of gas.
- Work done by gas during expansion.

**(JEE ADVANCED)**

**Sol:** Volume of a gas can be calculated by using simple formula

$$PV^\gamma = \text{constant of } P_1 V_1^\gamma$$

After calculating volume term, initial and final temperature can be calculated using following equation

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

As volume term and temperature term is known work done can be calculated either by using volume term or by using temperature term as follows:

$$\text{Using temperature term, } w = \frac{nR}{\gamma - 1} [T_2 - T_1]$$

$$\text{Using Volume term, } w = \frac{[P_2 V_2 - P_1 V_1]}{\gamma - 1}$$

$$\text{(a) We have } PV^\gamma = \text{Constant of } P_1 V_1^\gamma$$

$$\therefore 1.013 \times 10^6 \times 1^\gamma = 1.013 \times 10^5 \times V_2^\gamma \quad (\because \gamma = \frac{5}{3})$$

$$\therefore V_2 = 10^{\frac{3}{5}} = 3.98 \text{ dm}^3$$

Also, we have  $PV = nRT$

$$P = 1.013 \times 10^6, \quad V = 1 \text{ dm}^3 = 1 \times 10^{-3} \text{ m}^3, \quad n = 0.40, \quad R = 8.314$$

For initial condition

$$P = 1.013 \times 10^6 \times 10^{-3} = 0.40 \times 8.314 \times T_1$$

$$T_1 = 304.6 \text{ K}$$

also  $TV^{\gamma-1} = \text{constant}$  or  $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$\therefore 304.6 \times (1)^{\gamma-1} = T_2 \times (3.98)^{\gamma-1} \text{ or } T_2 = \frac{304.6}{(3.98)^{2/3}} \quad \left( \because \gamma = \frac{5}{3} \right)$$

(c) Work done during expansion

$$\begin{aligned} \text{(i) Either by : } W &= \frac{nR}{\gamma-1} [T_2 - T_1] \quad (\text{Since } T_2 \text{ and } T_1 \text{ are already evaluated}) \\ &= \frac{0.4 \times 8.314}{\left(\frac{5}{3}-1\right)} \times [121.28 - 304.6] = -923.7 \text{ J} \end{aligned}$$

$$\text{(ii) } W = \frac{[P_2V_2 - P_1V_1]}{\gamma-1} = \frac{1.013 \times 10^6 \times 1 \times 10^{-3} - 1.013 \times 10^5 \times 3.98 \times 10^{-3}}{\left(\frac{5}{3}-1\right)} = -923.7$$

## 7. SECOND LAW OF THERMODYNAMICS

First law showed the equivalence of work and heat.

$$\Delta U = q + W, \oint dU = 0 \text{ for cyclic process}$$

$$\Rightarrow q = -W$$

(Suggests engine can run in a cycle and convert heat into useful work)

But second law puts restriction on useful conversion of  $q$  to  $w$ . It follows from observation of directionality to natural or spontaneous process. It provides a set of principles for determining the direction of spontaneous change and also for determining equilibrium state of a system.

**Definition of Heat Reservoir:** A very large system of uniform  $T$ , which doesn't change regardless of the amount of heat added or withdrawn. It is also called 'heat bath'. Real System can come close to this idealization.

### Different statements of the Second Law

**Kelvin:** It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work at the same in the surroundings without transferring same heat to a colder reservoir.

**Clausius:** It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfers it to a hot reservoir at the same without converting some work into heat.

**Alternative Clausius statement:** All spontaneous processes are irreversible. (e.g. heat flows from hot to cold spontaneously and irreversibly)

### Mathematical statement:

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \text{ and } \oint \frac{dq_{\text{irrev}}}{T} < 0$$

$$\int \frac{dq_{\text{rev}}}{T} \text{ is a state function} \rightarrow \int dS \rightarrow dS = \oint \frac{dq_{\text{rev}}}{T}$$

### S = Entropy

$$\oint ds = 0 \rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{dq_{\text{rev}}}{T} > \int_1^2 \frac{dq_{\text{irrev}}}{T}$$

$$\text{for cycle } [1] \xrightarrow{\text{irrev}} [2] \xrightarrow{\text{rev}} [1]$$

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} + \int_2^1 \frac{dq_{\text{rev}}}{T} = \oint \frac{dq_{\text{irrev}}}{T} < 0$$

$$\int_1^2 \frac{dq_{\text{irrev}}}{T} - \Delta S < 0 \Rightarrow \Delta S > \int_1^2 \frac{dq_{\text{irrev}}}{T}$$

## 7.1 The Carnot Cycle – A Typical Heat Engine

All paths are reversible

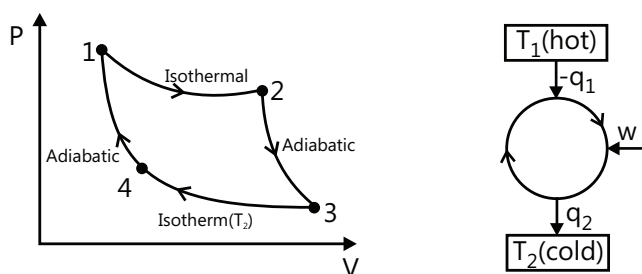


Figure 4.6: Carnot cycle

$$1 \rightarrow 2 \text{ isothermal expansion at } T_1 \text{ (hot)} \quad U = q_1 - W_1$$

$$2 \rightarrow 3 \text{ adiabatic expansion (} q = 0 \text{)} \quad U = W_1'$$

$$3 \rightarrow 4 \text{ isothermal compression at } T_2 \text{ (cold)} \quad U = q_2 + W_2$$

$$4 \rightarrow 1 \text{ adiabatic compression (} q = 0 \text{)} \quad U = W_2'$$

$$\text{Efficiency} = \frac{\text{Work output to surroundings}}{\text{Heat in at } T_1 \text{ (hot)}} = \frac{-(W_1 + W_1' + W_2 + W_2')}{q_1}$$

$$1^{\text{st}} \text{ Law} \Rightarrow \oint dU = 0 \Rightarrow q_1 + q_2 = -(W_1 + W_1' + W_2 + W_2')$$

$$\text{Efficiency} \equiv \varepsilon = \frac{q_1 + q_2}{q_1} = 1 + \frac{q_2}{q_1}$$

$$\text{Kelvin : } q_2 < 0 \rightarrow \text{Efficiency} \equiv \varepsilon < 1 \text{ (< 100\%)} \quad -W = q_1 \varepsilon = \text{Work output}$$

### Carnot cycle for an ideal gas

If cycle were run in reverse, then  $q_1 < 0$ ,  $q_2 < 0$ ,  $w > 0$ . It's a refrigerator.

$$1 \rightarrow 2 \quad \Delta U = 0: \quad q_1 = -W_1 = \int_1^2 p dV = RT_1 \ln \left( \frac{V_2}{V_1} \right)$$

$$2 \rightarrow 3 \quad q = 0: \quad W_2' = C_v(T_2 - T_1)$$

$$\text{Rev adiabatic} \Rightarrow \left( \frac{T_2}{T_1} \right) = \left( \frac{V_2}{V_3} \right)^{\gamma-1}$$

$$3 \rightarrow 4 \quad \Delta U = 0: \quad q_2 = -w_2 = \int_3^4 p dV = RT_2 \ln \left( \frac{V_4}{V_3} \right)$$

$$4 \rightarrow 1 \quad q = 0: \quad W_2' = C_v(T_1 - T_2)$$

$$\text{Rev adiabatic} \Rightarrow \left(\frac{T_1}{T_2}\right) = \left(\frac{V_4}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1}$$

$$\frac{q_2}{q_1} = \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)} = \left(\frac{-T_2}{T_1}\right)$$

$$\left(\frac{V_1}{V_4}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \Rightarrow \left(\frac{V_4}{V_3}\right) = \left(\frac{V_1}{V_2}\right) \Rightarrow \frac{-q_2}{q_1} = \frac{T_2}{T_1}$$

$$\text{Or} \quad \left(\frac{q_1}{T_1}\right) + \left(\frac{q_2}{T_2}\right) = 0 \Rightarrow \oint \frac{dq_{\text{rev}}}{T} = 0$$

Links heat engines to mathematical statement

$$\text{Efficiency } \varepsilon = 1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1} \rightarrow 100\% \text{ as } T_2 \rightarrow 0 \text{ K}$$

## 7.2 Entropy

Carnot cycle for a reversible ideal gas:

$$\text{Efficiency, } \varepsilon = \frac{-W}{q_{\text{rev}}} = 1 + \frac{q_2^{\text{rev}}}{q_1^{\text{rev}}} = 1 - \frac{T_2}{T_1} \Rightarrow \frac{q_2}{T_1} + \frac{q_2}{T_2} = 0 \Rightarrow \oint \frac{dq_{\text{rev}}}{T} = 0$$

The efficiency of any reversible engine has to be the same as the Carnot cycle:

$$\varepsilon = \frac{(-W)}{q_1} \quad \varepsilon' = \frac{(-W')}{q'_1} \quad \text{Assume } \varepsilon > \varepsilon'$$

(Left engine is less efficient than Carnot cycle)

Since the engine is reversible. We can run it backwards. Use the work  $(-W')$  out of the Carnot engine as work input  $(W)$  to run the left engine backwards.

Total work out = 0  $(-W' = W > 0)$

$$\text{But } \varepsilon' > \varepsilon \Rightarrow \frac{-W'}{q'_1} > \frac{-W}{q_1} \Rightarrow \frac{-W}{q'_1} > \frac{-W}{q_1} - \frac{W}{-q_1}$$

This contradicts the 2<sup>nd</sup> law (Clausius). This says that we have a net flow of heat into the hot reservoir. But no work is being done!

$\therefore$  The efficiency of any reversible engine is  $\varepsilon = 1 - T_1/T_2$

We can approach arbitrarily closely to any cyclic process using a series of only adiabats and isotherms.

$\therefore$  For any reversible cycle,  $\oint \frac{dq_{\text{rev}}}{T} = 0$

This defines Entropy a function of state

$$dS = \frac{\hat{d}q_{\text{rev}}}{T} \Rightarrow \Delta S = S_2 - S_1 = \int_1^2 \frac{\hat{d}q_{\text{rev}}}{T}$$

## PLANCESS CONCEPTS

Entropy is a state function, but to calculate  $\Delta S$  requires a reversible path.

An irreversible Carnot (or any other) cycle is less efficient than a reversible one

1  $\rightarrow$  2

$$(-W)_{\text{irrev}} < (-W)_{\text{rev}} \Rightarrow W_{\text{irrev}} > W_{\text{rev}}$$

$$\Delta U = q_{\text{irrev}} + W_{\text{irrev}} = q_{\text{rev}} + W_{\text{rev}}$$

$$\therefore q_{\text{irrev}} < q_{\text{rev}}$$

An irreversible isothermal expansion requires less heat than a reversible one.

$$S_{\text{irrev}} = 1 + \frac{q_2^{\text{rev}}}{q_1^{\text{irrev}}} < 1 + \frac{q_2^{\text{rev}}}{q_1^{\text{rev}}} = S_{\text{rev}} \quad (q_2 < 0)$$

$$\text{also } \frac{dq_{\text{irrev}}}{T} < \frac{dq_{\text{rev}}}{T} \Rightarrow \oint \frac{dq_{\text{irrev}}}{T} < 0$$

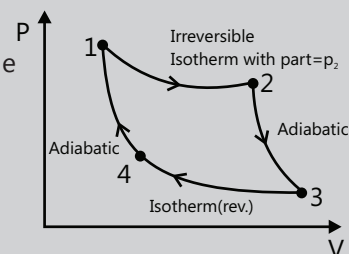


Figure 4.7: (a) Process Plot

Shrikant Nagori JEE 2009 AIR 30

The above equation (Note of Plancess Concept) leads to Clausius inequality

$$\oint \frac{dq}{T} \leq 0 \quad \text{contains} \quad \begin{cases} \frac{dq_{\text{rev}}}{T} = 0 \\ \frac{dq_{\text{irrev}}}{T} < 0 \end{cases}$$

Note that the entropy of an isolated system never decreases

Consider the system taken from 1 to 2, irreversibly as well as reversibly:

(i) The system is isolated and irreversibly (spontaneously) changes from 1 to 2.

(ii) The system is brought into contact with a heat reservoir and reversibly brought back from 2 to 1.

Path (A)  $q_{\text{rev}} = 0$  (isolated)

$$\text{Clausius } \oint \frac{dq}{T} \leq 0 \Rightarrow \int_1^2 \frac{dq_{\text{rev}}}{T} + \int_2^1 \frac{dq_{\text{rev}}}{T} \leq 0; \quad \int_2^1 \frac{dq_{\text{rev}}}{T} = S_1 - S_2 = \Delta S \leq 0$$

$$\Delta S = S_2 - S_1 \geq 0$$

This gives the direction of spontaneous change!

**Irreversible** Consider the universe as an isolated system containing our initial system and its surroundings.

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} > 0 \text{ therefore}$$

$$\Delta S_{\text{surr}} > -\Delta S_{\text{system}}$$

**Reversible**  $\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}} = 0$  therefore,

$$\Delta S_{\text{surr}} = -\Delta S_{\text{system}}$$

**Examples of a spontaneous process:**

(a) Connect two metal blocks thermally in an isolated system ( $\Delta U = 0$ )

Initially  $T_1 \neq T_2$

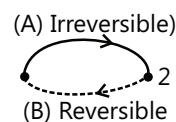


Figure 4.2: Cyclic process

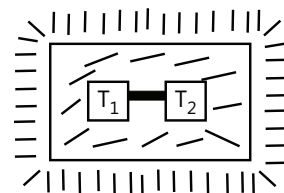


Figure 4.7: Spontaneity

$$dS = dS_1 - dS_2 - \frac{dq_2}{T_1} - \frac{dq_2}{T_1} - ds \frac{(T_2 - T_1)}{T_1 T_2} (dq_1 - dq_2)$$

$dS > 0$  for spontaneous process

$$\Rightarrow \quad \text{if } \left. \begin{array}{l} T_2 > T_1 \Rightarrow dq_1 > 0 \\ T_2 < T_1 \Rightarrow dq < 0 \end{array} \right\} \begin{array}{l} \text{in both cases heat flows} \\ \text{from hot to cold as expected} \end{array}$$

### (b) Joule expansion with on ideal gas

1 mol gas  $(2V, T) = 1 \text{ mol gas } (V, T)$

$$\Delta S_{\text{backwards}} = \int \frac{\hat{d}q_{\text{rev}}}{T} = - \int \frac{dW}{T} = \int_{2V}^V \frac{Rdv}{V} = R \ln \frac{1}{2}$$

Therefore,  $\Delta S - R \ln 2 > 0$  (Spontaneous)

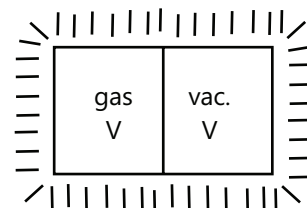


Figure 4.7: Joule expansion

### PLANCESS CONCEPTS

- Entropy of a system increases when the temperature of system increases.
- Entropy of a system also increases during isothermal expansion
- Standard molar entropy is the molar entropy of pure substances at 25°C and 1 bar pressure.
- Standard molar entropies increase as the complexity of a substance increases.
- The standard molar entropies of gases are higher than those of comparable solids and liquids at the same temperature.
- $\Delta S \geq 0$  for any process in an isolated system.
- At thermodynamic equilibrium  $\Delta S_{\text{total}} = 0$ .

Vaibhav Krishan (JEE 2009 AIR 22)

### Entropy change for an ideal gas:

In going from initial to final state the entropy changes,  $\Delta S$  for an ideal gas is given by the following relations,

(a) When  $T$  and  $V$  are two variables

$$\Delta S = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \text{ Assuming } C_v \text{ is constant}$$

(b) When  $T$  and  $P$  are two variables,

$$\Delta S = nC_p \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1} \text{ Assuming } C_p \text{ is constant}$$

(i) Thus for an Isothermal process ( $T$  constant)

$$\Delta S = nC_p \ln \frac{V_2}{V_1} \text{ or } = -nR \ln \frac{p_2}{p_1}$$

(ii) For isobaric process ( $p$  constant)

$$\Delta S = nC_p \ln \frac{T_2}{T_1} \text{ or } = nC_p \ln \frac{V_2}{V_1}$$

(iii) For isochoric process ( $V$  constant)

$$\Delta S = nC_v \ln \frac{T_2}{T_1} \text{ or } = nC_v \ln \frac{p_2}{p_1}$$

(iv) Entropy change during adiabatic expansion: In such process  $q=0$  at all stages. Hence  $\Delta S=0$ . Thus, reversible adiabatic processes are called isoentropic process.

## 7.2.2 Some Salient Features about Entropy Change

(a) For a reaction, entropy change  $\Delta S$  is given by

$$\Delta S = \sum S_{\text{product}} - \sum S_{\text{reactants}}$$

(b) The units of entropy change are  $\text{cal deg}^{-1} \text{mol}^{-1}$  and in S.I. units  $\text{J K}^{-1} \text{mol}^{-1}$

(c) At absolute zero temperature, i.e., zero Kelvin, the entropy of a pure crystal is zero. This is also referred as third law of thermodynamics.

**Note:** The entropies of  $\text{CO}$ ,  $\text{NO}$ ,  $\text{NO}_2$ , glassy solids, solid chlorine, etc., are not zero at absolute zero. These are exceptions to third law of thermodynamics.

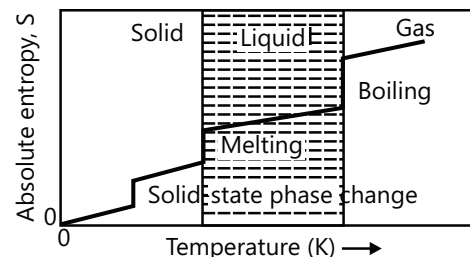


Figure 4.7: Plot of  $S$  vs  $T$

### PLANCESS CONCEPTS

**Misconception:** Efficiency is not equal to  $1 - T_1/T_2$  for all heat engines. It is only applicable to Carnot cycle. Maximum efficiency occurs only in Carnot's heat engine. But it is only a theoretical heat engine and practically such an engine is not possible because it involves reversible processes which take infinite time for completion of one cycle.

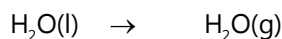
Vaibhav Krishan (JEE 2009 AIR 22)

**Illustration 12:** The enthalpy change, for the transition of liquid water to steam.  $\Delta H_{\text{vapour}}$  is  $40.8 \text{ kJ mol}^{-1}$  at  $373 \text{ K}$ . Calculate entropy change for the process. **(JEE MAIN)**

**Sol:** Here enthalpy and temperature is given, so entropy term can be calculated as follows:

$$\Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T}$$

The transition under consideration is :



$$\text{We know that, } \Delta S_{\text{vapour}} = \frac{\Delta H_{\text{vapour}}}{T}$$

$$\text{Given, } \Delta H_{\text{vapour}} = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 1000 \text{ J mol}^{-1}; \quad T = 373 \text{ K}$$

$$\text{Thus, } \Delta S_{\text{vapour}} = \frac{40.8 \times 1000}{373} = 109.38 \text{ J K}^{-1} \text{mol}^{-1}$$

**Illustration 13:** Heat supplied to a Carnot engine is  $2 \times 10^3 \text{ J}$ . How much useful work can be made by the engine working between  $290$  and  $373 \text{ K}$ ? **(JEE MAIN)**

**Sol:** Using the following equation calculate the work done



$$\eta = \frac{W_{\text{total}}}{q_2} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{W_{\text{total}}}{q_2} = \frac{T_2 - T_1}{T_2} \quad \text{or} \quad W = q_2 \frac{T_2 - T_1}{T_2} = 2 \times 10^3 \times \frac{373 - 290}{373} = 445 \text{ J}$$

**Illustration 14:** Calculation entropy change when 10 moles of an idea gas expands reversibly and isothermally from an initial volume of 10 litre to 100 litre at 300K. **(JEE MAIN)**

**Sol:** Here we are provided with initial volume and final volume so we have to use the following equation in order to calculate entropy term.

$$\Delta S = 2.303n R \log\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = 2.303n R \log\left(\frac{V_2}{V_1}\right) = 2.303 \times 10 \times 8.314 \log\left(\frac{100}{10}\right) = 191.24 \text{ J K}^{-1}$$

**Illustration 15:** Why would you expect a decrease in entropy as a gas condenses into liquid? Compare it with entropy decrease when a liquid sample is converted into solid? Or why is increase in entropy of the system greater for vaporization of a substance than for its melting? **(JEE MAIN)**

**Sol:** Gaseous molecules have free motion whereas liquid molecules have restricted motion or the entropy of gaseous molecules (more disorder) is higher than liquid molecules (relatively more ordered). Similarly, solid state has highly ordered arrangement thus possesses lowest entropy.

$$\Delta S_{\text{condensation}} = S_{(l)} - S_{(g)} (\Delta S = -ve; \text{ a decrease}); \Delta S_{\text{freezing}} = S_{(s)} - S_{(l)} (\Delta S = -ve; \text{ a decrease})$$

$\Delta S_{\text{condensation}}$  Is much higher than  $\Delta S_{\text{freezing}}$  for a substance as well as  $\Delta S_{\text{condensation}}$  is almost constant for different liquids because  $S_{(g)} \gg S_{(l)} \gg S_{(s)}$ .

**Illustration 16:** Determine the standard entropy change for the reaction given below.  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$  at 300K. If standard entropies of  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are 126.6, 201.20 and 68.0  $\text{J K}^{-1} \text{ mol}^{-1}$  respectively. **(JEE ADVANCED)**

**Sol:** Here we are provided with standard entropies of reactant and products so entropy of reaction can be calculated using following equation

$$\Delta S_{\text{Reaction}} = \sum S^{\circ}_{\text{product}} - \sum S^{\circ}_{\text{Reaction}}$$

$$\Delta S_{\text{Reaction}} = \sum S^{\circ}_{\text{product}} - \sum S^{\circ}_{\text{Reaction}}$$

$$= 2 \times S^{\circ}_{\text{H}_2\text{O}} - [2 \times S^{\circ}_{\text{H}_2} + S^{\circ}_{\text{O}_2}] = 2 \times 68 - [2 \times 126.6 + 201.20]$$

$$\Delta S = -318.4 \text{ J K}^{-1} \text{ mol}^{-1}$$

## 8. FUNDAMENTAL EQUATIONS, ABSOLUTE ENTROPY AND THE THIRD LAW

### 8.1 Fundamental Equations

From  $dU = Tds - PdV$

$$\Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T; \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

We can write similar equations for enthalpy

$$H = U + PV \Rightarrow dH = dU + d(PV) = dU + PdV + VdP$$

↖ inserting  $dU =$

$$\Rightarrow dH = TdS + VdP$$

The natural variables for  $H$  are then  $S$  and  $p$ .

$$\text{From } dH = TdS - VdP$$

$$\Rightarrow \left\{ \frac{\partial H}{\partial S} \right\}_p = T; \left\{ \frac{\partial H}{\partial P} \right\}_S = V$$

We can use these equations to find how  $S$  depends on  $T$ .

$$\text{From } dU = TdS + PdV$$

$$\Rightarrow \left\{ \frac{\partial S}{\partial U} \right\}_V = \frac{1}{T}; \left\{ \frac{\partial U}{\partial T} \right\}_V = C_V$$

$$\text{From } dH = TdS + VdP$$

$$\Rightarrow \left\{ \frac{\partial S}{\partial H} \right\}_p = \frac{1}{T}; \left\{ \frac{\partial H}{\partial T} \right\}_p = C_p$$

## 8.2 Absolute Entropy

Absolute entropy of an ideal gas

$$\bar{S}(P, T) = \bar{S}^0(T) - R \ln P \quad (P \text{ in bar})$$

$$\text{Then using } \left( \frac{\partial \bar{S}}{\partial T} \right)_p = \frac{C_p}{T} \text{ we should be able to get } \bar{S}^0(T)$$

Consider the following sequence of processes for the substance A

$$A(S, 0K, 1bar) \rightarrow A(S, T_m, 1bar) \rightarrow A(l, T_m, 1bar) \rightarrow (l, T_b, 1bar) \rightarrow (g, T_b, 1bar) \rightarrow (g, T, 1bar)$$

$$\bar{S}(T, 1bar) = \bar{S}^0(0K) + \int_0^{T_m} \frac{\bar{C}_p(s)}{T} dT + \frac{\Delta \bar{H}_{fus}}{T_m} + \int_{T_m}^{T_b} \frac{\bar{C}_p(l)}{T} dT + \frac{\Delta \bar{H}_{vapo}}{T_b} + \int_{T_b}^T \frac{\bar{C}_p(g)}{T} dT$$

Since  $\Delta S^0$  is positive for each of these processes. The entropy must have its smallest possible value at 0 K. If we take  $\bar{S}^0(0K) = 0$  for every pure substance in its crystalline solid state, then we could calculate the entropy at any other temperature. This leads us to the Third law!

## 8.3 Third Law of Thermodynamics

**Statement:** The entropy of all perfectly crystalline solids is zero at the absolute zero temperature. Since entropy is a measure of disorder, it can be interpreted that at absolute zero, a perfectly crystalline solid has a perfect order of its constituent particles.

Application of the third law of thermodynamics is that it helps in the calculation of absolute entropies of the substance at any temperature  $T$ .

$$S_T = 2.303 C_p \int_0^T \log T$$

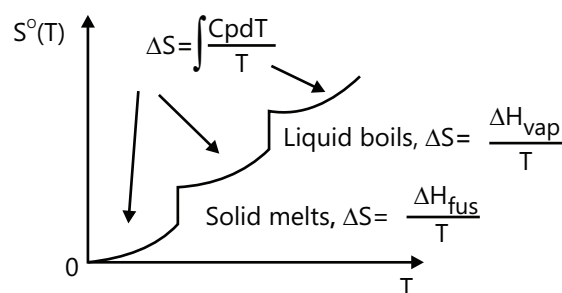


Figure 4. 8: Entropy plots for various processes

**Limitations of the Law:**

- (a) Glassy solids even at 0K has entropy greater than zero.  
 (b) Solids having mixtures of isotopes do not have zero entropy at 0 K.

**9. CRITERIA FOR SPONTANEITY AND GIBBS FREE ENERGY**

Gibbs free energy is defined as the energy available in the system for conversion into useful work.

At constant temperature and pressure.

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

- If  $(\Delta G)_{T,P} < 0$       Process is irreversible (spontaneous)  
 $(\Delta G)_{T,P} < 0$       Process is irreversible  
 $(\Delta G)_{T,P} < 0$       Process is impossible (non-spontaneous)

The use of Gibbs free energy has the advantage that it refers to the system only (and not spontaneous).

To summarize the spontaneity of chemical reaction is decided by two factors taken together.

- (i) The enthalpy factor    and    (ii) the entropy factor

The equation  $\Delta G = \Delta H - T\Delta S$  takes both the factors into consideration.

$(\Delta G_r)_{T,P}$	$(\Delta S_r)_{T,P}$	$(\Delta G_r)_{T,P}$	Remark
-ve	+ve	Always -ve	Reaction is spontaneous
+ve	-ve	Always +ve	Reaction is non-spontaneous
+ve	+ve	At low temperature, $\Delta G = +ve$	Non spontaneous
		At high temperature, $\Delta G = -ve$	Spontaneous
-ve	-ve	At low temperature, $\Delta G = -ve$	Spontaneous
		At high temperature, $\Delta G = +ve$	Non spontaneous

Variation of Gibb's function (G) with temperature and pressure:

$$G = H - TS = U + PV - TS; dG = dU + PdV - TdS + VdP - SdT; dG = VdP - SdT$$

At constant temperature,  $dG = VdP$       or       $\left(\frac{\partial G}{\partial P}\right)_T = V$

At constant pressure,  $dG = SdT$        $\Rightarrow$        $\left(\frac{\partial G}{\partial T}\right)_P = -S$

**Illustration 17:** Calculate the boiling point of bromine from the following data:

$\Delta H^\circ$  and  $S^\circ$  value of  $\text{Br}_2(l) \rightarrow \text{Br}_2(g)$  are 30.91 KJ/ mole and 93.2 J/mol. K respectively. Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature. **(JEE ADVANCED)**

**Sol:** We are provided with standard enthalpy and standard entropy so temperature can be calculated by following equation

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

As entropy and enthalpy do not vary with temperature,  $\Delta G$  becomes zero. Consider the process:  $\text{Br}_2(l) \rightarrow \text{Br}_2(g)$ . The b. p. of a liquid is the temperature which the liquid and the pure gas coexist in equilibrium at 1 atm.

$\therefore \Delta G = 0$

As it is given that  $\Delta H$  and  $\Delta S$  do not change with temperature

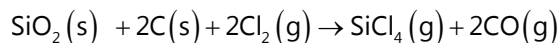
$$\Delta H = \Delta H^0 = 30.91 \text{ KJ}; \Delta S = \Delta S^0 = 93.2 \text{ J/K} = 0.0932 \text{ KJ/K}$$

We have,  $\Delta G = \Delta H - T\Delta S = 0$

$$\therefore T = \frac{\Delta H}{\Delta S} = \frac{30.91}{0.0932} = 331.6 \text{ K}$$

This is the temperature at which the system is in equilibrium, that is, the b. p. of bromine.

**Illustration 18:** Estimate the temperature range for which the following standard reaction is product favoured



(JEE ADVANCED)

$$\Delta H^0 = +32.9 \text{ KJ/mole and } \Delta S^0 = 226.5 \text{ J/mole.K}$$

**Sol:** In this problem, the factor  $\Delta S^0$  being positive, is favourable to spontaneity, whereas the factor  $\Delta H^0$  being positive is unfavourable. Thus the reaction becomes product-favoured above some temperature. We can set  $\Delta G^0$  equal to zero in the equation:  $\Delta G^0 = \Delta H^0 - T\Delta S^0$  and solve for the temperature at which the reaction is at equilibrium and above which the reaction becomes product-favoured as then  $\Delta G^0$  becomes negative.

$$T = \frac{\Delta H^0}{\Delta S^0} = \frac{+32.9}{+0.2265} = 145.25 \text{ K}$$

**Illustration 19:** For the water gas reaction.  $\text{C}(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + \text{H}_2(g)$ . The standard Gibbs free energy of reaction (at 1000K) is -8.1 KJ/mol. Calculate its equilibrium constant.

(JEE ADVANCED)

**Sol:** As standard free energy is given equilibrium constant can be calculated using the equation

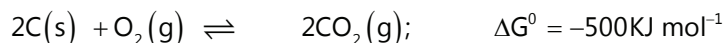
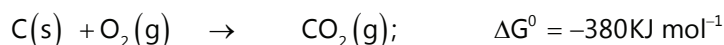
$$K = \text{antilog} \left( \frac{-\Delta G^0}{2.303RT} \right) \quad \dots (i)$$

$$\text{We know that, } K = \text{antilog} \left( \frac{-\Delta G^0}{2.303RT} \right) \quad \dots (ii)$$

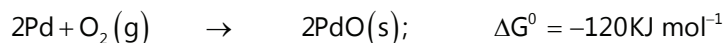
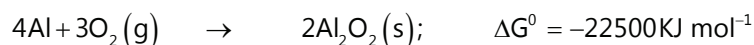
$$\text{Given that, } \Delta G^0 = -8.1 \text{ kJ/mol; } R = 8.314 \times 10^{-3} \text{ KJ K}^{-1} \text{ mol}^{-1}; T = 1000 \text{ K}$$

$$\text{Substituting these value in eq. (i), we get } K = \text{antilog} \left[ \frac{-(-8.1)}{2.030 \times 8.314 \times 10^{-3} \times 1000} \right] = 2.65$$

**Illustration 20:** The standard Gibbs free energies for the reactions at 1773 K are given below:

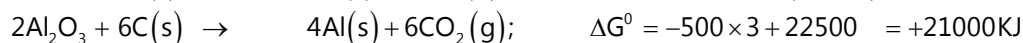
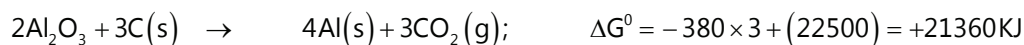


Discuss the possibility of reducing  $\text{Al}_2\text{O}_3$  and  $\text{PdO}$  with carbon at this temperature.



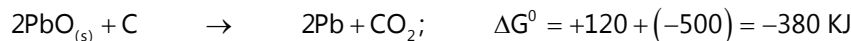
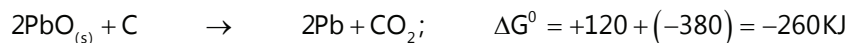
(JEE ADVANCED)

**Sol:** Let us consider the reduction of  $\text{Al}_2\text{O}_3$  by carbon

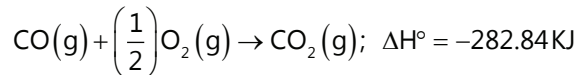


Positive value of  $\Delta G^0$  show that the reduction of  $\text{Al}_2\text{O}_3$  is not possible by any of the above methods.

Now, let us consider the reduction of PdO.



**Illustration 21:** Calculate  $\Delta G^\circ$  for the following reaction



Given,  $S^\circ_{\text{CO}_2} = 213.8 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $S^\circ_{\text{CO(g)}} = 197.9 \text{ JK}^{-1}\text{mol}^{-1}$ ,  $S^\circ_{\text{O}_2} = 205.0 \text{ JK}^{-1}\text{mol}^{-1}$ .

**(JEE ADVANCED)**

**Sol:** Here we are provided with standard entropies of reactant and products so entropy of reaction can be calculated using following equation

$$\Delta S_{\text{Reaction}} = \sum S^\circ_{\text{product}} - \sum S^\circ_{\text{Reaction}}$$

$$\Delta S^\circ = \sum S^\circ_{(\text{products})} - \sum S^\circ_{(\text{reactants})}$$

$$= [S^\circ_{\text{CO}_2}] - \left[ S^\circ_{\text{CO}} + \frac{1}{2} S^\circ_{\text{O}_2} \right] = 213.8 - \left[ 197.9 + \frac{1}{2} 205 \right] = -86.6 \text{ kJ}$$

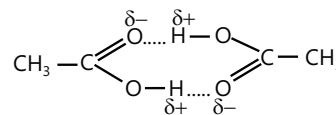
According to Gibbs-Helmholtz equation,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -282.84 - 298 \times (-86.6 \times 10^{-3}) = -282.84 + 25.807 = -257.033 \text{ kJ}$$

**Illustration 22:** Acetic acid  $\text{CH}_3\text{COOH}$  can form a dimer  $(\text{CH}_3\text{COOH})_2$  in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5 kJ per mole of dimer. If at  $25^\circ\text{C}$ , the equilibrium constant for the dimerization is  $1.3 \times 10^3$ . Calculate  $\Delta S^\circ$  for the reaction.  $2\text{CH}_3\text{COOH(g)} \rightarrow (\text{CH}_3\text{COOH})_2(\text{g})$

**(JEE MAIN)**

**Sol:** We are provided with equilibrium constant and we have to calculate entropy term. Entropy term cannot be calculated directly, first we have to find out free energy change using equilibrium constant and then from free energy calculate the entropy term.



$$\Delta G^\circ = -2.303RT \log K$$

$$= -2.303 \times 8.314 \times 298 \log (1.3 \times 10^3) = -17767.688 \text{ J} = -17.767 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ; \quad -17.767 = -66.5 - 298 \times \Delta S^\circ; \quad \Delta S^\circ = \frac{-66.5 + 17.767}{298} = -0.163 \text{ kJ}$$

## THERMOCHEMISTRY

Thermochemistry is the branch of chemistry which deals with the heat changes in a chemical reaction.

### 10. THERMOCHEMICAL EQUATIONS

A Thermochemical equation presents a chemical reaction stating the amount of heat released or absorbed during the process. A thermochemical equation gives:-

- The physical state or the phase of the reactants and the products using the symbols s, l, g or aq(aqueous).
- The allotropic form (if any) of the reactant.

- (c) It tells whether a reaction proceeds with the evolution of heat or with the absorption of heat, i.e. heat change involved in the system. Heat changes of the system, heat of reactant and product are represented by  $\Delta H$ ,  $H_R$  and  $H_p$  respectively.

$$\Delta H = H_p - H_R$$

Mathematically,

For Exothermic reactions,  $H_R > H_p$  or  $\Delta H$  is negative.

For endothermic reactions,  $H_p > H_R$  or  $\Delta H$  is positive.

## 11. HEAT OF REACTION AND KIRCHOFF'S EQUATION

### Relation Between $\Delta H$ and $\Delta E$

$$\Delta H = \Delta E + P\Delta V \quad \Delta H = \Delta E + \Delta n_{(g)}RT$$

Where  $\Delta n_{(g)}$  = Number of moles of gaseous products-number of moles of gaseous reactants

Thus, is  $\Delta n_{(g)} = 0$ ,  $\Delta H = \Delta E$ ;  $\Delta n_{(g)} > 1$ ,  $\Delta H < \Delta E$ ;  $\Delta n_{(g)} < 1$ ,  $\Delta H < \Delta E$

For reactions involving only solids and liquids  $\Delta H = \Delta E$ ;  $\Delta H = 22.0$  kcal

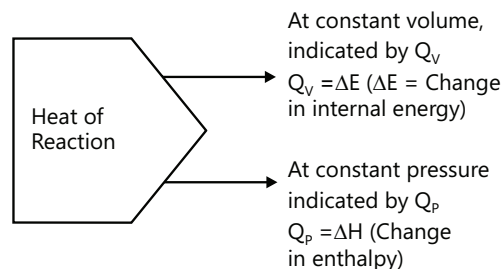


Figure 4.8: Heat of reaction

### Factors Affecting Heat of Reaction

Among the various factors affecting heat of reaction, viz amount of reactants, physical state of reactants and products, pressure and temperature, temperature is the most important. The variation of heat of reaction with temperature is given by.

### Kirchoff's Equations

- (a) For heat of reactions at constant pressure,  $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

- (b) For heat of reactions at constant volume,  $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$

Where  $\Delta H_2$  = Heat of reaction at temperature  $T_2$  at constant pressure

$\Delta H_1$  = Heat of reaction at temperature  $T_1$  at constant pressure

$\Delta E_2$  = Heat of reaction at temperature  $T_2$  at constant pressure

$\Delta E_1$  = Heat of reaction at temperature  $T_1$  at constant pressure

$\Delta C_p$  = Difference of heat capacities of products and reactants at constant pressure

$\Delta C_v$  = Difference of heat capacities of products and reactants at constant volume.

## 12. ENTHALPIES FOR VARIOUS PROCESSES

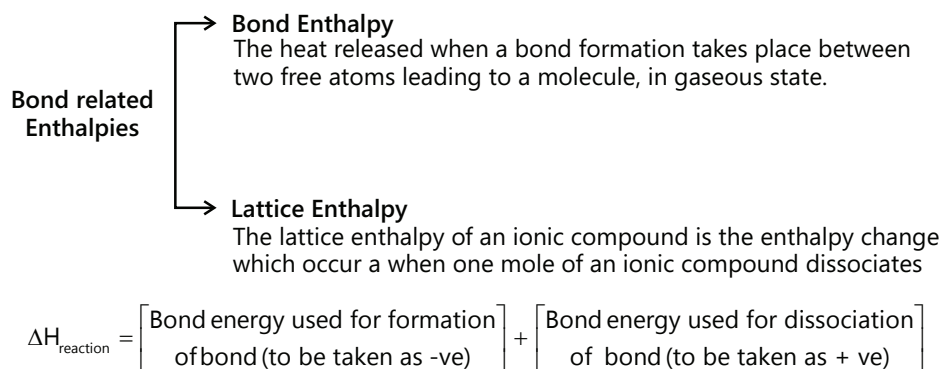
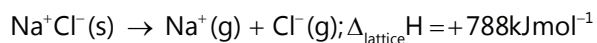


Figure 4.9: Enthalpies for various processes

$\Delta H_{\text{reaction}} = BE_{(R)} - BE_{(P)}$ , taking Bond Energies as +ve values.



#### Points to be noted:

- (a) The bond enthalpy of diatomic molecules like  $\text{H}_2$ ,  $\text{Cl}_2$ ,  $\text{O}_2$  etc. may be defined as the enthalpy change (always positive) when one mole of covalent bonds of a gaseous covalent substance is broken to form products in the gas phase, under conditions of constant pressure and temperature.

For example.  $\text{Cl}_2(g) \rightarrow 2\text{Cl}(g); \Delta H_{\text{Cl-Cl}} = +242 \text{ kJ mol}^{-1}$ ,  $\text{O}_2(g) \rightarrow 2\text{O}(g); \Delta H_{\text{O-O}} = +428 \text{ kJ mol}^{-1}$

- (b) In case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. In such case, mean bond enthalpy is used. Mean bond enthalpy may be defined as the average enthalpy change to dissociate a particular type of bond in the compounds.

- (c) In gas phase reaction, the standard enthalpy of reaction  $\Delta_r H^\circ$  is related with the bond enthalpies of reactants and products as  $\Delta_r H^\circ = \sum \text{bond enthalpies (reactants)} - \sum \text{bond enthalpies (products)}$

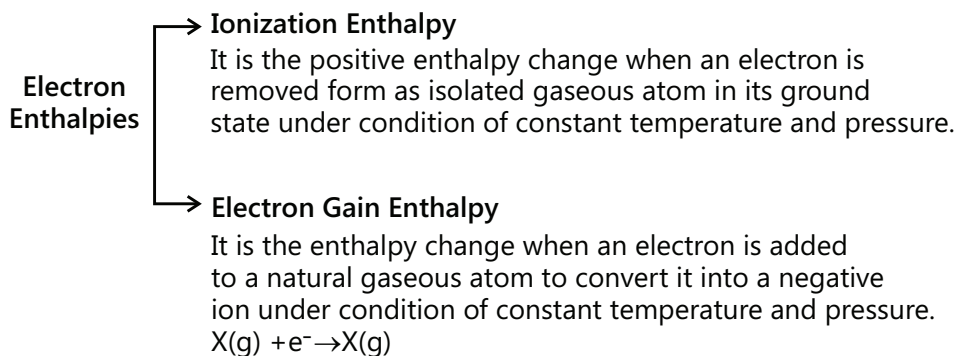


Figure 4.9: Types of Electron Enthalpy

## 12.1 Enthalpy of atomization ( $\Delta_a H$ )

It is the enthalpy change (always positive) when one mole of a substance is completely dissociated into atoms in the gaseous state, under constant pressure and temperature condition

For example,  $\text{H}_2(g) \rightarrow 2\text{H}(g); \Delta_f H = 435.0 \text{ kJ mol}^{-1}$ ,  $\text{CH}_4(g) \rightarrow \text{C}(g) + 4\text{H}(g); \Delta_f H = 1665 \text{ kJ mol}^{-1}$

## 12.2 Heat/Enthalpy of Vaporization

In a system, a liquid is boiled and some of the molecules are converted to gas. The Heat of Vaporization corresponds to the heat that the liquid lost when the molecules phase changed. The Enthalpy of Vaporization, conversely, is the amount of heat applied to the system to boil the liquid. As a result, the temperature of the liquid remained constant, while the given heat was absorbed to convert the molecules.  $\Delta H_{\text{vap}} = \text{Heat of Vaporization}$

## 12.3 Standard Enthalpy of Formation

The definition of the standard enthalpy of formation is the change in enthalpy when one mole of a substance, in the standard state of 1 atm of pressure and temperature of 298.15 K, is formed from its pure elements under the same conditions.

For most chemistry problems involving standard enthalpies of formation, you will need the equation for the standard enthalpy change of formation:

$$\Delta H_f \text{ reaction} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{Reactants})$$

Although this equation looks complicated, it essentially states that the standard enthalpy change of formation is equal to the **sum of the standard enthalpies of formation of the products** subtracted by the **sum of the standard enthalpies of formation of the reactants**.

There is an exception to  $\Delta H_f^\circ$  values. In general practice, reference state, i.e.,  $\Delta H_f^\circ$  of P is taken to be white P despite that this allotropic form not being the most stable form but simply the most reproducible form.

### PLANCESS CONCEPTS

If we have a simple chemical equation with the variables A, B and C representing different compounds:  
 $A + B \rightleftharpoons C$

and we have the standard enthalpy of formation values as such:

$$\Delta H_f^\circ [A] = 433 \text{ KJ/mol}$$

$$\Delta H_f^\circ [B] = -256 \text{ KJ/mol}$$

$$\Delta H_f^\circ [C] = 523 \text{ KJ/mol}$$

The equation for the standard enthalpy change of formation is as follows:

$$\Delta H_{\text{reaction}}^\circ = \Delta H_f^\circ [C] - (\Delta H_f^\circ [A] + \Delta H_f^\circ [B])$$

$$\Delta H_{\text{reaction}}^\circ = (1\text{mol})(523 \text{ KJ/mol}) - ((1\text{mol})(433 \text{ KJ/mol}) + (1\text{mol})(-256 \text{ KJ/mol}))$$

Since we have one mole of A, B and C, we multiply the standard enthalpy of formation of each reactant and product by 1 mole, which eliminates the mol denominator

$$\Delta H_{\text{reaction}}^\circ = \mathbf{346 \text{ KJ}}$$

We get the answer of 346 kJ, which is the standard enthalpy change of formation for the creation of variable "C".

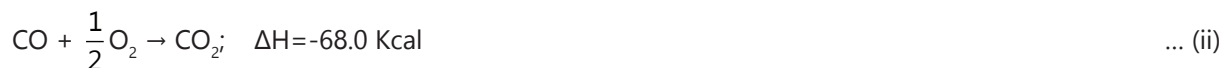
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**Illustration 23:** What is the basic difference between enthalpy of formation and enthalpy of reaction? Illustrate with suitable example. **(JEE ADVANCED)**

**Sol:** Enthalpy of formation is the heat change during the formation of a compound from its components, e.g., enthalpy of formation of  $\text{CO}_2$  is  $-94.3 \text{ Kcal}$ .

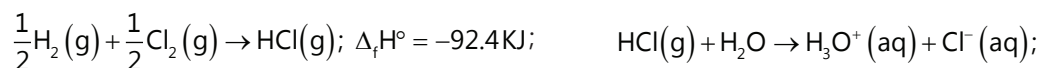


Enthalpy of reaction is the heat change during the completion of any reaction, e.g.,



In some cases enthalpy of reaction and enthalpy of formation may be same as eq. (i) also enthalpy of reaction.

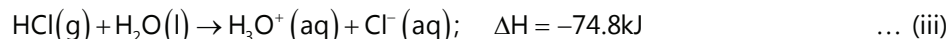
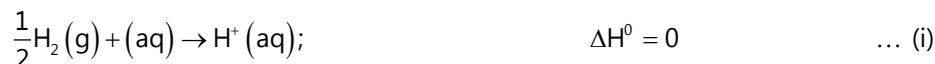
**Illustration 24:** Calculate  $\Delta_f H^\circ$  for chloride ion from the following data: **(JEE ADVANCED)**



$$\Delta_f H^\circ \text{ of } \text{H}_3\text{O}^+(\text{aq}) = 0.0 \text{ KJ}$$



**Sol:** Given,



By inspection method: eqs. (ii) + (iii) – (i) reveals that



i.e. Heat of Formation of  $\text{Cl}^-(\text{aq}) = -167.2 \text{ KJ}$

## 12.4 Enthalpy of Combustion

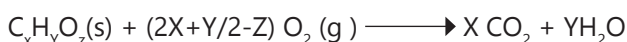
The standard enthalpy of combustion is the enthalpy change when one mole of a reactant completely burns in excess oxygen under standard thermodynamic conditions (although experimental values are usually obtained under different conditions and subsequently adjusted).

Expressed as  $H_{\text{comb}}$  or  $H_c$  when the enthalpy required is not combustion, it can be denoted as  $H_{\text{total}}$ . Enthalpies of combustion are typically measured using bomb calorimetry, and have units of energy (typically kJ); strictly speaking, the enthalpy change per mole of substance combusted is the standard molar enthalpy of combustion (which typically would have units of  $\text{kJ mol}^{-1}$ ).

### 12.4.1 Bomb Calorimetry

#### (a) Purpose of Bomb Calorimetry Experiments

Bomb calorimetry is used to determine the enthalpy of combustion,  $\Delta_{\text{comb}} H$ , for hydrocarbons:



Since combustion reactions are usually exothermic (give off heat),  $\Delta_{\text{comb}} H$  is typically negative. (However, be aware that older literature defines the "heat of combustion" as  $\Delta_{\text{comb}} H$ , so as to avoid compiling tables of negative numbers!

#### (b) Construction of a Bomb Calorimeter

**Apparatus:** Sample, oxygen, the stainless steel bomb, and water.

**Role of Dewar:** The dewar prevents heat flow from the calorimeter to the rest of the universe, i.e.,

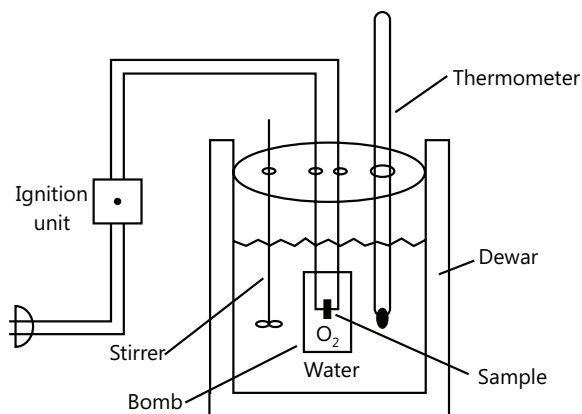
$$q_{\text{calorimeter}} = 0$$

Since the bomb is made from stainless steel, The combustion reaction will occur at constant volume with no work, since the Bomb is of Stainless steel i.e.,

$$W_{\text{calorimeter}} = PdV = 0$$

Hence,  $\Delta U$ , change in internal energy, is zero, for the calorimeter

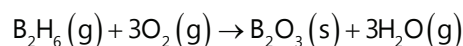
$$\Delta U_{\text{calorimeter}} = q_{\text{calorimeter}} + W_{\text{calorimeter}} = 0$$



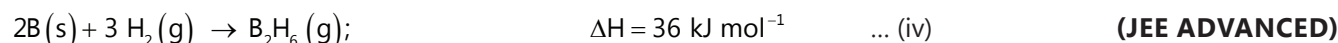
**Figure. 4.9** Bomb calorimeter

The calorimeter is isolated from the rest of the universe. This is the thermodynamic interpretation of the above equation.

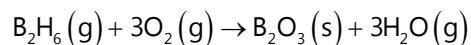
**Illustrations 25:** Diborane is a potential rocket fuel, which undergoes combustion according to the reaction,



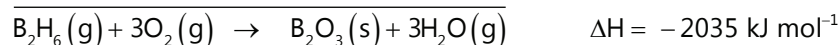
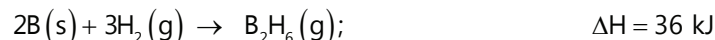
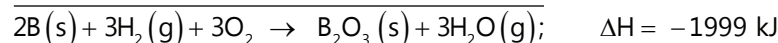
From the following data calculate the enthalpy change for the combustion of Diborane



**Sol:** To get,



By inspection method (i) + 3 x (ii) + 3 x (iii) - (iv)



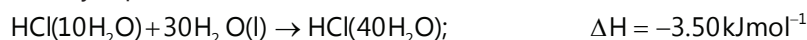
## 12.5 Enthalpy of Solution

The enthalpy change of solution is the enthalpy change when 1 mole of an ionic substance dissolves in water to give a solution of infinite dilution. The other terms used for enthalpy of solution are;

**(a) Integral enthalpy of dilution:** It is the change in enthalpy when a solution containing 1 mole of a solute is diluted from one concentration to other, e.g.,



Also by eqs. (i) and (ii)



i.e. integral enthalpy of dilution of  $\text{HCl}(10\text{H}_2\text{O})$  to  $\text{HCl}(40\text{H}_2\text{O})$  is  $-3.50 \text{ kJ mol}^{-1}$

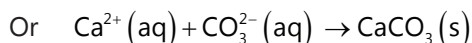
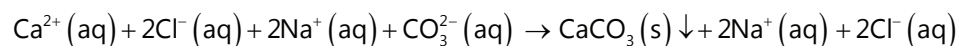
**(b) Differential enthalpy of solution:** It is the change in enthalpy when 1 mole of a solute is dissolved in excess of a solution of known concentration so that there occurs no appreciable change in the concentration of solution.

**(c) Differential enthalpy of dilution:** It is the change in enthalpy when 1 mole of a solvent is added to a large volume of the solution of known concentration so that there occurs no change in the concentration of solution.

**Illustration 26:** Calculate the enthalpy change when infinitely dilute solutions of  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  are mixed for respectively. **(JEE MAIN)**

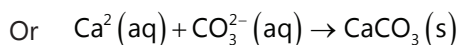
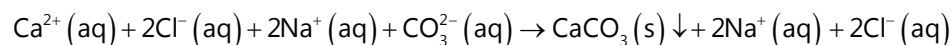
**Sol:** The given reaction on mixing two solutions is  $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl}$

At infinite dilution, each species is 100% dissociated and thus,



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At infinite dilution, each species is 100% dissociated and thus,



$$\begin{aligned} \therefore \Delta H &= \sum_{\text{Product}}^0 - \sum_{\text{Reactant}}^0 = \Delta_f H^\circ \text{CaCO}_3 - \left[ \Delta_f H^\circ \text{Ca}^{2+} + \Delta_f H^\circ \text{CO}_3^{2-} \right] \quad \because (H^\circ = \Delta H_{\text{formation}}^\circ) \\ &= -288.5 - (-129.80 - 161.65) ; = 2.95 \text{ kcal} \end{aligned}$$

## 12.6 Enthalpy of Hydration, $\Delta_{\text{hyd}}H$

The negative enthalpy change observed when one mole of an anhydrous (or partly hydrated) combines with the required number of moles of water to form a specific hydrate at the specified temperature and pressure.

For example:  $\text{MgSO}_4(\text{s}) + 7\text{H}_2\text{O}(\text{l}) \rightarrow \text{MgSO}_4(\text{s}) \cdot 7\text{H}_2\text{O}(\text{s}) ; \quad \Delta_{\text{hyd}}H = -106.6 \text{ kJ mol}^{-1}$

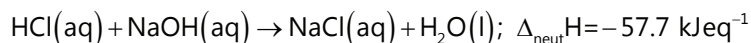
## 12.7 Enthalpy of Transition

It is the enthalpy change when one mole of one allotropic form changes to another under constant temperature and pressure.

For example:  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond}) ; \Delta_{\text{tra}}H = 1.90 \text{ kJ mol}^{-1}$

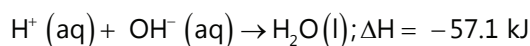
## 12.8 Enthalpy of Neutralization $\Delta_{\text{neut}}H$

It is the enthalpy change (always negative) when one g-equivalent of an acid and one g-equivalent of a base undergo complete neutralization in aqueous solution and all the reactants & products are at the same specified temperature and pressure.



The enthalpy of neutralization of strong acid and strong base is always constant (-57.7 kJ) independent from the acid and base taken. However the magnitude of enthalpy change of neutralization decreases when any one of the acid or base taken is weak.

**Illustration 27:** Whenever an acid is neutralized by a base, the net reaction is



Calculate the heat evolved for the following experiments:

- (i) 0.50 mole of HCl solution is neutralized by 0.50 mole of NaOH solution.
- (ii) 0.50 mole of  $\text{HNO}_3$  solution is mixed with 0.30 mole of KOH solution.
- (iii) 100 mL of 0.2 M HCl is mixed with 100 mL of 0.3 M
- (iv) 400 mL of 0.2 M  $\text{H}_2\text{SO}_4$  is mixed with 600 mL of 0.1 M KOH solution.

**(JEE ADVANCED)**

**Sol:** According to the reaction,  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ ;  $\Delta H = -57.1 \text{ kJ}$

When 1 mole of ions and 1 mole of ions are neutralized, 1 mole of water is formed and 57.1 kJ of energy is released.

- (i) 0.50 mole HCl  $\equiv$  0.50 mole  $\text{H}^+$  ions

0.50 mole NaOH  $\equiv$  0.50 mole  $\text{OH}^-$  ions

On mixing, 0.50 mole of water is formed.

Heat evolved for the formation of 0.50 mole of water =  $57.1 \times 0.5 = 28.55 \text{ kJ}$

- (ii) 0.50 mole  $\text{HNO}_3 \equiv$  0.50 mole  $\text{H}^+$  ions

0.30 mole KOH  $\equiv$  0.30 mole  $\text{OH}^-$  ions

i.e., 0.30 mole of ions react with 0.30 mole of  $\text{OH}^-$  ions to form 0.30 mole of water molecules.

Heat evolved in the formation of 0.3 mole of water =  $57.1 \times 0.3 = 17.13 \text{ kJ}$

- (iii) 100 mL of 0.2 M HCl will give  $\left(\frac{0.2}{1000} \times 100\right) = 0.02$  mole of  $\text{H}^+$  ions and 100 mL of 0.3 M NaOH will give

$\left(\frac{0.3}{1000} \times 100\right) = 0.03$  mole of  $\text{H}^+$  ions i.e., 0.02 mole of ions react with 0.02 mole of ions to form 0.02 mole of water molecules. Heat evolved in the formation of 0.02 mole of water =  $0.02 \times 57.1 = 1.142 \text{ kJ}$

- (iv) 400 mL of 0.2 M  $\text{H}_2\text{SO}_4$  will give  $\left(\frac{2 \times 0.2}{1000} \times 400\right) = 0.16$  mole of  $\text{H}^+$  ions and 600 mL of 0.1 M KOH will give

$\left(\frac{0.1}{1000} \times 600\right) = 0.06$  mole of  $\text{OH}^-$  ions i.e., 0.06 mole of ions react with 0.06 mole of ions to form 0.06 mole of water molecules.

Heat evolved in the formation of 0.06 mole of water =  $0.06 \times 57.1 = 3.426 \text{ kJ}$

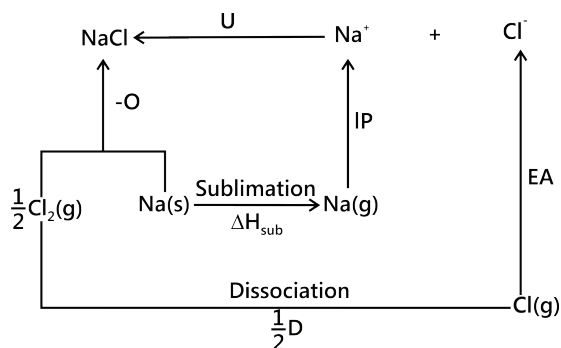
## 12.9 Enthalpy of Sublimation $\Delta_{\text{sub}} H$

It is the enthalpy change when one mole of solid substance changes from solid state to gases state under conditions of constant temperature and pressure.

For example  $\text{Na}_{(\text{s})} \xrightarrow[\Delta_{\text{a}}]{\text{Substance}} \text{Na}_{(\text{g})} \Delta_{\text{a}} H = x \text{ kJ mol}^{-1}$

## 12.10 Born Haber Cycle

It is a series of steps (chemical processes) used to calculate the lattice energy of ionic solids, which is difficult to determine experimentally. You can think of BH cycle as a special case of Hess's law, which states that the overall energy change in a chemical process can be calculated by breaking down the process into several steps and adding the energy change from each step.

**Example: Sodium chloride**

Steps Involved :

- (a) Sublimation ( $\Delta H_{\text{sub}}$ ) : Solid sodium changes into gaseous sodium.
- (b) Ionization (IP) : gaseous sodium changes into sodium ion.
- (c) Dissociation (D) : Dissociation of chlorine molecule.
- (d) Electron affinity (EA) : Gaseous chlorine atom changes into chloride ions.
- (e) Combination of ions to form neutral molecule.

$$\text{Total energies evolved in the above reaction} = \Delta H_{\text{sub}} + \frac{1}{2} \text{D} + \text{IP} - \text{EA} + \text{U}$$

$$\text{Thus according to Hess's law, } -Q = \Delta H_{\text{sub}} + \frac{1}{2} \text{D} + \text{IP} - \text{EA} + \text{U}$$

**Illustration 28:** Which ions are present in  $\text{MgO}(\text{s})$ ?

Calculate the enthalpy change for the reaction  $\text{Mg}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{MgO}(\text{s})$

What kind of enthalpy change is this? Standard enthalpy of formation of  $\text{MgO}$  is

**(JEE MAIN)**

$$\Delta H_{\text{atm}(\text{O})} = +249 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{atm}(\text{Mg})} = +148 \text{ kJ mol}^{-1}$$

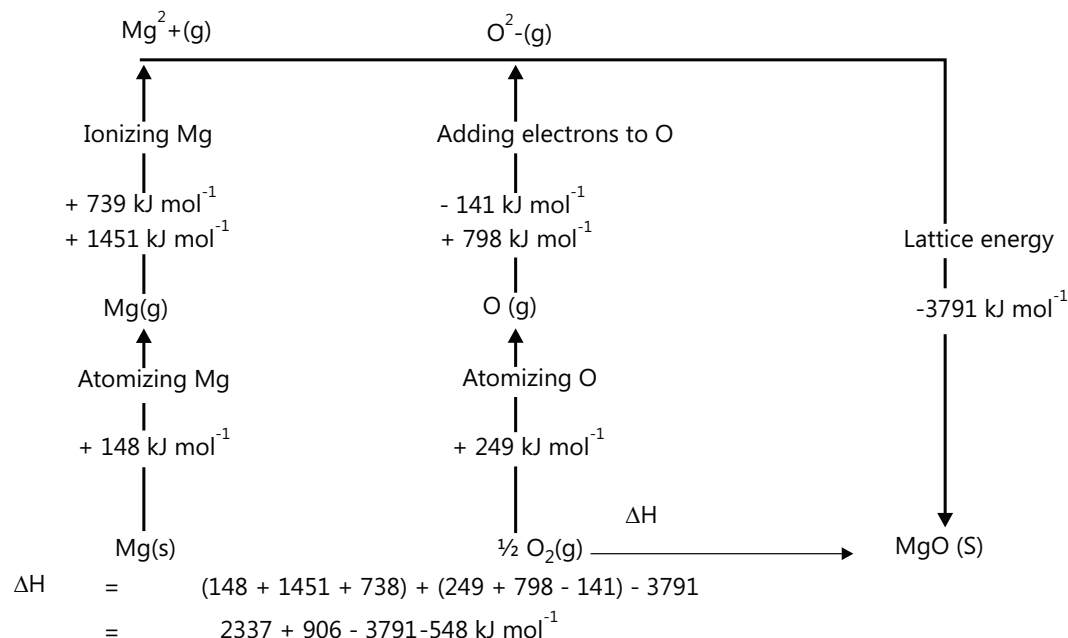
$$\Delta H_{\text{1st Ionisation energy}(\text{Mg})} = +738 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{2st Ionisation energy}(\text{Mg})} = +1451 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{1st electron affinity}(\text{O})} = +141 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{2st electron affinity}(\text{O})} = +798 \text{ kJ mol}^{-1}$$

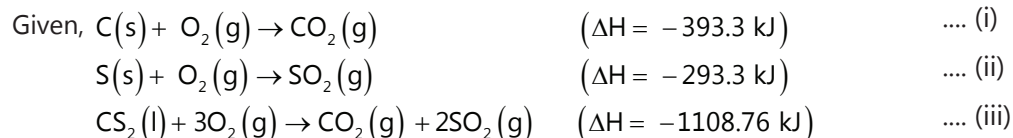
$$\Delta H_{\text{lattice energy}(\text{MgO})} = +3791 \text{ kJ mol}^{-1}$$

**Sol:**

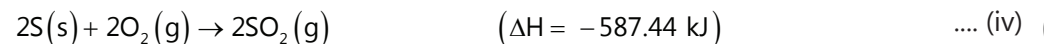
The actual value for this reaction is  $-602 \text{ kJ mol}^{-1}$ . This is because there is a degree of covalent bonding in  $\text{MgO}$ . Therefore the bonds formed are slightly stronger than those predicted by a purely ionic model.

**Illustration 29:** Calculate the standard heat of formation of Carbon disulphide (l). Given that the standard heats of Combustion of Carbon (s), Sulphur (s) and Carbon disulphide (are  $-393.3$ ,  $293.7$  and  $1108.76 \text{ kJ}$  respectively).

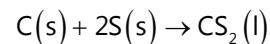
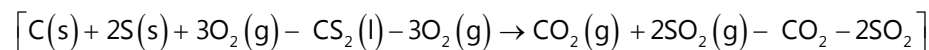
**Sol:** Required equation is  $\text{C(s)} + 2\text{S(s)} \rightarrow \text{CS}_2(\text{l})$ ;  $\Delta H_f = ?$



**First method:** Multiply the eq. (ii) by 2.



Adding eqs. (i) and (iv) and subtracting eq. (iii),

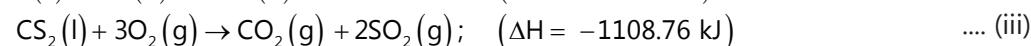
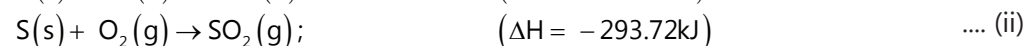
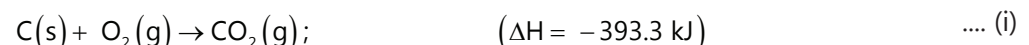


This is the required equation.

Thus,  $= -393.3 - 587.44 + 1108.76 = 128.02 \text{ kJ}$

Standard heat of formation of  $\text{CS}_2(\text{l}) = 128.02 \text{ kJ}$

**Second Method:**



From eqs. (i) and (ii),

Enthalpy of  $\text{CO}_2 = -393.3 \text{ kJ}$ ; Enthalpy of  $\text{SO}_2 = -293.72 \text{ kJ}$ ;

Enthalpy of  $\text{O}_2 = 0$  (By convention)

$\Delta H$  of eq. (iii) Enthalpies of products Enthalpies of reactants

$$-1108.76 = -393.3 + 2(-293.72) - \Delta H_{\text{CS}_2(l)}$$

$$\Delta H_{\text{CS}_2(l)} = (1108.76 - 980.74) = 128.02 \text{ kJ}$$

$$\text{Enthalpy of } \text{CS}_2(l) = 128.02 \text{ kJ}$$

### PLANCESS CONCEPTS

Enthalpy of reaction refers to entire chemical equation and not to any particular reactant or products. Alternatively, enthalpy of a reaction is the rate of change of Enthalpy of the system with the extent of reaction at constant P and T. If all the chemical species in a chemical equation are present in the respective standard state, i.e., at  $P=1 \text{ atm}$  (better to say  $1 \text{ Bar}$ ) and  $T = 298 \text{ K}$ , the enthalpy of reaction is referred as standard enthalpy of reaction.

For reaction involving only solid or liquid state. (and if  $\Delta V = 0$  of reactants and products,  $\Delta H = \Delta U$ , If temperature range is not small or  $C_p$  varies appreciably with temperature, Then,  $C_p = \alpha + \beta T + \gamma T^2$  Where  $\alpha$ ,  $\beta$  and  $\gamma$  are constant for given species  $\therefore \Delta C_p = \Delta \alpha + \Delta \beta T + \Delta \gamma T^2$

**Nikhil Khandelwal JEE 2009 AIR 94**

## 13. TROUTON'S RULE

**Trouton's rule:** According to this rule, the ratio of heat of vaporization and the normal boiling point of a

liquid is approximately equal to  $88 \text{ J/mol}$ , i.e.,  $\frac{\Delta_{\text{vap}} H}{T_b (\text{in K})} = 88 \text{ J/mol}$

## PROBLEM-SOLVING TACTICS

If we have a simple chemical equation with the variables A, B and C representing different compounds:  $A + B \rightleftharpoons C$

and we have the standard enthalpy of formation values as such:

$$\Delta H_f^\circ [A] = 433 \text{ kJ/mol}$$

$$\Delta H_f^\circ [B] = -256 \text{ kJ/mol}$$

$$\Delta H_f^\circ [C] = 523 \text{ kJ/mol}$$

The equation for the standard enthalpy change of formation is as follows:

$$\Delta H_{\text{reaction}}^\circ = \Delta H_f^\circ [C] - (\Delta H_f^\circ [A] + \Delta H_f^\circ [B])$$

$$\Delta H_{\text{reaction}}^\circ = (1\text{mol})(523 \text{ kJ/mol}) - ((1\text{mol})(433 \text{ kJ/mol}) + (1\text{mol})(-256 \text{ kJ/mol}))$$

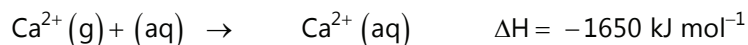
Since we have one mole of A, B and C, we multiply the standard enthalpy of formation of each reactant and product by 1 mole, which eliminates the mol denominator

$$\Delta H_{\text{reaction}}^\circ = 346 \text{ kJ}$$

We get the answer of  $346 \text{ kJ}$ , which is the standard enthalpy change of formation for the creation of variable "C".

Estimating enthalpies of solution from lattice enthalpies and hydration enthalpies

The hydration enthalpies for calcium and chloride ions are given by the equations:

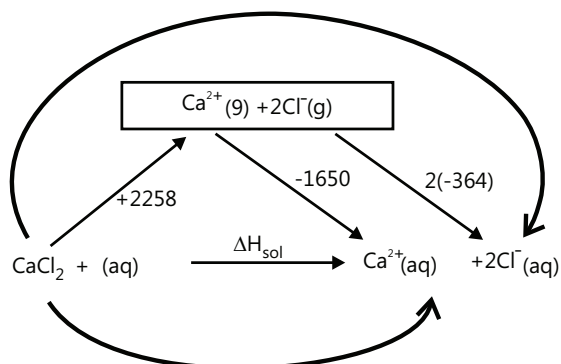


The following cycle is for calcium chloride, and includes a lattice dissociation enthalpy of  $+2258 \text{ kJ mol}^{-1}$ . We have to use double the hydration enthalpy of the chloride ion because we are hydrating 2 moles of chloride ions. Make sure you understand exactly how the cycle works.

So,

$$\Delta H_{\text{sol}} = +2258 - 1650 + 2(-364)$$

$$\Delta H_{\text{sol}} = -120 \text{ kJ mol}^{-1}$$

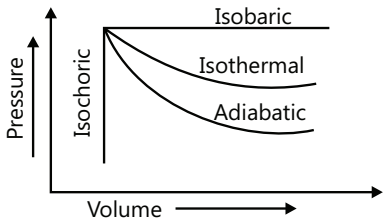


Whether an enthalpy of solution turns out to be negative or positive depends on the relative sizes of the lattice enthalpy and the hydration enthalpies. In this particular case, the negative hydration enthalpies more than made up for the positive lattice dissociation enthalpy.

## POINTS TO REMEMBER

S. No	Terms	Description
1	System, surrounding and Boundary	A specified part of the universe which is under observation is called the system and the remaining portion of the universe which is not a part of the system is called the surroundings. The system and the surroundings can interact across the boundary.
2	Types of System	Open System $\Delta E \neq 0, \Delta m \neq 0$ Closed System $\Delta E \neq 0, \Delta m = 0$ Isolated System $\Delta E = 0, \Delta m = 0$
3	Thermodynamic Processes	<b>(a) Isothermal process</b> Occurs at constant temperature; $\Delta T = 0$ <b>(b) Adiabatic process</b> Occurs without exchange of heat With surrounding, $q = 0$ . <b>(c) Isobaric process</b> Occurs at constant pressure, $\Delta p = 0$ <b>(d) Isochoric process</b> Occurs at constant pressure $\Delta V = 0$
4	Intensive and extensive properties	Those properties which do not depend on the mass of the sample are intensive properties whereas the others are extensive properties.
5	State Function	Those functions which do not depend on path followed during the change and depend only upon the initial and final state of the system.



S. No	Terms	Description
6	Sign Conventions for Heat and work	Heat absorbed by the system = q positive Heat evolved by the system = q negative Work done on the system = w positive Work done by the system = w negative
7	First law of Thermodynamics	First law of thermodynamics deals with the conservation of energy. $\Delta E = q + W$ Also, $q = nC_v \Delta T$ In rev Isothermal Expansion of gas, $q = -W = P_{\text{ext}} \Delta V (\Delta E = 0)$ $q = -W = nRT \ln \frac{V_2}{V_1}$ In rev Isothermal Expansion of gas, $W = -q = -nC_v \Delta T = nC_v (T_1 - T_2)$ $pV^\gamma = \text{constant}$ , where $\gamma = \frac{C_p}{C_v}$ $TV^\gamma = \text{constant}$ and Also, In adiabatic rev process, $P^{1-\gamma} T^\gamma = \text{constant}$
8	Graphical Representation of four Basic thermodynamic processes	Graphical representation of four basic thermodynamic Process. 
9	Enthalpy (H)	$H = E + PV \Rightarrow dE + PdV + VdP$ At constant pressure $dH = dE + pdV (\because dP = 0) = Q_p = C_p \Delta T$
10	Entropy (S)	$S = \frac{q_{\text{rev}}}{T}$ ; $\Delta S = nC_v \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)$ $= nC_p \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{P_1}{P_2} \right)$
11	Gibbs Free Energy (G)	$G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S$ at constant temperature. Also, $dG = Vdp - SdT$ At constant temperature, $\Delta G = nRT \ln (P_2 / P_1)$
12	Criteria for Spontaneity	For a spontaneous process, entropy of universe must increase, i.e., $\Delta S_{\text{univ}} > 0$ or $\Delta G < 0$ (a) If $\Delta H < 0$ and $\Delta S > 0$ , $\Delta G$ is always negative, always spontaneous. (b) If $\Delta H > 0$ and $\Delta S < 0$ , $\Delta G$ is always positive, always non-spontaneous. (c) If $\Delta H > 0$ and $\Delta S > 0$ , $\Delta G$ process will be spontaneous at higher temperature but non-spontaneous at lower temperature. (d) If $\Delta H < 0$ and $\Delta S < 0$ , $\Delta G$ process will be spontaneous at Lower temperature but non-spontaneous at higher temperature.

S. No	Terms	Description
13	Standard Molar Enthalpy of formation ( $\Delta H_f^0$ )	It is the enthalpy change associated with the formation of one mole of a substance in the standard state from the constituent elements in their standard state. It can be either positive or negative.
14	Standard Molar Enthalpy of combustion ( $\Delta H_{\text{comb}}^0$ )	It is the heat evolved when one mole of a substance in the standard state is oxidized completely. ( $\Delta H_{\text{comb}}^0$ ) is always negative.
15	Standard Enthalpy reaction ( $\Delta H_{\text{rxn}}^0$ )	<p>It is the net enthalpy change associated with a reaction. It is determined with the help of <math>\Delta H_f^0</math> or <math>\Delta H_{\text{comb}}^0</math> as</p> $\Delta H_{\text{rxn}}^0 = \sum \Delta H_f^0 (\text{products}) - \sum \Delta H_f^0 (\text{reactants})$ <p>Or</p> $\Delta H_{\text{rxn}}^0 = \sum \Delta H_{\text{comb}}^0 (\text{reactants}) - \sum \Delta H_{\text{comb}}^0 (\text{products})$ <p>By convention <math>\Delta H_f^0</math> of pure element is taken to be zero.</p>
16	Calorimetry	<p>If a reaction is carried out in a calorimeter, the enthalpy change of a reaction can be determined as <math>q = m\Delta T</math></p> <p>Where, <math>m</math> = mass of calorimeter content</p> <p><math>S</math> = specific heat of calorimeter content</p> $\Delta T = T_{\text{final}} - T_{\text{initial}} = \text{change in temperature of calorimeter}$
17	Bond Dissociation Energy and Bond Enthalpy	<p>Bond dissociation energy is the average energy required to break a specific type of bond in a molecule.</p> <p><b>Bond enthalpy of a Compound:</b> It is the total energy required to convert one mole of gaseous substance into their constituent atoms.</p> <p>In term of bond-enthalpy, <math>\Delta H_{\text{rxn}}^0</math> can be determined as</p> $\Delta H_{\text{rxn}}^0 = \sum \text{BE}(\text{reactants}) - \sum \text{BE}(\text{products})$
18	Resonance Energy	<p>It is the energy released by the conjugated system due to delocalization of electrons. It is the difference in enthalpy change (between one determined Experimentally (calorimetrically) and other calculated Theoretically)</p> $\Rightarrow \Delta H (\text{RE}) = \Delta H_{(\text{exp})} - \Delta H_{(\text{theo})}$
19	Enthalpy of Neutralization	It is the heat liberated when one gram equivalent of a strong acid or base is neutralized completely. Hence, all neutralization reactions are exothermic in nature.
20	Enthalpy of Hydration ( $\Delta H_{\text{hyd}}^0$ )	<p>It is the heat evolved when one mole of a substance is hydrated to a certain specific degree of hydration,</p> <p>e.g, <math>\text{CuSO}_4 (\text{s}) + 5\text{H}_2\text{O} (\text{l}) \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O} (\text{s})</math></p> <p>Enthalpy of hydration,</p>
21	Lattice Energy ( $U_0$ )	<p><b>Lattice Energy (<math>U_0</math>)</b> It is the heat liberated when one mole of an ionic compound in its standard state is formed from ions in their gaseous state,</p> <p>e.g. <math>\text{Na}^+ (\text{g}) + \text{Cl}^- (\text{g}) \rightarrow \text{NaCl} (\text{s}); \Delta H = U_0</math></p>

## Solved Examples

### JEE Main/Boards

**Q.1** Calculate the increase in internal energy of 1 kg of water at 100° C when it is converted into steam at the same temperature and at 1 atm (100 kPa). The density of water and steam are 1000 kg m<sup>-3</sup> and 0.6 kg m<sup>-3</sup> respectively.

The latent heat of vaporization of water =  $2.25 \times 10^6 \text{ J kg}^{-1}$

**Sol:** Mass and density of water and steam is provided so from the given data calculate the increase in volume. Pressure term is given so by using pressure volume relationship calculate the work done by the system. Change in internal energy can be calculated using heat and work relation.

The volume of 1 kg of water

$$= \frac{1}{1000} \text{ m}^3 \text{ and of 1 kg of steam} = \frac{1}{0.6} \text{ m}^3$$

The increase in volume

$$= \frac{1}{0.6} \text{ m}^3 - \frac{1}{1000} \text{ m}^3 = (1.7 - 0.001 \text{ m}^3 \approx 1.7 \text{ m}^3)$$

The work done by the system is

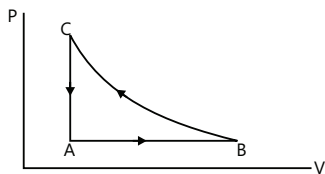
$$p\Delta V = (100 \text{ kPa})(1.7 \text{ m}^3) = 1.7 \times 10^5 \text{ J.}$$

The heat given to convert 1 kg of water into steam =  $2.25 \times 10^6 \text{ J}$ .

The change in internal energy is

$$\Delta U = \Delta Q - \Delta W = 2.25 \times 10^6 \text{ J} - 1.7 \times 10^5 \text{ J} = 2.08 \times 10^6$$

**Q.2** Consider the cyclic process ABCA on a sample of 2.0 mol of an ideal gas as shown in figure. The temperatures of the gas at A and B are 300 K and 500 K respectively. A total of 1200 J heat is withdrawn from the sample in the process. Find the work done by the gas in part BC. Take  $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$



**Sol:** The change in internal energy during the cyclic process is zero. Hence, the heat supplied to the gas is equal to the work done by it. Work done can be calculated by pressure volume relationship.

The change in internal energy during the cyclic process is zero. Hence, the heat supplied to the gas is equal to the work done by it. Hence,

$$W_{AB} = P_A (V_B - V_A) = nR(T_B - T_A)$$

$$= (2.0 \text{ mol})(8.3 \text{ J K}^{-1} \text{ mol}^{-1})(200 \text{ K}) = 3320 \text{ J.}$$

The work done by the gas during the process CA is zero as the volume remains constant. From (i),

$$3320 \text{ J} + W_{BC} = -1200 \text{ J} = -4520 \text{ J}$$

**Q.3** A mole of a monoatomic ideal gas at 1 atm and 273 K is allowed to expand adiabatically against a constant pressure of 0.395 bar until equilibrium is reached.

(a) What is the final temperature?

(b) What is the final volume?

(c) How much Work is done by the gas?

(d) What is the change in internal energy?

**Sol:** Let the initial and final volumes of the gas be  $V_1$  and  $V_2 \text{ m}^3$  respectively. Given that the initial pressure ( $P_1$ )  $1 \times 10^5 \text{ Pa}$ , final temperature be  $T_2$

$$\text{We have, } P_1 V_1 = n_1 R T_1$$

$$V_1 = \frac{1 \times 8.314 \times 273}{1 \times 10^5} = 0.022697 \text{ m}^3$$

For an adiabatic expansion of 1 mole of monoatomic ideal gas against a constant external pressure ( $P_2$ ), work done is given as

$$W = -P_2 (V_2 - V_1) = C_v (T_2 - T_1) = \frac{3R}{2} (T_2 - T_1)$$

$$\text{Or } -0.395 \times 10^5 (V_2 - 0.022697) = \frac{3 \times 8.314}{2} (T_2 - 273) \dots (i)$$

Again,

$$P_2 V_2 = n R T_2;$$

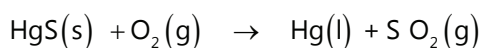
$$0.395 \times 10^5 \times V_2 = 1 \times 8.314 \times T_2 \dots (ii)$$

Solving eqns. (i) and (ii), we get,

(a) The final temperature,  $T_2 = 207 \text{ K}$

(b) The final volume  $V_2 = 0.043578 \text{ m}^3$

**Q.4** Metallic mercury is obtained by roasting mercury (II) sulphide in a limited amount of air. Estimate the temperature range in which the standard reaction is product-favored.



$$\Delta H^\circ = -238.6 \text{ kJ/mole and } \Delta S^\circ = +36.7 \text{ J/mole K}$$

**Sol:** Assume that  $\Delta H$  and  $\Delta S$  values do not depend on temperature. As  $\Delta H^\circ$  is negative and  $\Delta S^\circ$  is positive, using the equation  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   $\Delta G^\circ$  Will be negative at all temperatures and so the reaction is product - favored at all temperatures. In this problem, both the factors  $\Delta H^\circ$  and  $\Delta S^\circ$  are favourable to spontaneity.

**Q.5** An ideal gas has a molar heat capacity at constant pressure  $C_p = 2.5 R$ . The gas is kept in a closed vessel of Volume  $0.0083 \text{ m}^3$ , at a temperature of  $300 \text{ K}$  and a pressure of  $1.6 \times 10^6 \text{ Nm}^{-2}$ . An amount  $2.49 \times 10^4 \text{ J}$  of Heat energy is supplied to the gas. Calculate the final temperature and pressure to the gas.

**Sol:** First calculate the number of moles (amount of gas) by using ideal gas equation, temperature can be calculated using internal energy and  $n$ . after calculating temperature pressure ( $P_2$ ) can be calculated using following equation

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

We have,  $C_v = C_p - R = 2.5R - R = 1.5R$ .

The amount of the gas (in moles) is  $n = \frac{PV}{RT}$

$$= \frac{(1.6 \times 10^6 \text{ N m}^{-2}) \times (0.0083 \text{ m}^3)}{(8.3 \text{ J K}^{-1} \text{ mol}^{-1})(300 \text{ K})} = 5.33 \text{ mol}$$

As the gas is kept in a closed vessel, its volume is constant,

Thus, we have

$$\Delta Q = n C_v \Delta T \quad \text{or} \quad \Delta T = \frac{\Delta Q}{nC_v}$$

$$= \frac{2.49 \times 10^4 \text{ J}}{(5.3 \text{ mol})(1.5 \times 8.3 \text{ J K}^{-1} \text{ mol}^{-1})} = 377 \text{ K}$$

The final temperature is  $300 \text{ K} + 377 \text{ K} = 677 \text{ K}$ .

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

Here  $V_1 = V_2$ . Thus,

$$P_2 = \frac{T_2}{T_1} P_1 = \frac{677}{300} \times 1.6 \times 10^6 \text{ N m}^{-2} = 3.6 \times 10^6 \text{ N m}^{-2}.$$

**Q.6** Oxygen gas weighting 64 is expanded from 1 atm to 0.25 atm at  $30^\circ\text{C}$ . Calculate entropy change, assuming the gas to be ideal.

**Sol:** First find out value of  $n$  and then  $\Delta S$  can be determined by using following equation

$$\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$$

$$\Delta S = 2.303nR \log\left(\frac{P_1}{P_2}\right)$$

$$n = \frac{w}{\text{m.wt}} = \frac{64}{32} = 2 \quad = 2.303 \times 2 \times 8.314 \log\left(\frac{1}{0.25}\right)$$

$$= 23.053 \text{ J K}^{-1}$$

**Q.7** An aluminium container of mass 100 g contains 200 g of ice at  $-20^\circ\text{C}$ . Heat is added to the system at a rate of  $100 \text{ cal s}^{-1}$ . What is the temperature of the system after 4 minutes? Draw a rough sketch showing the variation in the temperature of the system as a function of time. Specific heat capacity of ice =  $0.5 \text{ cal g}^{-1}^\circ\text{C}^{-1}$ , specific heat capacity of aluminium =  $0.2 \text{ cal g}^{-1}^\circ\text{C}^{-1}$ , specific heat capacity of water =  $1 \text{ cal g}^{-1}^\circ\text{C}^{-1}$ , and latent heat of fusion of ice =  $80 \text{ cal g}^{-1}$ .

**Sol:** Total heat supplied to the system in 4 minutes is  $Q = 100 \text{ cal s}^{-1} \times 240 \text{ s} = 2.4 \times 10^4 \text{ cal}$ . The heat required to take the system from  $-20^\circ\text{C}$  to  $0^\circ\text{C}$

$$= (100 \text{ g}) \times (0.2 \text{ cal g}^{-1}^\circ\text{C}^{-1} \times (20^\circ\text{C})) + (200 \text{ g}) \times (0.5 \text{ cal g}^{-1}^\circ\text{C}^{-1} \times (20^\circ\text{C}))$$

$$= 400 \text{ cal} + 2000 \text{ cal} = 2400 \text{ cal}.$$

$$\text{The time taken in this process} = \frac{2400}{100} \text{ s} = 24 \text{ s. The}$$

$$\text{heat required to melt the ice at } 0^\circ\text{C} = (200 \text{ g}) \times (80 \text{ cal g}^{-1}) = 16000 \text{ cal}.$$

$$\text{The time taken in this process} = \frac{16000}{100} \text{ s} = 160 \text{ s}.$$

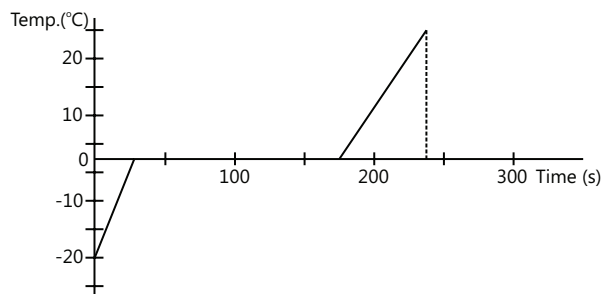
If the final temperature is  $\theta$ , the heat required to take the system to the final temperature is

$$= (100 \text{ g}) \times (0.2 \text{ cal g}^{-1}^\circ\text{C}^{-1}) \theta + (200 \text{ g}) \times (1 \text{ cal g}^{-1}^\circ\text{C}^{-1}) \theta.$$

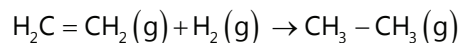
$$\text{Thus, } 2.4 \times 10^4 \text{ cal} = 2400 \text{ cal} + 16000 \text{ cal} + (220 \text{ cal}^\circ\text{C}^{-1}) \theta$$

$$\text{Or, } \theta = \frac{5600 \text{ cal}}{220 \text{ cal}^\circ\text{C}^{-1}} = 25.5^\circ\text{C}.$$

The variation in the temperature as function of time is sketched in figure



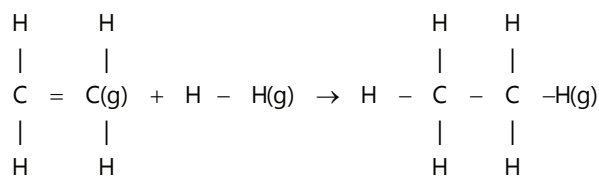
**Q.8** Calculate the enthalpy of the reaction



The bond energies of

C–H, C=C and H–H are 99, 83, 147 and 104 kcal respectively.

**Sol:** The reaction is:



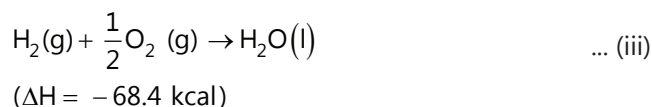
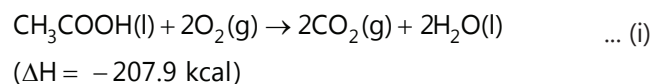
$\Delta H = ?$

$\Delta H =$  Sum of bond energies of reactants – Sum of bond energies of products

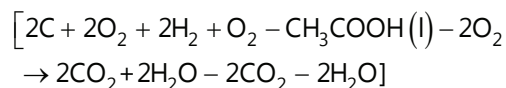
$$= [\Delta H_{\text{C}=\text{C}} + 4 \times \Delta H_{\text{C}-\text{H}} + \Delta H_{\text{H}=\text{H}}] - [\Delta H_{\text{C}-\text{C}} + 6 \times \Delta H_{\text{C}-\text{H}}]$$

$$= (147 + 4 \times 99 + 140) - (83 + 6 \times 99) = -30 \text{ Kcal}$$

**Q.9** Calculate the heat of formation of acetic acid from the following data:



**Sol: First method:** The required equation is  $2\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) = \text{CH}_3\text{COOH}(\text{l})$ ;  $\Delta H = ?$  This equation can be obtained by multiplying eq. (ii) by 2 and also eq. (iii) by 2 and adding both and finally subtracting eq. (i).



$$\Delta H_{\text{CH}_3\text{COOH}(\text{l})} = 2 \times (-94.48) + 2 \times (-68.4) - (-207.9)$$

$$= -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

**Second method:** From eqs. (ii) and (iii)

Enthalpy of  $\text{CO}_2 = -94.48 \text{ kcal}$

Enthalpy of  $\text{H}_2\text{O} = -68.4 \text{ kcal}$

Enthalpy of  $\text{O}_2 = 0$  (by convention)

$\Delta H$  of eq. (i) = Enthalpies of products – Enthalpies of reactants

$$-207.9 = 2 \times (-94.48) + 2 \times (-68.4) - \Delta H_{\text{CH}_3\text{COOH}(\text{l})}$$

$$\Delta H_{\text{CH}_3\text{COOH}(\text{l})} = -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9$$

$$= -117.86 \text{ kcal}$$

**Q.10** 100 cm<sup>3</sup> of 0.5 N HCl solutions at 299.95 K were mixed with 100 cm<sup>3</sup> 0.5 N NaOH solution at 299.75 K in a thermos flask. The final temperature was found to be 302.65 K. Calculate the enthalpy of neutralization of HCl. Water equivalent of thermos flask is 44 g.

**Sol:** Here we are not provided with initial temperature. So by averaging the temperature of acid and base find out the initial temperature and thus rise in temperature and enthalpy of neutralization. The initial average temperature of the acid and the base.

$$= \frac{299.95 + 299.75}{2} = 299.85 \text{ K}$$

$$\text{Rise in temperature} = (302.65 - 299.85) = 2.80 \text{ K}$$

Heat evolved during neutralization

$$= (100 - 100 + 44) \times 4.184 \times 2.8 = 2858.5 \text{ J}$$

$\therefore$  Enthalpy of neutralization

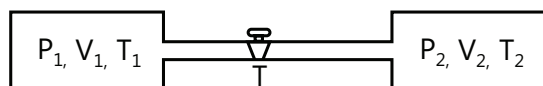
$$= -\frac{2858.5}{100} \times 1000 \times \frac{1}{0.50} = -57.17 \text{ kJ}$$

## JEE Advanced/Boards

**Q.1** Two vessels of volumes  $V_1$  and  $V_2$  contain the same ideal gas. The pressures in the vessels are  $P_1$  and  $P_2$  the temperatures are  $T_1$  and  $T_2$  respectively. The two vessels are now connected to each other through a narrow tube. Assuming that no heat is exchange between the surrounding and the vessels, find the common pressure and temperature attained after the connection.

**Sol:** In order to find out the common pressure and temperature attained after the connection, first we have to find out what is the amount of gas present in vessel one and two the formula to be used is

$$\gamma = \frac{C'_p}{C'_v} = \frac{n_1 C'_p + n_2 C'_p}{n_1 C'_v + n_2 C'_v}$$



The amount of the gas in vessel 1 is

$$n_1 = \frac{P_1 V_1}{RT_1} \text{ and that in vessel 2 is } n_2 = \frac{P_2 V_2}{RT_2}$$

If  $P'$  and  $T'$  be the common pressure and temperature after the connection is made, the amounts are

$$n_1' = \frac{P' V_1}{RT'} \text{ and } n_2' = \frac{P' V_2}{RT'}$$

We have  $n_1 + n_2 = n_1' + n_2'$

$$\text{or } \frac{P_1 V_1}{RT_1} + \frac{P_2 V_2}{RT_2} = \frac{P' V_1}{RT'} + \frac{P' V_2}{RT'}$$

$$\text{or } \frac{P'}{T'} = \frac{1}{V_1 + V_2} \left( \frac{P_1 V_1}{T_1} + \frac{P_2 V_2}{T_2} \right)$$

$$\text{or } \frac{T'}{P'} = \frac{T_1 T_2 (V_1 + V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1} \quad \dots (i)$$

As the vessels have fixed volume, no work is done by the gas plus the vessels system. Also no heat is exchanged with the surrounding. Thus, the internal energy of the total system remains constant.

The internal energy of an ideal gas is

$$T' = \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$$

The internal energy of the gases before the connection

$$= \frac{C_v P_1 V_1}{R} + \frac{C_v P_2 V_2}{R}$$

$$\text{and after the connection} = \frac{C_v P' (V_1 + V_2)}{R}$$

Neglecting the change in internal energy of the vessels (the heat capacity of the vessels is assumed negligible),

$$\frac{C_v P_1 V_1}{R} + \frac{C_v P_2 V_2}{R} = \frac{C_v P' (V_1 + V_2)}{R} \quad \text{Or,}$$

$$P' = \frac{P_1 V_1 + P_2 V_2}{V_1 + V_2}$$

$$\text{From (i), } T' = \frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$$

**Q.2** 4 mole of an ideal gas having  $\gamma = 1.67$  are mixed with 2 mole of another ideal gas having  $\gamma = 1.4$ . Find the equivalent value of  $\gamma$  for the mixture.

**Sol:** The problem can be solved using the following two equations,

$$\gamma = \frac{C'_p}{C'_v} \quad \text{And} \quad C'_p = C'_v + R$$

$C'_v$  = Molar heat capacity of the first gas,

$C'_v$  = Molar heat capacity of the second gas,

$C'_v$  = Molar heat capacity of the mixture

$C'_v$  = Molar heat capacity of the first gas,

$C'_v$  = Molar heat capacity of the second gas,

$C'_v$  = Molar heat capacity of the mixture

and similar symbols for other quantities. Then,

$$\gamma = \frac{C'_p}{C'_v} = 1.67 \quad \text{and } C'_p = C'_v + R$$

$$\text{This gives } C'_v = \frac{3}{2}R \quad \text{and } C'_p = \frac{5}{2}R.$$

$$\text{Similarly, } \gamma = 1.4. \text{ Gives } C'_v = \frac{5}{2}R. \text{ and } C'_p = \frac{7}{2}R.$$

Suppose the temperature of the mixture is increased by  $dT$ . The increase in the internal energy of the first gas  $= n_1 C'_v dT$ .

The increase in internal energy of the second Gas  $= n_2 C'_v dT$  and the increase in internal energy of the Mixture  $= (n_1 + n_2) C'_v dT$

$$\text{Thus, } (n_1 + n_2) C'_v dT = n_1 C'_v dT + n_2 C'_v dT;$$

$$C'_v = \frac{n_1 C'_v + n_2 C'_v}{n_1 + n_2} \quad \dots (i)$$

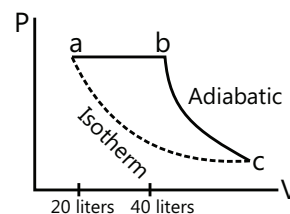
$$C_p = C_v + R = \frac{n_1 C'_v + n_2 C'_v}{n_1 + n_2} + R$$

$$= \frac{n_1 (C'_v + R) + n_2 (C'_v + R)}{n_1 + n_2} = \frac{n_1 C'_p + n_2 C'_p}{n_1 + n_2} \quad \dots (ii)$$

From (i) and (ii),

$$\gamma = \frac{C'_p}{C'_v} = \frac{n_1 C'_p + n_2 C'_p}{n_1 C'_v + n_2 C'_v} = \frac{4 \times \frac{5}{2}R + 2 \times \frac{7}{2}R}{4 \times \frac{3}{2}R + 2 \times \frac{5}{2}R} = 1.54$$

**Q.3** Two moles of helium gas ( $\gamma = 5/3$ ) are initially at  $27^\circ$  and occupy a volume of 20 liters. The gas is first expanded at constant pressure until the volume is doubled. Then it undergoes



an adiabatic change until the temperature returns to its initial value. (a) Sketch the process in a p-V diagram (b) What is the final volume and pressure of the gas? (c) What is the work done by the gas?

**Sol:** (a) The process is shown in figure. During the part ab, the pressure is constant.

We have,

$$\frac{P_a V_a}{T_a} = \frac{P_b V_b}{T_b} \quad \text{or} \quad T_b = \frac{V_b}{V_a} T_a = 2T_a = 600 \text{ K.}$$

During the part bc, the gas is adiabatically returned to the temperature  $T_a$ . The point b and the point c are on the same isotherm. Thus, we draw an adiabatic curve from b and an isotherm from a and look for the point of intersection c. That is the final state.

(b) From the isotherm ac,

$$P_a V_a = P_c V_c \quad \dots(i)$$

and from the adiabatic curve bc,

$$P_b V_b^\gamma = P_c V_c^\gamma \quad \text{or} \quad P_a (2V_a)^\gamma = P_c V_c^\gamma \quad \dots(ii)$$

Dividing (ii) by (i),

$$2^\gamma (V_a)^{\gamma-1} = (V_c)^{\gamma-1};$$

$$V_c = 2^{\gamma/(\gamma-1)} V_a = 4\sqrt{2} V_a = 113 \text{ liters}$$

From (i),

$$P_c = \frac{P_a V_a}{V_c} = \frac{nRT_a}{V_c} = \frac{2 \text{ mol} \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{113 \times 10^{-3} \text{ m}^3}$$

$$= 4.4 \times 10^4 \text{ Pa.}$$

(c) Work done by the gas in the part

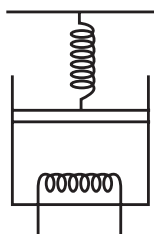
$$\begin{aligned} ab &= P_a (V_b - V_a) = P_b V_b - P_a V_a = nRT_2 - nRT_1 \\ &= 2 \text{ mol} \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (600 \text{ K} - 300 \text{ K}) = 4980 \text{ J} \end{aligned}$$

The net work done in the adiabatic part

$$bc = \frac{P_b V_b - P_c V_c}{\gamma - 1} = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{4980 \text{ J}}{5/3 - 1} = 7470 \text{ J.}$$

The net work done by the gas =  $4980 \text{ J} + 7470 \text{ J} = 12450 \text{ J}$

**Q.4** 2.00 mol of a monatomic ideal gas ( $U = 1.5 nRT$ ) is enclosed in an adiabatic, fixed vertical cylinder fitted with a smooth, light adiabatic piston. The piston is connected to a vertical spring of spring constant  $200 \text{ N m}^{-1}$  as shown in figure. The area of cross



section of the cylinder is  $20.0 \text{ cm}^2$ . Initially, the spring is at  $300 \text{ K}$ . The atmospheric and the temperature of the gas is  $300 \text{ K}$ . The atmospheric pressure is  $100 \text{ kPa}$ . The gas is heated slowly for some time by means of an electric heater so as to move the piston up through  $10 \text{ cm}$ . Find (a) the work done by the gas (g) the final temperature of the gas and (c) the heat supplied by the heater.

**Sol:** (a) The force by the gas on the piston is  $F = P_o A + kx$ . Where  $P_o = 100 \text{ kPa}$  is the atmospheric pressure,  $A = 20 \text{ cm}^2$  is the area of cross section,  $k = 200 \text{ N m}^{-1}$  is the spring constant and  $x$  is the compression of the spring. The work done by the gas as the piston moves through  $l = 10 \text{ cm}$  is

$$\begin{aligned} W &= \int_0^l F dx = \int_0^l (P_o A + kx) dx \\ &= (100 \times 10^3 \text{ Pa}) \times (20 \times 10^{-4} \text{ m}^2) \times (10 \times 10^{-2} \text{ m}) \\ &\quad + \frac{1}{2} (200 \text{ N m}^{-1}) \times (10 \times 10^{-2} \text{ m})^2 \\ &= 20 \text{ J} + 1 \text{ J} = 21 \text{ J.} \end{aligned}$$

(b) The initial temperature is  $T_1 = 300 \text{ K}$ . Let the final temperature be  $T_2 = 300 \text{ K}$ . Let the final temperature be we have

$$nRT_1 = P_o V_o \text{ and } nRT_2 = P_o V_o + \left( P_o + \frac{kl}{A} \right) (V_o + Al)$$

$$= nRT_1 + P_o Al + kl^2 + \frac{kl nRT_1}{AP_o} \quad \text{Or}$$

$$\begin{aligned} T_2 &= T_1 + \frac{P_o Al + kl^2}{nR} + \frac{klT_1}{AP_o} \\ &= (300 \text{ K}) + \frac{20 \text{ J} + 2 \text{ J}}{(2.0 \text{ mol}) (8.3 \text{ J K}^{-1} \text{ mol}^{-1})} \\ &\quad + \frac{(200 \text{ N m}^{-1}) \times (10 \times 10^{-2} \text{ m}) \times (300 \text{ K})}{(20 \times 10^{-4} \text{ m}^2) \times (100 \times 10^3 \text{ Pa})} \end{aligned}$$

$$= 300 \text{ K} + 1.325 \text{ K} + 30 \text{ K} \approx 331 \text{ K}$$

(c) The internal energy is  $U = 1.5 nRT$ . The change in internal energy is  $\Delta U = 1.5 nR\Delta T$

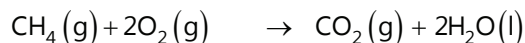
$$= 1.5 \times (2.00 \text{ mol}) \times (8.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (31 \text{ K}) = 772 \text{ J.}$$

$$\Delta Q = \Delta U + \Delta W = 772 \text{ J} + 21 \text{ J} = 793 \text{ J}$$

**Q.5** How much heat is produced in burning a mole of  $\text{CH}_4$  under standard conditions if reactants and products are brought to  $298 \text{ K}$  and  $\text{H}_2\text{O} (\text{l})$  is formed? What is the maximum amount of useful work that can be



accomplished under standard conditions by this system?



$$\Delta H_f^\circ : -74.8 \quad 0 \quad -393.5 \quad -285.85 \text{ KJ}$$

$$\Delta G_f^\circ : -50.8 \quad 0 \quad -394.4 \quad -236.8 \text{ KJ}$$

**Sol:**  $\Delta H_f^\circ = (-393.5) + (2 \times -285.85) - 74.8 - 2 \times 0 \text{ KJ/mole}$

Now the free energy change for a process,  $\Delta G$ , equals the maximum useful work that can be done by the system at constant temperature and pressure.

$$\therefore W_{\max} = \Delta G = (2 \times -236.8) + (-394.4) - 50.8 - 2 \times 0 \\ = -817.2 \text{ KJ mole CH}_4$$

**Q. 6** A heat engine operates between a cold reservoir at temperature  $T_2 = 300 \text{ K}$  and a hot reservoir at temperature  $T_1$ . It takes  $200 \text{ J}$  heat from the hot reservoir and delivers  $120 \text{ J}$  of heat to the cold reservoir in a cycle. What could be the minimum temperature of the hot reservoir?

**Sol:** The work done by the engine in a cycle is  $W = 200 \text{ J} - 120 \text{ J} = 80 \text{ J}$ .

The efficiency of the engine is

$$n = \frac{W}{Q} = \frac{80 \text{ J}}{200 \text{ J}} = 0.40$$

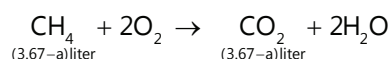
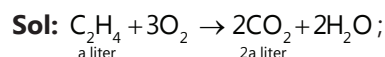
From Carnot's theorem, no engine can have efficiency greater than that of a Carnot engine.

$$\text{Thus, } T_1 \leq \frac{300 \text{ K}}{0.60} \quad \text{or } T_1 \geq 500 \text{ K}$$

$$\text{Or, } T_1 \leq \frac{300 \text{ K}}{0.60} \quad \text{or } T_1 \geq 500 \text{ K}$$

The minimum temperature of the hot reservoir has to be  $500 \text{ K}$ .

**Q.7** A gas mixture of  $3.67 \text{ liter}$  of ethylene and methane on complete combustion at  $25^\circ\text{C}$  produces  $6.11 \text{ liter}$  of  $\text{CO}_2$ . Find out the heat evolved on burning  $1 \text{ liter}$  of the gas mixture. The heats of combustion of ethylene and methane are  $-1423$  and  $-891 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ .



Given,  $2a + 3.67 - a = 6.11$ ;  $a = 2.44 \text{ liter}$

Volume of ethylene in mixture =  $2.44 \text{ liter}$

Volume of ethylene in mixture =  $1.23 \text{ liter}$

Volume of ethylene in  $1 \text{ liter}$  mixture

$$= \frac{2.44}{3.67} = 0.6649 \text{ litre}$$

Volume of ethylene in  $1 \text{ liter}$  mixture

$$= \frac{1.23}{3.67} = 0.3351 \text{ litre}$$

$24.45 \text{ liter}$  of gas at  $25^\circ\text{C}$  corresponds to  $1 \text{ mole}$ .

Thus, heat evolved by burning  $0.6649 \text{ liter}$  of ethylene

$$= \frac{1423}{24.5} \times 0.6649 = -38.69 \text{ kJ}$$

and heat evolved by burning  $0.3351 \text{ liter}$  of methane

$$= -\frac{891}{24.45} \times 0.3351 = -12.21 \text{ kJ}$$

So, total heat evolved by burning  $1 \text{ liter}$  mixture

$$= -38.68 - 12.21 = -50.90 \text{ kJ}$$

**Q.8** The enthalpies of neutralisation of a strong acid HA and weaker acid HB by NaOH are  $-13.7$  and  $-12.7 \text{ kcal/eq}$ . When one equivalent of NaOH is added to a mixture containing  $1$  equivalent of HA and HB; the enthalpy change was  $-13.5 \text{ kcal}$ . In what ratio is the base distributed between HA and HB?

**Sol:** Let  $x$  equivalent of HA and  $y$  equivalent of HB are taken in the mixture

$$x + y = 1 \quad \dots (i)$$

$$x \times 13.7 + y \times 12.7 = 13.5 \quad \dots (ii)$$

Solving eqs. (i) and (ii), we get

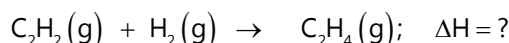
$$x = 0.8, y = 0.2$$

$$x : y = 4 : 1$$

**Q.9** Given the following standard heats of reactions:

(a) heat of formation of water =  $-68.3 \text{ kcal}$ , (b) heat of combustion of  $\text{C}_2\text{H}_2 = 310.6 \text{ kcal}$ . Calculate the heat of the reaction for the hydrogenation of acetylene at constant volume and  $25^\circ\text{C}$ .

**Sol:** The required equation is



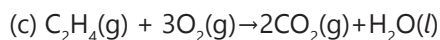
Given, (a)  $\text{H}_2(\text{g}) + 1/2\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$

$$(\Delta H = -68.3 \text{ kcal}) \quad \dots (i)$$

(b)  $\text{C}_2\text{H}_2(\text{g}) + 5/2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$

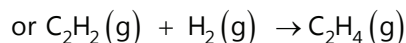
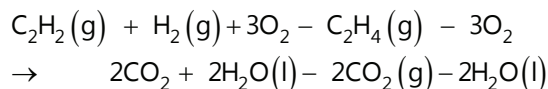
$$(\Delta H = -310.6 \text{ kcal}) \quad \dots (ii)$$





$$(\Delta H = -337.2 \text{ kcal}) \quad \dots (iii)$$

The required equation can be achieved by adding eqs. (i) and (ii) and subtracting (iii).



$$\begin{aligned} \Delta H &= -68.3 - 310.6 - (-337.2) \\ &= -378.9 + 337.2 = -41.7 \text{ kcal} \end{aligned}$$

We know that,

$$\Delta H = \Delta E + \Delta nRT \text{ or } \Delta H = \Delta E - \Delta nRT$$

$$\begin{aligned} \Delta n &= (1 - 2) = -1, R = 2 \times 10^{-3} \text{ kcal mol}^{-1}\text{K}^{-1} \text{ and } T \\ &= (25 + 273) = 298 \text{ K} \end{aligned}$$

Subtracting the values in above equation,

$$\begin{aligned} \Delta E &= -41.7 - (-1)(2 \times 10^{-3})(298) \\ &= -41.7 + 0.596 = -41.104 \text{ kcal} \end{aligned}$$

**Q.10** Using the data (all values in kilocalorie per mole at 25°C). Given below, calculate the bond energy of C-C and C-H bonds.

$$\Delta H_{\text{combustion of ethane}}^{\circ} = -372.0$$

$$\Delta H_{\text{(combustion of propane)}}^{\circ} = -530.0$$

$$\Delta H^{\circ} \text{ for } \text{C}_{(\text{graphite})} \rightarrow \text{C}(g) = +172.0$$

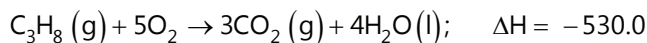
Bond energy of H-H Bond = +104.0;

$$\Delta H_f^{\circ} \text{ of } \text{H}_2\text{O}(l) = -68.0$$

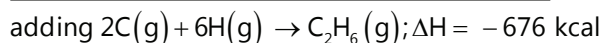
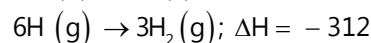
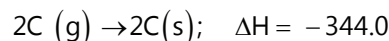
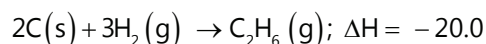
$$\Delta H_f^{\circ} \text{ of } \text{CO}_2(g) = -94.0$$

$$\text{Sol: } \text{C}_2\text{H}_6(g) + \frac{7}{2} \text{O}_2 \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l); \Delta H = -372.0$$

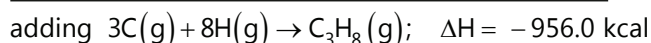
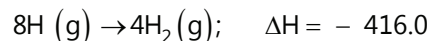
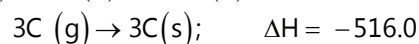
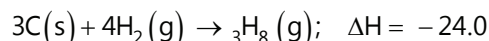
$$\Delta H_f^{\circ}(\text{C}_2\text{H}_6) = 2x(-94.0) + 3x(-68.0) + 372.0 = -20 \text{ kcal}$$



$$\Delta H_f^{\circ}(\text{C}_3\text{H}_8) = 2x(-94.0) + 4x(-68.0) + 530.0 = -24 \text{ kcal}$$



So, enthalpy of formation of 6C-H bonds and one C-C bond is -676.0 kcal.



So, enthalpy of formation of 8C-H and 2C-C bonds is -956 kcal

Let the bond energy of C-C be x and of C-H be y kcal.

$$\text{In ethane} \quad x + 6y = 676$$

$$\text{In propane} \quad 2x + 8y = 956$$

$$\text{So solving,} \quad x = 82 \text{ and } y = 99$$

Thus, bond energy of C-C = 82 kcal and bond energy of C-H = 99 kcal.

## JEE Main/Boards

### Exercise 1

**Q.1** Predict sign of work done in following reactions at constant pressure.

Initial state      Final state



**Q.2** The gas is cooled such that it loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and  $\Delta E$ ?

**Q.3** The enthalpy of combustion of glucose is -2808 kJ mol<sup>-1</sup> and 25°C. How many grams of glucose do you need to consume [Assume wt = 62.5kg].

(a) To climb a flight of stairs rising through 3m.

(b) To climb a mountain of altitude 3000m?

**Q.4** Water expand when it freezes. Determine amount of work, in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1L of ice.

**Q.5** Lime is made commercially by decomposition of limestone,  $\text{CaCO}_3$ . What is the change in internal energy when 1.00 mole of solid  $\text{CaCO}_3$  ( $V = 34.2\text{ml}$ ) absorbs 177.9 kJ of heat and decomposes at  $25^\circ\text{C}$  against a pressure of 1.0 atm to give solid  $\text{CaO}$ . (Volume = 16.9 ml) and  $\text{CO}_2(\text{g})$  ( $V=24.4\text{L}$ )?

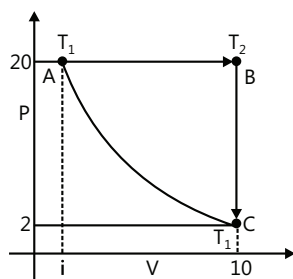
**Q.6** The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of  $\text{H}_2$  at 1.5 atm pressure is  $\Delta H = -0.31\text{ kJ}$ . What is the  $\Delta U$ ?

**Q.7** What is  $\Delta E$  when 2.0 mole of liquid water vaporises at  $100^\circ\text{C}$ ? The heat of vaporisation,  $\Delta H_{\text{vap}}$  of water at  $100^\circ\text{C}$  is  $40.66\text{ kJmol}^{-1}$ .

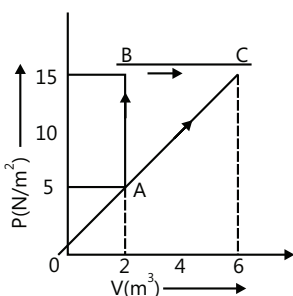
**Q.8** If 1.0 kcal of heat is added to 1.2 L of  $\text{O}_2$  in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate  $\Delta E$  and  $\Delta H$  of the pressure.

**Q.9** 1 mole of ice at  $0^\circ\text{C}$  and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find  $\Delta H$  and  $\Delta E$  if the latent heat of fusion of ice is 80 Cal/gm and latent heat of vaporisation of liquid water at  $0^\circ\text{C}$  is 596 Cal per gram and the volume of ice in comparison to that of water (vapour) is neglected.

**Q.10** The molar enthalpy of vaporization of benzene at its boiling point (353 K) is  $30.84\text{ kJmol}^{-1}$ . What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5A current in order to vaporise 7.8g of the sample at its boiling point?



**Q.11** Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext. pressure of 1 atm. Calculate  $q$ ,  $w$ ,  $\Delta U$  &  $\Delta H$ . Calculate the corresponding value of all if the above process is carried out reversibly.



**Q.12** Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at  $25^\circ\text{C}$ .

**Q.13** A real gas obeys the equation  $P(V_m - b) = RT$ , where ( $b = 0.1\text{ L/mol}$ ), if 2 moles of gas is slowly compressed from 1.2 litre to 0.6 litre at 300K then work done in the process is:

**Q.14** The moles of a ideal gas at 200 K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas  $C_V$  is  $27.5\text{ JK}^{-1}\text{ mol}^{-1}$  in this temperature range. Calculate  $q$ ,  $w$ ,  $\Delta U$ ,  $\Delta H$  and final  $V$  and final  $P$ .

**Q.15** 2 moles of an ideal gas undergoes isothermal compression along three different paths

(i) Reversible compression from  $P_i = 2\text{ bar}$  and  $V_i = 4\text{ L}$  to  $P_f = 20\text{ bar}$

(ii) A single stage compression against a constant external pressure of 20 bar, and

(iii) A two stage compression consisting initially of compression against a constant external pressure of 10 bar until  $P_{\text{gas}} = P_{\text{ext}}$  followed by compression against a constant pressure of 20 bar until  $P_{\text{gas}} = P_{\text{ext}}$ .

**Q.16** One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps:

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre.

(AB) Isobaric expansion to return the gas to the original volume of 10 litres with  $T$  going from  $T_1$  to  $T_2$ .

(BC) Cooling at constant volume to bring the gas to the original pressure and temperature.

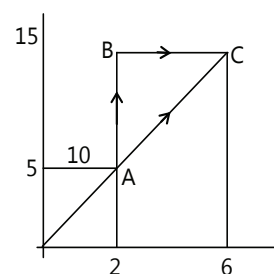
The steps are shown schematically in the figure show.

(a) Calculate  $T_1$  and  $T_2$ .

(b) Calculate  $\Delta E$ ,  $q$  and  $w$  in calories, for each step and for the cycle.

**Q.17** The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the:

(a) Path along which work done is least.



(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.

(c) Amount of heat supplied to the gas to go from A to B, if internal energy change to gas is 10 J.

**Q.18** The standard enthalpy for the reaction  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$  is - 285.76 kJ at 298 K. Calculate the value of  $\Delta H$  at 373K. The molar heat capacities at constant pressure ( $C_p$ ) in the given temperature range of  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ , and  $\text{H}_2\text{O}(\text{l})$  are respectively 38.83, 29.16 and 75.312  $\text{JK}^{-1}\text{mol}^{-1}$ .

**Q.19** Methane (Considered to be an ideal gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by  $C_p = 22.34 + 48.1 \times 10^{-3} T$  where  $C_p$  is in  $\text{JK}^{-1}\text{mol}^{-1}$ . Calculate molar (a)  $\Delta H$  (b)  $\Delta U$ .

**Q.20** One mole of NaCl(s) on melting absorbed 30.5 KJ of heat and its entropy is increased by 28.8  $\text{JK}^{-1}$ . What is the melting point of sodium chloride?

**Q.21** Oxygen is heated from 300 to 600 at a constant pressure of 1 bar. What is the increase in molar entropy? The molar heat capacity in  $\text{JK}^{-1}\text{mol}^{-1}$  for the  $\text{O}_2$  is  $C_p = 25.5 + 13.6 \times 10^{-3} T - 42.5 \times 10^{-7} T^2$

**Q.22** Calculate  $S_f^\circ$  at 298 K of ; (i) NaCl(s), (ii)  $\text{NH}_4\text{Cl}(\text{s})$  & (iii) diamond. The values of  $S^\circ$  of Na,  $\text{Cl}_2$ , NaCl,  $\text{NH}_4\text{Cl}$ ,  $\text{N}_2$ ,  $\text{H}_2$ , diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69  $\text{JK}^{-1}\text{mol}^{-1}$  respectively.

**Q.23** A cannot cycle has an efficiency of 40%. Its low temperature reservoir is at 7°C, what is the temperature of source?

**Q.24** Calculate entropy of a substance at 600 K using the following data.

(i) Heat capacity of solid from 0 K to normal melting point 200 K.  $C_{pm}(\text{s}) = 0.035 T \text{ JK}^{-1}\text{mol}^{-1}$ .

(ii) Enthalpy of fusion = 7.5 kJ  $\text{mol}^{-1}$ .

(iii) Enthalpy of vaporisation = 30 kJ  $\text{mol}^{-1}$ .

(iv) Heat capacity of liquid from 200 K to normal boiling point 300K.  $C_{pm}(\text{l}) = 60 + 0.016T \text{ JK}^{-1}\text{mol}^{-1}$ .

(v) Heat capacity of gas from 300 K to 600 J at 1 atm.  $C_{pm}(\text{g}) = 50.0 \text{ JK}^{-1}\text{mol}^{-1}$ .

**Q.25** Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The entropy change is +182.4  $\text{JK}^{-1}$  for the reaction as stated.  $\Delta H_{\text{combustion [glucose]}} = -2808 \text{ KJ}$

**Q.26** The entropies of  $\text{H}_2(\text{g})$  and  $\text{H}(\text{g})$  are 130.6 and 114.6  $\text{J mol}^{-1} \text{ K}^{-1}$  respectively at 298 K. Using the data given below calculate the bond energy of  $\text{H}_2$  (in kJ/mol):

$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g}); \Delta G^\circ = 406.62 \text{ kJ/mol}$

**Q.27** Calculate the heat produce when 3.785 lit of octane ( $\text{C}_6\text{H}_{18}$ ) reacts with oxygen to form CO and water vapour at 25°C. The density of octane is 0.7025 g/ml. Heat of combustion of  $\text{C}_6\text{H}_{18}$  is -1302.7 kcal/mol.

$\Delta H_f^\circ \text{CO}_2(\text{g}) = -94.05 \text{ kcal mol}^{-1}$ ;

$\Delta H_f^\circ \text{CO}(\text{g}) = -26.41 \text{ kcal mol}^{-1}$

$\Delta H_f^\circ \text{H}_2\text{O}(\text{l}) = -68.32 \text{ kcal mol}^{-1}$ ;

$\Delta H_f^\circ \text{H}_2\text{O}(\text{g}) = -57.79 \text{ kcal mol}^{-1}$

**Q.28** Calculate  $\Delta H_1$  and  $\Delta H_2$ .

(i) Cis -2-butene  $\rightarrow$  trans-2- butene,  $\Delta H_1$

(ii) Cis -2-butene  $\rightarrow$  1- butene,  $\Delta H_2$

(iii) Trans-2- butene is more stable than Cis -2-butene

(iv) Enthalpy of combustion of 1- butene,

$\Delta H = -649.8 \text{ kcal/mol}$

(v)  $9\Delta H_1 + 5\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans-2- butene,  $\Delta H = -647.1 \text{ kcal/mol}$ .

**Q.29** Calculate the bond energy of Xe – F from the following data

Ionization energy of Xe = 279 kcal/mol

Electron affinity of F = 85 kcal/mol

Bond energy of F - F = 38 kcal/mol and

Enthalpy change of reaction:  $\text{XeF}_4(\text{g}) \rightarrow \text{Xe}^+(\text{g}) + \text{F}^-(\text{g}) + \text{F}_2(\text{g}) + \text{F}(\text{g})$ ,  $\Delta H = 292 \text{ kcal}$

**Q.30** Using the data (all values are in kJ/mol at 25°C) given below:

$\Delta H_{\text{combustion}}^\circ$  (ethane) = -1559.8

$\Delta H_{\text{combustion}}^\circ$  (ethane) = -1410.9

$\Delta H^\circ_{\text{combustion}}$ (acetylene)	= -1299.7
$\Delta H^\circ_{\text{combustion}}$ (acetaldehyde)	= -1192.3
$\Delta H^\circ_f$ $\text{CO}_2(\text{g})$	= -393.5
$\Delta H^\circ_f$ of $\text{H}_2\text{O}(\text{l})$	= -285.8
$\Delta H^\circ_f$ for $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{g})$	= -716.68
Bond energy of H - H	= -435.94
Bond energy of O = O	= -498.34

Calculate the following bond energies:

- (i) C - C  
 (ii) C - H  
 (iii) C = O (iv) C = C (v) C  $\equiv$  C

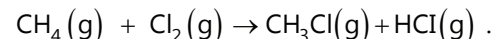
## Exercise 2

### Single Correct Choice Type

**Q.1** For which of the following change  $\Delta H \neq \Delta E$ ?

- (A)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$   
 (B)  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 (C)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$   
 (D)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

**Q.2** The reactions



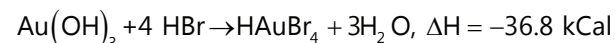
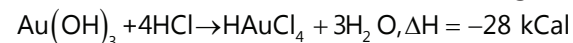
has  $\Delta H = -25 \text{ kCal}$

Bond	Bond Energy kCal
$\text{E}_{\text{C-Cl}} \rightarrow$	84
$\text{E}_{\text{H-Cl}} \rightarrow$	103
$\text{E}_{\text{C-H}} \rightarrow$	x
$\text{E}_{\text{Cl-Cl}} \rightarrow$	y
x : y = 9 : 5	

From the given data, what is the bond enthalpy of Cl-Cl bond

- (A) 70 kCal (B) 80 kCal  
 (C) 67.75 kCal (D) 57.75 kCal

**Q.3** Reactions involving gold have been of particular interest to a chemist. Consider the following reactions,



In an experiment there was an absorption of 0.44 kCal when one mole of  $\text{HAuBr}_4$  was mixed with 4 moles of

HCl. What is the percentage conversion of  $\text{HAuBr}_4$  into  $\text{HAuCl}_4$ ?

- (A) 0.5 % (B) 0.6 % (C) 5 % (D) 50 %

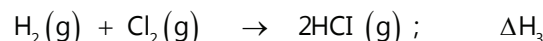
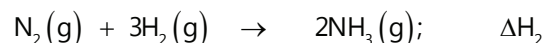
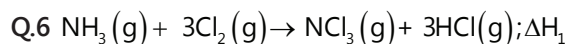
**Q.4** If  $x_1$ ,  $x_2$  and  $x_3$  are enthalpies of H-H, O=O and O-H bonds respectively, and  $x_4$  is the enthalpy of vaporization of water, estimate the standard enthalpy of combustion of hydrogen

- (A)  $x_1 + \frac{x_2}{2} - 2x_3 + x_4$  (B)  $x_1 + \frac{x_2}{2} - 2x_3 - x_4$   
 (C)  $x_1 + \frac{x_2}{2} - x_3 + x_4$  (D)  $2x_3 - x_1 - \frac{x_2}{2} - x_4$

**Q.5** For the allotropic change represented by the equation  $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$ ,

$H = 1.9 \text{ kJ}$ . If 6 g of diamond and 6 g of graphite are separately burnt to yield  $\text{CO}_2$ , the enthalpy liberated in first case is

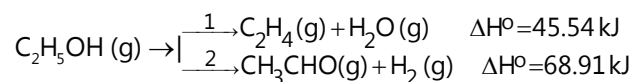
- (A) Less than in the second case by 1.9 kJ  
 (B) More than in the second case by 11.4 kJ  
 (C) More than in the second case by 0.95 kJ  
 (D) Less than in second case by 11.4 kJ



The enthalpy of formation of  $\text{NCl}_3(\text{g})$  in the terms of  $\Delta H_1$ ,  $\Delta H_2$  and  $\Delta H_3$  is

- (A)  $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$   
 (B)  $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$   
 (C)  $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$   
 (D) None of these

**Q.7** Ethanol can undergo decomposition to form two sets of products



If the molar ratio of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO}$  is 8: 1 in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is.

- (A) 65.98 kJ (B) 48.137 kJ  
 (C) 48.46 kJ (D) 57.22 kJ

**Q.8** A reversible heat engine A (based on Carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at  $T_2$ . A second reversible engine B absorbs the same amount of heat as rejected by the engine A, from the reservoir at  $T_2$  and rejects energy to a reservoir at 360 K. If the efficiencies of engines A and B are the same then the temperature  $T_2$  is

- (A) 680 K (B) 640 K  
(C) 600 K (D) None of these

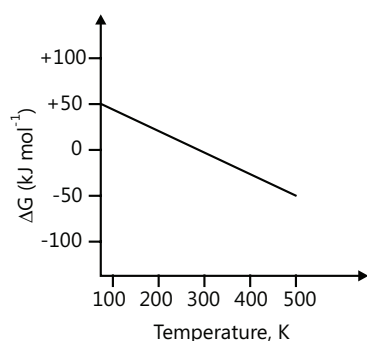
**Q.9** The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically

- (A)  $\frac{3}{2}R \ln\left(\frac{300}{200}\right)$  (B)  $\frac{5}{2}R \ln\left(\frac{573}{273}\right)$   
(C)  $3R \ln\left(\frac{573}{273}\right)$  (D)  $\frac{5}{2}R \ln\left(\frac{573}{473}\right)$

**Q.10** What is the free energy change (G) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure?

- (A) Zero cal (B) 540 cal  
(C) 517.13 cal (D) 510 cal

**Q.11** What can be concluded about the values of  $\Delta H$  and  $\Delta S$  from this graph?



- (A)  $\Delta H > 0, \Delta S > 0$  (B)  $\Delta H > 0, \Delta S < 0$   
(C)  $\Delta H < 0, \Delta S > 0$  (D)  $\Delta H < 0, \Delta S < 0$

**Q.12** If  $\Delta H_{\text{vaporization}}$  of substance X (l) (molar mass: 30 g/mol) is 300 J/mol at its boiling point 300 K, then molar entropy change for reversible condensation process is

- (A) 30 J/mol K (B) -300 J/mol K  
(C) -30 J/mol K (D) None of these

**Q.13** The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm is:

- (A) 1.385 cal/K (B) -1.2 cal/K  
(C) 1.2 cal/K (D) 2.77 cal/K

## Previous Years' Questions

**Q.1** Assuming that water vapour is an ideal gas, the internal energy (U) when 1 mol of water is vaporized at 1 bar pressure and 100°C, (Given: Molar enthalpy of vaporization of water at 1 bar and 373 K = 41 kJ mol<sup>-1</sup> and  $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$ ) will be **(2007)**

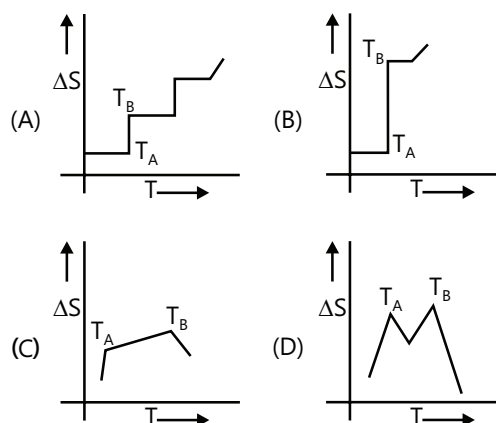
- (A) 4100 kJ mol<sup>-1</sup> (B) 3.7904 kJ mol<sup>-1</sup>  
(C) 37.904 kJ mol<sup>-1</sup> (D) 41.00 kJ mol<sup>-1</sup>

**Q.2** For the reaction,  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ;  $\Delta H = 560 \text{ kJ}$

Two moles of CO and one mole of  $\text{O}_2$  are taken in a container of volume 1 L. They completely form two moles of  $\text{CO}_2$ , the gases deviate appreciably from ideal behavior. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of  $\Delta U$  at 00 K (1 L atm = 0.1 kJ) **(2006)**

- (A) 563 (B) 575 (C) 585 (D) 595

**Q.3** If for a given substance melting point is  $T_B$  and freezing point is  $T_A$ , then correct variation shown by graph between entropy change and temperature is **(2001)**



**Q.4** Identify the correct statement regarding a spontaneous process **(2007)**

- (A) For a spontaneous process in an isolated system, the change in entropy is positive.  
(B) Endothermic processes are never spontaneous  
(C) Exothermic processes are always spontaneous  
(D) Lowering of energy in the reaction process is the only criterion for spontaneity.

**Q.5** If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point then **(2002; 2005)**

- (A)  $\Delta H$  is -ve,  $\Delta S$  is +ve  
 (B)  $\Delta H$  and  $\Delta S$  both are +ve  
 (C)  $\Delta H$  and  $\Delta S$  both are -ve  
 (D)  $\Delta H$  is +ve,  $\Delta S$  is -ve

**Q.6** The enthalpy of vaporization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vaporization is  $75 \text{ J mol}^{-1} \text{ K}$ . The boiling point of the liquid at 1 atm is **(2004)**

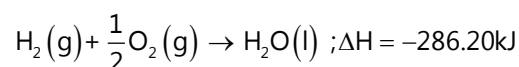
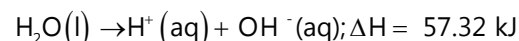
- (A) 250K (B) 400K  
 (C) 450K (D) 600K

**Q.7** The standard molar heat of formation of ethane,  $\text{CO}_2$  and water (l) are respectively -2.1, -94.1 and -68.3 kcal. The standard molar heat of combustion of ethane will be, **(1986)**

- (A) -372 kcal (B) 162 kcal  
 (C) -240 kcal (D) 183.5 kcal

**Q.8** On the basis of the following thermochemical data:

$$(\Delta_f G^\circ \text{H}^+_{(\text{aq})} = 0)$$



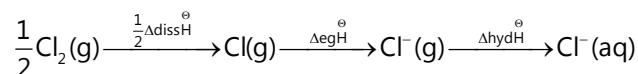
The value of enthalpy of formation of  $\text{OH}^-$  ion at  $25^\circ\text{C}$  is **(2009)**

- (A) -22.88 kJ (B) -22.8.88 kJ  
 (C) +228.88 kJ (D) -343.52 kJ

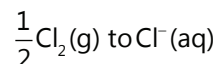
**Q.9** Standard molar enthalpy of formation of  $\text{CO}_2$  is equal to **(1997; 2001)**

- (A) Zero  
 (B) The standard molar enthalpy of combustion of gaseous carbon  
 (C) The sum of standard molar enthalpies of formation of CO and  $\text{O}_2$   
 (D) The standard molar enthalpy of combustion of carbon (graphite)

**Q.10** Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below



The energy involved in the conversion of



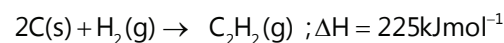
(Using the data  $\Delta_{\text{diss}}^\circ \text{HCl}_2 = 240 \text{ kJmol}^{-1}$ ,  $\Delta_{\text{eq}}^\circ \text{H}_{\text{Cl}} = -349 \text{ kJmol}^{-1}$ ,  $\Delta_{\text{hyd}}^\circ \text{H}_{\text{Cl}} = -381 \text{ kJmol}^{-1}$ ) will be **(2008)**

- (A) -610  $\text{kJmol}^{-1}$  (B) -850  $\text{kJmol}^{-1}$   
 (C) +120  $\text{kJmol}^{-1}$  (D) +152  $\text{kJmol}^{-1}$

**Q.11** If the bond dissociation energies of XY,  $\text{X}_2$  and  $\text{Y}_2$  (all diatomic molecules) are in the ratio of 1:1: 0.5 and  $\Delta_f H$  for the formation of XY is  $-200 \text{ kJmol}^{-1}$ . The bond dissociation energy of  $\text{X}_2$  will be **(2005)**

- (A) 100  $\text{kJmol}^{-1}$  (B) 800  $\text{kJmol}^{-1}$   
 (C) 300  $\text{kJmol}^{-1}$  (D) 400  $\text{kJmol}^{-1}$

**Q.12** Using the data provided, calculate the multiple bond energy ( $\text{kJ mol}^{-1}$ ) of a C=C bond in  $\text{C}_2\text{H}_2$ . That energy is (take the bond energy of a C-H bond as  $350 \text{ kJ mol}^{-1}$ )



**(2012)**

- (A) 1165 (B) 837 (C) 865 (D) 815

**Q.13** In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy ( $dG$ ) and change in entropy ( $dS$ ), satisfy the criteria **(2003)**

- (A)  $(dS)_{(V,E)} < 0, (dG)_{(T,P)} < 0$   
 (B)  $(dS)_{(V,E)} > 0, (dG)_{(T,P)} < 0$   
 (C)  $(dS)_{(V,E)} = 0, (dG)_{(T,P)} = 0$   
 (D)  $(dS)_{(V,E)} = 0, (dG)_{(T,P)} > 0$

**Q.14** For a particular reversible reaction at temperature T,  $\Delta H$  and  $\Delta S$  were found to be both +ve. If is the temperature  $T_e$  at equilibrium, the reaction would be spontaneous when **(2003)**

- (A)  $T = T_e$  (B)  $T_e > T$   
 (C)  $T > T_e$  (D)  $T_e$  is 5 time T



**Q.15** For which one of the following reactions,  $\Delta H$  is not equal to  $\Delta E$  (1995)

- (A)  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$   
 (B)  $\text{C}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$   
 (C)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$   
 (D)  $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightleftharpoons \text{NaCl}(\text{aq}) + \text{H}_2\text{O}$

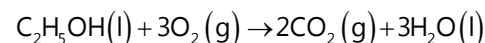
**Q.16** A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of  $q$  and  $w$  for the process will be:

(2013)

( $R = 8.314 \text{ J/mol K}$ ) ( $\ln 7.5 = 2.01$ )

- (A)  $q = +208 \text{ J}$ ,  $w = -208 \text{ J}$   
 (B)  $q = -208 \text{ J}$ ,  $w = -208 \text{ J}$   
 (C)  $q = -208 \text{ J}$ ,  $w = +208 \text{ J}$   
 (D)  $q = +208 \text{ J}$ ,  $w = +208 \text{ J}$

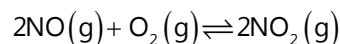
**Q.17** For complete combustion of ethanol,



The amount of heat produced as measured in bomb calorimeter, is  $1364.47 \text{ kJ mol}^{-1}$  at 25°C. Assuming ideality the enthalpy of combustion,  $\Delta_c H$ , for the reaction will be ( $R = 8.314 \text{ kJ mol}^{-1}$ ) (2014)

- (A)  $-1366.95 \text{ kJ mol}^{-1}$  (B)  $-1361.95 \text{ kJ mol}^{-1}$   
 (C)  $-1460.50 \text{ kJ mol}^{-1}$  (D)  $-1350 \text{ kJ mol}^{-1}$

**Q.18** The following reaction is performed at 298 K



The standard free energy of formation of  $\text{NO}(\text{g})$  is  $86.6 \text{ kJ/mol}$  at 298 K. What is the standard free energy of formation of  $\text{NO}_2(\text{g})$  at 298 K? ( $K_p = 1.6 \times 10^{12}$ )

(2015)

- (A)  $R(298) \ln(1.6 \times 10^{12}) - 86600$   
 (B)  $86600 + R(298) \ln(1.6 \times 10^{12})$   
 (C)  $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$   
 (D)  $0.5 \left[ 2 \times 86,600 - R(298) \ln(1.6 \times 10^{12}) \right]$

**Q.19** The heats of combustion of carbon and carbon monoxide are  $-393.5$  and  $-283.5 \text{ kJ mol}^{-1}$ , respectively. The heat of formation (in kJ) of carbon monoxide per mole is: (2016)

- (A) 676.5 (B)  $-676.5$   
 (C)  $-110.5$  (D) 110.5

## JEE Advanced/Boards

### Exercise 1

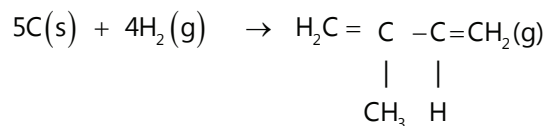
**Q.1** When 2 moles of  $\text{C}_2\text{H}_6(\text{g})$  are completely burnt 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of  $\text{C}_2\text{H}_6(\text{g})$ . Given  $\Delta_f H$  for  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are  $-395$  &  $286 \text{ kJ}$  respectively.

**Q.2** Calculate standard enthalpies of formation of carbon – di – sulphide. Given the standard enthalpy of combustion of carbon (s), sulphur (s) and carbon – di – sulphide are:  $-393.3$ ,  $-293.72$  and  $-1108.76 \text{ kJ mol}^{-1}$  respectively.

**Q.3** From the following data at 25° C, calculate the standard enthalpy of formation of  $\text{FeO}(\text{s})$  and of  $\text{Fe}_2\text{O}_3(\text{s})$ .

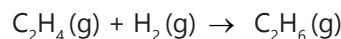
Reaction	$\Delta_r H^\circ (\text{kJ/mole})$
(A) $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{C}(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{CO}(\text{g})$	492.6
(B) $\text{FeO}(\text{s}) + \text{C}(\text{g}) \rightarrow \text{Fe}(\text{s}) + 3\text{CO}(\text{g})$	155.8
(C) $\text{C}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-393.51
(D) $\text{CO} + 11\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-282.98

**Q.4** Using bond enthalpy data, calculate enthalpy of formation of isoprene.



Given: C – H = 98.8 k Cal; H – H = 104 k Cal;  
C – C = 83 k Cal; C = C = 147 k Cal &  
C(s) → C (g) = 171 k Cal

**Q.5** Using the bond enthalpy data given below, calculate the enthalpy change for the reaction



Data:

Bond	C – C	C = C	C – H	H – H
Bond Enthalpy	336.81 kJ 1mol	606.68 kJ 1mol	410.87 kJ 1mol	431.79 kJ 1mol

**Q.6** Using the given data calculate enthalpy of formation of acetone (g). [All values in kJmol<sup>-1</sup>] bond enthalpy of:

C – H = 413.4;	C – C = 347.0;	(C = O = 728.0;
(O = O) = 495.0;	H – H = 435.8;	$\Delta_{\text{sub}}\text{H of C} = 718.4$

**Q.7** Calculate the enthalpy change when infinitely dilute solution of CaCl<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> are mixed  $\Delta_f\text{H}^\circ$  for Ca<sup>2+</sup> (aq), CO<sub>3</sub><sup>2-</sup> (ap) and CaCO<sub>3</sub> (s) are – 129.80, – 161.65, – 288.5 k Cal mol<sup>-1</sup> respectively.

**Q.8** The enthalpies of neutralization of NaOH & NH<sub>4</sub>OH by HCl are – 13680 Cal and – 12270 Cal respectively. What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH<sub>4</sub>Cl in solution? Assume that NH<sub>4</sub>OH and NaCl are quantitatively obtained.

**Q.9** 1.00 Lit sample of a mixture of CH<sub>4</sub> (g) and O<sub>2</sub> (g) measured at 25° C and 740 bar was allowed to react at constant pressure in a Calorimeter which together with its contents had a heat capacity of 1260 Cal/K. The complete combustion of methane to CO<sub>2</sub> and H<sub>2</sub>O caused a temperature rise, in the Calorimeter, of  $\Delta\text{H}^\circ_{\text{comb}}(\text{CH}_4) = -215 \text{ k Cal mol}^{-1}$ .

**Q.10** Two solution initially 25°C were mixed in an adiabatic constant pressure Calorimeter one contains 400 ml of 0.2 M weak mono protic acid solution. The other contains 100 ml of 0.80 M NaOH. After mixing temperature increased to 26.2°C. How much heat is

evolved in the neutralization of 1 mole of acid? Assume of solution 1.0 g/cm<sup>3</sup>, and specific heat of solution 4.2 J/g-K Neglect heat capacity of the Calorimeter.

**Q.11** Calculate the electron gain enthalpy of fluorine atom using the following data. Make Born – Haber's cycle. All the values are in kJ mol<sup>-1</sup> at 25°C  $\Delta\text{H}_{\text{diss}}(\text{F}_2) = 160$ ,  $\Delta_f\text{H}(\text{NaF(s)}) = 571$ , I. E. [Na (g)] = 494,  $\Delta\text{H}_{\text{vap}}[\text{Na(s)}] = 101$ . Lattice enthalpy of NaF(s) = 894.

**Q.12** Calculate the enthalpy of combustion of methyl alcohol at 298 K from the following data

Bond	C – H	C – O	O – H	O = O	C = O
Bond Enthalpy (kJ mol <sup>-1</sup> )	414	351.5	464.5	494	711

Resonance energy of CO<sub>2</sub> = – 143 kJ mol<sup>-1</sup>

Latent heat of vaporization of methyl alcohol = 35.5 kJ mol<sup>-1</sup>

Latent heat of vaporization of water = 40.6 kJ mol<sup>-1</sup>

**Q.13** Calculate work done in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1atm to final pressure of 2 atm Initial temperature = 300 K.

- (a) If process is carried out reversibly  
(b) If process is carried out irreversible against 2atm external pressure.

Computer the final volume reached by gas in two cases and describe the work graphically.

**Q.14** One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure Calculate.

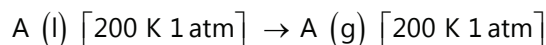
- (a) Work done by the gas  
(b) The heat exchanged by the gas in path CA and AB  
(c) Net heat absorbed by the gas in the path BC.  
(d) The max temperature attained by the gas during the cycle.

**Q.15** One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of  $\Delta S_{\text{gas}}$  and  $\Delta S_{\text{total}}$  under the following conditions.

- (i) Expansion is carried out reversibly.  
(ii) Expansion is carried out irreversibly where 836.8 J of heat is less absorbed than in  
(iii) Expansion is free.



**Q.16** The enthalpy change for vaporization of liquid 'A' at 200 K and 1 atm is 22 kJ 1 mol. Find out  $\Delta S_{\text{vaporization}}$  for liquid 'A' at 200 K? The normal boiling point of liquid 'A' is 300 K.



Given:  $C_{p,m}(A, g) = 30 \text{ J } 1 \text{ mol}^{-1} \text{ K}^{-1}$ ,  $C_{p,m}(A, l) = 40 \text{ J } 1 \text{ mol}^{-1} \text{ K}^{-1}$ ;

Use:  $\ln(312) = 0.405$

**Q.17** One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{suit}}$  and  $\Delta S_{\text{total}}$  in

- When the process carried out reversibly.
- When the process carried out irreversibly (one step)

**Q.18** Compute  $\Delta_r G$  for the reaction  $\text{H}_2\text{O}(l, 1 \text{ atm}, 323 \text{ K}) \rightarrow \text{H}_2\text{O}(g, 1 \text{ atm}, 323 \text{ K})$

Given that:  $\Delta_{\text{vap}} H$  at 373 K = 40.639 kJ mol<sup>-1</sup>,  $C_p(\text{H}_2\text{O}, l) = 75.312 \text{ J } \text{K}^{-1} \text{ mol}^{-1}$ ,

$C_p(\text{H}_2\text{O}, g) = 33.305 \text{ J } \text{K}^{-1} \text{ mol}^{-1}$ .

**Q.19** 10g of neon initially at a pressure of 506.625 kPa and temperature of 473 K expand adiabatically to a pressure of 202.65 kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.

- Expansion is carried out reversibly.
- Expansion occurs against a constant external pressure of 202.65 kPa.
- Expansion is a free expansion.

**Q.20** At 298 K,  $\Delta H_{\text{combustn}}^\circ(\text{sucrose}) = -5737 \text{ KJ } 1 \text{ mol}$  and  $\Delta G_{\text{combustn}}^\circ(\text{sucrose}) = -6333 \text{ KJ } 1 \text{ mol}$ .

**Q.21** The standard enthalpy of formation of FeO &  $\text{Fe}_2\text{O}_3$  is -65 kCal mol<sup>-1</sup> and -197 kCal mol<sup>-1</sup> respectively. A mixture of two oxides contains FeO &  $\text{Fe}_2\text{O}_3$  in the mole ratio 2:1. If by oxidation, it is changed into a 1:2 mole ratio mixture, how much of thermal energy will be released per mole of the initial mixture?

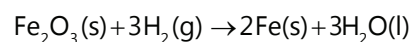
**Q.22** The enthalpies of neutralization of a weak acid HA & a weak acid HB by NaOH are -6900 cal equivalent & -2900 cal equivalent respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was -3900 Calories. In what ratio is the base distributed between HA & HB?

**Q.23** Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess HgO with 41.84 kJ of heat at

- Constant pressure.
- Constant volume

Given:  $\Delta H_f^\circ(\text{HgO}(s)) = -90.8 \text{ kJ } \text{mol}^{-1}$  &  $M(\text{Hg}) = 200.6 \text{ g } \text{mol}^{-1}$

**Q.24** For reduction of ferric oxide by hydrogen,



$\Delta H_{298}^\circ = -35.1 \text{ kJ}$ . The reaction was found to be too exothermic to be convenient. It is desirable that  $\Delta H^\circ$  should be at the most -26 kJ. At what temperature is it possible?

$C_p[\text{Fe}_2\text{O}_3] = 104.5$ ,  $C_p[\text{Fe}(s)] = 25.5$ ,  
 $C_p[\text{H}_2(l)] = 75.3$ ,  $C_p[\text{H}_2(g)] = 28.9$

(All in J/mol)

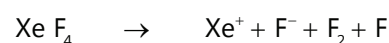
**Q.25** An intimate mix of ferric oxide and Al is used as solid rocket fuel. Calculate the fuel value per gm and fuel value per CC of the mix. Enthalpy of formation & densities are:

$\Delta H_f^\circ(\text{Al}_2\text{O}_3) = -399 \text{ kCal/mole}$ ;

$\Delta H_f^\circ(\text{Fe}_2\text{O}_3) = -199 \text{ kCal/mole}$ ,

Density of  $\text{Fe}_2\text{O}_3 = 5.2 \text{ g/cc}$ ; density of Al = 2.7 g/cc.

**Q.26** Calculate the enthalpy change for the reaction



The average Xe-F bond enthalpy is 34 kCal/mol, first I.E. of Xe is 279 kCal/mol, electron affinity of is 85 kCal/mol & bond dissociation enthalpy of  $\text{F}_2$  is 38 kCal/mol.

**Q.27** Calculate the proton gain enthalpy of  $\text{NH}_3(g)$  from the following data (in kJ/mole)

$\Delta H_{\text{dissociation}}^\circ(\text{H}_2(g)) = 218$ ;  $\Delta H_{\text{dissociation}}^\circ(\text{Cl}_2(g)) = 124$

$\Delta H_{\text{formation}}^\circ(\text{NH}_3(g)) = -46$ ;  $\Delta H_f^\circ(\text{NH}_4\text{Cl}(s)) = -314$

Lattice enthalpy of  $\text{NH}_4\text{Cl}(s) = -683$

Ionization enthalpy of H = 1310

Electron affinity of Cl = 348.

**Q.28** During one of his adventures, Chacha Chaudhary got trapped in an underground cave which was sealed two hundred years back. The air inside was poisonous, having some amount of carbon monoxide in addition

to  $O_2$  and  $N_2$ . Sabu, being huge, could not enter the cave. So, in order to save Chacha Chaudhary, he started sucking the poisonous air out of the cave by mouth. Each time he used to fill his lungs with cave air and exhale it out in the surroundings. In the meantime, fresh air from the surroundings effused into the cave till the pressure was again one atmosphere. Each time Sabu sacked out some air, the pressure in the cave dropped to half its initial value of one atmosphere.

An initial sample of air taken from the cave measured 11.2 mL at STP and gave 7J on complete combustion at constant pressure.

(i) If the safe level of CO in the atmosphere is less than 0.001% by volume, how many times does Sabu need to suck out air in order to save Chacha Chaudhary?

(ii) Sabu should rescue Chacha Chaudhary within 6 minutes else he will die. Precious 80 seconds are wasted in thinking of a way to rescue him. At maximum, how much time should each cycle of inhaling-exhaling take?

$\Delta H^\circ_{\text{comb}}(\text{CO}) = -280 \text{ kJ mol}^{-1}$ . Neglect any use of Graham's Law.

**Q.29** Find the Bond enthalpy (in kJ/mol) of one "three centre two electron bond" in  $B_2H_6$

$\{B-H-B \rightarrow 2B(g) + H(g)\}$  from the given data.

$$\Delta H^\circ_t [BH_3(g)] = 100 \text{ kJ/mole}$$

$$\Delta H^\circ_t [B_2H_6(g)] = 36 \text{ kJ/mole}$$

$$\Delta H_{\text{atm}} [B(s)] = 565 \text{ kJ/mole}$$

$$\Delta H_{\text{atm}} [H_2(g)] = 436 \text{ kJ/mole}$$

**Q.30** The heat of neutralization of:

(i)  $CHCl_2-COOH$  by NaOH is 12830 cal;

(ii) HCl by NaOH is 13680 cal

(iii)  $NH_4OH$  by HCl is 12270 cal.

What is the heat of neutralization of dichloroacetic acid by  $NH_4OH$ . Calculate also the heats of ionization of dichloroacetic acid and  $NH_4OH$ .

## Exercise 2

### Single Correct Choice Type

**Q.1** Hydrazine, a component of rocket fuel, undergoes combustion to yield  $N_2$  and  $H_2O$ .

$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$  What is the enthalpy combustion of  $N_2H_4$  (kJ/mole).

Given Reaction	$\Delta H/\text{kJ}$
$2NH_3(g) + 3N_2O(g) \rightarrow 4N_2(g) + 3H_2O(l)$	1011 kJ
$N_2O(g) + 3H_2(g) \rightarrow N_2H_4(l) + H_2O(l)$	-317 kJ
$4NH_3(g) + O_2(g) \rightarrow 2N_2H_4(l) + 2H_2O(l)$	286 kJ
$H_2(g) + 1/2O_2(g) \rightarrow H_2O(l)$	-385 kJ

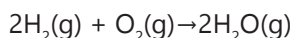
(A) -620.5 (B) -622.75

(C) 1167.5 (D) +622.75

**Q.2** Find  $\Delta_r U^\circ$  for the reaction  $4HCl(g) + O_2(g) \rightarrow 2Cl_2 + 2H_2O(g)$  at 300 K. Assume all gases are ideal.

Given:  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

$$\Delta_r H^\circ_{300} = -184.5 \text{ kJ/mole}$$

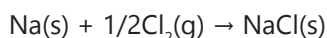


$$\Delta_r H^\circ_{300} = -483 \text{ kJ/mole (Use } R = 8.3 \text{ J/mole)}$$

(A) 111.5 kJ/mole (B) -109.01 kJ/mole

(C) -111.5 kJ/mole (D) None of these

**Q.3** The enthalpy changes at the following reactions at  $27^\circ\text{C}$  are



$$\Delta_r H = -411 \text{ kJ/mol}$$



$$\Delta_r H = -811 \text{ kJ/mol}$$

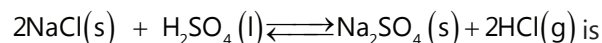


$$\Delta_r H = -1382 \text{ kJ/mol}$$



$$\Delta_r H = -92 \text{ kJ/mol; } R = 8.3 \text{ J/K-mol}$$

From these data, the heat change of reaction at constant volume (in kJ/mol) at  $27^\circ\text{C}$  for the purpose



(A) 67 (B) 62.02 (C) 71.98 (D) None

**Q.4** For the reaction at 300K  $A(g) + B(g) \rightarrow C(g)$

$$\Delta E = -3.0 \text{ kcal; } \Delta S = -10.0 \text{ cal/K; value of } G \text{ is?}$$

(A) -600 cal (B) -6600 cal

(C) -6000 cal (D) None

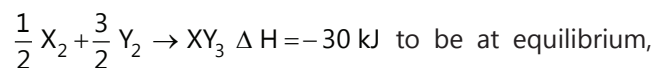
**Q.5** What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure?

(A) 80 cal (B) 540 cal (C) 620 cal (D) Zero

**Q.6** The enthalpy of tetramerization of X in gas phase ( $4X(g) \rightarrow X_4(g)$ ) is  $-100 \text{ kJ/mol}$  at  $300 \text{ K}$ . The enthalpy of vaporisation for liquid X and  $X_4$  are respectively  $30 \text{ kJ/mol}$  and  $72 \text{ kJ/mol}$  respectively.  $\Delta S$  for tetramerization of X in liquid phase is  $-125 \text{ J/Kmol}$  at  $300 \text{ K}$ , what is the  $\Delta G$  at  $300 \text{ K}$  for tetramerization of X in liquid phase?

- (A)  $-52 \text{ kJ/mol}$  (B)  $-89.5 \text{ kJ/mol}$   
(C)  $-14.5 \text{ kJ/mol}$  (D) None of these

**Q.7** Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_3$  are  $60$ ,  $40$  and  $50 \text{ JK}^{-1}\text{mol}^{-1}$ , respectively. For the reaction



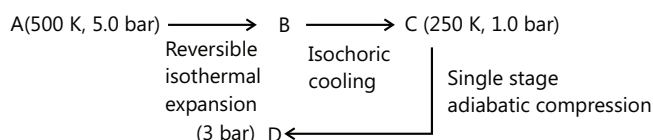
to be at equilibrium, the temperature will be

- (A)  $1250 \text{ K}$  (B)  $500 \text{ K}$  (C)  $750 \text{ K}$  (D)  $1000 \text{ K}$

**Q.8** When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into contact into thermal contact and isolated from its surrounding. The total change in entropy of system is given by

- (A)  $C \ln \frac{T_c + T_h}{2T_c}$  (B)  $C \ln \frac{T_2}{T_1}$   
(C)  $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$  (D)  $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

**Q.9** Two moles of an ideal gas ( $C_m = 312 \text{ R}$ ) is subjected to following change of state.



The correct statement is 1 are:

- (A) The pressure at B is  $2.0 \text{ bar}$   
(B) The temperature at D is  $450 \text{ K}$   
(C)  $\Delta H_{CD} = 1000 \text{ R}$   
(D)  $\Delta U_{BC} = 375 \text{ R}$

### Multiple Correct Choice Type

**Q.10** From the following data at  $25^\circ\text{C}$

Reaction	$\Delta_f H^\circ \text{ kJ/mol}$
$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g})$	42

$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	-242
$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	436
$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$	495

Which of the following statement(s) is/ are correct:

- (A)  $\Delta_f H^\circ$  for the reaction  $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$  is  $925.5 \text{ kJ/mol}$   
(B)  $\Delta_f H^\circ$  for the reaction  $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$  is  $502 \text{ kJ/mol}$   
(C) Enthalpy of formation of  $\text{H}(\text{g})$  is  $-218 \text{ kJ/mol}$   
(D) Enthalpy of formation of  $\text{OH}(\text{g})$  is  $42 \text{ kJ/mol}$

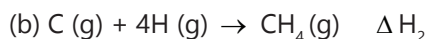
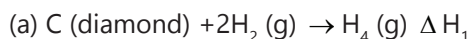
**Q.11** Which of the following is true?

- (A) For the reaction  $\text{CaCO}_3(\text{calcite}) \rightarrow \text{CaCO}_3(\text{aragonite})$

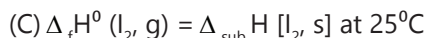
Given:  $\Delta_f G_{298}^\circ(\text{calcite}) = -1128.8 \text{ kJ/mol}$ ,  $\Delta_f G_{298}^\circ(\text{aragonite}) = -1127.75 \text{ kJ/mol}$ ,

Then calcite forms in thermodynamically more stable at standard conditions.

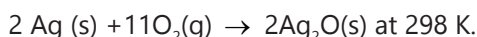
- (B) For the reaction,



Then more heat is evolved in reaction (b)



- (D) For the exothermic reaction



$$\Delta H < \Delta U$$

**Q.12** Which of the following statement (s) is /are true?

- (A) When  $(\Delta_{\text{system}})_{\text{TP}} < 0$ ; the reaction must be exothermic  
(B)  $\Delta_f H^\circ(\text{S, monoclinic}) \neq 0$

(C) If dissociation enthalpy of  $\text{CH}_4(\text{g})$  is  $1656 \text{ kJ/mol}$  and  $\text{C}_2\text{H}_6(\text{g})$  is  $2812 \text{ kJ/mole}$ , then value of C-C bond enthalpy will be  $328 \text{ kJ/mole}$

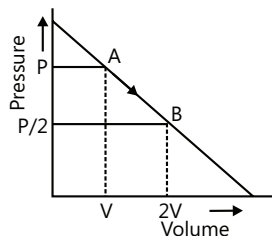
- (D) If  $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$

$$\Delta_f H^\circ = -56 \text{ kJ/mol}$$

$\Delta_f H^\circ(\text{H}_2\text{O, g}) = -242 \text{ kJ/mole}$ ; Enthalpy of vaporization of liquid water =  $44 \text{ kJ/mol}$  then  $\Delta_f H^\circ(\text{H}_2\text{O, g})$

$$= -142 \text{ kJ/mole};$$

**Q.13** An ideal gas is taken from state A (Pressure  $P$ , Volume  $V$ ) to the state B (Pressure  $P/2$ , Volume  $2V$ ) along a straight line path in PV diagram as shown in the adjacent figure



Select the correct statement(s) among the following

- (A) The work done by gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along the isotherm
- (B) In the T-V diagram, the path AB become part of the parabola
- (C) In the P-T diagram, the path AB become part of the hyperbola
- (D) In going from A to B the temperature  $T$  of the gas first increases to a maximum value then decreases.

**Q.14** The normal boiling point of a liquid 'A' is 350K.  $\Delta H_{\text{vap}}$  at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume  $\Delta H_{\text{vap}}$  to be independent of pressure).

- (A)  $\Delta S_{\text{vaporisation}} > 100 \text{ J/Kmole}$  at 350 K and 0.5 atm
- (B)  $\Delta S_{\text{vaporisation}} > 100 \text{ J/Kmole}$  at 350 K and 0.5 atm
- (C)  $\Delta S_{\text{vaporisation}} > 100 \text{ J/Kmole}$  at 350 K and 2 atm
- (D)  $\Delta S_{\text{vaporisation}} > 100 \text{ J/Kmole}$  at 350 K and 2 atm

**Q.15** Which statement is are correct?

- (A) Final temperature in reversible adiabatic expansion is lesser than in irreversible adiabatic expansion
- (B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase
- (C) When an ideal gas is subjected to adiabatic expansion it gets cooled.
- (D) Entropy increases in atomisation of dihydrogen

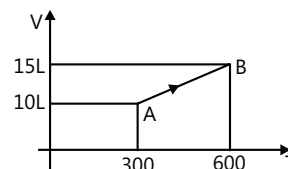
**Q.16** Which one is (are) correct statement?

- (A)  $W_{\text{adiabatic}} > W_{\text{isothermal}}$  in an ideal gas compression from same initial state to same final volume
- (B) The value of  $\gamma \frac{C_p}{C_v}$  remains constant for diatomic gas at all temperature

(C) Entropy increases when an ideal gas expanded isothermally

(D)  $\Delta S_r$  and  $\Delta H_r$  both are +ve for the decomposition of  $\text{Mg C}_3(\text{s})$

**Q.17** If one mole monoatomic ideal gas was taken through process AB as shown in figure, then select correct option(s).



- (A)  $W_{AB} = -2496.52 \text{ J}$
- (B)  $q_{AB} = 5237.82 \text{ J}$
- (C)  $H_{AB} = 3741.3 \text{ J}$
- (D)  $S_{AB}$  is +ve

**Q.18** Which of the following statement(s) is/are correct?

(A) Reversible isothermal compression of an ideal gas represents the limiting minimum value of the work done (w) by the surrounding on the system for isothermal process.

(B) In an irreversible process, the cyclic integral of work is not zero.

(C) For thermodynamic changes in adiabatic process

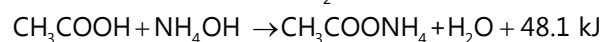
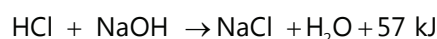
$$T \left( \frac{C_{pm}}{R} \right) P = \text{constant}$$

**Q.19** Which of the following is true for reversible adiabatic process involving an ideal gas?

- (A) Gas with higher  $\gamma$  has high magnitude of slope in a P (y-axis) vs T (x-axis) curve
- (B) Gas with higher  $\gamma$  has high magnitude of slope in a V (y-axis) vs T (x-axis) curve
- (C) Gas with higher  $\gamma$  has high magnitude of slope in a P (y-axis) vs V (x-axis) curve
- (D) Gas with higher  $\gamma$  has high magnitude of slope in a P (y-axis) vs V (x-axis) curve

**Q.20** 100 ml 0.5 N  $\text{H}_2\text{SO}_4$  (strong acid) is neutralised with 200 ml 0.2M  $\text{NH}_4\text{OH}$  in a constant pressure Calorimeter which results in temperature rise of  $1.4^\circ\text{C}$ . If heat capacity of Calorimeter content is  $1.5 \text{ kJ}/^\circ\text{C}$ . Which statement is /are correct

Given:



- (A) Enthalpy of neutralisation of HCl v/s  $\text{NH}_4\text{OH}$  is  $-52.5 \text{ kJ/mol}$   
 (B) Enthalpy of dissociation (ionization) of  $\text{NH}_4\text{OH}$  is  $4.5 \text{ kJ/mol}$   
 (C) Enthalpy of dissociation of  $\text{CH}_3\text{COOH}$  is  $4.6 \text{ kJ/mol}$   
 (D)  $\Delta H$  For  $2\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{H}(\text{aq.}) + 2\text{OH}^-$  is  $114 \text{ kJ}$

**Q.21** Which of the following does not represent  $\Delta H$  formation of the product.

- (A)  $\frac{1}{2}\text{H}_2(\text{g}) + (\text{aq}) \rightarrow \text{H}^+(\text{aq})$   
 (B)  $\frac{2}{3}\text{O}_3(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{e}^-$   
 (C)  $\text{NH}_4^+(\text{g}) + \text{Cl}^-(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$   
 (D)  $\text{P}_4(\text{black}) + 5\text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})$   
 (E) Reaction representing  $\Delta H_{\text{combustion}}$  of C (graphite)

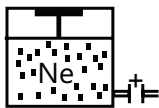
**Q.22** Which of the following statements is /are false?

- (A)  $\Delta S$  for  $\frac{2}{3}\text{N}_2(\text{g}) \times \text{N}(\text{g})$  is positive  
 (B)  $\Delta G_{\text{system}}$  is always zero for a reversible process in a closed system  
 (C)  $\Delta G^0$  for an ideal gas is a function of temperature and pressure  
 (D) Entropy of a closed system is always maximized at equilibrium

**Q.23** In isothermal ideal gas compression:

- (A)  $W$  is +ve (B)  $\Delta H$  is zero  
 (C)  $\Delta S_{\text{gas}}$  is +ve (D)  $\Delta G$  is +ve

**Q.24** A piston cylinder device initially contains  $0.2 \text{ m}^3$  neon (assume ideal) at  $200 \text{ kPa}$  inside at  $T_1^\circ\text{C}$ . A valve is now opened and neon is allowed to escape until the volume reduces to half the initial volume. At the same time heat transfer with outside at  $T_2^\circ\text{C}$  ensures a constant temperature inside. Select correct statement(s) for given process



- (A)  $\Delta U$  must be zero (B)  $\Delta U$  cannot be zero  
 (C)  $q$  may be +ve (D)  $q$  may be -ve

### Assertion Reasoning Type

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I  
 (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I

- (C) Statement-I is false, statement-II is true.  
 (D) Statement-I is true, statement-II is false

**Q.25 Statement-I:** There is no change in enthalpy of an ideal gas during compression constant temperature.

**Statement-II:** Enthalpy of an ideal gas is a function of temperature and pressure.

**Q.26 Statement-I:** Due to adiabatic free expansion, temperature of a real gas always increases.

**Statement-II:** If a real gas is at inversion temperature then no change in temperature is observed in adiabatic free expansion.

**Q.27 Statement-I:**  $\text{S}_8(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$ , represents complete combustion of  $\text{S}_8(\text{s})$ .

**Statement-II:** On complete combustion, the element from its amide, having maximum oxidation state.

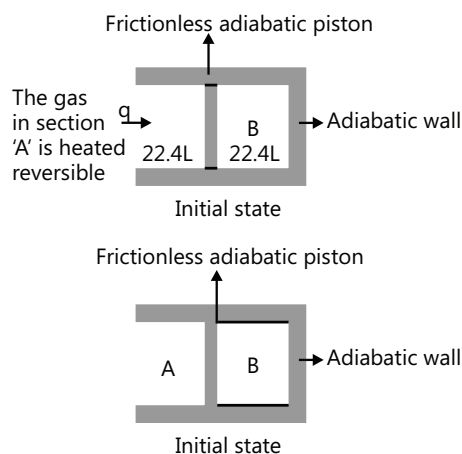
**Q.28 Statement-I:** The enthalpy of neutralization of the reaction between HCl and NaOH is –

$13.7 \text{ kCal/mol}$ . If the enthalpy of neutralization of oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) by a strong base is  $-25.4 \text{ kCal/mol}$ , then the enthalpy changes ( $\Delta H$ ) of the process  $\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{H}^+ + \text{C}_2\text{O}_4^{2-}$  is  $11.7 \text{ kCal/mol}$ .

**Statement-II:**  $\text{H}_2\text{C}_2\text{O}_4$  is a weak acid

### Comprehension Type

**Paragraph 1:** A cylindrical container of volume  $44.8$  liters is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is  $27.3 \text{ K}$  and  $1 \text{ atm}$ . Now gas in section 'A' is slowly heated till the volume of section B becomes  $(1/8)^{\text{th}}$  of initial volume.



Given:  $R = 2 \text{ cal/mol-K}$ ,  $C_{vm}$  of monoatomic gas  $= \frac{3}{2} R$ ,  
At 1 atm &  $0^\circ\text{C}$  ideal gas occupy 22.4 liter.

**Q.29** What will be the final pressure in container B?

- (A) 2 atm (B) 8 atm  
(C) 16 atm (D) 32 atm

**Q.30** Find temperature in container A will be

- (A) 1638 K (B) 6988 K  
(C) 3274 K (D) 51 K

**Q.31** Change in enthalpy for section A in k Cal

- (A) 48.3 (B) 80.53  
(C) 4.83 (D) 8.05

**Paragraph 2:** The vapor pressure of  $\text{H}_2\text{O}(\text{l})$  at 353 K is 532 mm Hg. The external pressure on  $\text{H}_2\text{O}(\text{l})$  taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (=0.9 kg) of  $\text{H}_2\text{O}(\text{l})$  at 33 K is increased to 1 atm. Temperature remained constant. Now, heat is supplied keeping pressure constant till 0.45 L of  $\text{H}_2\text{O}(\text{l})$  (=0.45 kg) is evaporated to form  $\text{H}_2\text{O}(\text{g})$  at 373 K. carefully observe the diagrams provided and form given data, answer the following questions

Given:

Specific heat of  $\text{H}_2\text{O} = 4.2 \text{ J/gm}^\circ\text{C}$

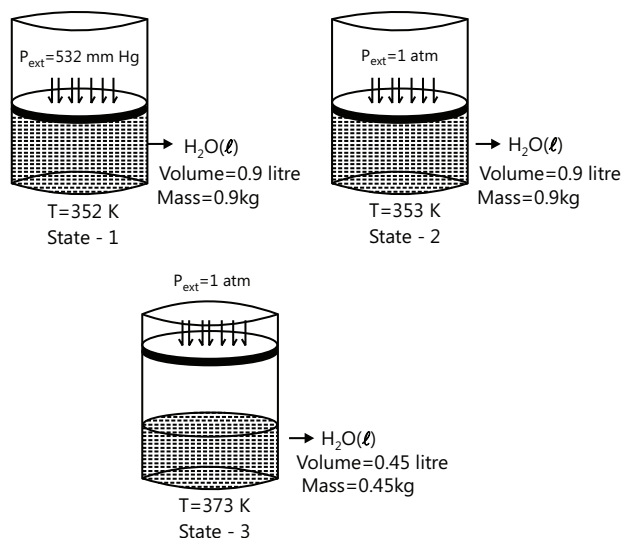
Use  $H_{\text{vap}}$  at 373 K and 1 atm = +40 kJ/mol

1L atm = 100 Joule

1 atm = 760 mm Hg

$R = 8 \text{ Joule/mole K}$

(Assume internal energy of liquid to be dependent only on temperature).



**Q.32**  $\Delta H$  When system is taken from state 1 to state 2 (Joule)?

- (A) Zero (B) 0.27 (C) 27 (D) 90

**Q.33** Total change in  $\Delta U$  going from state 1 to 3 (kJ)?

- (A) 75.6 (B) 1075.6 (C) 1001 (D) 74.6

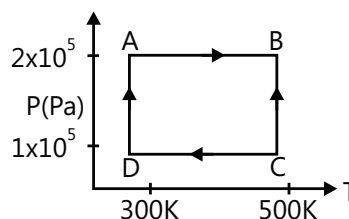
**Q.34** Total change in enthalpy going from state 1 to 3 (kJ)?

- (A) 75.6 (B) 1075.6 (C) 1001 (D) 74.6

**Q.35** What is the work done in going from state 1 to state 3 in Joules?

- (A) Zero (B) 74.6 (C) 90 (D) 31.5

**Paragraph 3:** Two moles of helium gas are taken over the ABCDA, as shown in the P-T diagram



**Q.36** Assuming the gas to be ideal the work done by the gas in taking it from A to B is

- (A) 200 R (B) 300 R (C) 400 R (D) 500 R

**Q.37** The work done on the gas in taking it from D to A is-

- (A) -414R (B) +414 R (C) -690 R (D) +690 R

**Q.38** The work done on the gas in the cycle ABCDA is-

- (A) Zero (B) 276 R (C) 1076 R (D) 1904 R

### Match the Columns

**Q.39** Match the column I with column II:

Column I (Ideal Gas)	Column II (Related equations)
(A) Reversible isothermal process	(p) $W = 2.303nRT \log (P_2/P_1)$
(B) Reversible adiabatic process	(w) $W = nC_{vm}(T_2 - T_1)$
(C) Irreversible adiabatic process	(r) $W = -2.303nRT \log (V_2/V_1)$
(D) Irreversible isothermal process	(s) $W = \int_{V_2}^{V_1} P_{\text{ext}} dV$



**Q.40** Match the column I with column II.

Note that column I may have more than one matching options in column II

Column I	Column II
(A) Reversible adiabatic compression	(p) $\Delta S_{\text{system}} > 0$
(B) Reversible vaporisation	(q) $\Delta S_{\text{system}} < 0$
(C) Free expansion of ideal gas in vacuum	(r) $\Delta S_{\text{surrounding}} < 0$
(D) Dissociation of $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(s) $\Delta S_{\text{surrounding}} = 0$

## Previous Years' Questions

**Q.1** The species which by definition has zero standard molar enthalpy of formation at 298 K is **(2010)**

- (A)  $\text{Br}_2(\text{g})$  (B)  $\text{Cl}_2(\text{g})$  (C)  $\text{H}_2\text{O}(\text{g})$  (D)  $\text{CH}_4(\text{g})$

**Q.2** The value of  $\log_{10} K$  for a reaction  $\text{A} \rightleftharpoons \text{B}$  is (Given:  $\Delta_r H^\circ_{298\text{K}} = -54.07 \text{ kJ mol}^{-1}$ ,

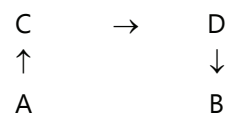
$\Delta_r S^\circ_{298\text{K}} = 10 \text{ JK}^{-1}$  and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ;  $2.303 \times 8.314 \times 298 = 5705$ ) **(2007, 3M)**

- (A) 5 (B) 10 (C) 95 (D) 100

**Q.3** For the process  $\text{H}_2\text{O}(\text{l}) (1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O}(\text{g}) (1 \text{ bar}, 373 \text{ K})$ , the correct set of thermodynamic parameters is **(2007, 3M)**

- (A)  $\Delta G = 0$ ,  $\Delta S = +ve$  (B)  $\Delta G = 0$ ,  $\Delta S = -ve$   
 (C)  $\Delta G = +ve$ ,  $\Delta S = 0$  (D)  $\Delta G = -ve$ ,  $\Delta S = +ve$

**Q.4** The direct conversion of A to B is difficult, hence it is carried out by the following shown path



Given that  $\Delta S_{(\text{A} \rightarrow \text{C})} = 50 \text{ eu}$   
 $\Delta S_{(\text{C} \rightarrow \text{D})} = 30 \text{ eu}$   
 $\Delta S_{(\text{D} \rightarrow \text{B})} = 20 \text{ eu}$

where eu is entropy unit. Then  $\Delta S_{(\text{A} \rightarrow \text{B})}$  is **(2006, 3M)**

- (A) +100 eu (B) +60 eu  
 (C) -100 eu (D) -60 eu

**Q.5** A monatomic ideal gas undergoes a process in which the ratio of P to V at any instant is constant and equals to 1. What is the molar heat capacity of the gas? **(2006, 3M)**

- (A)  $\frac{4R}{2}$  (B)  $\frac{3R}{2}$  (C)  $\frac{5R}{2}$  (D) 0

**Q.6** Among the following, intensive property is (properties are): **(2010)**

- (A) Molar Conductivity (B) Electromotive force  
 (C) Resistance (D) Heat capacity

**Q.7** Among the following, the state function(s) is (are) **(2009)**

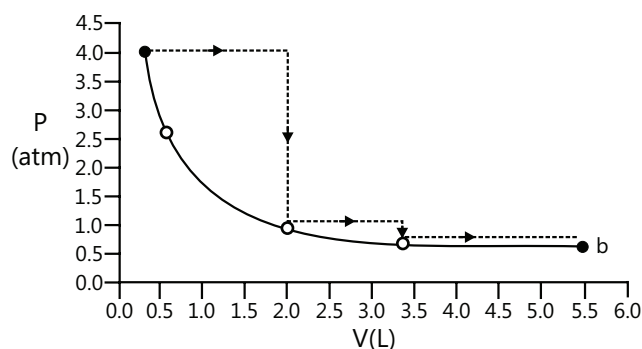
- (A) Internal energy  
 (B) Irreversible expansion work  
 (C) Reversible expansion work  
 (D) Molar enthalpy

**Q.8** In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is  $2.5 \text{ kJ K}^{-1}$ , the numerical value for the enthalpy of combustion of the gas in  $\text{mol}^{-1}$  is **(2009)**

**Q.9** For the reaction,  $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2$ ;  $\Delta H = -560 \text{ kJ}$ . Two moles of CO and one mole of  $\text{O}_2$  are taken in a container of volume 1 L. They completely form two moles of  $\text{CO}_2$ , the gases deviate appreciably from ideal behaviour. If the pressure in the vessel changes from 70 to 40 atm, find the magnitude (absolute value) of  $\Delta U$  at 500 K. (1 L atm = 0.1 kJ) **(2006, 3M)**

**Q.10** 100 mL of a liquid contained in an isolated container at a pressure of 1 bar. The pressure is steeply increased to 100 bar. The volume of the liquid is decreased by 1 mL at this constant pressure. Find the  $\Delta H$  and  $\Delta U$ . **(2004, 2M)**

**Q.11** One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is  $W$ , and that along the dotted line path is  $W_d$ , then the integer closest to the ratio  $\frac{W_d}{W_s}$  is **(2010)**



Read the following questions and answer as per the direction given below:

(A) Statement-I is true; statement-II is true; statement-II is the correct explanation of statement-I.

(B) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement-I.

(C) Statement-I is true; statement-II is false.

(D) Statement-I is false; statement-II is true

**Q.12 Statement-I:** The heat absorbed during the isothermal expansion of an ideal gas against vacuum is zero

**Statement-II:** The volume occupied by the molecules of an ideal gas is zero. (2000, 2M)

**Q.13 Statement-I:** For every chemical reaction at equilibrium, standard Gibbs' energy of reaction is zero.

**Statement-II:** At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs' energy. (2008, 3M)

**Q.14 Statement-I:** There is a natural asymmetry between converting work to heat and converting heat to work.

**Statement-II:** No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work. (2008, 3M)

**Q.15** Match the transformations in column I with appropriation options in column II. (2011)

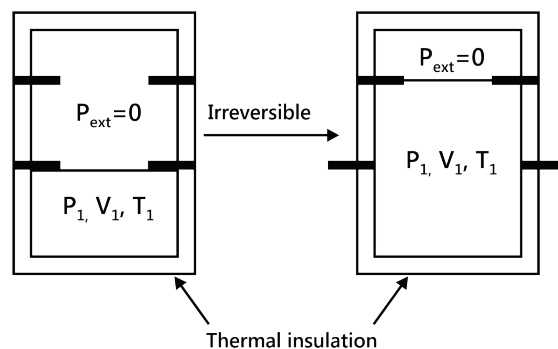
Column I	Column II
(A) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$	(p) Phase transition
(B) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$	(q) Allotropic change
(C) $2\text{H} \rightarrow \text{H}_2(\text{g})$	(r) $\Delta H$ is positive
(D) $P_{(\text{white, solid})} \rightarrow P_{(\text{red, solid})}$	(s) $\Delta S$ is positive
	(t) $\Delta S$ is negative

**Q.16.** The standard enthalpies of formation of  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$  and glucose(s) at 25°C are  $-400 \text{ kJ/mol}$ ,  $-300 \text{ kJ/mol}$  and  $-1300 \text{ kJ/mol}$ , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is (2013)

(A)  $+2900 \text{ kJ}$  (B)  $-2900 \text{ kJ}$

(C)  $-16.11 \text{ kJ}$  (D)  $+16.11 \text{ kJ}$

**Q.17** An ideal gas in a thermally insulated vessel at internal pressure =  $P_1$ , volume =  $V_1$  and absolute temperature =  $T_1$  expands irreversibly against zero external pressure, as shown in the diagram. The final internal pressure, volume and absolute temperature of the gas are  $P_2$ ,  $V_2$  and  $T_2$ , respectively. For this expansion, (2014)



(A)  $q = 0$

(B)  $T_2 = T_1$

(C)  $P_2 V_2 = P_1 V_1$

(D)  $P_2 V_2^\gamma = P_1 V_1^\gamma$

**Q.18** For the process  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$  at  $T = 100^\circ\text{C}$  and 1 atmosphere, the correct choice is (2015)

(A)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surrounding}} > 0$

(B)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surrounding}} < 0$

(C)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surrounding}} > 0$

(D)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surrounding}} < 0$

**Q.19** One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ( $\Delta S_{\text{sur}}$ ) in  $\text{JK}^{-1}$  is (1 L atm = 101.3 J) (2016)

(A) 5.763 (B) 1.013

(C) -1.013 (D) -5.763



# PlancEssential Questions

## JEE Main/Boards

### Exercise 1

Q.1            Q. 10            Q. 11  
Q. 15        Q. 16            Q. 17  
Q. 28

### Exercise 2

Q. 3            Q. 8            Q. 11  
Q.18        Q. 25            Q. 34  
Q. 37

## JEE Advanced/Boards

### Exercise 1

Q. 3            Q. 6            Q.10  
Q. 19        Q.22            Q. 24  
Q. 28

### Exercise 2

Q. 7            Q.8            Q. 9  
Q.10        Q.13            Q.16  
Paragraph 2    Paragraph 3

## Answer Key

## JEE Main/Boards

### Exercise 1

**Q.1** (i) W, (ii)-W, (iii)-W (iv)-W  
**Q.2**  $q = -65 \text{ J}$ ;  $w = 20 \text{ J}$ ;  $\Delta E = -45 \text{ J}$   
**Q.3** (a) 0.47 gm, (b) 0.47 kg  
**Q.4** -10 J  
**Q.5**  $q = 177.9 \text{ kJ}$ ,  $W = 2.5 \text{ kJ}$ ;  $\Delta E = 175.4 \text{ kJ}$   
**Q.6** 0.3024 kJ  
**Q.7**  $\Delta E = 75.11 \text{ kJ}$   
**Q.8**  $\Delta E = 0.993 \text{ Kcal}$ ,  $\Delta H = 1 \text{ Kcal}$   
**Q.9**  $\Delta H = 12168 \text{ calories}$ ;  $\Delta E = 11623 \text{ calories}$   
**Q.10**  $\Delta E = 27.91 \text{ kJ mol}^{-1}$ ,  $t = 514 \text{ sec}$ .  
**Q.11**  $W_{\text{in}} = 9353.25 \text{ J}$ ,  $W_{\text{in}} = +17288.47 \text{ J}$ ,  $\Delta U = \Delta H = 0$   
**Q.12**  $W = -3.988 \text{ kJ}$   
**Q.13** 4.59 kJ

**Q.14**  $q = 0$ ;  $w = \Delta U = 4.12 \text{ kJ}$ ;  $\Delta H = 5.37 \text{ kJ}$   $V_f = 11.8 \text{ dm}^3$ ,  $P = 5.21 \text{ atm}$

**Q.15** (i) 18.424 bar L;  
(ii) 72 bar L;  
(iii) 40 bar L

Magnitude of work is maximum in single stage compression.

**Q.16** (a)  $T = 243.60 \text{ K}$ ;  $T = 2436.0 \text{ K}$ ,  
(b)  $\Delta E = 0$ ;  $q = W = +3262.88 \text{ cal}$

**Q.17** (a) AC, (b) 170 J, (c) 10 J

**Q.18**  $\Delta H_{373}(\text{H}_2\text{O (l)}) = -284.11 \text{ kJ}$

**Q.19** (a)  $13.064 \text{ kJ mol}^{-1}$ , (b)  $10.587 \text{ kJ mol}^{-1}$

**Q.20**  $T = 1059 \text{ K}$

**Q.21**  $21.18 \text{ JK}^{-1} \text{ Mol}^{-1}$

**Q.22** (i) -90.5  
(ii) -374.5  
(iii) -3.26 (all in  $\text{J mol}^{-1} \text{ K}^{-1}$ )

**Q.23**  $196.66^\circ \text{C}$

**Q.24** 205.08 JK<sup>-1</sup> mol<sup>-1</sup>**Q.25** -2864.5 KJ**Q.26** 436 kJ mol**Q.27** Heat produced = -15549.7 kcal**Q.28**  $\Delta H_1 = 0.96$  kcal,  $\Delta H_2 = 1.74$  kcal**Q.29** Bond energy = 34 kcal/mol ;  $\Delta H = 136$ **Q.30** (i) 97.81 kJ (ii) 454.64 kJ

(iii) 804.26 kJ (v) 733.48 kJ

## Exercise 2

### Single Correct Choice Type

**Q.1** D**Q.2** D**Q.3** C**Q.4** B**Q.5** C**Q.6** A**Q.7** B**Q.8** C**Q.9** C**Q.10** C**Q.11** A**Q.12** C**Q.13** D

## Previous Years' Questions

**Q.1** C**Q.2** A**Q.3** A**Q.4** A**Q.5** B**Q.6** B**Q.7** A**Q.8** B**Q.9** D**Q.10** A**Q.11** B**Q.12** D**Q.13** B**Q.14** C**Q.15** C**Q.16** A**Q.17** A**Q.18** D**Q.19** C

## JEE Advanced/Boards

### Exercise 1

**Q.1** -88 kJ mol**Q.2** 128.02 kJ**Q.3** -266.3 kJ 1mol and -824.2 kJ 1 mol**Q.4** +20.6 k Cal**Q.5** -120.08 kJ /mol**Q.6** -192.3 kJ mol<sup>-1</sup>**Q.7** 2.95 kCal**Q.8** -1410 Cal**Q.9** 9.82 mol % CH<sub>4</sub>**Q.10** -31.5 kJ mole**Q.11** -352 kJ mol<sup>-1</sup>**Q.12** -669.7 kJ mole<sup>-1</sup>**Q.13** (a)  $T_2 = 395.8$ ;  $V_2 = 16.24$  L;  $W_{\text{rev}} = 1194.72$  J.(b)  $V_{1/2} = 17.24$  L  $T_{1/2} = 420$  K $W_{\text{rev}} = 1496.52$  J.**Q.14**  $w = P^0 V^0$ ;  $q_{CA} = -\frac{5}{2} P^0 V^0$ ;  $q_{AB} = 3 P^0 V^0$ ;

$$q_{BC} - \frac{1}{2} P^0 V^0 T_{\text{max}} = \frac{25}{8} \left( \frac{P^0 V^0}{R} \right)$$

**Q.15** (i)  $\Delta S_{\text{gas}} = \Delta S_{\text{surr}}$  and  $\Delta S_{\text{total}} = 0$ ,(ii)  $\Delta S_{\text{total}} = 2.808$  JK<sup>-1</sup>(iii)  $\Delta S_{\text{total}} = 9.134$  JK<sup>-1</sup>**Q.16** 74.05 J/K**Q.17** (i) Rev. Process  $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$ ;

$$\Delta S_{\text{surr}} = -\frac{3}{2} R \ln 10;$$

(ii) In process  $\Delta S_{\text{sys}} = -\frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = -\frac{3}{2} R$  (0.9)

$$\Delta S_{\text{total}} = -\frac{3}{2} R (1.403)$$

**Q.18**  $\Delta G = 5.59 \text{ kJ mol}^{-1}$ **Q.19** (i)  $\Delta S_{\text{sys}} = 0$ ;  $\Delta S = 0$  and  $\Delta S_{\text{total}} = 0$ ;(ii)  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 0.957 \text{ JK}^{-1}$ (iii)  $\Delta S_{\text{sys}} = \Delta S_{\text{total}} = 3.81 \text{ JK}^{-1}$ **Q.20**  $24 \text{ kJ/mol}$ **Q.21** Heat released =  $11.16 \text{ Kcal}$  per mol of initial mixture.**Q.22** 1: 3**Q.23** (a)  $92.435 \text{ g}$  (b)  $93.715 \text{ g}$ **Q.24**  $404.18 \text{ K}$ **Q.25**  $0.9345 \text{ k cal g}^{-1}$ ,  $3.94 \text{ k Cal cm}^{-3}$ **Q.26**  $292 \text{ kCal/mol}$ **Q.27**  $-718 \text{ kJ/mol}$ **Q.28** (i) 13 times, (ii)  $21.54 \text{ sec}$ **Q.29**  $\text{EB-H-B} = 455 \text{ kJ/mole}$ **Q.30**  $-11420 \text{ cal}$ 

## Exercise 2

### Single Correct Choice Type

**Q.1** A**Q.2** C**Q.3** B**Q.4** A**Q.5** D**Q.6** C**Q.7** C**Q.8** D**Q.9** A

### Multiple Correct Choice Type

**Q.10** A, D**Q.11** A, B, C, D**Q.12** B, C**Q.13** A, B, D**Q.14** A, C**Q.15** A, C, D**Q.16** A, C, D**Q.17** B, D**Q.18** A, B**Q.19** C, D**Q.20** A, B, D**Q.21** A, B, C, D**Q.22** B, C, D**Q.23** A, B, D**Q.24** B, C, D

### Assertion Reasoning Type

**Q.25** D**Q.26** D**Q.27** D**Q.28** D

### Comprehension Type

**Paragraph 1:****Q.29** D**Q.30** A**Q.31** B**Paragraph 2:****Q.32** C**Q.33** C**Q.34** B**Q.35** B**Paragraph 3:****Q.36** C**Q.37** B**Q.38** B

### Match the Columns

**Q.39**  $A \rightarrow p, r, s$ ;  $B \rightarrow q, s$ ;  $C \rightarrow q, s$ ;  $D \rightarrow s$ **Q.40**  $A \rightarrow s$ ;  $B \rightarrow p, r$ ;  $C \rightarrow p, s$ ;  $D \rightarrow p, r$

## Previous Years' Questions

<b>Q.1</b> B	<b>Q.2</b> C	<b>Q.3</b> A	<b>Q.4</b> B	<b>Q.5</b> A	<b>Q.6</b> A,B
<b>Q.7</b> A, D, C	<b>Q.8</b> 9	<b>Q.9</b> -563 KJ	<b>Q.10</b> 9900	<b>Q.11</b> 2	<b>Q.12</b> B
<b>Q.13</b> D	<b>Q.14</b> B	<b>Q.15</b> $A \rightarrow p, r, s; B \rightarrow r, s; C \rightarrow t; D \rightarrow p, q, t$			<b>Q.16</b> C
<b>Q.17</b> C	<b>Q.18</b> B	<b>Q.19</b> C			

## Solutions

### JEE Main/Boards

#### Exercise 1

**Sol 1:** (i)  $H_2O(g) \rightarrow H_2O(l)$

Volume of system  $\downarrow$ es

$$W = -P\Delta V$$

$\therefore W$  +ve

(ii)  $H_2O(s) \rightarrow H_2O(g)$

V system  $\downarrow$ es

$$W = -P\Delta V$$

$\Delta V > 0, \therefore W$  -ve

(iii)  $H_2O(s) \rightarrow H_2O(l)$

V  $\downarrow$ es,  $W = -\Delta V, \Delta V < 0$

$\therefore W$  +ve

(iv)  $CaCO_3 \rightarrow CaO(s) + CO_2(g)$

V  $\uparrow$  es,

$\therefore \Delta V > 0, \therefore W < 0$

**Sol 2:**  $Q = -65 \text{ J}$

$$W = 20 \text{ J}$$

(Contraction work done system)

$$\Delta E = Q + W$$

$$= 20 - 65 = -45 \text{ J}$$

**Sol 3:**  $H_{\text{combustion}} = -2808 \text{ kJ/mol}$

(i) Energy  $\times$  Eff = Change in potential energy.

$$\therefore \frac{\text{Mass of glucose}}{180} \times 2808 \times 10^3 \times \frac{25}{100}$$

$$= 62.25 \times 3 \times 9.8$$

$$= 0.47 \text{ kg}$$

**Sol 4:**  $W = -P\Delta V$

$$= -1 \times (1.1 - 1)$$

$$= -0.1 \text{ atm}$$

$$= -0.1 \times 10^5 \times 10^{-3} \text{ J} = -10 \text{ J}$$

**Sol 5:**  $CaCO_3 \xrightarrow[34.2 \text{ ml}]{16.9 \text{ ml} \quad 24.4 \text{ L}} CaO + CO_2$

$$Q = +177.9 \text{ kJ}$$

$$W = -P\Delta V$$

$$= -1 \times (24.4 + 16.9 \times 10^{-3} - 34.2 \times 10^{-3})$$

$$= -1 \times (24.4 - 17.3 \times 10^{-3})$$

$$= -2438.27$$

$$\therefore Q + W = \Delta E$$

$$177.9 \times 10^3 - 2438.27 = \Delta E$$

$$\therefore \Delta E = 175.462 \text{ kJ}$$

**Sol 6:**  $W = -P\Delta V$

$$= -1.5(50 - 50 - 50) \times 10^{-3}$$

$$= -1.5 \times -50 \times 10^{-3} \times 10^5 \times 10^{-3}$$

$$W = 15 = 0.0075$$

$$H = -0.31$$

$$\Delta V = \Delta H - \Delta(PV)$$

$$\Delta V = -0.31 \text{ kJ} + 0.15 \text{ kJ} = 0.3025$$

**Sol 7:**  $\Delta H_{\text{vap}} = 40.66 \text{ kJ/mol}$

$$\Delta H_{\text{gas}} = 2 \times 40.66 \text{ kJ}$$

$$PV = nRT$$

$$1 \times V = 2 \times 0.0821 \times 373$$

$$V = 61.2466 \text{ L}$$

$$\Delta PV = 1(\Delta V) = 1(V_g - V_L)$$

$$2 \text{ moles } \therefore \text{Mass of H}_2\text{O} = 36 \text{ g}$$

$$d = 1 \text{ gm/cm}^3$$

$$\therefore V = 36 \text{ cm}^3 = 36 \times 10^{-3} \text{ L}$$

$$\therefore \Delta V = \frac{(61.2466 - 36 \times 10^{-3}) \times 10^2}{1000}$$

$$V_L \ll V_g \quad \Delta V = V_g$$

$$\Delta V = \Delta H - \Delta PV$$

$$= 81.32 - 6.125 = 75.1216$$

**Sol 8:**  $Q = 1 \text{ Kcal}$

$$P = 1 \text{ atm}$$

$$W = -\int P dV = -\int dV = -P\Delta V$$

$$= -1(1.5 - 1.2) \times 10^5 \times 10^{-3} \text{ J}$$

$$= \frac{0.3 \times 10^2}{1000} \text{ kJ} = 0.03 \text{ kJ}$$

$$4.18 \text{ J} = 1 \text{ cal}$$

$$\therefore 1 \text{ J} = \frac{1}{4.18} \text{ cal}$$

$$\therefore 0.03 \text{ kJ} = -7.18 \times 10^{-3} \text{ kcal}$$

$$\Delta E = Q + W$$

$$= 1 - 7.8 \times 10^{-3}$$

$$= 0.993 \text{ kcal}$$

$$\Delta H = \Delta E + \Delta(PV)$$

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

$$= 0.993 + 7.8 \times 10^{-3}$$

$$= 1 \text{ k Cal}$$

**Sol 9:**  $V_{\text{vapour}} = \frac{nRT}{P} = \frac{1 \times 0.0821 \times 273}{4.6 / 760}$

$$= 3703.07 \text{ L}$$

$$\Delta H = \Delta H_{\text{fusion}} + \Delta H_{\text{vap}} + H$$

$$0^\circ\text{C} \rightarrow 0^\circ\text{C}$$

$$\text{ice} \quad \text{water}$$

$$\Delta H = nC_p\Delta T$$

$$\Delta T = 0, \therefore \Delta H_{\text{process}} = 0$$

$$\Delta H_{\text{total}} = (80 + 596) \times 18 = 12168 \text{ cal}$$

$$\Delta E = \Delta H - (\Delta PV)$$

$$= \Delta H - P\Delta V$$

$$= 12168 - \frac{4.6}{760} \times 3703.07$$

$$= 12168 - 536.20$$

$$= 11623 \text{ cal}$$

**Sol 10:**  $\Delta H_{\text{vap}} = 30.84 \text{ kJ/mol}$

$$V_{\text{vap}} = \frac{1 \times 0.0821 \times 353}{1}$$

$$= 28.9 \text{ L}$$

$$W = -P\Delta V = +PV_{\text{vap}}$$

$$= +0.0821 \times 353 = 2.89 \text{ kJ}$$

$$\Delta E = \Delta H - \Delta PV$$

$$= +30.84 - 2.89$$

$$= 27.91 \text{ kJ/mol}$$

$$\text{We know } VIT = Q$$

$$Q + W = \Delta E$$

$$\therefore Q = \Delta E - W$$

$$= \Delta E + \Delta PV = \Delta H$$

$$\therefore 12 \times 0.5 \times t = 30.84 \times 10^3 \times \frac{7.8}{78}$$

$$t = 514 \text{ sec.}$$

**Sol 11:**  $p_i = 4 \text{ atm } p_t = 1 \text{ atm}$

$$\text{Const. external pressure of 1 atm.}$$

$$4V_i = 5 \times 0.082 \times 300$$

$$\therefore V_i = 30.79$$

$$V_t = 4 V_i = 123.16$$

$$\Delta V = nC_v\Delta T$$

$$\Delta T = 0 \Rightarrow \Delta V = 0$$

$$\Delta H = nC_p\Delta T = 0$$

$$W_{\text{rev}} = \int -PdV = -\int \frac{nRT}{V} dV = -nRT \ln V_2/V_1$$

$$= -nRT \ln 4 = -5 \times 8.314 \times 300 \ln 4 = -17228.47 \text{ J}$$

$$W_{\text{air}} = -P\Delta V = -P\Delta V = -1(123.16 - 30.79) \times 10^{-5} \times 10^3 \\ = 9353.25 \text{ J}$$

**Sol 12:**  $5 \times V_i = 1 \times V_f \quad \therefore \frac{V_f}{V_i} = 5$

$$w = -\int P dV = -\int \frac{nRT}{V} dV = -nRT \ln \frac{V_f}{V_i} \\ = -1 \times 8.314 \times 298 \times \ln 5 = -3.988 \text{ kJ}$$

**Sol 13:**  $P(V_m - b) = RT$

$$P = \frac{RT}{V_m - b} \\ w = -\int P dV = -\int \frac{RT}{V - b} dV = -\int_{V_i}^{V_f} \frac{RT}{V - nb} dV$$

$$= -nRT \ln \left( \frac{V_f - nb}{V_i - nb} \right) \\ = -2 \times 8.314 \times 300 \times \ln \left( \frac{0.6 - 2 \times 0.1}{1.2 - 2 \times 0.1} \right)$$

$$= \frac{600}{1000} \times 8.314 \ln \left( \frac{1.2 - 0.2}{0.6 - 0.2} \right) \text{ kJ}$$

$$= 0.6 \times 8.314 \ln \left( \frac{1}{0.4} \right) = 4.59 \text{ kJ}$$

**Sol 14:**  $2 \times V = 200 \times 3 \times 0.0821$

$$V = 8.21 \times 3 \quad V_i = 24.63 \text{ L}$$

$$V^{r-1} = \text{Constant}$$

$$\frac{T_i}{T_f} = \left( \frac{V_f}{V_i} \right)^{r-1}$$

$$\frac{200}{250} = \left( \frac{V_f}{24.63} \right)^{r-1}$$

$$C_v = 27.5$$

$$C_p = C_v + R = 27 + 8.314$$

$$r = \frac{C_p}{C_v} = \frac{27.5 + 8.314}{27.5} = 1.302$$

$$\left( \frac{200}{250} \right)^{\frac{1}{0.31}} = \frac{V_f}{24.63}$$

$$V_f = 11.79 \text{ L} \quad V_f = 11.8 \text{ dm}^3$$

$$\Delta V = n\ell\Delta T = 3 \times 27.5 \times 50 = 4215 = 9.12 \text{ KJ}$$

$$q = 0 \text{ (idealistic process)}$$

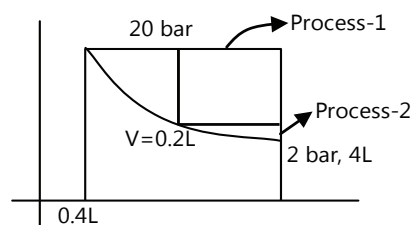
$$\therefore \Delta V = W = 4.12 \text{ kJ}$$

$$\Delta H = nC_p \Delta T = 3 \times 50 \times 35.81 = 5.37 \text{ kJ}$$

$$\frac{P_f V_f}{T_f} = \frac{P_i V_i}{T_i}$$

$$\therefore P_f = \frac{2 \times 24.63 \times 256}{200 \times 11.8}; P_f = 5.21 \text{ atm}$$

**Sol 15:**



$$V_f = \frac{2 \times 4}{20} = 0.4$$

Process 1

$$W = -nRT \ln \frac{V_f}{V_i} = PV \ln(V_f / V_i)$$

$$= -2 \times 8.314 \times \ln \left( \frac{0.4}{4} \right) \times T$$

$$W_{\text{rev}} = 18.424 \text{ bar L}$$

(ii) Single stage compression

$$w = -P\Delta V = -20 \times (0.4 - 4)$$

$$= 3.6 \times 20 = 72 \text{ bar lit}$$

2 stage process

$$W = -\sum P_1 \Delta V_1$$

$$= -20 \times [0.4 - 0.8] - 10[0.8 - 4]$$

$$= 20 \times 0.4 + 10 \times 3.2$$

$$= 32 + 8 = 40$$

Magnitude of work is in single stage conversion.

**Sol 16:** Momentum gas  $C_v = \frac{3R}{2}$ ,  $r = \frac{5}{3}$

$$n = 1 \text{ mole}$$

$$P_1 V_1 = nRT_1$$

$$2 \times 10 = 1 \times 0.0821 T_1$$

$$\therefore T_1 = 243.60 \text{ K}$$

In step (BC)

$$W = 0$$

Volume const.

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \quad \frac{20}{2} = \frac{T_2}{243.60}$$

$$\therefore T_2 = 2436 \text{ K}$$

$$W = 0 \text{ as } dV = 0 \quad q = \Delta V = nC_V \Delta T$$

$$= \frac{3}{2}R \times 2 \times (-2436 + 243.6)$$

$$= 3 \times 8.314 \times 2192.4$$

$$= -54682.841 \text{ J}$$

In process A – B

$$W = -PdV$$

$$= -P\Delta V$$

$$= -20 \times (10-1)$$

$$= -180 \text{ bar lit}$$

$$= \frac{-180 \times 10^5 \times 10^{-3}}{4.18} \text{ cal.}$$

$$\Delta V = nC_V \Delta T$$

$$= \frac{3}{2}R \times 2 \times (2436 - 243.6) = 54682.841 \text{ J}$$

$$Q = \Delta V - W$$

$$= \frac{54682.841}{4.18} + \frac{18000}{4.18} = 17388.24 \text{ J}$$

In process (CA)

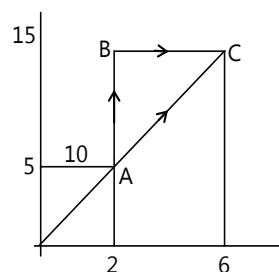
$$\Delta T = 0 \Rightarrow \Delta V = 0$$

$$Q = W = -\int PdV = +PV \ln \frac{V_i}{V_f}$$

$$= +20 \times 1 \times \lambda n \left( \frac{20}{1} \right) = \frac{59.914 \times 100}{4.18}$$

$$W_{\text{total}} = \frac{5991.46}{4.17} - \frac{18000}{4.17} = -3262 \text{ cal.}$$

**Sol 17:**



Work done is area under the PV curve

$\therefore$  Work done under A–C curve is least.

$$Q_{AC} = 200 \text{ J}$$

$$W_{AC} = -\int PdV$$

$$\left( P = \frac{5}{2}V \right) \text{ along AC}$$

$$W_{AC} = -\int_2^6 \frac{5}{2}V dV$$

$$W_{AC} = -\frac{5}{4}V^2 \Big|_2^6$$

$$= -\frac{5}{4}(6^2 - 4) = -\frac{5}{4} \times 4(9-1)$$

$$= -5 \times 8 = -40$$

$$V = Q + W$$

$$V_C - V_A = 200 - 40$$

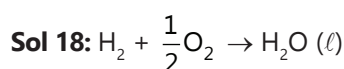
$$V_C = 10 + 200 - 40$$

$$V_C = 170 \text{ J}$$

From A–B

$$W = 0 \text{ as } \Delta V = 0$$

$$\therefore Q = \Delta V = 10 \text{ J}$$



$$\Delta H_{\text{reac}} = -285.76$$

$$\Delta H_{(373)} = \Delta H_{298} + \int_{298}^{373} nC_p \Delta T$$

$$\Delta H_{373} = -285.76 + \int 75.312 - 38.83 - \frac{29.16}{2}$$

$$= -285.76 \times 10^3 + 21.902 \text{ T} \Big|_{298}^{375}$$

$$= -285.76 \times 10^3 + 21.902 \times 75$$

$$\Delta H_{373} = -284.11 \text{ kJ}$$

**Sol 19:**  $\Delta H = nC_p \Delta T$

$$10^5 \times V = 8.314 \times 298 ;$$

$$V = 24.77 \text{ l, } T_f = 2T = 596;$$

$$V_f = 2V = 24.77 \times 2 = 49.54;$$

$$\Delta H = n \int C_p dV = \int C_p dT ;$$

$$\begin{aligned}
&= \int_{298}^{596} (22.34 + 4.81 \times 10^{-3} T) dT \\
&= 22.34T + \frac{48.1}{2} \times 10^{-3} T^2 \\
&= 22.34 \times 298 + \frac{48.1}{2} \times 10^{-3} (596^2 - 298^2) \\
&= 6657.32 + 6407.21 \\
\Delta H &= 13.064 \\
\Delta V &= \Delta H - \Delta PV = H - P\Delta V \\
&= 13.064 - \frac{10^5 \times 24.77}{1000} \times 10^{-3} \\
&= 13.064 - 2.477 = 10.587
\end{aligned}$$

**Sol 20:**  $Q = 30.5 \text{ kJ}$ 

$$\Delta S = 28.8$$

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

$$28.8 = \frac{30.5 \times 10^3}{T} \quad \therefore T = 1059 \text{ K}$$

**Sol 21:**  $T_1 = 300$ ;  $T_2 = 600$ ,  $P = 1 \text{ bar}$ 

$$\Delta S = \int n \frac{C_p dT}{T} + nR \ln \frac{P_2}{P_1}$$

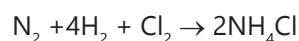
$$\begin{aligned}
\Delta S &= \int n \frac{C_p dT}{T} \\
&= \int \frac{n \times 25.5 + 13.6 \times 10^{-3} - 42.5 \times 10^{-7} T^2}{T}
\end{aligned}$$

$$\begin{aligned}
\Delta S &= 25.5 \ln \frac{T_2}{T_1} + 13.6 \times 10^{-3} T \Big|_{300}^{600} \\
&\quad - 42.5 \times 10^{-7} (T_2^2 - T_1^2) \\
&= 25.5 \ln 2 + 13.6 \times 10^{-3} \times 300 \\
&\quad - 42.5 \times 10^{-7} (600^2 - 300^2) \\
&= 17.67 + 4.08 - 0.1475 \\
&= 21.18 \text{ J K}^{-1} \text{ mol}^{-1}
\end{aligned}$$

**Sol 22:**  $2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl}$ 

$$\begin{aligned}
\Delta S &= 2 \times S_{\text{NaCl}} - S_{\text{Cl}_2} - 2 \times S_{\text{Na}} \\
&= 2 \times 72 - 223 - 2 \times 51
\end{aligned}$$

$$\Delta S = -181/2 = -90.5$$



$$\begin{aligned}
\Delta S &= (2 \times S_{\text{NH}_4\text{Cl}} - S_{\text{Cl}_2} - S_{\text{V}_2} - 4S_{\text{H}_2}) / 2 \\
&= 2 \times 95 - 223 - 192 - 4 \times 131 \\
&= -749/2 = -374.5
\end{aligned}$$

$$C_{\text{graphite}} - C_{\text{diamond}}$$

$$\Delta S = S_{\text{diamond}} - S_{\text{graphite}}$$

$$= 2.43 - 5.69 = -3.26$$

**Sol 23:** Efficiency = 40%

$$0.4 = 1 - \frac{T_L}{T_H}$$

$$\frac{T_L}{T_H} = 0.6$$

$$\frac{273 + 7}{T_H} = 0.6$$

$$\therefore T_H = \frac{280}{0.6} = 466.6 \text{ K} = 193.66^\circ\text{C}$$

**Sol 24:**

$$\int_0^{600} S = \int_0^{200} S + \frac{H_{\text{fus}}}{T} + \frac{T_{\text{vap}}}{T} + \int_{200}^{300} S + \int_{300}^{600} S$$

$$S_{600} = \int_0^{200} \frac{dT^{0.034T}}{T} + \frac{7.5 \times 10^3}{200} + \int_{200}^{300} \frac{60 + 0.016T}{T}$$

$$+ \frac{30 \times 10^3}{300} + \int_{300}^{600} \frac{50.dT}{T}$$

$$= 7 + 0.035 (200 - 0) + 37.5 + 60 \lambda n \left( \frac{300}{200} \right)$$

$$+ 0.016(300 - 200) + \frac{30000}{600} + 50 \lambda n \left( \frac{600}{300} \right)$$

$$= 37.5 T + 24.328 + 1.6 + 34.657 + 100 = 205.08 \text{ J}$$

**Sol 25:**  $\Delta H_{\text{combust}} = -2808$ 

$$\Delta S = 182.4$$

$$T = 37^\circ = 310 \text{ K}$$

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

$$= \left( -2808 - \frac{310 \times 182.4}{1000} \right) \text{ kJ}$$

$$\Delta G = -2864.5$$



**Sol 26:**  $\text{H}_2 \rightarrow 2\text{H}^\circ$  130.6 114.6

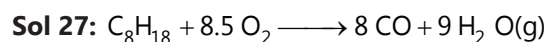
$$\Delta S^\circ = 2 \times 114.6 - 130.6 = 98.6$$

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

$$406.62 \times 10^3 = \Delta H^\circ - 298 \times 98.6$$

$$\Delta H^\circ = \left( 406.62 + \frac{298 \times 98.6}{1000} \right) \text{KJ}$$

$$\Delta H^\circ = 436 \text{ KJ/mol H}_2$$



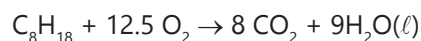
$$V = 3.785 \times 10^3 \text{ ml}$$

$$d = 0.702 \text{ g/ml}$$

$$\therefore \text{Mass} = 0.7025 \times 3.785 \times 10^3 \text{ g} = 2658.9625$$

$$\text{Moles} = \frac{2658.9625}{114} = 23.33 \text{ moles}$$

given



$$\Delta H = -130.27$$

$$\Delta H_{\text{comb}} = -n\Delta H_{\text{f reactant}} - n\Delta H_{\text{f product}}$$

$$-1302.7 = \Delta H_{\text{f C}_8\text{H}_{18}} + 12.5$$

$$\times \text{O}_2 - 8 \times \Delta H_{\text{CO}_2} - 9 \times \Delta H_{\text{f H}_2\text{O}}$$

$$\therefore \Delta H_{\text{f C}_8\text{H}_{18}} = 13027 + 8 \times (-94.05) + 9 \times (-68.32)$$

$$\frac{\Delta H_{\text{reactant}}}{\text{mol C}_8\text{H}_{18}} = 8 \Delta H_{\text{f O}} + 9 + \Delta H_{\text{H}_2\text{O(g)}} - 8.9 \times \Delta H_{\text{f O}_2}$$

$$- \Delta \Delta H_{\text{f C}_8\text{H}_{18}} + 64.58$$

$$= 8 \times (-26.41) + 9 \times (-57.79) - 666.80$$

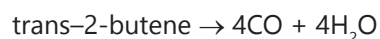
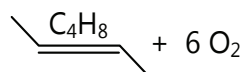
$$\therefore \Delta H \text{ for given conditions} =$$

$$\Delta H_{\text{reac}} \times 23.33$$

$$= -666.80 \times 23.32 = -15549.7$$



$$\text{cis-2-butene} = \text{trans-2-butene} - \Delta H_2$$



$$\text{Trans } \Delta H_{\text{comb}}^\circ = \underbrace{4\Delta H_{\text{CO}_2} + 4\Delta H_{\text{H}_2\text{O}}}_{\Delta H} + \Delta H_{\text{f C}_4\text{H}_8}$$

trans

$$\Delta H_{\text{comb}}^\circ = 4\Delta H_{\text{CO}_2} + 4\Delta H_{\text{H}_2\text{O}} - \Delta H_{\text{f C}_4\text{H}_8}$$

1-butene Cis

$$\Delta H_{\text{f trans-2}} = \Delta H' + 649.8 \text{ Kcal}$$

$$\Delta H_{\text{f 1-butene}} = \Delta H' + 647.1 \text{ Kcal}$$

$$\Delta H_1 = \Delta H_{\text{f trans}} - \Delta H_{\text{f cis}}$$

$$\Delta H_2 = \Delta H_{\text{f buten}} - \Delta H_{\text{f cis}}$$

$$\Delta H_1 - \Delta H_2 = \Delta H_{\text{f trans}} - \Delta H_{\text{f cis}}$$

$$= 649.8 - 647.1$$

$$\Delta H_1 - \Delta H_2 = 2.7$$

$$\Delta H_1 + 5\Delta H_2 = 0$$

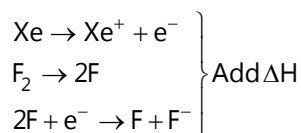
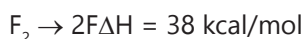
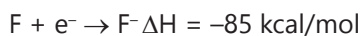
$$\Delta H_1 - \Delta H_2 = -2.7$$

$$\Delta H_1 + \frac{9}{4}\Delta H_1 = -2.7$$

$$\Delta H_1 = -0.964 \text{ kcal}$$

$$\Delta H_2 = \frac{9}{5} \times 0.964 \text{ kcal}$$

$$= 1.74 \text{ kcal}$$

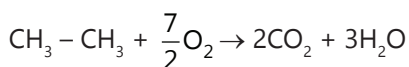


$$\Delta H = -4 \times \text{B.E.}_{\text{Xe-F}}$$

$$-\Delta H_{\text{ion}} - \Delta H_{\text{+gain enthalpy}} - \Delta H_{\text{Bond energy}}$$

$$292 = -4 \times x + 297 + 85 + 38$$

$$x = \frac{292 - 279 + 85 + 38}{4} = 34$$



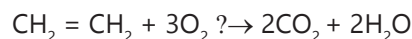
$$\Delta H_{\text{comb}}^\circ = E_{\text{C-C}} + 6E_{\text{C-H}}$$

$$+ \frac{7}{2} E_{\text{O=O}} - 2\Delta H_{\text{f CO}_2} - 3\Delta H_{\text{f H}_2\text{O}}^\circ$$

$$-1559.8 = E_{\text{C-C}} + 6E_{\text{C-H}} + \frac{7}{2} (498.34) - 2(-39.5) - 3(-285.8)$$

$$E_{C-C} + 6E_{C-H} = -1460.01$$

Combustion of Ethene:



$$\Delta H^\circ_{\text{Comb}} = E_{C=C} + 4E_{C-H}$$

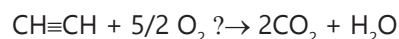
$$+ E_{O=O} - 2\Delta H_{f,CO_2} - 2\Delta H_{f,H_2O}$$

$$-1410.9 = E_{C=C} + 4E_{C-H}$$

$$+ 3(498.34) - 2(-393.5) - 2(-285.8)$$

$$E_{C=C} + 4E_{C-H} = -1274.48$$

Combustion of Acetylene:



$$\Delta H^\circ_{\text{comb}} = E_{C \equiv C} + 2E_{C-H} + 2E_{C-H}$$

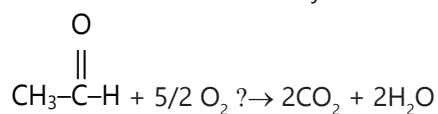
$$+ 5/2 E_{O=O} - 2\Delta H_{f,CO_2} - 2\Delta H_{f,H_2O}$$

$$-1299.7 = E_{C \equiv C} + 2E_{C-H}$$

$$+ 5/2(498.34) - 2(-393.5) - 2(-285.8)$$

$$E_{C \equiv C} + 2E_{C-H} = -1412.45$$

Combustion of Acetaldehyde:



$$\Delta H^\circ_{\text{comb}} = E_{C-C} + E_{C=O} + 4E_{C-H}$$

$$+ 5/2 E_{O=O} - 2\Delta H_{f,CO_2} - 2\Delta H_{f,H_2O}$$

## Exercise 2

### Single Correct Choice Type

**Sol 1: (D)**  $\Delta H = \Delta E + \Delta n_g T$

Case-I =  $\Delta n_g = 2 - 1 - 1 = 0$

Case-II =  $\Delta n_g = 0 - 0 = 0$

Case-III =  $\Delta n_g = 1 - 1 = 0$

Case-IV =  $\Delta n_g = 2 - 3 - 1 = -2 \neq 0$

$\therefore$  In option (Δ)  $\Delta H = \Delta E$

**Sol 2: (D)**  $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$$\Delta H = -25$$

$$-25 = 4 \times C-H + 4Cl$$

$$-Cl - 3 \times CH - 1C - Cl - 1H - Cl$$

...(i)  $-25 = 4x + y - 3x - 84 - 103$

$$y - x = 162$$

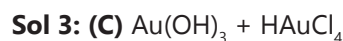
$$x = \frac{9}{5} y$$

$$\frac{9}{5} x + \frac{1}{5} x = 162$$

$$\frac{14}{5} y = 162$$

$$y = 57.75 \text{ k cal}$$

....(ii)



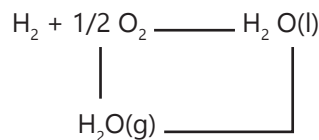
$$36.8 + x \times -28 = 0.44$$

$$x(36.8 - 28) = 0.44$$

$$x = 0.05$$

**Sol 4: (B)**

.....(iii)

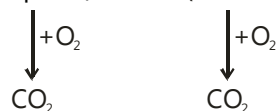


$$\Delta H_{\text{comb}} = BE(H - 11) + 1/2 B.E(O=O - 2 \times B.E(OH))$$

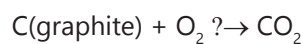
B.E. (vap)

$$= x_1 + x/2 - 2 \times x_3 - x_4$$

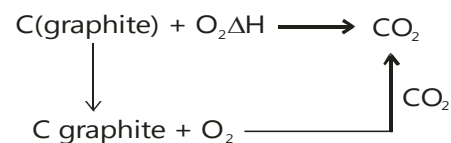
**Sol 5: (C)**



$$\Delta H = 1.9 \text{ kJ}$$

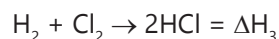
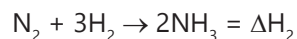
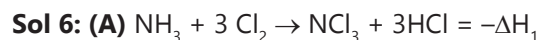


$$\Delta H = \Delta H_{f,CO_2}$$



$$\Rightarrow \Delta H' = \Delta H_{f,CO_2} + \Delta H_{C-C \text{ graphite}}$$

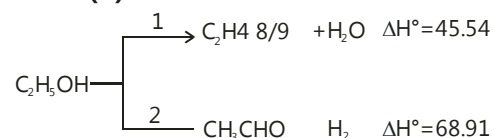
$$\Delta H' = \Delta H_f - 1.9$$



$-\Delta H_1 = 3\Delta H_f \text{HCl} + \Delta H_{f\text{NCl}_3} - \Delta H_f \text{NO}_3$

$\therefore \Delta H_{f\text{NCl}_3} = \frac{\Delta H_2}{2} - \frac{3\Delta H_3}{2} - \Delta H_1$

**Sol 7: (B)**



Molar ratio of  $\text{C}_2\text{H}_4$  to  $\text{CH}_3\text{CHO} = 8:1$

$\therefore$  Enthalpy per unit

$8x + x = 0$

$\therefore x = 1/9$

$\therefore \Delta H = \frac{1}{9} \times 45.54 + \frac{8 \times 68.91}{9} = 48.137$

**Sol 8: (C)**  $E_1 = 1 - \frac{T_2}{1000}$

$E_1 = 1 - \frac{360}{T_2}$

$\therefore 1 - \frac{T_2}{1000} = 1 - \frac{360}{T_2}$

$\therefore (T_2)^2 = 360 \times 1000$

$T_2 = 600$

**Sol 9: (C)** Isochoric  $\therefore V_1 = V_2$

$\Delta S = nC_v \ln \frac{T_2}{T_1} = nR \ln \frac{V_2}{V_1}$

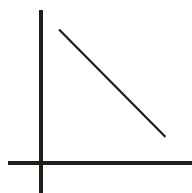
$\therefore \Delta S = 2 \times \frac{3R}{2} \ln \left( \frac{300+273}{200+273} \right)$

$= 3R \ln \left( \frac{573}{473} \right)$

**Sol 10: (C)**  $\Delta G = \Delta dP = \int \frac{nRT}{P} dP$

$= nRT \ln \frac{P_2}{P_1} = 517.13$

**Sol 11: (A)**



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

$y = \Delta H - x \Delta S$

Slope is -ve

$\therefore \Delta S < 0$

$\therefore \Delta S > 0$  and intercept  $> 0$

$\therefore \Delta H > 0$

**Sol 12: (C)**  $\Delta H_{\text{vap}} = 300/\text{g}$  at  $T = 300 \text{ K}$

$= 300 \times 30 \text{ J/mol}$

$\Delta S \text{ mole} = \frac{\Delta H_{\text{moles}}}{T} = \frac{300 \times 30}{300} = 30 \text{ J/mol}$

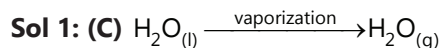
**Sol 13: (D)**  $P \times 20 = 2 \times 0.0821 \times 243.6 \text{ K}$

$P_i = 2 \text{ atm}$   $P_f = 1 \text{ atm}$

$\Delta S = -4R \ln \frac{P_2}{P_1}$

$= 2 \times \frac{8.314}{4.19} \ln 2 = 2.77$

## Previous Years' Questions



$\Delta n_g = 1 - 0 = 1$

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

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

$= 41 - 8.3 \times 10^{-3} \times 373 = 37.9 \text{ kJ mol}^{-1}$

**Sol 2: (A)**  $\Delta H = \Delta U + \Delta(PV)$

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

$\Delta U = \Delta H - V\Delta P = -560 - 1 \times 30 \times 0.1$

Absolute value = 563 kJ.

**Sol 3: (A)** For a pure substance,  $T_A$  and  $T_B$  represent the same temperature. Hence, A is a correct choice.

**Sol 4: (A)** For a spontaneous process in an isolated system, the change in entropy is positive.

**Sol 5: (B)** For a reaction to be spontaneous,  $\Delta G$  must be negative. According to the equation -

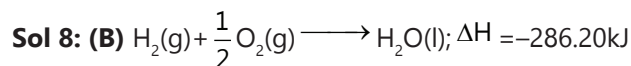
$\Delta G = \Delta H - T\Delta S$

If  $\Delta H$  and  $\Delta S$  both are positive, then term  $T \cdot \Delta S$  will be

greater than  $\Delta H$  at high temperature and consequently  $\Delta G$  will be negative at high temperature.

**Sol 6: (B)**  $dS = \frac{dQ_{\text{rev}}}{T}$ ;  $T = \frac{30 \times 10^3}{75}$ ;  $T = 400 \text{ K}$

**Sol 7: (A)**  $\text{C}_2\text{H}_6 + \frac{7}{2} \text{O}_2 \longrightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$  substitute the values.



$$\Delta H_r = \Delta H_f(\text{H}_2\text{O}, \text{l}) - \Delta H_f(\text{H}_2, \text{g}) - \frac{1}{2} \Delta H_f(\text{O}_2, \text{g})$$

$$-286.20 = \Delta H_f(\text{H}_2\text{O}(\text{l}))$$

$$\text{So, } \Delta H_f(\text{H}_2\text{O}, \text{l}) = -286.20$$



$$\Delta H_r = \Delta H_f^\circ(\text{H}^+, \text{aq}) - \Delta H_f^\circ(\text{OH}^-, \text{aq}) - \Delta H_f^\circ(\text{H}_2\text{O}, \text{l})$$

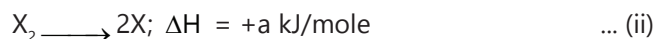
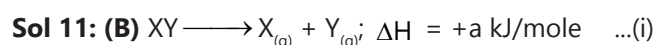
$$57.32 = 0 + \Delta H_f^\circ(\text{OH}^-, \text{aq}) - (-286.20)$$

$$\Delta H_f^\circ(\text{OH}^-, \text{aq}) = 57.32 - 286.20 = -228.88 \text{ kJ}$$

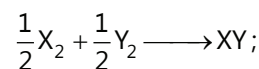
**Sol 9: (D)** Standard molar heat enthalpy ( $H^\circ$ ) of a compound is equal to its standard heat of formation from most stable states of initial components.

**Sol 10: (A)**  $\Delta H = \frac{240}{2} - 349 - 381$

$$= 120 - 349 - 381 = -610 \text{ kJ/mol}$$



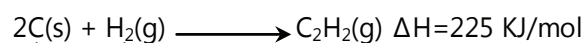
$$\frac{1}{2} \times (\text{ii}) + \frac{1}{2} \times (\text{iii}) - (\text{i}), \text{ gives}$$



$$\Delta H = \left( +\frac{a}{2} + \frac{0.5a}{2} - a \right) \text{ kJ / mole}$$

$$+\frac{a}{2} + \frac{0.5a}{2} - a = -200; a = 800$$

**Sol 12: (D)**



$$\therefore \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{\text{C=C}} = +225$$

$$\therefore \varepsilon_{\text{C=C}} = 1740 - 700 - 225 = +815 \text{ kJ/mol.}$$

**Sol 13: (B)**  $(dS)_{V,E} > 0, (dG)_{T,P} < 0$

**Sol 14: (C)**  $\Delta G = \Delta H - T\Delta S$  [ $\Delta H = +ve$ ;  $\Delta S = +ve$ ]

$$\Delta G = +ve - T_e(+ve)$$

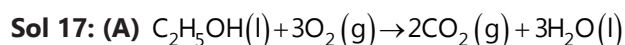
if  $T > T_e$  then  $\Delta G = -ve$  (spontaneous).

**Sol 15: (C)** In this reaction  $\Delta n = 2 - 4 = -2$  so  $\Delta H \neq \Delta E$

**Sol 16: (A)** The process is isothermal expansion Hence,  $q = -w$ ;  $\Delta u = 0$

$$q = +208 \text{ J}$$

$$w = -208 \text{ J (expansion work)}$$



Bomb calorimeter gives  $\Delta U$  of the reaction

So, as per question

$$\Delta U = -1364.47 \text{ kJ mol}^{-1}$$

$$\Delta n_g = -1$$

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

$$= -1364.47 - \frac{1 \times 8.314 \times 298}{1000}$$

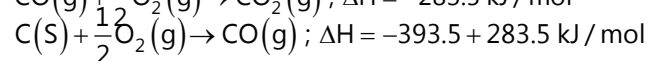
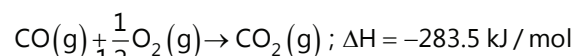
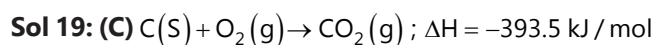
$$= -1366.93 \text{ kJ mol}^{-1}$$

**Sol 18: (D)**

$$2\Delta G_{f(\text{NO}_2)}^\circ - [2\Delta G_{f(\text{NO})}^\circ + \Delta G_{f(\text{O}_2)}^\circ] = \Delta G_r^\circ = -RT \ln K_p$$

$$2\Delta G_{f(\text{NO}_2)}^\circ - [2 \times 86,600 + 0] = -RT \ln K_p$$

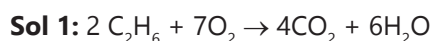
$$2\Delta G_{f(\text{NO}_2)}^\circ = 0.5 \left[ 2 \times 86,600 - R(298) \ln(1.6 \times 10^{12}) \right]$$



$$= -110 \text{ kJ / mol}$$

## JEE Advanced/Boards

### Exercise 1

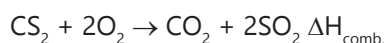


$$\Delta H_{\text{comb}} = \Delta H \text{ for reactants} - \Delta H_f \text{ products}$$

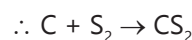
$$3120 = 2 \times \Delta H_f (\text{C}_2\text{H}_6) - 4 \times \Delta H$$

$$+ \text{CO}_2 - 6 \Delta H_{\text{H}_2\text{O}}$$

$$\therefore \Delta H_f (\text{C}_2\text{H}_6) = \frac{3120 - 4 \times 395 - 6 \times 286}{2} = 88 \text{ KJ}$$



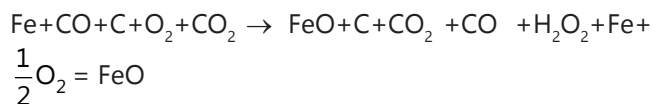
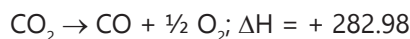
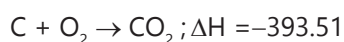
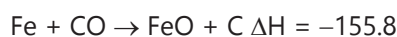
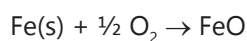
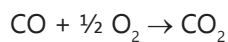
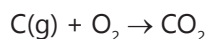
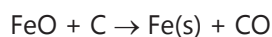
$$= -1108.76$$



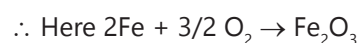
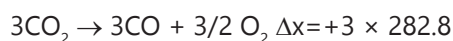
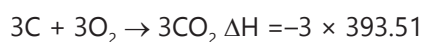
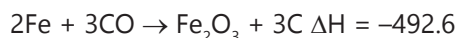
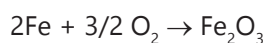
$$-\Delta H_3 + \Delta H_1 + 2\Delta H_2$$

$$= 1108.76 - 393.3 - 2 \times 293.72$$

$$\Delta H = 128.02$$



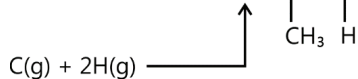
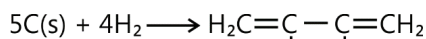
$$\therefore \Delta H_f = -155.8 - 393.51 + 282.98 = -266.33$$



$$\Delta H_2 = -492.6 - 3 \times 393.51 + 3 \times 282.98$$

$$= -824.2$$

**Sol 4:**



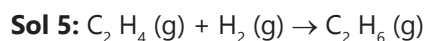
$\Delta H_{\text{atom}}$

$$= \Delta H_{\text{C(s)} \rightarrow \text{C(B)}} + \Sigma \text{BE}_{\text{(Reactants)}} - \Sigma \text{BE}_{\text{(products)}}$$

$\Delta H_{\text{formation}}$

$$= 5 \times 171 + [4 \times 104 - 2 \times 83 - 2 \times 147 - 8 \times 98.8]$$

$$= 20.6 \text{ K cal}$$



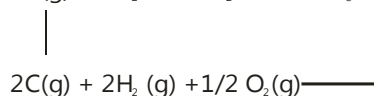
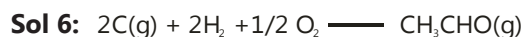
$$\Delta H_{\text{reaction}} = \Sigma \text{BE}_{\text{reactants}} - \Sigma \text{BE}_{\text{products}}$$

$$= 1 \times \text{C}=\text{C} + 4 \times \text{C}-\text{H} - 1 \times \text{C}-\text{C} + 6 \times (\text{H})$$

$$= 1 \times \text{C}=\text{C} - 1 \times \text{C}-\text{C} = 2 \times \text{C}-\text{H}$$

$$= 606.68 + 431.79 - 336 - 81 - 2 \times 410.87$$

$$= -120.08$$

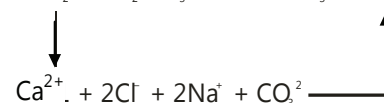


$$\therefore \Delta H_f = 2 \times \Delta H_{\text{sub}} + \Sigma \text{BE}_{\text{reactants}} - \Sigma \text{BE}_{\text{products}} = 2 \times 718.4$$

$$+ \left[ 2 \times 435.8 + \frac{495}{2} - 4 \times 413.4 - 728.0 - 347.0 \right]$$

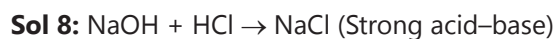
$$= -192.73$$

**Sol 7:**

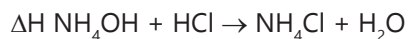


$$\Delta H_{\text{reac.}} = -288.5 + 129.80 + 1261.65$$

$$= 2.98 \text{ k cal}$$



$$\therefore \Delta H^0 = -1368 \text{ cal}$$



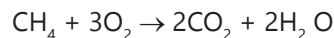
$$\therefore \Delta H' = \Delta H - 1\Delta H_{\text{diss}} - 12270$$

$$= -13680 + \Delta H_{\text{diss}}$$

$$\therefore \Delta H_{\text{diss}} = 1410$$

**Sol 9:**  $\text{CH}_4(\text{g}) + \text{O}_2(\text{g})$  at  $T = 298 \text{ K}$   $P = \frac{740}{766} \text{ atm}$

$$v = 1 \text{ L}$$



$$PV = nRT$$

$$\frac{740}{760} \times 1 = n \times 0.0821 \times 298$$

$$\therefore n_{\text{E}} = 0.04$$

$$\Delta H_{\text{rec}} = 1260 \times 0.667$$

$$0.667 \times 1260 = n_{\text{CH}_4} \times \Delta H_{\text{CO}}$$

$$340 = n_{\text{CH}_4} \times 215 \times 10^3$$

$$n_{\text{CH}_4} = 0.0039$$

$$\therefore n_{\text{CH}_4} = \frac{0.0039}{0.04} \times 100 = 9.82\%$$



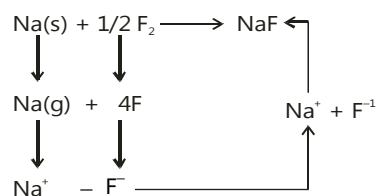
$$400 \times 0.2 \quad 100 \times 0.8$$

$$V_{\text{t}} = 400 + 100 = 500 \text{ cm}^3$$

$$n = 1 \text{ g/cm}^3$$

$$\therefore \Delta H = \frac{-500 \times 4.2 \times \Delta T}{1000} = -31.5 \text{ KJ}$$

**Sol 11:**

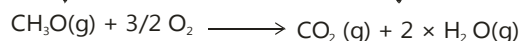
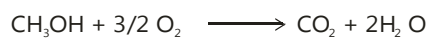


$$\therefore \Delta H_{\text{f}} = \Delta H_{\text{sap}} + \frac{\Delta \text{BE}}{2} + \text{I.E.} \Delta H_{\text{EG}} + \text{L.E.}$$

$$-57 = 101 + \frac{160}{2} + 494 + \Delta H_{\text{EG}} \quad 894$$

$$\Delta H_{\text{EG}} = -352$$

**Sol 12:**



Resonance eng of  $\text{CO}_2 + 43$

$$\therefore \Delta H_{\text{cob}} = +35.5 +$$

$$\Sigma \text{B.E.}_{\text{react}} - \Sigma \text{B.E.}_{\text{products}} - 40.0 \times 2$$

$$= 35.5 + 3/2 \times 494 + 351.5 + 464.5 + 3 \times 414 - 2 \times 711 - 143 - 2 \times 40.6 - 464.5 = -669.7$$

**Sol 13:** (A)  $C_v = 3R/2r = 5/3$

$$P_i = 1 \text{ atm}; P_f = 2 \text{ atm}$$

$$T_i = 300 \text{ K}$$

$$1 \times V = 300 \times 1 \times 0.082$$

$$V_i = 24.63$$

$$1 \times (24.63)^r = 2 \times V_i^r$$

$$\therefore W_{\text{adiabatic}} = \int -PdV = - \int \frac{CdV}{V^{1-r}} = 1194.72 \text{ J}$$

$$P^{1-r}T^r = \text{Const.}$$

$$P_f^{1-\frac{5}{3}} T_f^{\frac{5}{3}} = P_i^{1-\frac{5}{3}} T_i^{\frac{5}{3}} \quad P_f$$

$$2^{-2300} \left( \frac{T}{300} \right)^5 = 1$$

$$\frac{T}{300} = 4^{\frac{1}{5}}$$

$$T = 4^{1/5} \times 300$$

$$T_f = 395.85$$

(B)  $1 \times V_1 = 1 \times R \times T_1 = 300 R$

$$PV = nRT$$

$$nC_v \Delta T = -P_2 (V_2 - V_1)$$

$$2 \times V_f = 1 \times R \times T_f$$

$$1 \times \frac{3R}{2} (T_2 - T_1) = -2 (V_2 - V_1)$$

$$\frac{3R}{2} (T_2 - 300) = T_f \times R + 2 V_1$$

$$\frac{3R}{2} (T_2 - 300) = -T_f \times R + 2 \times 300 R$$

$$\frac{3T}{2} - 450 = -T_f \quad 1 + 600$$

$$\frac{5T}{2} = 1050$$

$$T_f = \frac{2100}{5}$$

$$V_f = 420 \text{ k}$$

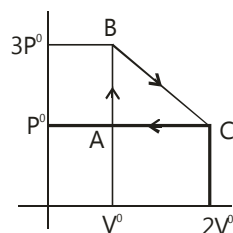
$$T_f = \frac{R \times 420}{2} = 210 R = 17.24$$

$$\therefore W = -2 (V_2 - V_1) = -2 (210 R - 300 R)$$

$$= 180 R = 1496.525 \text{ J}$$

**Sol 14:**  $C_V = 3R/2$   $n = 1$

Work done by gas = Area under P – V curve



$$= \text{Area of } \triangle ABC$$

$$= \frac{1}{2} \times (3P_0 - P_0) \times (2V_0 - V_0)$$

$$= \frac{-2P_0V_0}{2} = -P_0V_0$$

$$\Delta V_{\text{cycle}} = 0$$

$$\therefore W_{d1} = Q_{\text{process}} = P_0V_0$$

$$W_{AB} = 0 \quad Q_{AB} = \Delta V_{AB} = nC_V\Delta T$$

$$= \frac{3R\Delta T}{2} = \frac{3}{2} \Delta PV$$

$$= \frac{3}{2} \times (3P_0V_0 - 2P_0V_0) = 3P_0V_0$$

$$W_{AC} = P_0 \times (V_0 - 2V_0) = P_0V_0$$

$$\Delta V_{AC} = nC_V\Delta T = \frac{3}{2} \Delta P_0V_0$$

$$\frac{3}{2} P_0 (V_0 - 2V_0) = -\frac{3}{2} P_0V_0$$

$$\therefore Q = \Delta U - W$$

$$= -3/2 P_0V_0 - P_0V_0$$

$$-5/2 P_0V_0$$

$$Q_{AB} + Q_{BC} + Q_{CA} = Q_{\text{plou}} = P_0V_0$$

$$-5/2 P_0V_0 + 3P_0V_0 + Q_{BC} = P_0V_0$$

$$\therefore Q_{BC} = \frac{P_0V_0}{2}$$

$$\text{at B temp} = \frac{3P_0V_0}{R}$$

$$\text{at } \Delta \text{ temp} = \frac{P_0V_0}{R}$$

$$\text{at B temp} = \frac{2P_0V_0}{R}$$

from B – C

P – V curve is

$$P = mV + C$$

$$(3P_0 = mV_0 + C) \times 2$$

$$P_0 = 2mV_0 + C$$

$$5P_0 = C$$

$$3P_0 = mV_0 + 5P_0$$

$$\therefore m = \frac{-2P_0}{V_0}$$

$$\therefore P = \frac{-2P_0}{V_0} V + 5P_0$$

$$\left( 5P_0 - \frac{2P_0}{V_0} V \right) V = RT$$

$$T = R \left( 5P_0V - \frac{2P_0}{V_0} V^2 \right)$$

$$\frac{dT}{dV} = 0 \text{ at } 5P_0 - \frac{4P_0}{V_0} V = 0$$

$$\therefore V_0 = 5/4 V$$

$$T = R \left[ 5P_0 \times 5/4 V_0 - 2 \frac{P_0}{V_0} \times \frac{25}{16} V_0 \right]$$

$$T_{\text{max}} = R \left( \frac{25}{4} - \frac{25}{8} \right) P_0V_0 = \frac{25}{8} \frac{P_0V_0}{R}$$

**Sol 15:** (i)  $\Delta S_{\text{gas}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$

$$\Delta S_{\text{gas}} = R \times \ln 3 = 9.13$$

$$\text{Reverse } \therefore \Delta S_{\text{gas}} = -\Delta S_{\text{surr}} \therefore \Delta S_{\text{total}} = 0$$

$$\Delta S_{\text{surr}} = -\frac{Q_{\text{rev}}}{T}$$

$$9.134 = \frac{-Q_{\text{rev}}}{298}$$

$$\therefore Q_{\text{rev}} = 2775.572$$

$$\therefore Q_{\text{avg}} = -2775.572 + 836.8$$

$$\therefore \Delta S_{\text{total}} = 9.134 + \frac{-2775.572}{278} + \frac{836.8}{298}$$

$$= \frac{836.8}{298} = 2.808 \text{ J/k}$$

(iii) In case of free expansion  $Q = 0$ 

$$\therefore \Delta S_{\text{surr.}} = 0$$

$$\therefore \Delta S_{\text{system}} = \Delta S_{\text{total}} = 9.134 \text{ J}$$

**Sol 16:**  $\text{Ag}(\ell) \rightarrow \text{Ag}$ 

$$\Delta H_{\text{avg}} = 22 \text{ KJ}$$

$$\Delta S_{300} = \frac{\Delta T}{T} = \frac{22 \times 10^3}{300} = \frac{220}{3} \text{ J}$$

$$\int_{300}^{200} \Delta S = \int \frac{nC_p}{T} - nR \, dP$$

$$\therefore P_2 = P_1 = 100$$

$$\Delta S_{200} \frac{-220}{3} = C_p \ln \frac{T_2}{T_1} - C_p(\ell) \ln \frac{T_2}{T_1}$$

$$\Delta S_{-200/3} = (30 - 40) \ln \left( \frac{200}{300} \right)$$

$$\Delta S = \frac{220}{3} + 10 \ln (3/2)$$

$$= 22/3 + 10 \times 0.405 = 74.05 \text{ J/k}$$

 $V = \text{constant}$ **Sol 17:**  $\Delta S_{\text{sys}} = nC_v \ln T_2/T_1$ 

$$= 1 \times \frac{3R}{2} \ln (1000/10)$$

$$= \frac{3R}{2} \ln 10$$

$$\therefore \Delta S_{\text{total}} = 0$$

$$\therefore \Delta S_{\text{surr.}} = \Delta S_{\text{system}} = -3/2 k \ln (10)$$

(ii) Irreversible Process

$$\Delta S_{\text{system}} = -3/2 R \ln (10)$$

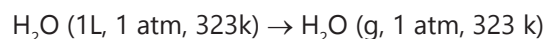
$$W + Q = \Delta U$$

$$W = 0 \text{ as } dV = 0 \therefore Q = \Delta U = nC_v \Delta T$$

$$= \frac{3R}{2} \times 900$$

$$\therefore \Delta S_{\text{total}} = \frac{3R}{2} (0.9 - \lambda n 10)$$

$$= -\frac{3R}{2} \times 1.403$$

**Sol 18:**

$$\Delta H_{\text{vap}} \text{ H at } 373 = 40.639 = 2.1$$

$$\Delta H_{373} = 40.639 \times 10^3 \text{ J}$$

$$\Delta H_{323} = 38.54 \text{ KJ}$$

$$\Delta S_{373} = \frac{\Delta H_{\text{vap}}}{373} = \frac{40639}{373} = 108.95 \text{ J}$$

$$\int_{373}^{323} \frac{nC_p dT}{T}$$

$$= (33.305 - 75.312) \ln (T_2/T_1)$$

$$= -42.00 \ln (373/325)$$

$$\Delta S_{323} = 108.95 - 6.04$$

$$= 102.349$$

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

$$= 38.54 - \frac{102.349 \times 323}{1000} = 5.54 \text{ kJ/mol}$$

**Sol 19:** Adiabatic expansion

$$\therefore P = 0 \therefore \Delta S_{\text{surr}} = 0$$

$$\therefore \Delta S_{\text{total}} = \Delta S_{\text{system}}$$

(i) Case-I: Reversible process,

$$\therefore \Delta S_{\text{system}} = \Delta S_{\text{total}} = 0$$

(ii) Case-II: Irreversible  $P_{\text{ext}}$ 

$$= 262.65 \text{ KPa}$$

$$\Delta S_{\text{system}}$$

Neon  $\rightarrow$  monoatomic

$$C_v = 3R/2 \text{ r} = 5/3$$

$$P^{1-r} = \text{const.}$$

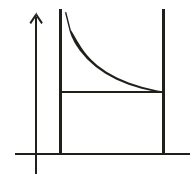
$$P \propto T^{r/r-1}$$

$$\frac{P_2}{P_1} = \left( \frac{T_2}{T_1} \right)^{r/r-1}$$

$$\frac{202.65}{506.65} \left( \frac{T_2}{473} \right)^{\left( \frac{5/3}{2/3} \right)}$$

$$\therefore T_f = 327.85$$

$$V_{\text{ex}} = 20.26 \text{ J}$$



$$PV = nRT$$

$$n \times \frac{3R}{2} \Delta T = -P_{\text{ext}} (V_2 - V_1)$$



$$n \times \frac{3R}{2} \Delta T = -P_{\text{ext}} \left( \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

$$\therefore w = nC_p \ln T_2/T_1 - nP \ln (P_2/P_1)$$

$$= -2.85 + 3.81 = 0.957 \text{ KJ}$$

(iii) In case of free expansion

$$\therefore \Delta S = -ne \lambda n (P_2/P_1)$$

$$= \frac{-10}{20} \times 8.314 \lambda n \left( \frac{202.65}{506.625} \right) = 3.81 \text{ J/k}$$

**Sol 20:**  $\Delta_r C_p = 0$

$$\therefore \Delta H_{298}^0 = \Delta H_{373}^0$$

$$\Delta S_{298}^0 = \Delta H_{373}^0$$

$$P-V \text{ work} = T\Delta S^0$$

$$\therefore -6333 = -5737 - 298 \rightarrow \Delta S^0$$

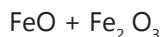
$$\Delta S^0 = 2$$

Additional non-PV work

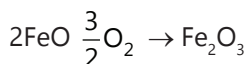
$$= (310 - 298) \times 2 = 24 \text{ kJ/mol}$$

**Sol 21:**  $\Delta H_{f \text{ FeO}} = -65 \text{ k}$

$$\Delta H_{f \text{ Fe}_2\text{O}_3} = -197 \text{ k Cal}$$



initially



$$2-2x \quad 1+x$$

$$\text{Finally } \frac{1+x}{1-2x+2+x} = \frac{2}{3}$$

$$\frac{1+x}{3-x} = \frac{2}{3}$$

$$3 + 3x = 6 - 3x$$

$$6x = 3 \Rightarrow x = 0.5$$

$\therefore$  1 mole of FeO  $\rightarrow$  converts to  $\text{Fe}_2\text{O}_3$

$$\Delta H = \frac{\Delta H_{f \text{ Fe}_2\text{O}_3}}{2} - \Delta H_{f \text{ FeO}}$$

$$= -197/2 + 65 = -33.5$$

$$\therefore \Delta H/\text{mole} = -11.167$$

**Sol 22:**  $\Delta H_{\text{diss}} (H_A) = -6900 + 13400$

$$\Delta H_{\text{diss}} (H_B) = -2900 + 13400$$

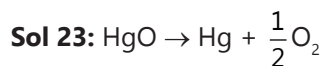
$$x - 6900 + (1 - x) \times -2900 = -3900$$

$$69 \times x + (1 - x) \times 29 = 39$$

$$40x = 10$$

$$n = 0.25\%$$

$\therefore$  25% is given to HA and 75% to HB



At constant pressure

$$\therefore \Delta H = 41.84$$

$$\therefore 41.84 = \frac{m}{200.6} \times 90.8$$

$$\therefore m = 92.435$$

(b)  $\Delta v = 41.84$

$$\Delta H = \Delta U + \Delta PT$$

$$= \Delta U + \Delta nRT$$

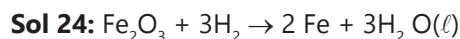
$$= \Delta U + \frac{m}{2 \times 200.6} \times 8 \times 314 \times 298$$

$$\therefore \left( 41.34 + \frac{8.314 \times 298 \times m}{400.12 \times 1000} \right) = \frac{m \times 90.8}{200.6}$$

$$41.84 = \left( \frac{90.8}{200.6} - \frac{1.238}{200.6} \right) m$$

$$41.84 = 0.446 n$$

$$m = 93.715 \text{ g}$$



$$\Delta H_{298}^0 = -35.1$$

$$\Delta H_{\text{max}}^0 = -265$$

$$\int_{298}^T \Delta H = n(\Delta C_{p \text{ Products}} - \Delta C_{\text{rad}}) \Delta T = 0$$

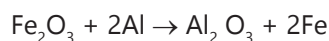
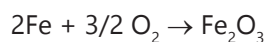
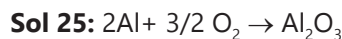
$$\Delta H_T - \Delta H_{298} (2 \times 25.5 + 3 \times 75.3$$

$$- 104.5 - 3 \times 28.9) [T - 28]$$

$$-26 + 35.1 = \frac{85.7}{10^3} (T_{-298})$$

$$\frac{9100}{85.7} = T - 298$$

$$T_f = 404.18 \text{ K}$$



$$\Delta H_f^\circ = \Delta H_{Al_2O_3}^\circ - \Delta H_{Fe_2O_3}^\circ = -399 + 199 = -200 \text{ k cal/mol} \quad \therefore \text{Proton gain} = -718 \text{ kJ/mol}$$

2 mole of mixture

$\therefore$  Mole of  $Fe_2O_3$  and  $\frac{1}{2}$  mole of  $Al_2$

$\therefore$  Mass of  $Fe_2O_3 = 160$

Mass of  $Al = 27 \times 2 = 54$

$\therefore$  Mass total = 214

$\therefore \Delta H/\text{mol} = -200$

$$\Delta H/g = \frac{-200}{2 \times 214} = 0.9345 \text{ g}$$

Mole mix mass 2 mole of  $Al = 54 \text{ (g)}$

$d = 2.7 \text{ g/cc}$

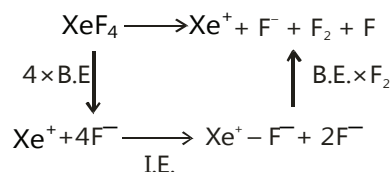
$$\therefore V_1 = \frac{54}{2.7} = 20$$

$$V_2(Fe_2O_3) = \frac{160}{5.2} = 30.77$$

$V_{\text{total}} = 50.77 \text{ cc}$

$$\therefore \Delta H = \frac{-200}{50.77} = 3.94 \text{ k cal}$$

**Sol 26:**

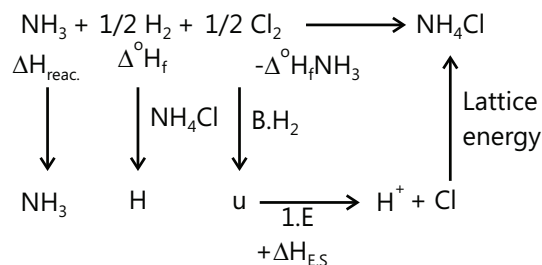


$+\Delta H_{\text{EQ}} = \text{electron affinity} = -85$

$$= 4 \times 34 + 279 - 85 - 38 = 292 \text{ k cal/mol}$$

**Sol 27:**  $N_2 + 3H_2 \rightarrow 2NH_3$   $\Delta^\circ H = -46 \times 2$

$\Delta H_f^\circ = -46$



$$\therefore \Delta H_{\text{rea}} = \frac{\text{B.E.H}_2}{2} + \frac{\text{B.E.Cl}}{2}$$

$+ \text{I.E.H}_2 + \Delta H_{\text{EG Cl}} + \text{Lattice} + \text{Protein gain}$

$$-314 + 46 = \frac{218}{2} + \frac{124}{2} + 1310$$

$$-348 + \text{proton gain} - 683$$

$$\text{Sol 28: } 10^{-3} \times 1.2 \times 1 = 0.0820 \times 273 \times x$$

$$\therefore n_t = 0.5 \times 10^{-3}$$

$\text{CO (will at)} = ?$

$\text{CO} + \text{H}_2\text{O}_2 = \text{CO}_2$ ;  $\Delta H = -280 \text{ KJ}$

$$\therefore n_{\text{CO}} + 280 \times 10^3 = 7$$

$$\therefore n_{\text{CO}} = \frac{7}{280} \times 10^{-3} = 2.5 \times 10^{-5}$$

Proportion by volume

$$\Rightarrow \frac{n_{\text{CO}}}{n_t} = \frac{2.5 \times 10^{-5}}{5 \times 10^{-3}} = 0.05$$

$$\frac{n_{\text{CO}}}{n_{\text{CO}_t}} = 0.001 \% y$$

$$10^{-5} = 0.05 \times (1/2)$$

After each cycle

$$n_{\text{CO}_t} = \frac{1}{2} n_{\text{CO}}$$

$$\therefore \frac{n_{\text{CO}}}{n_{\text{CO}_t}} = \frac{1}{2} \ell n$$

$$2 \times 10^{-4} = (0.5)^n$$

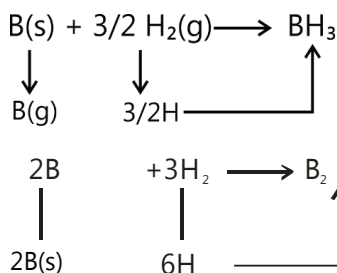
$$\therefore n = 13$$

$$13 \times x + 80 = 6 \times 60$$

$$x = \frac{360 - 80}{13}$$

$$x = 21.54 \text{ sec}$$

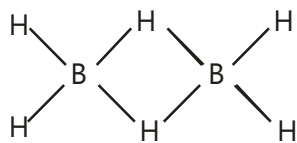
**Sol 29:**



$$\Delta H_f^\circ = \Delta H_B + \frac{3}{2} \Delta H_6 H - 3 \times \text{B.E. (B-H)}$$

$$100 = 565 + 436 \times \frac{3}{2} - 3 \times x$$

$$\therefore X = 373 \text{ H} - = a$$



3 – centre, 2 – electron bond

$$\Delta H_{\text{f}}^{\circ} \text{B}_2\text{H}_6 - 36 = 2 \times 565 + 436 \times 3 - 4 \times x$$

**Sol 30:**  $\text{CHCl}_2 - \text{COOH}$  by  $\text{NaOH} = 12850$

$\text{HCl}$  by  $\text{NaOH}$  is 13680

$\text{NH}_4\text{OH}$  by  $\text{HCl}$  is 12270

$\text{CHCl}_2\text{COOH} + \text{NaOH}$

$\rightarrow \text{CHCl}_2\text{COONa} + \text{H}_2\text{O}$

$\text{NH}_4\text{OH} + \text{HCl} \rightarrow \text{NH}_4\text{Cl} + \text{H}_2\text{O}$

$\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$  (2) – (3) gives

$\text{CHCl}_2 + \text{NH}_4\text{OH} \rightarrow \text{CHCl}_2\text{COONa} + \text{NH}_4\text{Cl}$

$$\therefore \Delta H_{\text{reac}} = -12830 - 12270 + 413680 = -11420$$

$$\Delta H_{\text{diss}} \text{ of } \text{CHCl}_2\text{COOH} = 13680 - 12830 = 850$$

$$\Delta H_{\text{diss}} \text{ NH}_4\text{OH} = 13680 - 12270 = 1410$$

## Exercise 2

### Single Correct Choice Type

**Sol 1 : (A)**  $\text{N}_2\text{H}_4(\text{l}) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$

$a \rightarrow (1) 2\text{NH}_3 + 3\text{N}_2\text{O} \rightarrow 4\text{N}_2 + 3\text{H}_2\text{O}$

$b \rightarrow (2) \text{N}_2\text{O} + 3\text{H}_2 \rightarrow \text{N}_2\text{H}_4 + \text{H}_2\text{O}$

$c \rightarrow (3) 4\text{NH}_3 + \text{O}_2 \rightarrow 2\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l})$

$d \rightarrow (4) \text{H}_2 + \frac{1}{2} \text{O}_2(\text{r}) \rightarrow 2\text{N}_2\text{H}_4(\text{l}) + 2\text{H}_2\text{O}$

$$4a = 1$$

$$b + 2c = -1$$

$$c + d/2 = 1$$

$$3a + b + 2c + d = 2$$

$$b + 2c = -1$$

$$c + d/2 = 1$$

$$3 \times \frac{1}{4} - 1 + d = 2$$

$$d = 9/4$$

$$c = 1 - \frac{8}{9} = -\frac{1}{9}$$

$$b - \frac{2}{8} = -1$$

$$b = -1 + \frac{1}{4} = -\frac{3}{4}$$

$$\therefore \Delta H = \frac{1011}{4} + \frac{1}{8}$$

$$\times 286 - \frac{285 \times 9}{4} + \frac{317 \times 3}{4}$$

$$\Delta H = -620.5$$

**Sol 2: (C)**  $\text{HCl} + \text{O}_2 \rightarrow 2 \text{Cl}_2 + 2\text{H}_2\text{O}$

$$\Delta H_{\text{reac.}} = -2 \times \Delta H_1 + \Delta H_2$$

$$= 2 \times 184.5 + 483 = 114$$

$$\Delta H = \Delta V + \Delta ng$$

$$-114 = \Delta V + -1 \times 8.3 \times 300$$

$$\Delta V = -1115.5$$

**Sol 3: (B)**  $\Delta H_{\text{reac.}} = \Delta H_{\text{f}} + \text{Na}_2\text{SO}_4 + 2\Delta H \text{ HCl}$

$$-2 \Delta H_{\text{f}} \text{ NaCl} - \Delta H_{\text{f}} \text{ H}_2\text{SO}_4$$

$$= -1382 - 2 \times 92 + 2 \times 441 + 811$$

$$\Delta V = \Delta H - ngRT = 62.02$$

$$\Delta H = -67$$

**Sol 4: (A)**  $\text{A}(\text{g}) + \text{B}(\text{g}) \rightarrow \text{C}$

$$\Delta E = -3 \text{ k Cal}$$

$$\Delta H = \Delta E + \Delta_{\text{ng}} R$$

$$= -3 - \frac{1 \times 1.987 \times 300}{1000}$$

$$\Delta H = -3.60$$

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

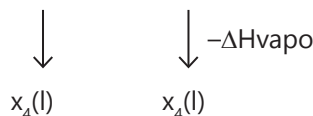
$$= -3.5 + \frac{300 \times -10}{1000} 0.6 \text{ k cal} \Rightarrow 600 \text{ cal}$$

$$\textbf{Sol 5: (D)} \Delta S = \frac{\Delta H_{\text{vap}}}{T}$$

$$\therefore T\Delta S - \Delta H = -\Delta G = 0$$

$$\therefore \Delta G = 0$$

**Sol 6: (C)**



$$\Delta S = -125 \text{ J/k}$$

$$-100 \times 4 = -4 \times 30 - 32 + 4x$$

$$\Theta x = 52$$

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

$$= -52 - \left( \frac{-125 \times 300}{1000} \right)$$

$$= -52 + \frac{123 \times 3}{10}$$

$$\Delta H = -14.5$$

**Sol 7: (C)**  $\frac{1}{2} x_2 + \frac{3}{2} y_2 \rightarrow xy_3$   $\Delta H = -30$

Reactive at equals

$$\therefore \Delta G = 0$$

$$\therefore \Delta H - T\Delta S = 0$$

$$\Delta H = T\Delta S$$

$$\Delta S = \left( 50 - \frac{3}{2} \times 40 - \frac{60}{2} \right)$$

$$-30 \times 10^3 = T \times (50 - 60 - 30)$$

$$T = \frac{30 \times 10^3}{40}$$

$$T = 750 \text{ K}$$

**Sol 8: (D)**



(Sizes here mass is equal)

$$n \times C_p (T_f - T_H) + n \times C_p (T_f - T_C) = 0$$

$$\therefore 2 T_f = T_H + T_C$$

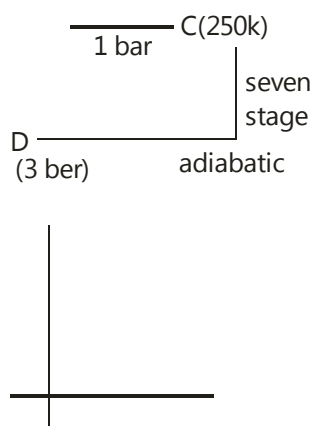
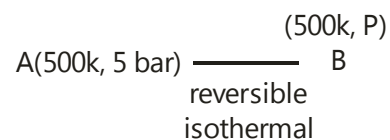
$$T_f = \frac{T_H + T_C}{2}$$

$$\therefore \Delta S = C \ln \frac{T_2}{T_1} + C \ln \frac{T_2}{T_1} \lambda n$$

$$= C \ln \left[ \frac{T_f}{T_H} \right] + C \ln \frac{T_f}{T_H}$$

$$= C \ln \left[ \frac{(T_H + T_C)^2}{T_H T_C} \right]$$

**Sol 9: (A)** ( $V = 3/2 R$ )



$$10^5 \times 5 \times V = 80314 \times 2 \times 500 \times 100$$

$$V_i = 8.31$$

$$4 \times 2 \times 10^{-3} \text{ m}^3$$

$$V_i = 16.628 \text{ L}$$

$$\frac{P}{1} = \frac{500}{250}$$

$$\therefore P_B = 2 \text{ bar}$$

$$P_V = \frac{3}{2} R, \frac{1}{r} = \frac{C_v}{C_p} = \frac{3R/2}{3R/2 + R} = \frac{3}{5}$$

$$r = 5/3$$

$$PV^r = \text{Const.}$$

$$P \left( \frac{T}{P} \right)^r = \text{const.}$$

$$P^{1-r} T^r = \text{const.}$$

$$3^{1-5/3} T^{5/3} = 1^{1-5/3} \times (25)^{5/3}$$

$$\therefore \frac{T}{250} = 3^{2/5} \left( \frac{T}{250} \right)^{5/3} = 3^{2/5}$$

$$T_f = 387.9$$

$$\Delta V_{BC} = HC_V \Delta T$$

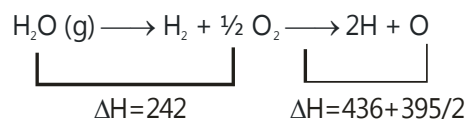
$$= \frac{2 \times 3R}{2} (250 - 500)$$

$$= 3R \times 250 = 0750 R$$

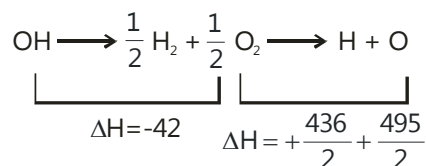
$$\Delta H_{CA} = nC_p \Delta T = 2 \times 5 \frac{R}{2} (357.90 - 250)$$

**Multiple Correct Choice Type**

**Sol 10: (A, D)**  $H_2O(g) \rightarrow 2H(g) + O(g)$



$$\therefore \Delta H_{\text{total}} = 242 + 436 + \frac{495}{2} = 925.5$$



$$\therefore \Delta H_{\text{total}} = -42 + \frac{436 + 495}{2} = 423.5$$

$$\Delta H_{\text{formation of H}} = \frac{436}{2} = 218$$

$$\Delta H_f \text{ OH} = 42 - 0 - 0 = 42$$

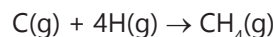
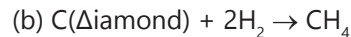
**Sol 11: (A, B, C, D)**  $\text{CaCO}_3$  (Calvin  $\rightarrow$   $\text{CaCO}_3$ /area)

$$\Delta_f G^\circ (\text{CalC}) = -1128.8$$

$$\Delta G^{\circ f} = -1127.75$$

$$\Delta G_{\text{avg}}^\circ > \Delta G_f^\circ (\text{CalC})$$

$\therefore$  Cal is more stable



More heat is evolved volume in case (b)

as  $\text{C diamond} \rightarrow \text{C}(\text{gas}) \Delta H > 0$

$$(c) \Delta_f H^\circ \text{I}_2(\text{g}) = \Delta_{\text{surr}} H \text{I}_2(\text{s}) \text{ at } 25^\circ \text{C}$$



$$= -ve + 1 \times RT$$

$$\therefore \Delta V > \Delta H$$

**Sol 12: (B, C)** (A)  $(\Delta G_{\text{system}}) < 0$  then react must be is fare

$$\Delta H - T\Delta S < 0$$

$$\Delta H > 0$$

(B)  $\Delta_f H^\circ (\text{S, Momenta k}) \neq 0$  true

$$\text{BE}_{\text{CH}_4} = 1654$$

$$\text{BE}_{\text{CH}} = \frac{1654}{4}$$

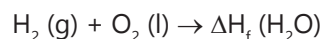
$$\text{BE}_{(\text{C}-\text{C})} = \text{B}_{\text{C}_2\text{H}_6} - 6 \times \text{B}_{\text{CH}}$$

$$28.2 - \frac{6 \times 1658}{4}$$

$$= 2812 - 2482 = 328$$



$$\Delta H = -56 \text{ KJ}$$



$$H_{\text{vep}} = 44 \text{ KJ cm}$$

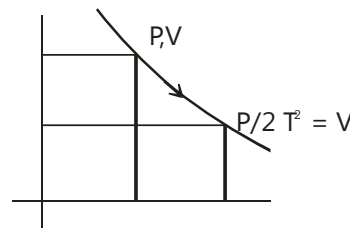
$$\therefore \Delta H_f(\text{H}_2\text{O}, \ell) = -44 - 242$$

$$= -286$$

$$-56 = -286 \Delta H(\text{OH}^-)$$

$$286 - 56 = \Delta H(\text{OH}^-); \text{Hf}(\text{OH}^-) = 230$$

**Sol 13: (A, B, D)**



$$P = mV + C$$

$$\frac{P}{2} 2m V + C$$

$$mV = \frac{P}{2}$$

$$\therefore m = \frac{-P}{2V}$$

$$\text{Process} = \frac{-P}{2V} \text{ volume} + \frac{3P}{2}$$

$$sw = -PdV$$

$$= \left( \frac{-P}{2V} x + \frac{3P}{2} \right) dV = -\frac{P}{fV^0} V^2 + \frac{3P}{2} \Big|_V^{2V}$$

$$= \frac{-P}{4V} (4V^0 - V^0) + \frac{3P}{2} \times V$$

$$= -\frac{3}{4} PV + \frac{3}{2} PV = \frac{3}{4} PV$$

$$PV \lambda n 2$$

$\lambda n 2 < \frac{3}{4} \therefore$  work done is higher

$$-\frac{2}{2V} x^2 + \frac{3}{2} PX = nRY$$

Parabolic bott

$$T = \frac{3PX}{2} - \frac{Px^2}{2V}$$

$$\frac{\delta T}{\delta x} = \frac{3P}{2} - \frac{Px}{V}$$

$$x = \frac{3}{2} V$$

$$\frac{\delta^2 T}{\delta x^2} = -P$$

T atomic max at  $\frac{3}{2} V$

$$V_{\text{atm}} = \frac{2V}{P} \left( \frac{3}{2}P - \text{pressure} \right)$$

$$\frac{2V}{P} \left( \frac{3P}{2} - \text{pressure} \right) \text{ Pressure} = T$$

**Sol 14: (A, C)** Normal boiling point = 350 K

$$\Delta H_{\text{vap}} = 3 \text{ TKJ}$$

$$\text{at } \Delta S = \frac{350 \times 10^3}{350} = 100 \text{ J}$$

(i)  $\Delta S$  at 1 atm 350 K = 100 J

at 0.5 350

$$P < P_{\text{vap}} \text{ CHO mol}$$

$$\Delta S > \Delta S_{\text{vap}} > 100$$

(ii) as at 2 at 350 K

$$\text{as } P > P_{\text{vap}}$$

$$S < S_{\text{val}}$$

**Sol 15: (A, C, D)** In adiabatic explained

$$w < 0,$$

$$Q = 0$$

$$\therefore \Delta V = w$$

$$\Delta V < 0$$

$$w_{\text{rev}} < \Delta_{\text{ice}}$$

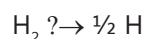
$$\therefore \Delta V_{\text{rev}} < \Delta_{\text{avg}}$$

$$\Delta T_{\text{rev}} < \Delta T_{\text{ice}}$$

$$\therefore T_{\text{f rev}} < T_{\text{f ice}}$$

(ii) K.E =  $\frac{3}{2} nRT$  dependent on temperature if T is constant then KE is constant for adiabatic expansion of gas

$$nC_V \Delta T = w < 0$$



$\Delta S > 0$ , STV as no. of molecules hence no. of molecules.

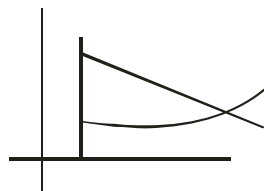
**Sol 16: (A, C, D)** At any common row on the p-v curve

$$P(V)^r$$

$$PV = C \text{ adiabatic}$$

$$P = C_1 r - r$$

$$P = C_1 V - r$$



$$\frac{\delta P}{\delta V} = -R$$

$$\frac{\delta P}{\delta V} = -r \frac{P}{V}$$

$$r > 1$$

Slope of adiabatic C is more negative than slope of isothermal

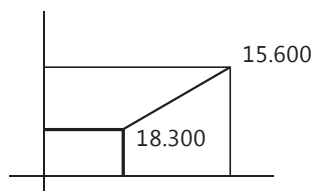
Adiabatic curve is above isothermal curve

Hence area under adiabatic curve > area under isothermal curve

Hence  $w_{\text{adiabatic}} > w_{\text{isothermal}}$

$$\delta = \frac{C_p}{C_v} \text{ not necessarily constant}$$

**Sol 17: (B, D)**



$$\Delta H_{AB} = nC_p \Delta T$$

$$= 1 \times \frac{5R}{2} \times 300 = 6235.5 \text{ J}$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} - \ln R \ln \frac{V_2}{V_1}$$

$$= \frac{3R}{2} \ln 2 + R \ln \left( \frac{15}{10} \right)$$

$$\therefore \Delta S > 0$$

$$V = mT + C$$

$$10 = 300m + C$$

$$15 = 600m + C$$

$$m = \frac{5}{300}$$

$$10 = \frac{5}{300} \times 100 + C$$

$$C = 5$$

$$V = \frac{T}{300} + 5$$

$$PV = R(V - 5) \times 60$$

$$P = R \left( 60 - \frac{300}{V} \right)$$

$$w = \left( \frac{300}{V} - 60 \right)$$

$$= (300 \ln V - 60 V) R = -1488.88 \text{ J}$$

$$\Delta V = nC_V \Delta T$$

$$= 1 \times \frac{3R}{2} \times 300 = 3746.3$$

$$q = -w + Q$$

$$= 1491.8 + 3746.3 = 5237.82$$

**Sol 18: (A, B)** Compressive  $\therefore w +ve$

(i) And reversible isothermal work is therefore the maximum value of isothermal work

(ii) Work is area under cyclic process

$$S_{rev} \neq 0 \therefore w \neq 0$$

For ideal gas  $T^r P^{1-r} = 0$

$$\frac{CP}{T^{CV}} \cdot \frac{-e}{T^{CV}} = 0$$

$$\frac{CP}{T^R} P^{-1} \text{ const.}$$

$$P = \frac{RT}{V_V - b} - \frac{a}{V^2}$$

$$w = - \int_{V_1}^{V_2} P dV$$

$$= -RT \ln \left[ \left( \frac{V_2 - b}{V_1 - b} \right) - a \left( \frac{1}{V_2} - \frac{1}{V_1} \right) \right]$$

**Sol 19: (C, D)**  $P V^r = \text{const.}$

$$\therefore P^{1-r} T^r = \text{const.}$$

$$V^{1+r} T^{-1} = \text{const.}$$

$$P T^{\frac{r}{1-r}} = w$$

$$P = G \times T$$

$$\frac{rP}{rT} = \frac{r-1}{r}$$

$$\frac{rP}{rT} = \frac{r}{r_1} P T^{-r} = 1 + \frac{1}{r-1} P T^{-r}$$

$$\therefore \frac{rP}{rT} > 0$$

$$V^0 = \cos T^{\frac{1}{1+r}-1}$$

$$\frac{rV}{rT} = \frac{1}{1+r} \quad GT = \frac{-r}{1+r}$$

$$\text{as } r \text{ is } \frac{rV}{rT} = \frac{1}{1+r} \quad VT^{-r} > 0$$

$$P = CV^{-r}$$

$$\frac{rP}{rV} = -rCV^{-r}$$

**Sol 20: (A, B, D)**  $\text{H}_2\text{SO}_4 + 2(\text{NH}_4)\text{OH} \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{O}$

$$\Delta H_{\text{reac.}} = 2 \times \Delta H_{\text{dissociation}} \text{ of } (\text{NH}_4)_2\text{OH} \times \text{moles of } \text{NH}_4\text{OH} \\ + 2 \times \text{moles of dissociation of } \text{H}_2\text{O}$$

$$\text{Given } -1.5 \times 1.4 = -0.05 \times 57 \times 2 + 2 \times 0.2 \Delta H_{\text{diss.}}$$

$$3.6 = 2 \times 0.2 \times 0.2 \times \Delta H$$

$$\therefore \Delta H_{\text{diss}} = 4.5 \text{ KJ}$$

$$\Delta H_{\text{reac}} (\text{HCl} - \text{NaOH}) = -57 + 4.5 = -52.5$$

$$\Delta H(\text{CH}_3\text{COOH} - \text{NH}_4\text{OH}) = -48.1$$

$$-48.1 = -57 + 4.5 + \Delta H_{\text{diss}} \text{ CH}_3\text{COOH}$$

$$\therefore \Delta H_{\text{diss}} \text{ CH}_3\text{COOH} = 4.4 \text{ KJ}$$

$$\Delta H \text{ for } 2\text{H}_2\text{O} (\text{l}) \rightarrow 2\text{H}^+ + 2\text{OH}^-$$

$$= 2 \times 57 = 114$$

**Sol 21: (A, B, C, D)** Only (g) +  $\text{O}_2 \rightarrow \text{CO}_2$

Replacement  $\Delta H_f$  of product

**Sol 22: (B, C, D)**  $\Delta S$  for  $\frac{1}{2} \text{H}_2 \rightarrow \text{N}$  is +ve true

as no. of molecules yes, entropy increase

$\Delta G_{\text{system}}$  is 0 for reversible process at standard conditions

$$\Delta G^0 \text{ i real} = VdP - SdT$$

Function of P,V,T not just P and T at equilibrium  $\Delta G$  is moles

Nothing fixed about  $\Delta S$

**Sol 23: (A, B, D)** In isothermal gas cylinder,

$$(A) w + ve \quad dV < 0 = w = -PdV$$

$$\therefore w + ve$$

$$(B) \Delta H = \Delta U = 0 \text{ as } \Delta T = 0$$

$$(C) \Delta S = R \ln \frac{V_2}{V_1}, = V_2 > V_1$$

$$\therefore \Delta S - ve$$

$$(D) \Delta G = -T\Delta S > 0 \text{ as } \Delta S < 0$$

**Sol 24: (B, C, D)** 0.2 m<sup>3</sup> Ne at 200 kPa at T<sub>i</sub>

$$V_f = \frac{1}{2} V_{B_i} = 0.1 \text{ m}^3$$

Temperature constant inside as gas volume < and pressure is constant to maintain temperature to maintain air temperature

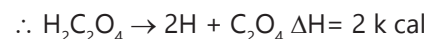
q may be +ve or -ve

$$\Delta V \neq 0 \text{ as } \Delta nRT \neq 0$$

**Assertion Reasoning Type****Sol 25: (D)** HCl + NaOH = -13.7

$$\therefore \Delta H_{\text{rest}} \times \text{Alkali} = -25\%$$

$$\Delta H_{\text{diss}} = +2 \times 13.7 - 25\% = 2$$

**Sol 26: (D)**  $\Delta H = nC_p \Delta T$ 

(For ideal gas,  $\Delta H$  is a function of compressor alone)

**Sol 27: (D)** Q = 0

$$w = \Delta V$$

$$\text{and } w < 0, \therefore \Delta U < 0$$

No comments can be made about temperature T might not increase

**Sol 28: (D)**  $\frac{1}{8} \text{S}_8(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{SO}_2(\text{g})$ 

$$S - (-2 \times 2) = 0$$

$$S = 4$$

Max oxidation state = 6

Assertion is wrong

**Comprehension Type****Paragraph 1:**

A	B
22.4L	22.4L
n	n

**Sol 29: (D)** T = 27.3 K P = 1 atm

In container B

$$V_f = \frac{V}{8} \quad V_i = PV^r = \text{const.}$$

$$1 \times \left(\frac{V_i}{V_f}\right)^{5/3} P_f r = 5/3$$

$$P_f = (8)^{5/3}$$

$$P_f = 32 \text{ atm}$$

$$\text{In container A, } V_f = 22.4 + \frac{7}{8} \times 22.5$$

$$= \frac{15}{8} \times 22.4$$

$$V_f = \frac{15}{8} V_i$$

$$P_f = 8 \text{ atm}$$

$$\text{Sol 30: (A)} \quad \frac{\frac{15}{8} \times 22.4}{T_f} = \frac{1 \times 22.4}{2 + .3}$$

$$C_f = \frac{273 \times 5}{8} = 1638$$

$$\text{Sol 31: (B)} \quad \Delta H_A = nC_p \Delta T = 1 \times \frac{5 \times 8.34}{2} \times (1638 - 27.5) = 80.53$$

**Paragraph 2:****Sol 32: (C)** (i) T = 532 mm Hg = 0.4 atm T = 353 K

$$V_i = 0.4 = 0.4 \text{ kg}$$

$$\Delta H = \Delta U + \Delta pV$$

Dependent only on temperature

$$\therefore \Delta H = \Delta pV = (1 - 0.7) \times 0.9 \text{ L}$$

$$= 0.3 \times 0.9 \text{ L} = 0.3 \times 0.9 \times 100 \text{ J} = 27 \text{ J}$$

**Sol 33: (C)** From 1 to 3

$$\Delta U = \Delta (nC_T)$$

$$\Delta mCT = 0.9 \times C \times (373 - 353) + \frac{0.4 \times 40}{18} = 1075.6$$

$$\text{Sol 34: (B)} \quad \Delta H = 1.8 \times 4.2 + \frac{450}{18} \times 80 = 1075.6$$

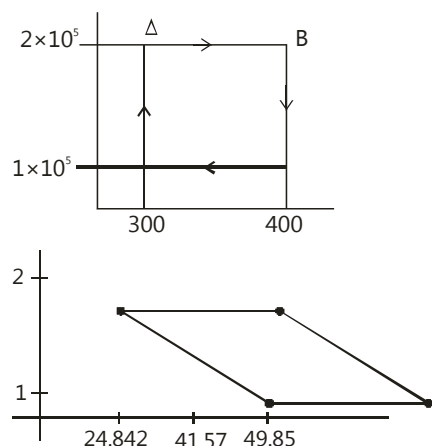
**Sol 35: (B)** Work done in 1 to 3

$$w_{1-2} = 0 \text{ as } \Delta U = 0$$

$$w_{2-3} = P_{\text{ext}} dU = \frac{0.45 \times 10^3}{18} \times \frac{0.0821 \times 373}{1000}$$

$$w_2 \text{ (10 KJ)}$$



**Paragraph 3:**

**Sol 36: (C)**  $w_{A \rightarrow B} - w = P \Delta V = nR \Delta T$   
 $= 2 \times 10^5 \times T$   
 $= 2 \times 8.314 \times 200 = 400 \text{ R}$

**Sol 37: (B)** Work done  $= -nRT \ln \frac{V_2}{V_1}$   
 $= -nRT \ln \frac{P_2}{P_1} = 2R \times 300 \ln \left( \frac{1}{2} \right)$   
 $= +600 R \times \ln 2 = +414 \text{ R}$

**Sol 38: (B)**

Net work done in cycle

$$\Rightarrow \ln A - B = P \Delta V = nR \Delta T$$

$$2R \times (500 - 300)$$

$$B - C = -nRT \ln \frac{P_2}{P_1} = 2R \times 500 \ln \left( \frac{1}{2} \right)$$

$$= -2R \times 500 \ln 2$$

$$C - D = P \Delta V - nRT = 2 \times R (300 - 500)$$

$$D - A = -2R \times 300 \ln (1/2) = 2R \times 300 \ln 2$$

$$\therefore \text{Total mole} = 2R (500 - 300) - 2R \times 500 \ln 2$$

$$= 2R (500 - 300) + 2 \times 300 \ln 2$$

$$= 2R (300 - 500) \ln 2$$

$$= 420 R \ln 2$$

$$= 276 \text{ R}$$

**Match the Columns****Sol 39:**  $A \rightarrow p, r, s$ ;  $B \rightarrow q, s$ ;  $C \rightarrow q, s$ ;  $D \rightarrow s$ 

(i) Reversible isothermal

$$P = -nRT \ln \frac{V_2}{V_1} = 2.303 nRT \log \frac{P_2}{P_1}$$

(p, r)

(ii) Reversible adiabatic =

$$w = \Delta U = nC_V (T_2 - T_1)$$

qs

(iii) Irreversible adiabatic  $= nC_V \Delta T = -P_{\text{ex}} dV$ (iv) Irreversible isothermal  $w = - \int P_{\text{ex}} dV$ **Sol 40:**  $A \rightarrow s$ ;  $B \rightarrow p, r$ ;  $C \rightarrow p, s$ ;  $D \rightarrow p, r$ 

Irreversible adiabatic compression

$$(A) Q = 0, \therefore \Delta S_{\text{surr}} = 0, \Delta S_{\text{system}} = 0$$

(B) Reversible vap

$$\Delta S_{\text{system}} > 0$$

as gaseous

Reversible, process  $\therefore \Delta S_{\text{total}} = 0$ 

$$\therefore \Delta S_{\text{surr}} < 0$$

(C) free expansion of ideal gas

$$Q = w = 0$$

$$\therefore \Delta S_{\text{surr}} = 0$$

Expansion  $\therefore \Delta S_{\text{system}} > 0$  $(\Delta)$  diss. of  $\text{CaCO}_3 (\text{s}) \rightarrow \text{CaO} (\text{s}) + \text{CO}_2 (\text{g})$ 

$$\Delta S_{\text{system}} > 0$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} = 0$$

$$\therefore \Delta S_{\text{surr}} < 0$$

**Previous Years' Questions****Sol 1: (B)** Elements in its standard state have zero enthalpy of formation.  $\text{Cl}_2$  is gas at room-temperature,  $\Delta H_f^\circ$  of  $\text{Cl}_2 (\text{g})$  is zero.

$$\text{Sol 2: (C)} \quad \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$= -54.07 \times 10^3 \text{ J} - 298 \times 10 \text{ J} = -57.05 \times 10^3 \text{ J}$$

$$\text{Also, } \Delta G^\circ = -2.303 RT \log K$$

$$\Rightarrow \log K = \frac{-\Delta G^\circ}{2.303 RT} = \frac{57.05 \times 10^3}{5705} = 10$$

**Sol 3: (A)** At transition point (373 K, 1.0 bar), liquid remains in equilibrium with vapour phase, therefore  $\Delta G = 0$ . As vaporisation occur, degree of randomness increase, hence  $\Delta S > 0$

**Sol 4: (B)** Entropy is a state function hence:

$$\begin{aligned}\Delta S_{A \rightarrow B} &= \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow D} + \Delta S_{D \rightarrow B} \\ &= 50 \text{ eu} + 30 \text{ eu} + (-20 \text{ eu}) = 60 \text{ eu}\end{aligned}$$

**Sol 5: (A)** Given,  $\frac{P}{V} = 1 \Rightarrow p = V$

Also from first law:  $dq = C_v dT + p dV$

For one mole of an ideal gas:  $pV = RT$

$$\Rightarrow p dV + V dp = R dT$$

From (i)  $p dV = V dp$

Substituting in Eq. (ii) gives

$$2p dV = R dT$$

$$\Rightarrow p dV = \frac{R}{2} dT \Rightarrow dq = C_v dT + \frac{R}{2} dT$$

$$\Rightarrow \int \frac{dq}{dT} = C_v + \frac{R}{2} = \frac{3}{2}R + \frac{R}{2} = 2R$$

**Sol 6: (A, B)** Resistance and heat capacity are mass dependent properties, hence they are extensive.

**Sol 7: (A, D, C)** Internal energy, molar enthalpy are state function. Also, reversible expansion work is a state function because among the given initial and final states, there can be only one reversible path.

**Sol 8:** Temperature rise  $= T_2 - T_1 = 298.45 - 298 = 0.45\text{K}$

$q = \text{heat-capacity} \times \Delta T = 2.5 \times 0.45 = 1.125 \text{ kJ}$

$$\Rightarrow \text{Heat produced per mol} = \frac{1.125}{3.5} \times 28 = 9 \text{ kJ}$$

**Sol 9:**  $\Delta H = \Delta U + \Delta(pV) = \Delta U + V \Delta p$

$$\Rightarrow \Delta U = \Delta H - V \Delta p$$

$$= -560 - 1 \times 30 \times 0.1 = -563 \text{ kJ}$$

**Sol 10:**  $\Delta U = q + W$

For adiabatic process,  $q = 0$ , hence  $\Delta U = W$

$$W = -p(\Delta V) = -p(V_2 - V_1)$$

$$\Rightarrow \Delta U = -100(99 - 100) = 100 \text{ bar mL}$$

$$\Delta H = \Delta U + \Delta(pV)$$

$$\text{where, } \Delta pV = p_2 V_2 - p_1 V_1$$

$$\Rightarrow \Delta H = 100 + (100 \times 99 - 1 \times 100) = 9900 \text{ bar mL}$$

**Sol 11:** Work-done along dashed path:

$$|-W| = \sum p \Delta V = 4 \times 1.5 + 1 \times 1 + \frac{2}{3} \times 2.5 = 8.65 \text{ L atm}$$

Work-done along solid path:  $-W = nRT \ln \frac{V_2}{V_1}$

$$= p_1 V_1 \ln \frac{V_2}{V_1} = 2 \times 2.3 \log \frac{5.5}{0.5}$$

$$= 2 \times 2.3 \log 11 = 4.79$$

$$\Rightarrow \frac{W_d}{W_s} = \frac{8.65}{4.79} = 1.80 \approx 2$$

**Sol 12: (B)** Statement-I is true.

$$dq = dE + p_{\text{ext}} dV = 0$$

$$\Delta T = 0 \therefore dE = 0; p_{\text{ext}} = 0 \therefore p_{\text{ext}} dV = 0$$

Statement-II is true. According to kinetic theory of gases, volume occupied by molecules of ideal gas is zero.

However, statement-II is not the correct explanation of statement-I.

**Sol 13: (D)** Statement-I is false. At equilibrium,  $\Delta G = 0$ ,  $G \neq 0$ .

Statement-II is true, spontaneous direction of reaction is towards lower Gibbs free energy.

**Sol 14: (B)** Statement-I is true, it is statement of first law of thermodynamics.

Statement-II is true, it is statement of second law of thermodynamics. However, statement-II is not the correct explanation of statement-I.

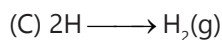
**Sol 15:**  $A \rightarrow p, r, s; B \rightarrow r, s; C \rightarrow t; D \rightarrow p, q, t$

1. (A)  $\text{CO}_2(\text{s}) \longrightarrow \text{CO}_2(\text{g})$

It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence  $\Delta S$  is positive

(B)  $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

It is a chemical decomposition, not a phase change. Thermal decomposition occurs at the expense of energy, hence endothermic. Product contains a gaseous species, hence,  $\Delta S > 0$ .



A new H-H covalent bond is being formed, hence  $\Delta H < 0$ .

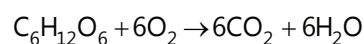
Also, product is less disordered than reactant,  $\Delta S < 0$ .

(D) Allotropes are considered as different phase, hence

$P_{(white, solid)} \longrightarrow P_{(red, solid)}$  is a phase transition as well as allotropic change.

Also, red phosphorus is more ordered than white phosphorus,  $\Delta S < 0$ .

**Sol 16: (C)** Combustion of glucose



$$\Delta H_{\text{combustion}} = (6 \times \Delta H_f CO_2 + 6 \times \Delta H_f H_2O)$$

$$-\Delta H_f C_6H_{12}O_6$$

$$= (6 \times -400 + 6 \times -300) - (-1300)$$

$$= -2900 \text{ kJ/mol}$$

$$= -2900/180 \text{ kJ/g}$$

$$= -16.11 \text{ kJ/g}$$

Hence (C) is correct.

**Sol 17: (C)** Since container is thermally insulated. So,  $q = 0$ , and it is a case of free expansion therefore  $W = 0$  and

$$\Delta E = 0$$

$$\text{So, } T_1 = T_2$$

$$\text{Also, } P_1 V_1 = P_2 V_2$$

**Sol 18: (B)** At  $100^\circ\text{C}$  and 1 atmosphere pressure

$H_2O(l) \rightleftharpoons H_2O(g)$  is at equilibrium. For equilibrium

$$\Delta S_{\text{total}} = 0 \text{ and } \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = 0$$

$$\therefore \Delta S_{\text{system}} > 0 \text{ and } \Delta S_{\text{surrounding}} < 0$$

**Sol 19: (C)**  $\Delta E = q + w$

$$0 = q - P_{\text{ext}} \Delta V$$

$$q = P_{\text{ext}} \Delta V = 3 \text{ atm } (2 - 1)L = 3 \text{ atm L}$$

$$= (3 \times 101.3) \text{ Joule}$$

$$\Delta S_{\text{surr}} = -\frac{q}{T} = \frac{3 \times 101.3}{300} = -1.013 \text{ Joule/K}$$