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.
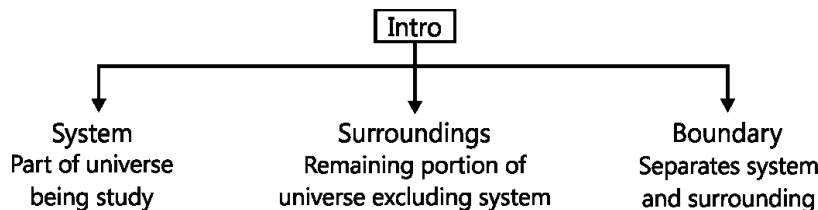
1.1 Definition of Thermodynamics

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.
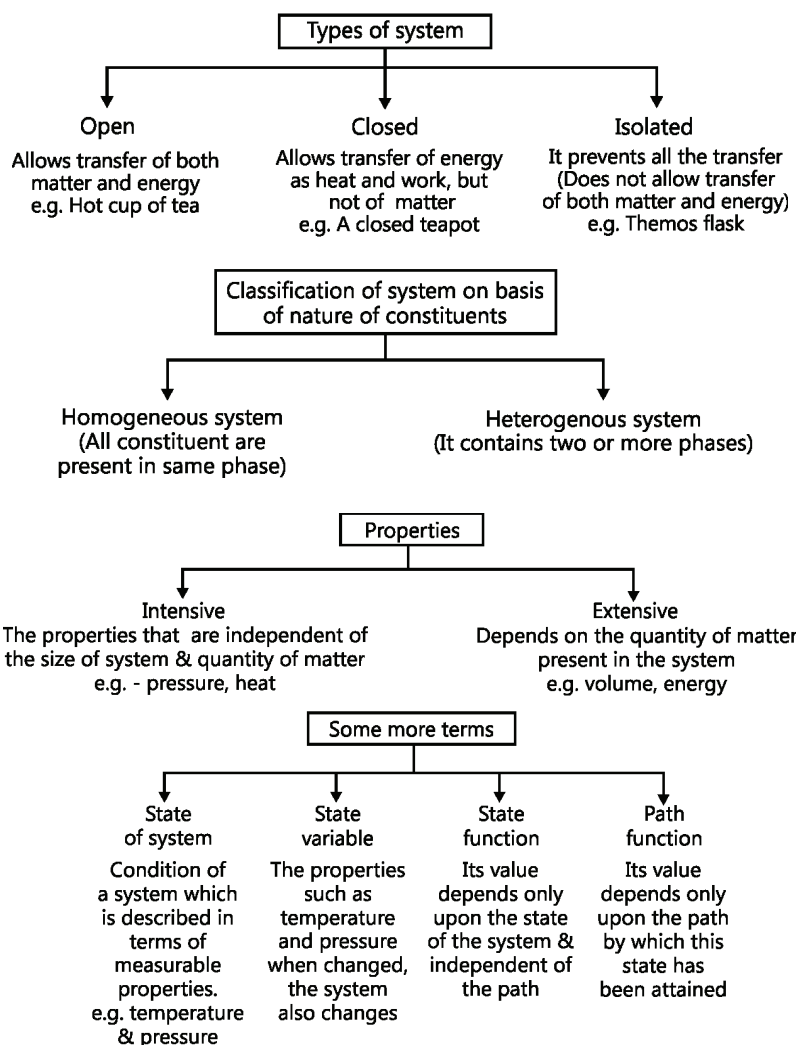
1.2 Importance of Thermodynamics

(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.


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                        ┌──────┐
                        │ Intro │
                        └──────┘
        ┌──────────────────┼──────────────────┐
        ▼                  ▼                  ▼
     System            Surroundings         Boundary
  Part of universe   Remaining portion of  Separates system
    being study      universe excluding system  and surrounding
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Flowchart 4.1: Terminology used 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, $\Delta H = H_{final} - H_{initial}$

Table 4.1: Difference between state and path functions

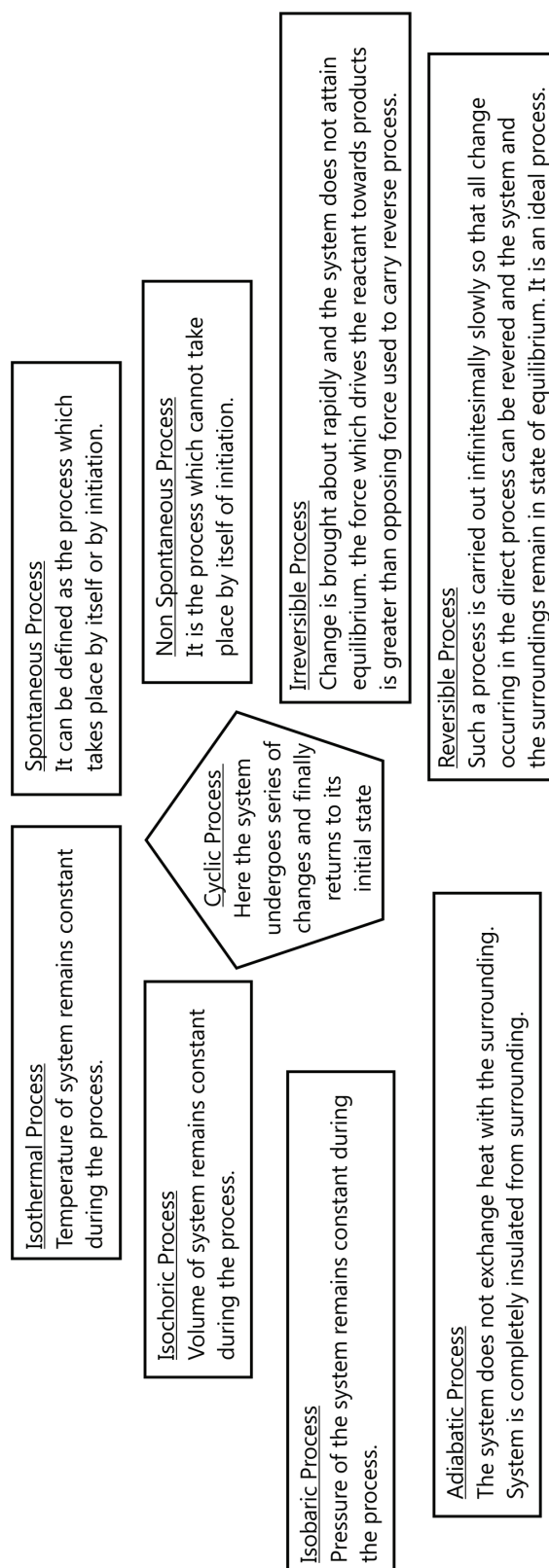| State Function	Path Function
Independent of path taken to establish property or value	Dependent on path taken to establish property or value
Can integrate using final and initial values.	Need multiple integrals and limits of integration in order to integrate.
Multiple steps result in same value.	Multiple 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.

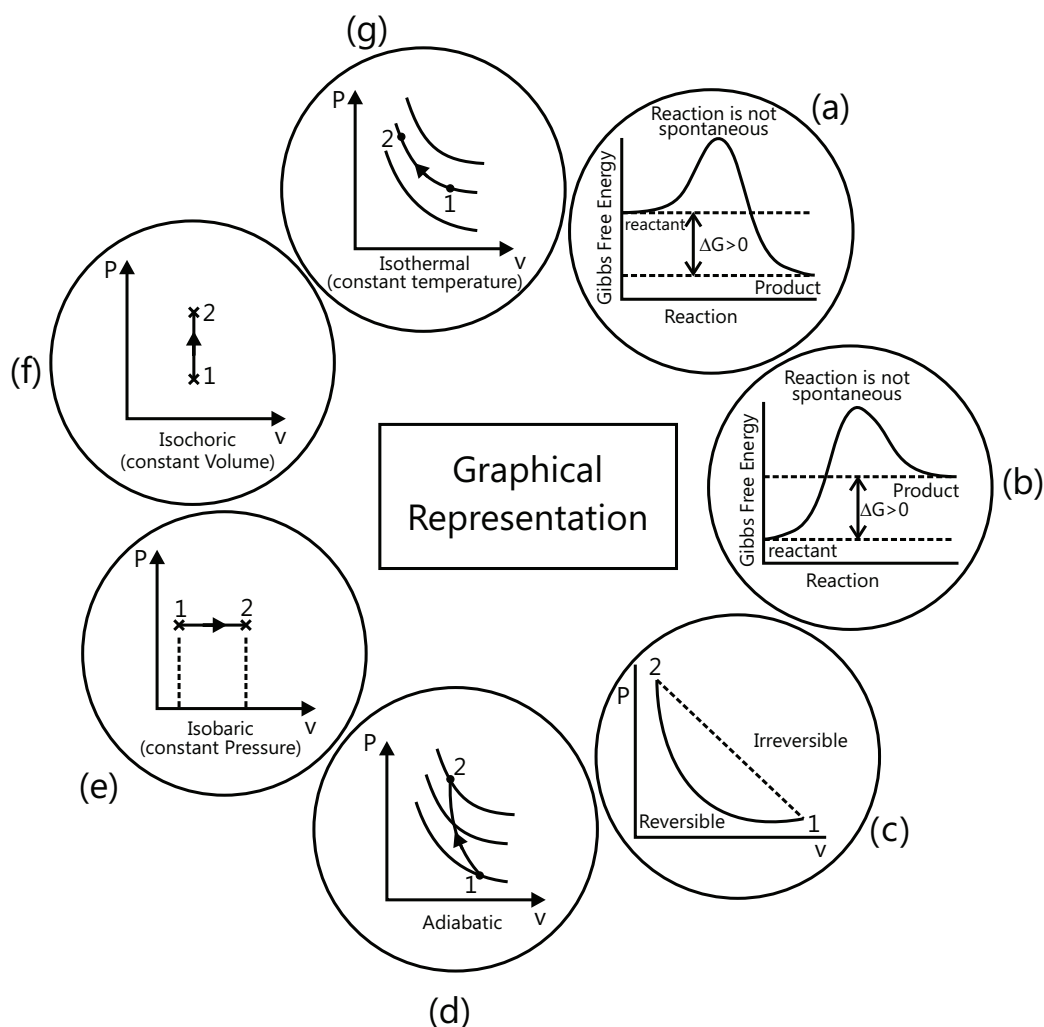## 3. INTRODUCTION TO VARIOUS PROCESSES

Spontaneous Process
It can be defined as the process which takes place by itself or by initiation.

Non Spontaneous Process
It is the process which cannot take place by itself of initiation.

Irreversible Process
Change is brought about rapidly and the system does not attain equilibrium. the force which drives the reactant towards products is greater than opposing force used to carry reverse process.

Reversible Process
Such a process is carried out infinitesimally slowly so that all change occurring in the direct process can be revered and the system and the surroundings remain in state of equilibrium. It is an ideal process.

Isothermal Process
Temperature of system remains constant during the process.

Cyclic Process
Here the system undergoes series of changes and finally returns to its initial state

Isochoric Process
Volume of system remains constant during the process.

Isobaric Process
Pressure of the system remains constant during the process.

Adiabatic Process
The system does not exchange heat with the surrounding. System is completely insulated from surrounding.

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.

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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.

$$\text{Work:} \qquad W = F.l$$

Applied Force   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**.
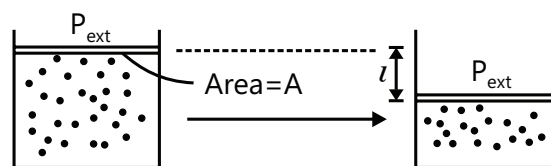
Mechanical Work $(=W) = P_{ext}(V_2 - V_1) = P_{ext}\,\Delta$

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

4.1.1 Convention

'–' Sign	W>0 Positive work	ΔV<0	Work is done ON the system
			BY the surroundings
'+' Sign	W<0 Negative work	ΔV>0	Work is done BY the system
			ON the surroundings

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

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

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

Path dependence of W:

Example: Type of Process: Reversible process
Condition: $= P_{ext} = P$
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
$V_1 \to V_2$ at $P = P_1$ Then $P_1 \to P_2$ at $V = V_2$	$P_1 \to P_2$ at $V = V_1$ Then $V_1 \to V_2$ at $P = P_2$
$W_{(1)} = -\int_{V_1}^{V_2} P_{ext}dV - \int_{V_1}^{V_2} P_{ext}dV$ $= -\int_{V_1}^{V_2} P_1 dV$ $= -P_1(V_2 - V_1)$ $\boxed{W_{(1)} = P_1(V_1 - V_2)}$	$W_{(2)} = -\int_{V_1}^{V_2} P_{ext}dV - \int_{V_1}^{V_2} P_{ext}dV$ $= -\int_{V_1}^{V_2} P_2 dV$ $= -P_2(V_2 - V_1)$ $\boxed{W_{(2)} = P_2(V_1 - V_2)}$

W>0 $\Longrightarrow$ 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

(a) External pressure is reduced to 1 atm in single step.

(b) External pressure is reduced to 5 atm in 1st operation and then 1 atm in next step.

(c) 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.

$$P \times V_1 = nRT$$

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

(a) $\qquad W = P\Delta V = -1 \times (10-1) = -9 \, L - atm$

$\qquad$ or $\quad W_{system} = -9 \, L - atm \qquad$ and $\qquad W_{surr} = +9 \, L - atm$

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

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

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

$\qquad\qquad = -19.630 - 5.074$

$\qquad\qquad = -24.704 \, L - atm$

$\qquad \because W_{sys} = -24.704 \, L - atm; \, W_{surr} = +24.704 \, L - atm$

(c) $\qquad W = -P \times \Delta V = -0 \times (10-1) = 0 L - atm$

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

| Gas expands | Gas compresses | Constant P |
| dv > 0, W > 0 | dv < 0, W < 0 | W = p (V₂-V₁) |
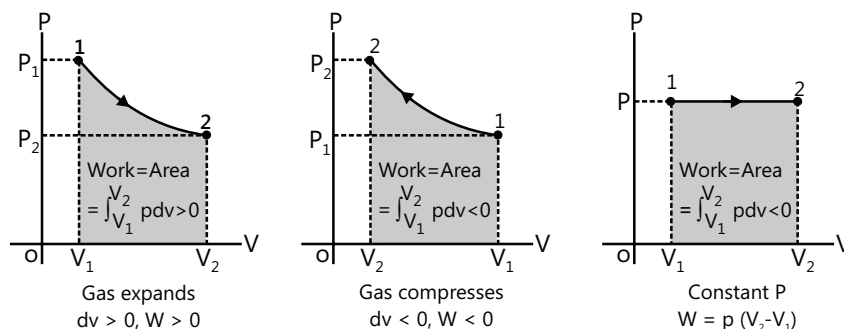
PLANCESS CONCEPTS

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.

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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

$W_{ab} = (120\,kPa)\,(250\,cc)$

$= 120 \times 10^3 \times 250 \times 10^{-6}\,J = 30\,J.$
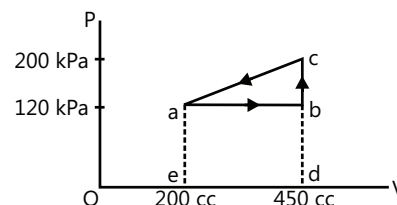
In the process b to c the volume remains constant and the work done is zero.

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 cab + baed $= \frac{1}{2}(80kPa)(250cc) + 30\,J = 10\,J + 30\,J = 40\,J.$

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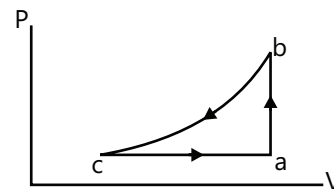
Sol: By using the following equation find out the missing terms

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

(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 $\Delta U = \Delta Q = 50\,J$

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

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

$\Delta U = -\Delta W = 40\,J$

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 $\Delta U = 1500J - 1590J = -90J$

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

$\Delta W = \Delta Q - \Delta U = -70\,J + 90\,J = 20\,J$

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 Δt =Tempearture 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 H_2O by $1^\circ C$).

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.

Cp Heat capacity at constant pressure	$\delta q = C_{path} dT$ or $C_{path} = \left(\dfrac{\delta q}{dT}\right)_{path}$	Cv Heat capacity at constant volume

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

Heat capacity $= \dfrac{dq}{dT}$
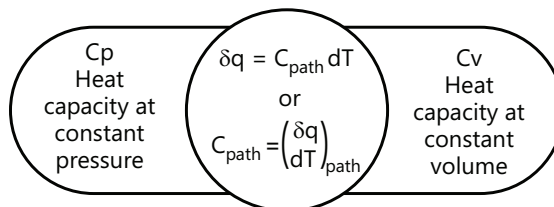
4.2.2 Relation of Work and Heat with Internal Energy

Temperature of water can be raised by-

Heating	Doing work
(a) With only heat $\quad T_1 \rightarrow T_2$	(b) With only work (Weight falls & churns propeller) $\quad T_1 \rightarrow T_2$
Figure 4.2: (a) Heating to raise temperature	**Figure 4.2:** (b) Doing work to raise temperature

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:

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

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°C to 100°C? Heat capacity of steel is 0.11 kcal/kg-K and heat capacity of water is 1 kcal/kg.K   **(JEE MAIN)**

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

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

$\Delta q = (mS\Delta T)_{Boiler} + (mS\Delta T)_{Water}$

= 900 x 0.11 x 90 + 400 x 1 x 90 = 44910 kcal

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

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

Illustration 6: Assume an ideal gas obeys $\dfrac{P}{V}$ = 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, $\dfrac{P}{V} = K \therefore K = \dfrac{1}{2} atm\, L^{-1}$ (initial condition)

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

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 $= \int PdV$ while in chemistry work $= -\int PdV$

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.

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5. ZEROTH LAW OF THERMODYNAMICS

It was introduced after the 1st and 2nd 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:

(a) 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.

(b) In accordance to the temperature increase in the thermocouples, proportional electrical output is received.
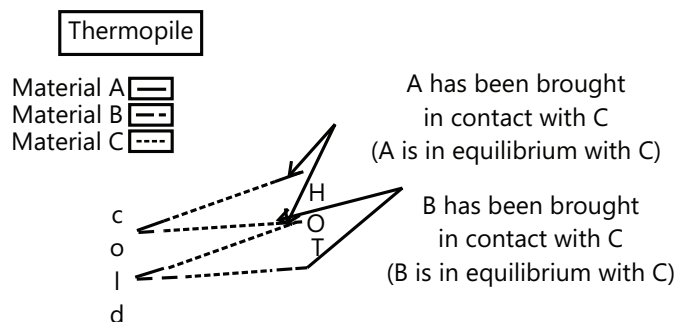
Figure 4.3: Thermopile

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, ΔE can be written as: $\Delta E = E_f - E_i$

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

(a) Either by allowing the heat to flow into the system (absorption) or out of the system (evolution).

(b) 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 $-\oint dq = \oint dw$

$$\Delta U_{system} = q + w;$$
$$\Delta U_{surroundings} = -q - w$$
$$\Rightarrow \Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0$$

Clausius statement of 1st 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
	$H_1 = E_1 + PV_1$	$H_2 = E_2 + PV_2$
$H_2 - H_1 = \Delta H = (E_2 + PV_2) - (E_1 + PV_1)$		
$= (E_2 - E_1) + P(V_2 - V_1)$		
$\Delta H = \Delta E + P\Delta V$		

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

When $\Delta n_g = 0$ $\Rightarrow$ $\Delta H = \Delta E$

When $\Delta n_g > 0$ $\Rightarrow$ $\Delta H > \Delta E$

When $\Delta n_g < 0$ $\Rightarrow$ $\Delta H < \Delta E$

Also $\Delta E = q_p - P\Delta V$ $q_p = \Delta E + P\Delta V$

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

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);

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial T}\right)_T dp$$

6.2 Degree of Freedom
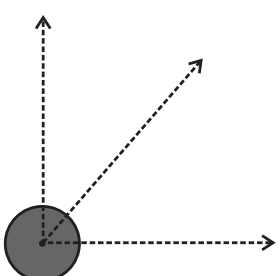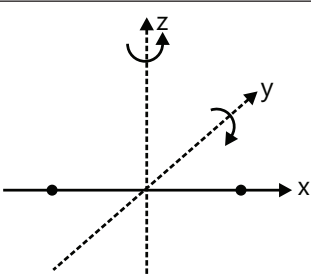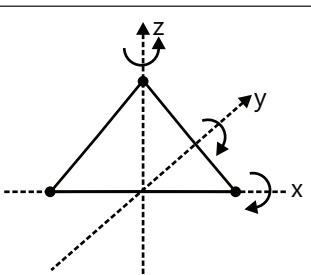
Degree of freedom of gas molecules

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
Degree of freedom of monoatomic gas	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	
Degree of freedom of a diatomic and linear polyatomic gas	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.	
Degree of freedom of nonlinear polyatomic gas	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.

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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 volum (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:

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

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

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,

$P\Delta V = nR\Delta T$ 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 $\gamma = \dfrac{C_p}{C_v}$ 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,

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

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

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

Work done in reversible isothermal expansion:

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

$dw = -(P_{ext} - dp)dV = -P_{ext}.dV = -PdV$

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

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

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

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

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

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

Figure 4.4: More work done to the   of the surroundings

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

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

Work done for Irreversible Isothermal Expansion:

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

(b) Intermediate expansion:

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

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

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

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 1st law $dU = -PdV \Rightarrow C_v dT = -PdV$ (along path)

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

Integrating on both the sides

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

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

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 monoatamic ideal gas : $\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$ $\qquad \left(> 1 \text{ generally} \right)$

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), $T = \frac{PV}{R}$

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

Figure 4.5: Comparison plots for different gases

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

For an isothermal process (T = constant)

$\Rightarrow \quad PV = $ constant.

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

Work done$= C_v . \Delta T = C_v \left(T_2 - T_1 \right) = -\frac{R}{\gamma - 1} \left(T_2 - T_1 \right)$

For n 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 ΔE which is equal to w is also zero. If $\Delta E = 0$, ΔT 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 $P_{ext.}$

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

or $\quad w = C_V(T_2 - T_1) = -RP_{ext}\left(\dfrac{T_2P_1 - T_1P_2}{P_1P_2}\right)$

6.5.3 Isobaric Process

In an Isobaric process, P = constant

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

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

6.5.4 Isochoric Process

Isochoric process is a Constant volume process, This implies, V = constant

$Q - W = \Delta U, \ W = \int PdV = 0$,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 = Constant, where n is a constant for a specific process

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

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

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

$P_1V_1^n = P_2V_2^n = PV^n$

$W = \int_1^2 PdV = \int_1^2 (P_1V_1^n)V^{-n}dV$

$= (P_1V_1^n)\int_1^2 V^{-n}dV = \dfrac{(P_1V_1^n)}{1-n}(V_2^{1-n} - V_1^{1-n}) = \dfrac{P_2V_2 - P_1V_1}{1-n}$

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, $W_{irr} = 0$

$$W_{irr} = 0$$

$$Q = 0$$

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

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

$$T_1 = T_2$$

Considering an ideal gas, the above case is true. But, the final states of reversible and irreversible adiabatic transformations will be different. Thus, ΔE and ΔH 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.

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

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

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

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

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

$$= 12.39 + P_1 (V_2 - V_1) + V_2 (P_2 - P_1)$$

$$= 12.39 + 2.463 \times (20 - 10) + 20 (1.642 - 2.463)$$

$$= 12.39 + 24.63 - 16.42 = 20.6 \, L - atm$$

Illustration 8: A mole of a monoatmomic 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^3 respectively. Given that the initial pressure (p_1) is 1×10^5 Pa, final pressure (p_2) is 0.395×10^5 Pa and the initial temperature is 273 K. Let the final Temperature be T_2.

We have,

$$P_1V_1 = n_1RT_1$$

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

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

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

Or $-0.395 \times 10^5\left(V_2 - 0.022697\right) = (3 \times 8.314)/2(T_2 - 273)$ .... (i)

Again, $p_2V_2 = nRT_2$

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

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^3 respectively. Find the rise in the temperature if the gas is compressed to 200 cm^3 (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

$$T_2V_2^{(\gamma-1)} = T_1V_1^{\gamma-1} \quad \text{or} \quad T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

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

Thus, $T_2V_2^{(\gamma-1)} = T_1V_1^{\gamma-1}$ or $T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = (300 \text{ K}) \times \left[\frac{800}{200}\right]^{0.4} = 522k$

Rise in temperature = $T_2 - T_1$ = 222 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)**

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

We have for one mole of an ideal gas PV = RT ...(ii) From Eq. (i) and (ii)

P^2V = constant or $PV^{1/2}$ = K (say) ... (iii)

From first law of thermodynamics,

$\Delta Q = \Delta U + \Delta W$ Or $C\Delta T = C_v \Delta T + \Delta W$ Or $C = C_v + \dfrac{\Delta W}{\Delta T}$ ... (iv)

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

$\therefore \quad \dfrac{\Delta W}{\Delta T} = 2R$

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

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

Solving this we get $\gamma = 1.5$

Now, $\gamma = 1 + \dfrac{2}{F}$

Or degree of freedom $\quad F = F + \dfrac{2}{\gamma - 1} = \dfrac{2}{1.5 - 1} = 4$

Illustration 11: 0.40 mole of a monoatomic gas fills a 1dm³ container to a pressure 1.013 $\times$ 10⁶ Pa. It is expanded reversibly and adiabatically until a pressure of 1.013 $\times$ 10⁵ Pa is reached. Calculate:

(a) What is final volume of gas?

(b) Initial and final temperature of gas.

(c) Work done by gas during expansion. **(JEE ADVANCED)**

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

PV^γ = 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:

Using temperature term, w $\quad = \dfrac{nR}{\gamma - 1}\left[T_2 - T_1\right]$

Using Volume term, w $\quad = \dfrac{\left[P_2 V_2 - P_1 V_1\right]}{\gamma - 1}$

(a) We have PV^γ = Constant of $P_1 V_1^\gamma$

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

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

Also, we have $PV = nRT$

$P = 1.013 \times 10^6, \qquad V = 1 dm^3 = 1 \times 10^3 m^3, \qquad n = 0.40, \qquad R = 8.314$

For initial condition

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

$T_1 = 304.6 K$

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

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

(c) Work done during expansion

(i) Either by : W $\quad = \dfrac{nR}{\gamma-1}\left[T_2 - T_1\right]\left(\text{Since } T_2 \text{ and } T_1 \text{ are already evaluated}\right)$

$\qquad = \dfrac{0.4 \times 8.314}{\left(\dfrac{5}{3}-1\right)} \times \left[121.28 - 304.6\right] = -923.7 \text{ J}$

(ii) W $= \dfrac{\left[P_2 V_2 - P_1 V_1\right]}{\gamma-1} = \dfrac{1.013 \times 10^6 \times 1 \times 10^{-3} - 1.013 \times 10^5 \times 3.98 \times 10^{-3}}{\left(\dfrac{5}{3}-1\right)} = -923.7$

7. SECOND LAW OF THERMODYNAMICS

First law showed the equivalence of work and heat.

$\Delta U = q + W, \oint dU = 0$ 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:

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

$\int \dfrac{dq_{rev}}{T}$ is a state function $- \int dS \;\to\; dS = \oint \dfrac{dq_{rev}}{T}$

S = Entropy

$\oint ds = 0 \to \Delta S = S_2 - S_1 = \int\limits_1^2 \dfrac{dq_{rev}}{T} > \int\limits_1^2 \dfrac{dq_{irrev}}{T}$

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

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

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

7.1 The Carnot Cycle – A Typical Heat Engine

All paths are reversible
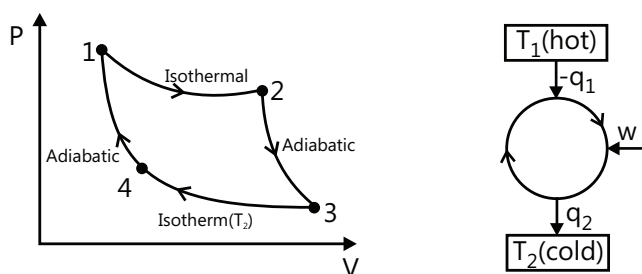
Figure 4.6: Carnot cycle

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

$2 \rightarrow 3$ adiabatic expansion (q = 0) $U = W_1'$

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

$4 \rightarrow 1$ adiabatic compression (q = 0) $U = W_2'$

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

1st Law $\Rightarrow \oint dU = 0 \Rightarrow q_1 + q_2 = -\left(W_1 + W_1' + W_2 + W_2'\right)$

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

Kelvin : $q_2 < 0 \rightarrow$ Efficiency $\equiv \varepsilon < 1 \left(< 100\%\right) -W = q_1\varepsilon =$ 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.

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

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

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

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

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

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

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

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

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

Links heat engines to mathematical statement

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

7.2 Entropy

Carnot cycle for a reversible ideal gas:

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

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

$\varepsilon = \dfrac{(-W)}{q_1}$ $\varepsilon' = \dfrac{(-W')}{q'_1}$ Assume $\in > \in'$

(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)

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

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

∴ The efficiency of any reversible engine is ε = 1 − T$_1$/T$_2$

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

∴ For any reversible cycle, $\oint \dfrac{dq_{rev}}{T} = 0$

This defines Entropy a function of state

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

PLANCESS CONCEPTS

Entropy is a state function, but to calculate ΔS requires a reversible path.

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

$1 \rightarrow 2$

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

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

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

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

Figure 4. 7: (a) Process Plot

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

also $\quad \dfrac{dq_{irrev}}{T} \quad < \quad \dfrac{dq_{rev}}{T} \quad \Rightarrow \quad \oint \dfrac{dq_{irrev}}{T} < 0$

Shrikant Nagori JEE 2009 AIR 30

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

$$\oint \frac{dq}{T} \le 0 \qquad \text{contains} \quad \begin{cases} \dfrac{\hat{d}q_{rev}}{T} = 0 \\ \dfrac{\hat{d}q_{irrev}}{T} < 0 \end{cases}$$

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.

(A) Irreversible)

(B) Reversible

Figure 4.2: Cyclic process

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

Clausius $\oint \dfrac{dq}{T} \le 0 \quad \Rightarrow \quad \int\limits_1^1 \dfrac{dq_{rev}}{T} + \int\limits_2^1 \dfrac{dq_{rev}}{T} \le 0 ; \qquad \int\limits_2^1 \dfrac{dq_{rev}}{T} = S_1 - S_2 = \Delta S \le 0$

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

This gives the direction of spontaneous change!

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

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

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

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

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

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 4.7: Spontaneity

$$dS = dS_1 - dS_2 - \frac{dq_2}{T_1} - \frac{dq_2}{T_1} - ds\frac{(T_2 - T_1)}{T_1T_2}(dq_1 - dq_2)$$

dS > 0 for spontaneous process

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

(b) Joule expansion with on ideal gas

1 mol gas $(2V, T)$ = 1 mol gas (V, T)

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

Therefore, Δ S-Rln2 > 0 (Spontaneous)
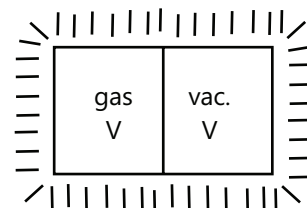
Figure 4.7: Joule expansion

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 $\Delta S_{total} = 0$.

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Entropy change for an ideal gas:

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

(a) When T and V are two variables

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

(b) When T and P are two variables,

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

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

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

    (ii) For isobaric process (p constant)

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

(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 ΔS is given by
$$\Delta S = \sum S_{product} - \sum S_{reactants}$$

(b) The units of entropy change are cal deg^{-1} mol^{-1} and in S.I. units J K^{-1} 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 CO, NO, 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

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

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

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

The transition under consideration is :

$$H_2O(l) \quad \rightarrow \quad H_2O(g)$$
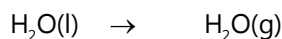
We know that, $\Delta S_{vapour} = \dfrac{\Delta H_{vapour}}{T}$

Given, $H_{vapour} = 40.8 \text{k.J mol}^{-1} = 40.8 \times 1000 \text{ Jmol}^{-1}; \qquad T = 373K$

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

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

Sol: Using the following equation calculate the work done

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

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

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.

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

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

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.

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

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

Illustration 16: Determine the standard entropy change for the reaction given below. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ at 300K. If standard entropies of $H_2(g)$. $O_2(g)$ and $H_2O(l)$ are 126.6. 201.20 and 68.0 JK^{-1} 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

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

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

$$= 2 \times S^2_{H_2O} - \left[2 \times S^{\circ}_{H_2} + S^{\circ}_{O_2}\right] = 2 \times 68 - \left[2 \times 126.6 + 201.20\right]$$

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

8. FUNDAMENTAL EQUATIONS, ABSOLUTE ENTROPY AND THE THIRD LAW

8.1 Fundamental Equations

From $dU = Tds - Pdv$

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

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.

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.

From $dU = TdS + PdV$

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

From $dH = TdS + VdP$

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

8.2 Absolute Entropy

Absolute entropy of an ideal gas

$$\overline{S}(P.T) = \overline{S}^0(T) - R\ln P \; (P \text{ in bar})$$

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

Consider the following sequence of processes for the substance A

Figure 4. 8: Entropy plots for various processes

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

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

Since ΔS° is positive for each of these processes. The entropy must have its smallest possible value at 0 K. If we take $\overline{S}^\circ(0K) = zero$ 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.

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

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.

$\left(\Delta G_r\right)_{T,P}$	$\left(\Delta S_r\right)_{T,P}$	$\left(\Delta G_r\right)_{T,P}$	Remark
-ve	+ve	Always –ve	Reaction is spontaneous
+ve	-ve	Always +ve	Reaction is non-spontaneous
+ve	+ve	At low temperature, ΔG=+ve	Non spontaneous
		At high temperature, ΔG=-ve	Spontaneous
-ve	-ve	At low temperature, ΔG=-ve	Spontaneous
		At high temperature, ΔG=+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 $\left(\dfrac{\partial G}{\partial P}\right)_T = V$

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

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

$\Delta H°$ and $S°$ value of Br_2 (l) $\rightarrow Br_2$ (g) are 30.91 KJ/ mole and 93.2 J/mol. K respectively. Assume that ΔH and ΔS 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, ΔG becomes zero. Consider the process: Br_2 (l) $\rightarrow Br_2$ (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 ΔH and ΔS do not change with temperature

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

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

∴ $T = \dfrac{\Delta H}{\Delta S} = \dfrac{30.91}{0.0932} = 331.6$ 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

$SiO_2(s) + 2C(s) + 2Cl_2(g) \rightarrow SiCl_4(g) + 2CO(g)$
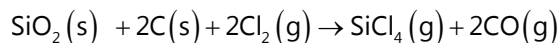
(JEE ADVANCED)

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

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

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

Illustration 19: For the water gas reaction. $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$. 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 = $ antilog $\left(\dfrac{-\Delta G°}{2.303RT} \right)$ ... (i)

We know that, $K = $ antilog $\left(\dfrac{-\Delta G°}{2.303RT} \right)$ ... (ii)

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

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

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

$C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta G^0 = -380$KJ mol^{-1}

$2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$; $\Delta G^0 = -500$KJ mol^{-1}
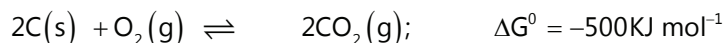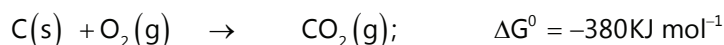
Discuss the possibility of reducing Al_2O_3 and PdO with carbon at this temperature.

$4Al + 3O_2(g) \rightarrow 2Al_2O_2(s)$; $\Delta G^0 = -22500$KJ mol^{-1}
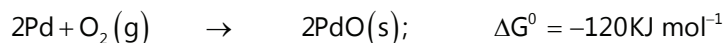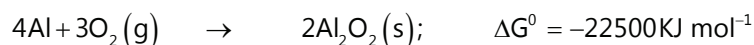
$2Pd + O_2(g) \rightarrow 2PdO(s)$; $\Delta G^0 = -120$KJ mol^{-1} **(JEE ADVANCED)**

Sol: Let us consider the reduction of Al_2O_3 by carbon

$2Al_2O_3 + 3C(s) \rightarrow 4Al(s) + 3CO_2(g)$; $\Delta G^0 = -380 \times 3 + (22500) = +21360$KJ

$2Al_2O_3 + 6C(s) \rightarrow 4Al(s) + 6CO_2(g)$; $\Delta G^0 = -500 \times 3 + 22500 = +21000$KJ
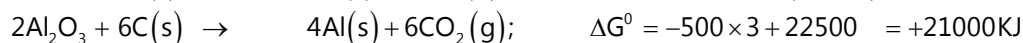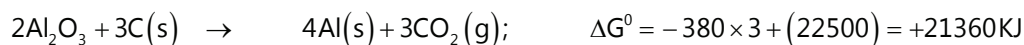
Positive value of $\Delta G°$ show that the reduction of Al_2O_3 is not possible by any of the above methods.

Now, let us consider the reduction of PdO.

$2PbO_{(s)} + C \quad \rightarrow \quad 2Pb + CO_2; \quad \Delta G^0 = +120 + (-380) = -260KJ$

$2PbO_{(s)} + C \quad \rightarrow \quad 2Pb + CO_2; \quad \Delta G^0 = +120 + (-500) = -380\ KJ$
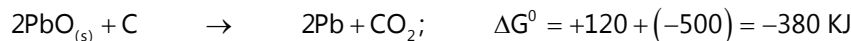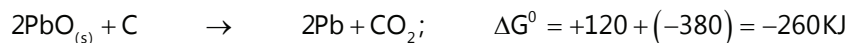
Illustration 21: Calculate $\Delta G°$ for the following reaction

$CO(g) + \left(\frac{1}{2}\right)O_2(g) \rightarrow CO_2(g); \quad \Delta H° = -282.84KJ$
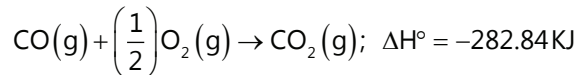
Given, $S°_{CO_2} = 213.8JK^{-1}mol^{-1}$, $S°_{CO_{(g)}} = 197.9JK^{-1}mol^{-1}$, $S°_{O_2} = 205.0JK^{(-1)}mol^{(-1)}$. **(JEE ADVANCED)**

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

$\Delta S_{Reaction} = \sum S°_{product} - \sum S°_{Reaction}$

$\Delta S° = \sum S°_{(products)} - \sum S°_{(reactants)}$

$= \left[S°_{CO_2}\right] - \left[S°_{CO} + \frac{1}{2}S°_{O_2}\right] = 213.8 - \left[197.9 + \frac{1}{2}205\right] = -86.6kJ$

According to Gibbs-Helmholtz equation,

$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -282.84 - 298 \times (-86.6 \times 10^{-3}) = -282.84 + 25.807 = -257.033kJ$

Illustration 22: Acetic acid CH_3COOH can form a dimer $(CH_3COOH)_2$ in the gas phase. The dimer is held together by two H-bonds with a total strength of 66.5kJ per mole of dimer. If at 25°C, the equilibrium constant for the dimerization is 1.3×10^3. Calculate $\Delta S°$ for the reaction. $2CH_3COOH(g) \rightarrow (CH_3COOH)_2(g)$ **(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.
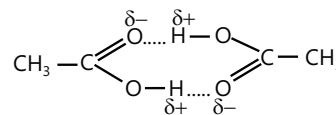
$\Delta G° = -2.303RT \log K$

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

$\Delta G^0 = \Delta H^0 - T\Delta S^0; \quad -17.767 = -66.5 - 298 \times \Delta S°; \quad \Delta S° = \frac{-66.5 + 17.767}{298} = -0.163kJ$

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:-

(a) The physical state or the phase of the reactants and the products using the symbols s, l, g or aq(aqueous)).

(b) 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 ΔH, H_R and H_p respectively. $$\Delta H = H_p - H_R$$

Mathematically,

For Exothermic reactions, $H_R > H_p$ or ΔH is negative.

For endothermic reactions, $H_p > H_R$ or ΔH is positive.

11. HEAT OF REACTION AND KIRCHOFF'S EQUATION

Relation Between ΔH and ΔE

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

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

At constant volume, indicated by Q_V
$Q_V = \Delta E$ (ΔE = Change in internal energy)

At constant pressure indicated by Q_P
$Q_P = \Delta H$ (Change in enthalpy)
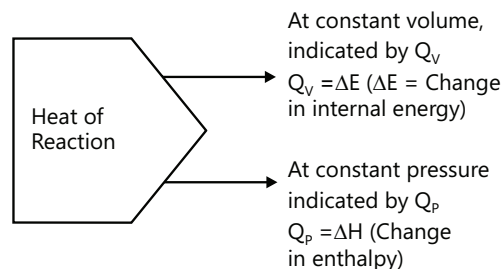
Figure 4.8: Heat of reaction

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 ΔH_2 = Heat of reaction at temperature T_2 at constant pressure

ΔH_1 = Heat of reaction at temperature T_1 at constant pressure

ΔE_2 = Heat of reaction at temperature T_2 at constant pressure

ΔE_1 = Heat of reaction at temperature T_1 at constant pressure

ΔC_p = Difference of heat capacities of products and reactants at constant pressure

ΔC_V = Difference of heat capacities of products and reactants at constant volume.

12. ENTHALPIES FOR VARIOUS PROCESSES

Bond Enthalpy
The heat released when a bond formation takes place between two free atoms leading to a molecule, in gaseous state.

Bond related Enthalpies

Lattice Enthalpy
The lattice enthalpy of an ionic compound is the enthalpy change which occur a when one mole of an ionic compound dissociates

$$\Delta H_{reaction} = \begin{bmatrix} \text{Bond energy used for formation} \\ \text{of bond (to be taken as -ve)} \end{bmatrix} + \begin{bmatrix} \text{Bond energy used for dissociation} \\ \text{of bond (to be taken as + ve)} \end{bmatrix}$$

Figure 4.9: Enthalpies for various processes

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

Na^+Cl^- (s) $\rightarrow$ Na^+(g) + Cl^-(g); $\Delta_{lattice}H = +788kJmol^{-1}$
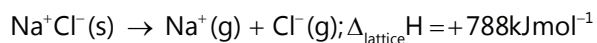
Points to be noted:

(a) The bond enthalpy of diatomic molecules like H_2, Cl_2, 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. Cl_2 (g) $\rightarrow$2Cl (g); $\Delta H_{Cl-Cl} = +242kJmol^{-1}$, O_2 (g) $\rightarrow$2O (g); $\Delta H_{O-O} = +428kJmol^{-1}$

(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 $\Delta_f H°$ is related with the bond enthalpies of reactants and products as $\Delta_f H° = \Sigma$ bond enthalpies (reactants) $-\Sigma$ bond enthalpies (products)

Electron Enthalpies

→ **Ionization Enthalpy**
It is the positive enthalpy change when an electron is removed form as isolated gaseous atom in its ground state under condition of constant temperature and pressure.

→ **Electron Gain Enthalpy**
It is the enthalpy change when an electron is added to a natural gaseous atom to convert it into a negative ion under condition of constant temperature and pressure.
X(g) $+e^- \rightarrow$X(g)

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, H_2(g)$\rightarrow$2H(g) ; $\Delta_f H = 435.0kJ$ mol^{-1} CH_4,(g)$\rightarrow$C(g)+4H(g) ; $\Delta_f H = 1665kJ$ 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. ΔH_{vap} = 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:

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

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 ΔH_f° values. In general practice, reference state, i.e., ΔH_f° 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:

$$\Delta H_f^\circ \left[A\right] = 433 \text{ KJ/mol}$$
$$\Delta H_f^\circ \left[B\right] = -256 \text{ KJ/mol}$$
$$\Delta H_f^\circ \left[C\right] = 523 \text{ KJ/mol}$$

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

$$\Delta H^\circ_{\text{reaction}} = \Delta H_f^\circ \left[C\right] - \left(\Delta H_f^\circ \left[A\right] + \Delta H_f^\circ \left[B\right]\right)$$
$$\Delta H^\circ_{\text{reaction}} = (1\text{mol})(523 \text{ kJ/mol}) - ((1\text{mol})(433 \text{ kJ/mol}) + (1\text{mol})(-256 \text{ kJ/mol}))$$

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

$$\Delta H^\circ_{\text{reaction}} = \textbf{346 kJ}$$

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

Shrikant Nagori JEE 2009 AIR 30

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 CO_2 is -94.3 =Kcal.

$$C + O_2 \rightarrow CO_2; \qquad \Delta H = -94.3 \text{ Kcal} \qquad \qquad \text{... (i)}$$

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

$$CO + \frac{1}{2}O_2 \rightarrow CO_2; \quad \Delta H = -68.0 \text{ Kcal} \qquad \qquad \text{... (ii)}$$

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)**

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g); \ \Delta_f H^\circ = -92.4 \text{ KJ}; \qquad HCl(g) + H_2O \rightarrow H_3O^+(aq) + Cl^-(aq);$$

$\Delta_f H^0 \text{ of } H_3O^+(aq) = 0.0 \text{ KJ}$

Sol: Given,

$$\frac{1}{2}H_2(g) + (aq) \rightarrow H^+(aq); \qquad\qquad \Delta H^0 = 0 \qquad\qquad \dots (i)$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g); \qquad\qquad \Delta H^0 = -92.4 \text{ kJ} \qquad\qquad \dots (ii)$$

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq); \quad \Delta H = -74.8 kJ \qquad\qquad \dots (iii)$$
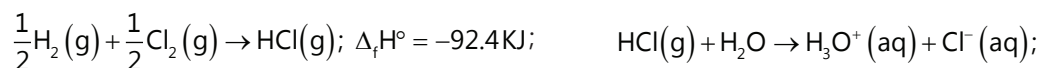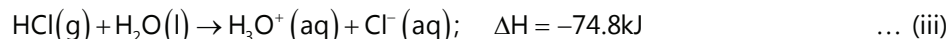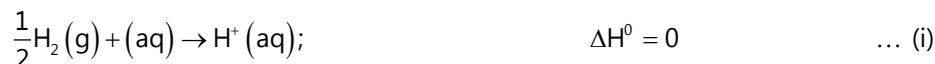
By inspection method : eqs. $(ii) + (iii) - (i)$ reveals that

$$\frac{1}{2}Cl_2(g) + (aq) \rightarrow Cl^-(aq); \qquad\qquad \Delta H = -167.2 \text{ KJ}$$

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

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_{comb} or H_c when the enthalpy required is not combustion, it can be denoted as H_{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 kJ mol^{-1}).

12.4.1 Bomb Calorimetry

(a) Purpose of Bomb Calorimetry Experiments

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

$$C_xH_yO_z(s) + (2X+Y/2-Z) O_2 (g) \longrightarrow X\ CO_2 + YH_2O$$
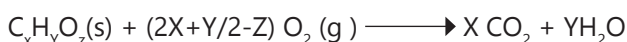
Since combustion reactions are usually exothermic (give off heat), $\Delta_{comb}H$ is typically negative. (However, be aware that older literature defines the "heat of combustion" as $\Delta_{comb}H$, so as to avoid compiling tables of negative numbers!

(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.,

$$q_{calorimeter} = 0$$

Figure. 4.9 Bomb calorimeter

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.,

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

Hence, ΔU, change in internal energy, is zero, for the calorimeter

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

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,

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$
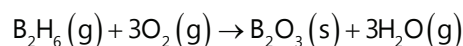
From the following data calculate the enthalpy change for the combustion of Diborane

$2B(s) + \dfrac{3}{2}O_2(g) \rightarrow B_2O_3(s);$ $\Delta H = -1273 kJ\ mol^{-1}$ ... (i)

$H_2(g) + \dfrac{1}{2}O_2(g) \rightarrow H_2O(l);$ $\Delta H = -286 kJ\ mol^{-1}$ ... (ii)

$H_2O(l) \rightarrow H_2O(g);$ $\Delta H = 44\ kJmol^{-1}$ ... (iii)

$2B(s) + 3 H_2(g) \rightarrow B_2H_6(g);$ $\Delta H = 36\ kJ\ mol^{-1}$ ... (iv)   **(JEE ADVANCED)**

Sol: To get,

$$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$$
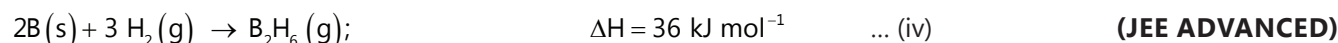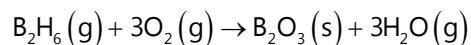
By inspection method (i) + 3 x (ii) + 3 x (iii) − (iv)

$2B(s) + (3/2)O_2(g) \rightarrow B_2O_3(s);$ $\Delta H = -1273\ kJ\ mol^{-1}$ ... (i)

$3H_2(g) + (3/2)O_2(g) \rightarrow 3H_2O(l);$ $\Delta H = -286\ x3$ ... (ii)

$3H_2O(l) \rightarrow 3H_2O(g);$ $\Delta H = 44\ x3$ ... (iii)

$2B(s) + 3H_2(g) + 3O_2 \rightarrow B_2O_3(s) + 3H_2O(g);$ $\Delta H = -1999\ kJ$

$2B(s) + 3H_2(g) \rightarrow B_2H_6(g);$ $\Delta H = 36\ kJ$

$B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$ $\Delta H = -2035\ kJ\ mol^{-1}$
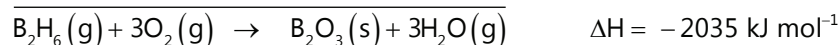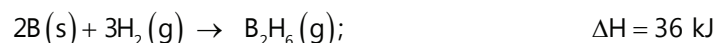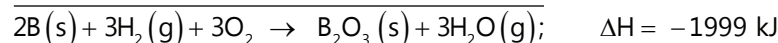
12.5 Enthalpy of Solution

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.,

$HCl(g) + 40H_2O \rightarrow HCl(40H_2O);$ $\Delta H = -73.0 kJmol^{-1}$ ...(i)

$HCl(g) + 10H_2O \rightarrow HCl(10H_2O);$ $\Delta H = -69.5 kJmol^{-1}$ ...(ii)

Also by eqs. (i) and (ii)

$HCl(10H_2O) + 30H_2O(l) \rightarrow HCl(40H_2O);$ $\Delta H = -3.50 kJmol^{-1}$
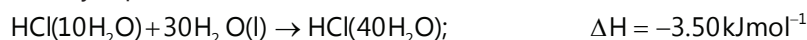
i.e. integral enthalpy of dilution of $HCl(10H_2O)$ to $HCl(40H_2O)$ is -3.50 kJ mol^{-1}

(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 $CaCl_2$ and Na_2CO_3 are mixed for respectively. **(JEE MAIN)**

Sol: The given reaction on mixing two solutions is $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

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

$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \downarrow + 2Na^+(aq) + 2Cl^-(aq)$

Or $\quad Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

The given reaction on mixing two solutions is $CaCl_2 \quad Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

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

$Ca^{2+}(aq) + 2Cl^-(aq) + 2Na^+(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \downarrow + 2Na^+(aq) + 2Cl^-(aq)$

Or $\quad Ca^2(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$
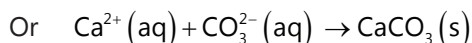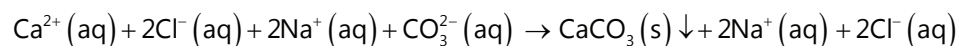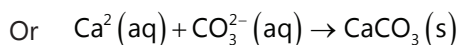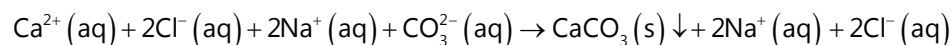
$\therefore \Delta H = \overset{0}{\underset{Product}{\sum}} - \overset{0}{\underset{Reactant}{\sum}} = \Delta_f H \overset{\circ}{\sum} CaCO_3 - \left[\Delta_f H^\circ Ca^{2+} + \Delta_f \overset{\circ}{\sum} CO_3^{2-} \right] \qquad \because (H^\circ = \Delta H^0_{formation})$

$\quad\quad = -288.5 - (-129.80 - 161.65) \, ; \, = 2.95 \text{ kcal}$

12.6 Enthalpy of Hydration, $\Delta_{Hyd}H$

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: $\quad MgSO_4(s) + 7H_2O(l) \rightarrow MgSO_4(s).7H_2O(s) \, ; \qquad \Delta_{hyd}H = -106.6 \text{ kJmol}^{-1}$

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

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

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.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l); \, \Delta_{neut}H = -57.7 \text{ kJeq}^{-1}$$
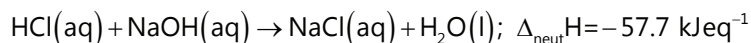
The enthalpy of neutralization of strong acid and strong base is always constant (-57.7 kJ) independent from the acid and base taken. However the magnitude of enthalpy change of neutralization decreases when any one of the acid or base taken is weak.

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

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l); \Delta H = -57.1 \text{ kJ}$$
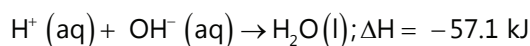
Calculate the heat evolved for the following experiments:

(i)   0.50 mole of HCl solution is neutralized by 0.50 mole of NaOH solution.

(ii) 0.50 mole of 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 H_2SO_4 is mixed with 600 mL of 0.1 M KOH solution.   **(JEE ADVANCED)**

Sol: According to the reaction, $H^+(aq) + OH^-(aq) \rightarrow H_2O(l); \quad \Delta H = -57.1 \, kJ$

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 H^+ ions

      0.50 mole NaOH $\equiv$ 0.50 mole OH^- ions

      On mixing, 0.50 mole of water is formed.

      Heat evolved for the formation of 0.50 mole of water = 57.1 x 0.5 = 28.55 kJ

(ii) 0.50 mole HNO_3 $\equiv$ 0.50 mole H^+ ions

      0.30 mole KOH 0.30 mole OH^- ions

      i.e., 0.30 mole of ions react with 0.30 mole of OH^- ions to form 0.30 mole of water molecules.

      Heat evolved in the formation of 0.3 mole of water = 57.1 x 0.3 = 17.13 kJ

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

      $\left(\dfrac{0.3}{1000} \times 100\right)$ = 0.03 mole of 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 x 57.1 = 1.142 kJ

(iv) 400 mL of 0.2 M H_2SO_4 will give $\left(\dfrac{2 \times 0.2}{1000} \times 400\right)$ = 0.16 mole of H^- ions and 600 mL of 0.1 M KOH will give

      $\left(\dfrac{0.1}{1000} \times 600\right)$ = 0.06 mole of 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 x 57.1 = 3.426 kJ

12.9 Enthalpy of Sublimation $\Delta_{Sub}H$

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 $Na_{(s)} \xrightarrow[\Delta_a]{Substance} Na_{(g)} \quad \Delta_a H = x \, kJ \, mol^{-1}$

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
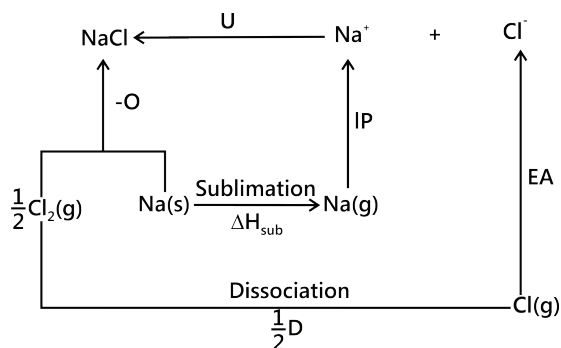
Steps Involved :

(a) Sublimation (ΔH_{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.

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

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

Illustration 28: Which ions are present in MgO(s)?

Calculate the enthalpy change for the reaction $Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$

What kind of enthalpy change is this? Standard enthalpy of formation of MgO is **(JEE MAIN)**

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

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

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

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

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

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

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

Sol:

$$\Delta H \quad = \quad (148 + 1451 + 738) + (249 + 798 - 141) - 3791$$
$$= \quad 2337 + 906 - 3791 - 548 \text{ kJ mol}^{-1}$$
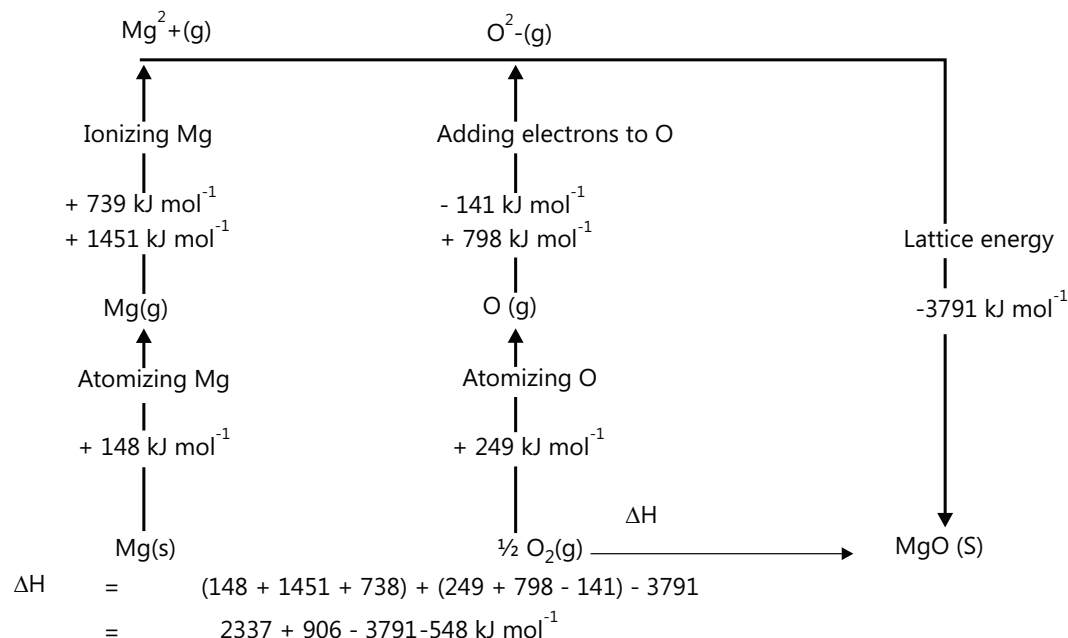
The actual value for this reaction is -602 kJ mol^{-1} This is because there is a degree of covalent bonding in MgO. Therefore the bonds formed are slightly stronger than those predicted by a purely ionic model.

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 kJ respectively.

Sol: Required equation is $C(s) + 2S(s) \rightarrow CS_2(l); \quad \Delta H_f = ?$

Given, $C(s) + O_2(g) \rightarrow CO_2(g)$ $\qquad (\Delta H = -393.3 \text{ kJ})$ $\qquad$ .... (i)

$\qquad S(s) + O_2(g) \rightarrow SO_2(g)$ $\qquad (\Delta H = -293.3 \text{ kJ})$ $\qquad$ .... (ii)

$\qquad CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$ $\quad (\Delta H = -1108.76 \text{ kJ})$ $\qquad$ .... (iii)
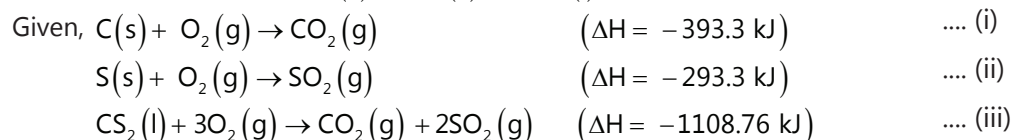
First method: Multiply the eq. (ii) by 2.

$$2S(s) + 2O_2(g) \rightarrow 2SO_2(g) \qquad (\Delta H = -587.44 \text{ kJ}) \qquad .... \text{(iv)}$$
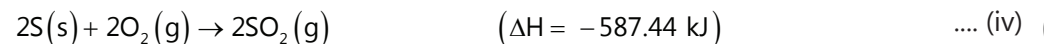
Adding eqs. (i) and (iv) and subtracting eq. (iii),

$$\left[C(s) + 2S(s) + 3O_2(g) - CS_2(l) - 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g) - CO_2 - 2SO_2\right]$$

$$C(s) + 2S(s) \rightarrow CS_2(l)$$
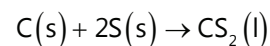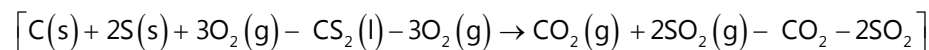
This is the required equation.

Thus, = -393.3 − 587.44 + 1108.76 = 128.02.kJ

Standard heat of formation of $CS_2(\ell)$ = 128.02 kJ

Second Method:

$C(s) + O_2(g) \rightarrow CO_2(g);$ $\qquad (\Delta H = -393.3 \text{ kJ})$ $\qquad$ .... (i)

$S(s) + O_2(g) \rightarrow SO_2(g);$ $\qquad (\Delta H = -293.72 \text{kJ})$ $\qquad$ .... (ii)

$CS_2(l) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g);$ $\quad (\Delta H = -1108.76 \text{ kJ})$ $\qquad$ .... (iii)
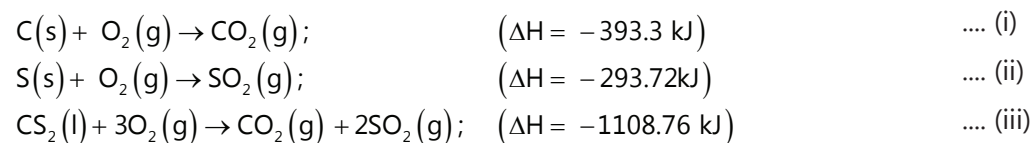
From eqs. (i) and (ii),

Enthalpy of CO_2 = -393.3 kJ; Enthalpy of SO_2 = -293.72 kJ;

Enthalpy of O_2 = 0 (By convention)

ΔH of eq. (iii) Enthalpies of products Enthalpies of reactants

-1108.76 = -393.3+2 (-293.72) - ΔHCS_2 (l)

ΔHCS_2 (l) = (1108.76-980.74) = 128.02 kJ

Enthalpy of CS_2 (l) = 128.02 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 atm (better to say 1 Bar) and T = 298 K, the enthalpy of reaction is referred as standard enthalpy of reaction.

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

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 J/mol, i.e., $\dfrac{\Delta_{vap} H}{T_b \left(\text{in K}\right)}$ = 88 J/mol

PROBLEM-SOLVING TACTICS

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

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

$$\Delta H_f^\circ \left[A\right] = 433 \text{ KJ/mol}$$
$$\Delta H_f^\circ \left[B\right] = -256 \text{ KJ/mol}$$
$$\Delta H_f^\circ \left[C\right] = 523 \text{ KJ/mol}$$

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

$$\Delta H^\circ_{reaction} = \Delta H_f^\circ \left[C\right] - \left(\Delta H_f^\circ \left[A\right] + \Delta H_f^\circ \left[B\right]\right)$$
$$\Delta H^\circ_{reaction} = (1\text{mol})(523 \text{ kJ/mol}) - ((1\text{mol})(433 \text{ kJ/mol}) + (1\text{mol})(-256 \text{ kJ/mol}))$$

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

$$\Delta H^\circ_{reaction} = 346 \text{ kJ}$$

We get the answer of 346 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:

$$Ca^{2+}(g) + (aq) \rightarrow Ca^{2+}(aq) \qquad \Delta H = -1650 \text{ kJ mol}^{-1}$$
$$Cl^{-}(g) + (aq) \rightarrow Cl^{-}(aq) \quad \Delta H = -364 \text{ kJ mol}^{-1}$$
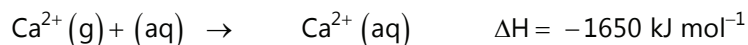
The following cycle is for calcium chloride, and includes a lattice dissociation enthalpy of +2258 kJ mol-1. We have to use double the hydration enthalpy of the chloride ion because we are hydrating 2 moles of chloride ions. Make sure you understand exactly how the cycle works.

So,
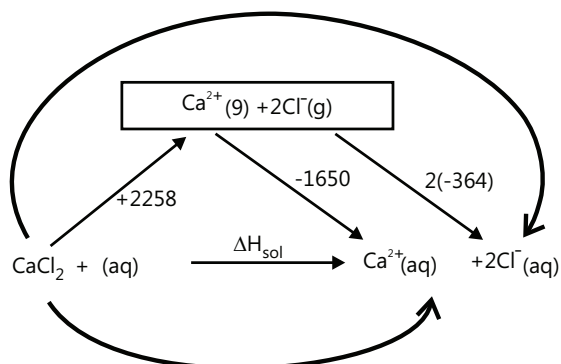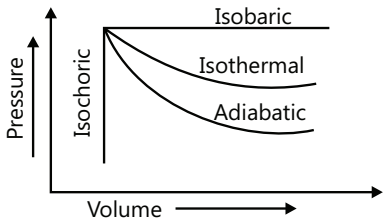
ΔHsol = +2258 - 1650 + 2(-364)

ΔHsol = -120 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	**(a) Isothermal process** Occurs at constant temperature; $\Delta T = 0$ **(b) Adiabatic process** Occurs without exchange of heat With surrounding, q = 0. **(c) Isobaric process** Occurs at constant pressure, $\Delta p = 0$ **(d) Isochoric process** 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, $\qquad q = nC_v \Delta T$ In rev Isothermal Expansion of gas, $q = -W = P_{ext} \Delta V (\Delta E = 0)$ $q = -W = nRT \ln \dfrac{V_2}{V_1}$ In rev Isothermal Expansion of gas, $W = -q = -nC_v \Delta T = nC_v (T_1 - T_2)$ $pV^{\gamma} = constant$, where $\gamma = \dfrac{C_p}{C_v}$ TV^{γ} constant and Also, In adiabatic rev process, $P^{1-\gamma}T^{\gamma} = constant$
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)	$S = \dfrac{q_{rev}}{T}; \; \Delta S = nC_v \ln\left(\dfrac{T_2}{T_1}\right) + nR \ln\left(\dfrac{V_2}{V_1}\right)$ $= nC_p \ln\left(\dfrac{T_2}{T_1}\right) + nR \ln\left(\dfrac{P_1}{P_2}\right)$
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., $\Delta S_{univ} > 0$ or $\Delta G < 0$ (a) If $\Delta H < 0$ and $\Delta S > 0$, ΔG is always negative, always spontaneous. (b) If $\Delta H > 0$ and $\Delta S < 0$, ΔG is always positive, always non-spontaneous. (c) If $\Delta H > 0$ and $\Delta S > 0$, ΔG process will be spontaneous at higher temperature but non-spontaneous at lower temperature. (d) If $\Delta H < 0$ and $\Delta S < 0$, ΔG process will be spontaneous at Lower temperature but non-spontaneous at higher temperature.

S. No	Terms	Description
13	Standard Molar Enthalpy of formation $\left(\Delta H^0_{f_m}\right)$	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 $\left(\Delta H^0_{comb}\right)$	It is the heat evolved when one mole of a substance is the standard state is oxidized completely. (ΔH^0_{comb}) is always negative.
15	Standard Enthalpy reaction $\left(\Delta H^0_{rxn}\right)$	It is the net enthalpy change associate with a reaction. It is determined with the help of $\Delta H^0_{f_m}$ or ΔH^0_{comb} as $$\Delta H^0_{rxn} = \sum \Delta H^0_{f_m}\ (\text{products}) - \sum \Delta H^0_{f_m}\ (\text{reactants}) \text{ Or}$$ $$\Delta H^0_{rxn} = \sum \Delta H^0_{comb}\ (\text{reactants}) - \sum \Delta H^0_{comb}\ (\text{products})$$ By convention ΔH^0_f of pure element is taken to be zero.
16	Calorimetry	If a reaction is carried out in a calorimeter, the enthalpy change of a reaction can be determined as q=mSΔT Where, m = mass of calorimeter contend S = specific heat of calorimeter content $\Delta T = T_{final} - T_{initial} = $ change in temperature of calorimeter
17	Bond Dissociation Energy and Bond Enthalpy	Bond dissociation energy is the average energy required to break a specific type of bond in a molecule. **Bond enthalpy of a Compound**: It is the total energy required to convert one mole of gaseous substance into their constituent atoms. In term of bond-enthalpy, ΔH^0_{rxn} can be determined as $$\Delta H^0_{rxn} = \sum BE(\text{reactants}) - \sum BE(\text{products})$$
18	Resonance Energy	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 $\Rightarrow \Delta H\ (RE) = \Delta H_{(exp)} - \Delta H_{(theo)}$
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 (ΔH^0_{hyd})	It is the heat evolved when one mole of a substance is hydrated to a certain specific degree of hydration, e.g, $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 + 5H_2O(s)$ En thalpy of hydration,
21	Lattice Energy (U_0)	**Lattice Energy** (U_0) It is the heat liberated when one mole of an ionic compound in its standard state is formed from ions in their gaseous state, e.g. $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$; $\Delta H - U_o$

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^{-3} and 0.6 kg m^{-3} respectively.

The latent heat of vaporization of water = 2.25×10^6 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

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

The increase in volume

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

The work done by the system is

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

The heat given to convert 1 kg of water into steam

$= 2.25 \times 10^6$ 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 R $= 8.3$ JK^{-1} mol^{-1}
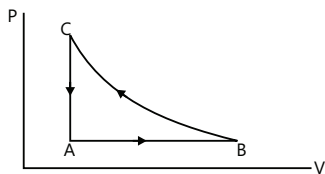
Sol: The change in internal energy during the cyclic process is zero. Hence, the heat supplied to the gas is equal to the work done by it. Work done can be calculated by pressure volume relationship.

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,

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

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

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

$3320 \text{ J} + W_{BC} = -1200 \text{ J} = -4520$ 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 m^3 respectively. Given that the initial pressure (P_1) 1 x 10^5 Pa, final temperature be T_2

We have, $P_1V_1 = n_1RT_1$

$V_1 = \dfrac{1 \text{ x8.314 x273}}{1 \text{ x10}^5} = 0.022697\text{m}^3$

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

$W = -P_2\left(V_2 - V_1\right) = Cv\left(T_2 - T_1\right) = \dfrac{3R}{2}\left(T_2 - T_1\right)$

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

Again,

$P_2V_2 = nRT_2$;

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

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

(a) The final temperature, T_2= 207 K

(b) The final volume V_2= 0.043578 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.

$HgS(s) + O_2(g) \rightarrow Hg(l) + S\,O_2(g)$
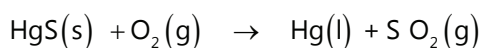
$\Delta H° = -238.6$ kJ/ mole and $\Delta S° = +36.7$ J / mole K

Sol: Assume that ΔH and ΔS values do not depend on temperature. As ΔH° is negative and ΔS° is positive, using the equation $\Delta G° = \Delta H° = T\Delta S°$ ΔG° Will be negative at all temperatures and so the reaction is product - favored at all temperatures. In this problem, both the factors ΔH° and ΔS° 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 losed vessel of Volume 0.0083 m³, at a temperature of 300 K and a pressure of $1.6 \times 10^6\ Nm^{-2}$. An amount $2.49 \times 10^4\,J$ 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 $n = \dfrac{PV}{RT}$

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

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

Thus, we have

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

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

The final temperature is 300 K + 377 K = 677K.

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

Here $V_1 = V_2$. Thus,

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

Q.6 Oxygen gas weighting 64 is expanded from 1 atm to 0.25 atm at 30°C. Calculate entropy change, assuming the gas to be ideal.

Sol: First find out value of n and then ΔS can be determined by using following equation

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

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

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

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

Q.7 An aluminium container of mass 100 g contains 200 g of ice at -20°C. Heat is added to the system at a rate of 100 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 cal g⁻¹ °C⁻¹, specific heat capacity of aluminium = 0.2 cal g⁻¹° C⁻¹, specific heat capacity of water = 1 cal g⁻¹° C⁻¹, and latent heat of fusion of ice = 80 calg⁻¹.

Sol: Total heat supplied to the system in 4 minutes is Q = 100 cal s⁻¹ x 240 s = 2.4 x 10⁴ cal. The heat require to take the system from – 20°C to 0°C

= (100g) x (0.2 cag⁻¹°C⁻¹ x (20°C) + (200g) x (0.5 cal⁻¹°C⁻¹ x (20°C)

= 400 cal + 2000 cal = 2400 cal.

The time taken in this process $= \dfrac{2400}{100}\,S = 24\ s$. The heat required to melt the ice at 0°C =(200g) x (80 cal⁻¹)

= 16000 cal.

The time taken in this process $= \dfrac{1600}{100}\,S = 160\ s$.

If the final temperature is θ, the heat required to take the system to the final temperature is

= (100g) × (0.2 cal⁻¹°C⁻¹) θ + (200g) × (0.5 cal⁻¹°C⁻¹) θ.

Thus, 2.4 x 10⁴ cal =2400 cal +16000 cal+(220 cal°C⁻¹) θ

Or, $\theta = \dfrac{5600\ cal}{200\ cal°\ C^{-1}} = 25.5°C.$

The variation in the temperature as function of time is sketched in figure
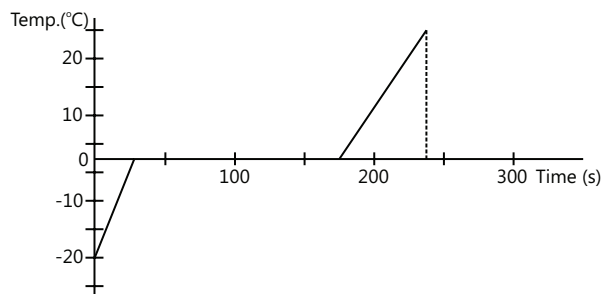
Q.8 Calculate the enthalpy of the reaction

$$H_2C = CH_2(g) + H_2(g) \rightarrow CH_3 - CH_3(g)$$
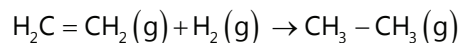
The bond energies of

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

Sol: The reaction is:

```
H      H                      H    H
|      |                      |    |
C  =  C(g)  + H  –  H(g)  →  H  –  C  –  C  –H(g)
|      |                      |    |
H      H                      H    H
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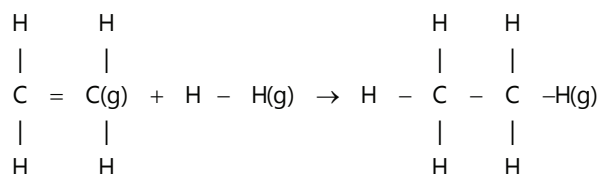
$\Delta H = ?$

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

$$= \left[\Delta H_{C=C} + 4 \times \Delta H_{C-H} + \Delta H_{H=H} \right] - \left[\Delta H_{C-C} + 6 \times \Delta H_{C-H} \right]$$
$$= (147 + 4 \times 99 + 140) - (83 + 6 \times 99) = -30 \text{ Kcal}$$

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

$$CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l) \qquad \text{... (i)}$$

$(\Delta H = -207.9 \text{ kcal})$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \text{... (ii)}$$

$(\Delta H = -94.48 \text{ kcal})$

$$H_2(g) + \frac{1}{2}O_2 (g) \rightarrow H_2O(l) \qquad \text{... (iii)}$$

$(\Delta H = -68.4 \text{ kcal})$
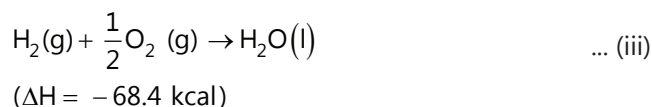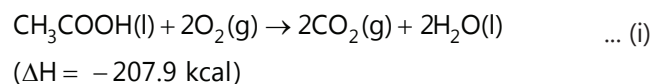
Sol: First method: The required equation is $2C(s) + 2H_2(g) + O_2(g) = CH_3COOH(l); \quad \Delta H = ?$ This equation can be obtained by multiplying eq. (ii) by 2 and also eq. (iii) by 2 and adding both and finally subtracting eq. (i).

$$\left[2C + 2O_2 + 2H_2 + O_2 - CH_3COOH(l) - 2O_2 \right.$$
$$\left. \rightarrow 2CO_2 + 2H_2O - 2CO_2 - 2H_2O \right]$$
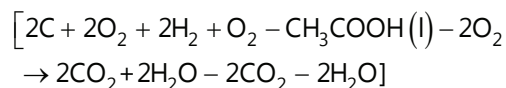
$$\Delta H_{CH_3COOH(l)} = 2x(-94.48) + 2x(-68.4) - (-207.9)$$

$$= -188.96 - 136.8 + 207.9$$

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

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

Enthalpy of $CO_2 = -94.48$ kcal

Enthalpy of $HO_2 = -68.4$ kcal

Enthalpy of $O_2 = 0$ (by convention)

ΔH of eq. (i) = Enthalpies of products – Enthalpies of reactants

$$-207.9 = 2 \, x(-94.48) + 2 \, (-68.4) - \Delta H_{CH_3COOH(l)}$$

$$\Delta H_{CH_3COOH(l)} = -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9$$

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

Q.10 100 cm³ of 0.5 N HCl solutions at 299.95 K were mixed with 100 cm³ 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.

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

Rise in temperature = (302.65 − 299.85) = 2.80 K

Heat evolved during neutralization

= (100 − 100 + 44) × 4.184 × 2.8 = 2858.5 J

∴ 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

$$\gamma = \frac{C'_P}{C'_V} = \frac{n_1 C'_p + n_2 C'_p}{n_1 C'_V + n_2 C'_V}$$
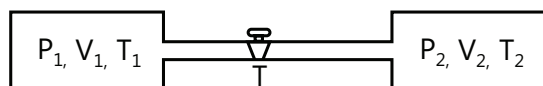
The amount if the gas in vessel 1 is

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

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

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

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

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

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

or $\dfrac{T'}{P'} = \dfrac{T_1 T_2 (V_1 + V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}.$ .... (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 if the total system remains constant.

The internal energy of an ideal gas is

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

The internal energy of the gases before the connection

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

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

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

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

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

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

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 γ for the mixture.

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

$$\gamma = \dfrac{C'_P}{C'_V} \qquad \text{And} \qquad C'_P = C'_V + R$$

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,

$\gamma = \dfrac{C'_P}{C'_V} = 1.67$ and $C'_P = C'_V + R$

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

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

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 $= (n_1 + n_2)C'_v\, dT$

Thus, $(n_1 + n_2)C'_v dT = n_1 C'_v dT + n_2 C'_v dT;$

$$C'_v = \dfrac{n_1 C'_v + n_2 C'_v}{n_1 + n_2} \qquad \text{...(i)}$$

$C_P = C_V + R = \dfrac{n_1 C'_v + n_2 C'_v}{n_1 + n_2}R$

$= \dfrac{n_1(C'_v + R) + n_2(C'_v + R)}{n_1 + n_2}$

$= \dfrac{n_1 C'_p + n_2 C'_p}{n_1 + n_2}$ ... (ii)

From (i) and (ii),

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

Q.3 Two moles of helium gas ($\gamma = 5/3$) are initially at 27° and occupy a volume of 20 liters. The gas is first expanded at constant pressure until the volume is doubled. Then it undergoes
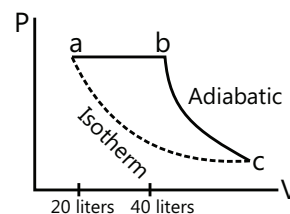
an adiabatic change until the temperature returns to its initial value. (a) Sketch the process in a p-V diagram (b) What is the final volume and pressure of the gas? (c) What is the work done by the gas?

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 and the point 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,

$$P_a V_a = P_c V_c \qquad \text{...(i)}$$

and from the adiabatic curve bc,

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

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

$$ab = P_a (V_b \; V_a) = P_b V_b - P_a V_a = nRT_2 - nRT_1$$

$$= 2 \text{ mol} \times (8..3 \text{ J K}^{-1}\text{mol}^{-1}) \times (600 \text{ K} - 300\text{K}) = 4980 \text{ J}$$

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 J + 7470 J = 12450 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 N m^{-1} as shown in figure. The area of cross
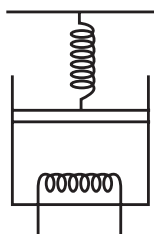
section of the cylinder is 20.0 cm^2. Initially, the spring is at 300 K. The atmospheric and the temperature of the gas is 300 K. the atmospheric pressure is 100 kPa. The gas is heated slowly for some time by means of an electric heater so as to move the piston up through 10 cm. Find (a) the work done 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 $F = P_0 A + kx$. Where $P_0 = 100\text{kPa}$ is the atmospheric pressure, $A = 20\text{cm}^2$ is the area of cross section, $k = 200 \text{ Nm}^{-1}$ is the spring constant and x is the compression of the spring. The work done by the gas as the piston moves through $l = 10$ cm is

$$W = \int_0^1 F dx \; P_0 A l + \frac{1}{2} kl^2$$

$$= (100 \times 10^3 \text{Pa}) \times (20 \text{ x}10^{-4} \text{ m}^2) \times (10 \times 10^{-2} \text{ m})$$

$$+ \frac{1}{2}(200 \text{ N m}^{-1}) \times (100 \times 10^{-4} \text{m}^2)$$

$$= 20 \text{ J} + 1 \text{ J} = 21 \text{ J.}$$

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

$$nRT_1 = P_0 V_0 \text{ and } nRT_1 = P_0 V_0 = \left(P_0 + \frac{kl}{A}\right)(V_0 + Al)$$

$$= nRT_1 + P_0 Al + kl^2 + \frac{kl \; nRT_1}{AP_0} \quad \text{Or}$$

$$T_2 = T_1 + \frac{P_0 Al + kl^2}{nR} + \frac{klT_1}{AP_0}$$

$$= (300\text{k}) + \frac{20 \text{ J} + 2\text{J}}{(2.0 \text{ mol})(8.3 \text{ J K}^{-1}\text{mol}^{-1})}$$

$$+ \frac{(200 \text{ N m}^{-1}) \times (10 \text{ x}10^{-2} \text{ m}) \times (300 \text{ K})}{(20 \text{ x}10^{-4} \text{ m}^2) \times (100 \times 10^3 \text{Pa})}$$

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

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

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

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

Q.5 How much heat is produced in burning a mole of CH_4 under standard conditions if reactants and products are brought to 298 K and H_2O (l) is formed? What is the maximum amount of useful work that can be

(c) $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + H_2O(l)$

($\Delta H = -337.2$ kcal)   ... (iii)

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

$C_2H_2(g) + H_2(g) + 3O_2 - C_2H_4(g) - 3O_2$
$\rightarrow \quad 2CO_2 + 2H_2O(l) - 2CO_2(g) - 2H_2O(l)$
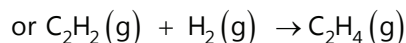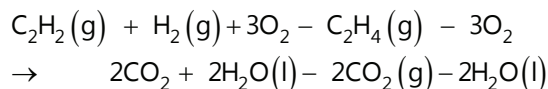
or $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$
$\Delta H = -68.3 - 310.6 - (-337.2)$
$\quad = -378.9 + 337.2 = -41.7$ kcal

We know that,

$\Delta H = \Delta E + \Delta nRT$ or $\Delta H = \Delta E - \Delta nRT$

$\Delta n = (1 - 2) = -1$, $R = 2 \times 10^{-3}$ kcal mol^{-1}K^{-1} and T

$= (25 + 273) = 298$K

Subtracting the values in above equation,

$\Delta E = -41.7 - (-1)(2 \times 10^{-3})(298)$

$\quad = -41.7 + 0.596 = -41.104$ kcal

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.

$\Delta H^{o}_{combustion\ of\ ethane} = -372.0$

$\Delta H^{o}_{(combustion\ of\ propane)} = -530.0$

ΔH^{o} for $C_{(graphite)} \rightarrow C(g) = +172.0$

Bond energy of H–H Bond $= +104.0$;

ΔH^{0}_{f} of $H_2O(l) = -68.0$

ΔH^{0}_{f} of $CO_2(g) = -94.0$

Sol: $C_2H_6(g) + \dfrac{7}{2}O_2 \rightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta H = -372.0$

$\Delta H^{o}_{f(C_2H_6)} = 2x(-94.0) + 3 \ x(-68.0) + 372.0 = -20$ kcal

$C_3H_8(g) + 5O_2 \rightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta H = -530.0$
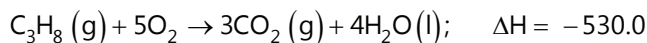
$\Delta H^{o}_{f(C_3H_8)} = 2 \ x(-94.0) + 4 \ x(-68.0) + 530.0 = -24$ kcal

$\qquad 2C(s) + 3H_2(g) \rightarrow C_2H_6(g)$; $\Delta H = -20.0$
$\qquad 2C(g) \rightarrow 2C(s)$; $\Delta H = -344.0$
$\qquad 6H(g) \rightarrow 3H_2(g)$; $\Delta H = -312$

adding $2C(g) + 6H(g) \rightarrow C_2H_6(g)$; $\Delta H = -676$ kcal
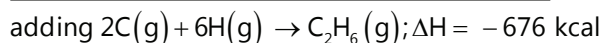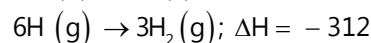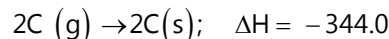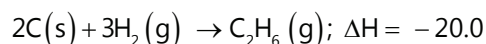
So, enthalpy of formation of 6C – H bonds and one C – C bond is – 676.0 kcal.

$\qquad 3C(s) + 4H_2(g) \rightarrow _3H_8(g)$; $\Delta H = -24.0$
$\qquad 3C(g) \rightarrow 3C(s)$; $\Delta H = -516.0$
$\qquad 8H(g) \rightarrow 4H_2(g)$; $\Delta H = -416.0$

adding $3C(g) + 8H(g) \rightarrow C_3H_8(g)$; $\Delta H = -956.0$ kcal
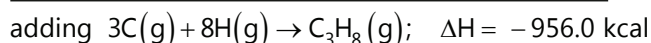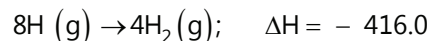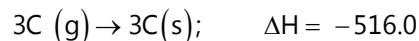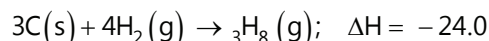
So, enthalpy of formation of 8C – H and 2C – C bonds is-956 kcal

Let the bond energy of C – C be x and of C – H be y kcal.

In ethane $x + 6y = 676$
In propane $2x + 8y = 956$
So solving, $x = 82$ 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
(i)	$H_2O(g)$	$\rightarrow$	$H_2O(l)$
(ii)	$H_2O(s)$	$\rightarrow$	$H_2O(g)$
(iii)	$H_2O(l)$	$\rightarrow$	$H_2O(s)$
(iv)	$CaCO_3(s)$	$\rightarrow$	$CaO(s) + CO_2(g)$

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 ΔE?

Q.3 The enthalpy of combustion of glucose is -2808 kJ mol^{-1} 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, $CaCO_3$. What is the change in internal energy when 1.00 mole of solid $CaCO_3$ (V = 34.2ml) absorbs 177.9 kJ of heat and decomposes at 25°C against a pressure of 1.0 atm to give solid CaO. (Volume = 16.9 ml) and $CO_2(g)$ (V=24.4L)?

Q.6 The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of H_2 at 1.5 atm pressure is ΔH = -0.31 KJ. What is the ΔU?

Q.7 What is ΔE when 2.0 mole of liquid water vaporises at 100°C? The heat of vaporisation, ΔH vap. of water at 100°C is 40.66 kJmol^{-1}.

Q.8 If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the pressure.

Q.9 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find ΔH and ΔE if the latent heat of fusion of ice is 80 Cal/gm and latent heat of vaporisation of liquid water at 0°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 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?
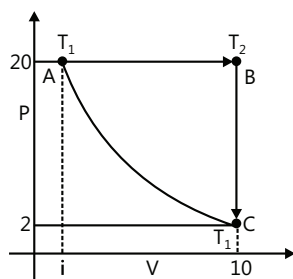
Q.11 Five moles of an ideal gas at 300 K, expanded isothermally from an initial pressure of 4 atm to a final pressure of 1 atm against a cont. ext.pressure of 1 atm. Calculate q, w, ΔU & ΔH. Calculate the corresponding value of all if the above process is carried out reversibly.
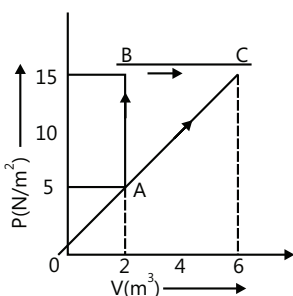
Q.12 Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C.

Q.13 A real gas obeys the equation P (V_m - b) - RT, where (b - 0.1 L/mol), if 2 moles of gas is slowly compressed from 1.2 later 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 JK^{-1} mol^{-1} in this temperature range. Calculate q, w, ΔU, ΔH 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 bar and V_i = 4L to P_f = 20 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 $P_{gas} = P_{ext}$, followed by compression against a constant pressure of 20 bar until $P_{gas} = P_{ext}$.

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 ΔE, 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.
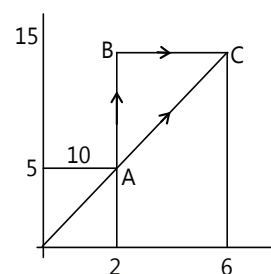
(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.

(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 $H_2(g)$ + $1/2 \, O_2(g) \rightarrow H_2O(l)$ is - 285.76 kJ at 298 K. Calculate the value of ΔH at 373K. The molar heat capacities at constant pressure (C_p) in the given temperature range of $H_2(g)$, $O_2(g)$, and $H_2O(l)$ are respectively 38.83, 29.16 and 75.312 $JK^{-1}mol^{-1}$.

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 x 10^{-3} T where C_p is in JK^{-1} mol^{-1}. Calculate molar (a) ΔH (b) ΔU.

Q.20 One mole of NaCl(s) on melting absorbed 30.5 KJ of heat and its entropy is increased by 28.8 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 $JK^{-1}mol^{-1}$ for the O_2 is C_p = 25.5 + 13.6 x 10^{-3} T - 42.5 x 10^{-7} T^2

Q.22 Calculate S_f° at 298 K of ; (i) NaCl(s), (ii) $NH_4Cl(s)$ & (iii) diamond. The values of S° of Na, Cl_2, NaCl, NH_4Cl, N_2, H_2, diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 $JK^{-1}mol^{-1}$ 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. $C_{pm}(s)$ = 0.035 T $JK^{-1}mol^{-1}$.

(ii) Enthalpy of fusion = 7.5 kJ mol^{-1}.

(iii) Enthalpy of vaporisation = 30 kJ mol^{-1}.

(iv) Heat capacity of liquid from 200 K to normal boiling point 300K. $C_{pm}(l)$= 60 + 0.016T $JK^{-1}mol^{-1}$.

(v) Heat capacity of gas from 300 K to 600 J at 1 atm. $C_{pm}(g)$ = 50.0 $JK^{-1}mol^{-1}$.

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 +182.4JK^{-1} for the reaction as stated. $\Delta H_{combustion \, [glucose]}$ = -2808 KJ

Q.26 The entropies of $H_2(g)$ and H(g) are 130.6 and 114.6 J mol^{-1} K^{-1} respectively at 298 K. Using the data given below calculate the bond energy of H_2 (in kJ/mol):

$H_2(g) \rightarrow 2H(g)$; $\Delta G°$ = 406.62 kJ/mol

Q.27 Calculate the heat produce when 3.785 lit of octane (C_6H_{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 C_6H_{18} is -1302.7 kcal/mol.

$\Delta H°_r CO_2(g)$ = -94.05 kcal mol^{-1};

$\Delta H°_r CO(g)$ = -26.41 kcal mol^{-1}

$\Delta H°_r H_2O(l)$ = -68.32 kcal mol^{-1};

$\Delta H°_r H_2O(g)$ = -57.79 kcal mol^{-1}

Q.28 Calculate ΔH_1 and ΔH_2.

(i) Cis -2-butene→trans-2- butene, ΔH_1

(ii) Cis -2-butene→1- butene, ΔH_2

(iii) Trans-2- butene is more stable than Cis -2-butene

(iv) Enthalpy of combustion of 1- butene,

ΔH = -649.8 kcal/mol

(v) $9\Delta H_1 + 5\Delta H_2 = 0$

(vi) Enthalpy of combustion of trans-2- butene, ΔH = -647.1 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: $XeF_4(g) \rightarrow Xe^+(g) + F^-(g) + F_2(g) + F(g)$, ΔH = 292 kcal

Q.30 Using the data (all values are in kJ/mol at 25°C) given below:

$\Delta H°_{combustion}$ (ethane)   = -1559.8

$\Delta H°_{combustion}$ (ethane)   = -1410.9

$\Delta H°_{combustion}$ (acetylene)   = -1299.7

$\Delta H°_{combustion}$ (acetaldyde)   = -1192.3

$\Delta H°_r$ $CO_2(g)$ = -393.5

$\Delta H°_r$ of $H_2O(l)$ = -285.8

$\Delta H°_r$ for C(graphite)→C(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 ≡ C

Exercise 2

Single Correct Choice Type

Q.1 For which of the following change $\Delta H \neq \Delta E$?

(A) $H_2(g) + I_2(g) \rightarrow 2HI(g)$

(B) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

(C) $C(s) + O_2(g) \rightarrow CO_2(g)$

(D) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Q.2 The reactions

$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g)$.
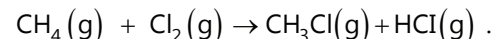
has $\Delta H = -25$ kCal

Bond	Bond Energy kCal
$\varepsilon_{C-Cl} \rightarrow$	84
$\varepsilon_{H-Cl} \rightarrow$	103
$\varepsilon_{C-H} \rightarrow$	x
$\varepsilon_{Cl-Cl} \rightarrow$	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,

$Au(OH)_3 + 4HCl \rightarrow HAuCl_4 + 3H_2O, \Delta H = -28$ kCal

$Au(OH)_3 + 4 HBr \rightarrow HAuBr_4 + 3H_2O, \Delta H = -36.8$ kCal
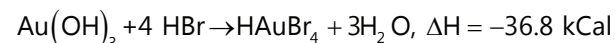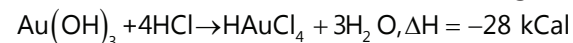
In an experiment there was an absorption of 0.44 kCal when one mole of $HAuBr_4$ was mixed with 4 moles of

HCl. What is the percentage conversation of $HAuBr_4$ into $HAuCl_4$?

(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) $x_1 + \dfrac{x_2}{2} - 2x_3 + x_4$ (B) $x_1 + \dfrac{x_2}{2} - 2x_3 - x_4$

(C) $x_1 + \dfrac{x_2}{2} - x_3 + x_4$ (D) $2x_3 - x_1 - \dfrac{x_2}{2} - x_4$

Q.5 For the allotropic change represented by the equation C (graphite) → C (diamond),

H = 1.9 kJ. If 6 g of diamond and 6 g of graphite are separately burnt to yield 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

Q.6 $NH_3(g) + 3Cl_2(g) \rightarrow NCl_3(g) + 3HCl(g); \Delta H_1$

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g); \qquad \Delta H_2$

$H_2(g) + Cl_2(g) \rightarrow 2HCl(g) ; \qquad \Delta H_3$
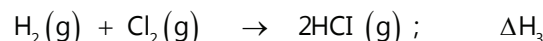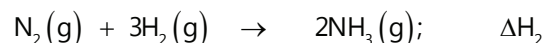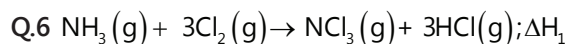
The enthalpy of formation of NCl_3 (g) in the terms of ΔH_1, ΔH_2 and ΔH_3 is

(A) $\Delta H_f = - \Delta H_1 + \dfrac{\Delta H_2}{2} - \dfrac{3}{2} \Delta H_3$

(B) $\Delta H_f = \Delta H_1 + \dfrac{\Delta H_2}{2} - \dfrac{3}{2} \Delta H_3$

(C) $\Delta H_f = \Delta H_1 - \dfrac{\Delta H_2}{2} - \dfrac{3}{2} \Delta H_3$

(D) None of these

Q.7 Ethanol can undergo decomposition to form two sets of products

$C_2H_5OH(g) \rightarrow \begin{vmatrix} \xrightarrow{\quad 1 \quad} C_2H_4(g) + H_2O(g) & \Delta H°=45.54\,kJ \\ \xrightarrow{\quad 2 \quad} CH_3CHO(g) + H_2(g) & \Delta H°=68.91\,kJ \end{vmatrix}$
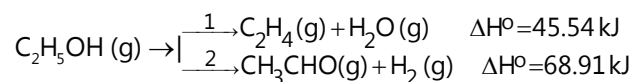
If the molar ratio of C_2H_4 to CH_3 CHO is 8: 1 in a set of product gases, then the enthalpy involved in the decomposition of 1 mole of ethanol is.

(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 1000K 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 360K.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 300^0C 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 100^0C and 1 atm pressure is converted into steam at 100^0C 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 ΔH and ΔS from this graph?
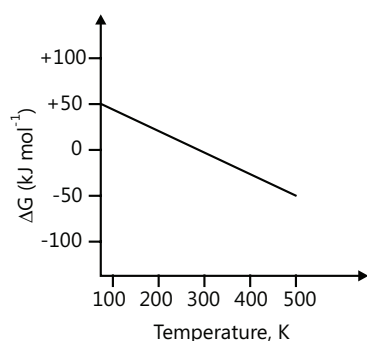
(A) $\Delta H > 0,\ \Delta S > 0$ (B) $\Delta H > 0,\ \Delta S < 0$

(C) $\Delta H < 0, \Delta S > 0$ (D) $\Delta H < 0,\ \Delta S < 0$

Q.12 If $\Delta H_{vaporization}$ of substance X (l) (molar mass: 30 g/mol) is 300 J/mol at it's 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 100^0C, (Given: Molar enthalpy of vaporization of water at 1 bar and 373 K = 41 kJ mol^{-1} an R=8.3 J mol^{-1}K^{-1}) will be   *(2007)*

(A) 4100 kJ mol^{-1} (B) 3.7904 kJ mol^{-1}

(C) 37.904 kJ mol^{-1} (D) 41.00 kJ mol^{-1}

Q.2 For the reaction, $2CO + O_2 \rightarrow 2CO_2;\ \ \Delta H = 560kJ$

Two moles of CO and one mole of O_2 are taken in a container of volume 1L. They completely form two moles of 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 ΔU 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_8 and freezing point is $T_{A'}$ then correct variation shown by graph between entropy change and temperature is   *(2001)*
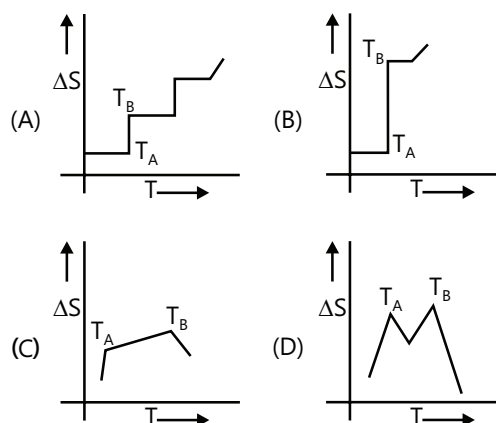
Q.4 Identify the correct statement regarding a spontaneous process   *(2007)*

(A) For a spontaneous process in an isolated system, the change in entropy is positive.

(B) Endothermic processes are never spontaneous

(C) Exothermic process 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) ΔH is $-$ve, ΔS is $+$ve

(B) ΔH and ΔS both are +ve

(C) ΔH and ΔS both are -ve

(D) ΔH is $+$ve, ΔS is $-$ve

Q.6 The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75 J mol^{-1} 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, 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:

$(\Delta_f G° H^+_{(aq)} = 0)$

$H_2O(l) \rightarrow H^+(aq) + OH^-(aq); \Delta H = 57.32$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) ; \Delta H = -286.20$kJ
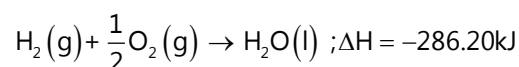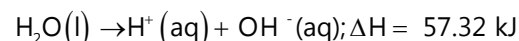
The value of enthalpy of formation of OH^- ion at $25°C$ is **(2009)**

(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 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 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

$$\frac{1}{2}Cl_2(g) \xrightarrow{\frac{1}{2}\Delta_{diss}\overset{\ominus}{H}} Cl(g) \xrightarrow{\Delta_{eg}\overset{\ominus}{H}} Cl^-(g) \xrightarrow{\Delta_{hyd}\overset{\ominus}{H}} Cl^-(aq)$$
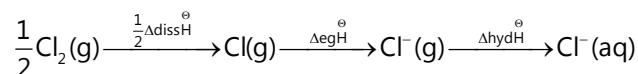
The energy involved in the conversion of

$$\frac{1}{2}Cl_2(g) \text{ to } Cl^-(aq)$$
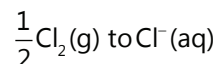
(Using the data $\Delta_{diss}HCl_2$= 240 kJmol^{-1}, $\Delta_{eq}H_{Cl}$ = -349 kJmol^{-1}, $\Delta_{hyd}H_{Cl}$ = -381kJmol^{-1}) will be **(2008)**

(A) -610 kJmol^{-1} (B)-850 kJmol^{-1}

(C) +120 kJmol^{-1} (D) +152 kJmol^{-1}

Q.11 If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1:1: 0.5 and $\Delta_f H$ for the formation of XY is -200kJmole^{-1}. The bond dissociation energy of X_2 will be **(2005)**

(A) 100 kJmol^{-1} (B) 800 kJmol^{-1}

(C) 300 kJmol^{-1} (D) 400 kJmol^{-1}

Q.12 Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C=C bond in $C_2 H_2$. That energy is (take the bond energy of a C $-$ H bond as 350 kJ mol^{-1})

$2C(s) + H_2(g) \rightarrow C_2H_2(g) ; \Delta H = 225$kJmol^{-1}

$2C(s) \rightarrow 2C(g); \quad \Delta H = 1410$kJmol^{-1}
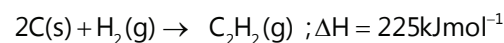
$H_2(g) \rightarrow 2H(g); \quad \Delta H = 330$kJmol^{-1} **(2012)**

(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, ΔH and ΔS 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, ΔH is not equal to ΔE *(1995)*

(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(B) $C(g) + O_2(g) \rightleftharpoons CO_2(g)$

(C) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(D) $HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O$

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 J/mol K) (ln 7.5 = 2.01)

(A) q = +208 J, w = -208 J

(B) q = - 208 J, w = -208 J

(C) q = -208 J, w = + 208 J

(D) q = +208 J, w = + 208 J

Q.17 For complete combustion of ethanol,

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
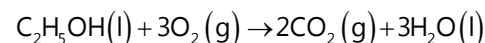
The amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol⁻¹ at 25°C. Assuming ideality the enthalpy of combustion, Δ_cH, for the reaction will be (R = 8.314 kJ mol⁻¹) *(2014)*

(A) -1366.95 kJ mol⁻¹   (B) -1361.95 kJ mol⁻¹

(C) -1460.50 kJ mol⁻¹   (D) -1350 kJ mol⁻¹

Q.18 The following reaction is performed at 298 K

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
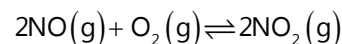
The standard free energy of formation of NO(g) is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_2(g)$ at 298 K? $(K_p = 1.6 \times 10^{12})$

(2015)

(A) $R(298) \ln(1.6 \times 10^{12}) - 86600$

(B) $86600 + R(298) \ln(1.6 \times 10^{12})$

(C) $86600 - \dfrac{\ln(1.6 \times 10^{12})}{R(298)}$

(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 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 C_2H_6 (g) are completely burnt 3120 kJ of heat is liberated. Calculate the enthalpy of formation, of $C_2H_6(g)$. Given Δ_fH for CO_2 (g) and H_2O (l) are – 395 & 286 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 kJ mol⁻¹ respectively.

Q.3 From the following data at 25° C, calculate the standard enthalpy of formation of FeO(s) and of Fe_2O_3 (s).

Reaction	Δ_r H° (kJ/mole)
(A) $Fe_2O_3(s) + 3C(g) \rightarrow$ $2Fe(s) + 3CO(g)$	492.6
(B) $FeO(s) + C(g) \rightarrow$ $Fe(s) + 3CO(g)$	155.8
(C) $C(g) + O_2(g) \rightarrow CO_2(g)$	-393.51
(D) $CO + 11O_2(g) \rightarrow CO_2(g)$	-282.98

Q.4 Using bond enthalpy data, calculate enthalpy of formation of isoprene.

$$5C(s) + 4H_2(g) \rightarrow H_2C = \underset{\underset{CH_3}{|}}{C} - \underset{\underset{H}{|}}{C} = CH_2(g)$$
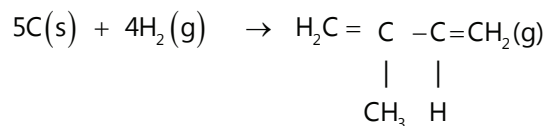
Given: C – H = 98.8 k Cal;   H – H = 104 k Cal;

           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

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$
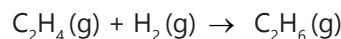
Data:

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⁻¹] bond enthalpy of:

C- H = 413.4;	C – C = 347.0;	(C = 0 = 728.0;
(0 = 0) = 495.0;	H – H = 435.8;	Δ_{sub}H of C = 718.4

Q.7 Calculate the enthalpy change when infinitely dilute solution of $CaCl_2$ and Na_2CO_3 are mixed $\Delta_f H°$ for Ca^{2+} (aq), CO_3^{-2} (ap) and $CaCO_3$ (s) are – 129.80, - 161.65, - 288.5 k Cal mol⁻¹ respectively.

Q.8 The enthalpies of neutralization of NaOH & NH_4OH by HCl are - 13680 Cal and - 12270 Cal respectively. What would be the enthalpy change if one gram equivalent of NaO H is added to one gram equivalent of NH_4Cl in solution? Assume that NH_4OH and NaCl are quantitatively obtained.

Q.9 1.00 Lit sample of a mixture of CH_4 (g) and O_2 (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_2 and H_2O caused a temperature rise, in the Calorimeter, of$\Delta H°_{comb}$ (CH_4) = -215 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/cm³, 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⁻¹ at 25°C ΔH_{diss} (F_2) = 160, $\Delta_f H$ (NaF(s)) =571, I. E. [Na (g)] = 494, ΔH_{vap}[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⁻¹)	414	351.5	464.5	494	711

Resonance energy of CO_2 = - 143 kJ mol⁻¹

Latent heat of vaporization of methyl alcohol = 35.5 kJ mol⁻¹

Latent heat of vaporization of water = 40.6 kJ mol⁻¹

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 ΔS_{gas} and ΔS_{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 22kJ 1mol. Find out $\Delta S_{vaporization}$ for liquid 'A' at 200 K? The normal boiling point of liquid 'A' is 300 K.

$$A\ (l)\ \left[200\ K\ 1\ atm\right] \to A\ (g)\ \left[200\ K\ 1\ atm\right]$$
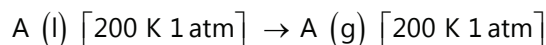
Given: $C_{p.m}(A, g) = 30$ J 1 mol-K, $C_{p,,m}(A, l) = 40$ J1mol – K; Use: ln (312) = 0.405

Q.17 One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate $\Delta S_{system,}$ ΔS_{suit} and ΔS_{total} in

(i) When the process carried out reversibly.

(ii) When the process carried out irreversibly (one step)

Q.18 Compute $\Delta_r G$ for the reaction H_2O (l, 1 atm, 323 K) $\to H_2O$ (g, 1 atm, 323 K)

Given that: $\Delta_{vap}H$ at 373 K = 40.639 kJmol^{-1}, $C_p(H_2O,l)$ = 75.312 J K^{-1} mol^{-1},

$C_p(H_2O,G)$ = 33.305 J K^{-1} mol^{-1}.

Q.19 10g of neon initially at a pressure of 506.625kPa and temperature of 473 K expand adiabatically to a pressure of 202.65kPa. Calculate entropy change of the system and total entropy change for the following ways of carrying out this expansion.

(i) Expansion is carried out reversibly.

(ii) Expansion occurs against a constant external pressure of 202.65kPa.

(iii) Expansion is a free expansion.

Q.20 At 298 K, $\Delta H°_{combustn}$ (sucrose) = -5737 KJ^{-1} mol and $\Delta G°_{combustn}$ (sucrose) = -6333 KJ 1 mol.

Q.21 The standard enthalpy of formation of FeO & Fe_2O_3 is – 65 kCal mol^{-1} and -197 kCalmol^{-1} respectively. A mixture of two oxides contains FeO & Fe_2O_3 in the mole ratio 2:1. If by oxidation, it is changed into a 1:2 mole ration 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

(a) Constant pressure.

(b) Constant volume

Given: $\Delta H°_f$ (HgO(s) = -90.8 kJ mol^{-1} & M (Hg) = 200.6 g mol^{-1}

Q.24 For reduction of ferric oxide by hydrogen,

$$Fe_2O_3(s) + 3H_2(g) \to 2Fe(s) + 3H_2O(l)$$
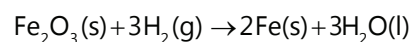
$\Delta H°_{298}$ = -35.1 kJ. The reaction was found to be too exothermic to be convenient. It is desirable that $\Delta H°$ should be at the most – 26kJ. At what temperature is it possible?

$$C_P\left[Fe_2O_3\right] = 104.5,\quad C_P\left[Fe(s)\right] = 25.5,$$
$$C_P\left[H_2(l)\right] = 75.3,\ C_P\left[H_2(g)\right] = 28.9$$

(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:

$$\Delta H°_f\left(Al_2O_3\right)\ = -399k\ Cal/mole;$$

$$\Delta H°_f\left(Fe_2O_3\right)\ = -199k\ Cal/mole,$$

Density of $Fe_2\ O_3$ = 5.2 g/cc; density of Al = 2.7 g/cc.

Q.26 Calculate the enthalpy change for the reaction

$$Xe\ F_4 \quad \to \qquad Xe^+ + F^- + F_2 + F$$
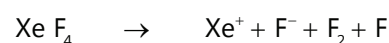
The average Xe–F bond enthalpy is 34 K Cal/mol, first I E. of Xe is 279 k Cal/mol, electron affinity of is 85 k Cal/mol & bond dissociation enthalpy of F_2 is 38k Cal/mol.

Q.27 Calculate the proton gain enthalpy of NH_3 (g) from the following data (in kJ/mole)

$\Delta H°_{dissociation:}$ $H_2(g)$ = 218; $\qquad \Delta H°_{dissociation:}$ $Cl_2(g)$ = 124

$\Delta H°_{formation:}$ $NH_3(g)$ = -46; $\qquad \Delta H°_f$:NH_4 Cl(s) = -314

Lattice enthalpy of NH_4 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?

$\Delta H°_{comb}(CO) = -280 kJmol^{-1}$. 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→2B (g) +H (g)} from the given data.

$\Delta H°_t [BH_3 (g)] = 100$ kJ/mole

$\Delta H°_t [B_2H_6 (g)] = 36$ kJ/mole

$\Delta H_{atm} [B(s)] = 565$ kJ/mole

$\Delta H_{atm} [H_2 (g)] = 436$ 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.

$N_2H_4(l) + O_2 (g) →N_2(g) + 2H_2O(l)$ What is the enthalpy combustion of N_2H_4 (kJ/mole).

Given Reaction	ΔH/kJ
$2NH_3(g) + 3N_2O(g) → 4N_2(g) + 3H_2O(l)$	1011 kJ
$N_2O(g) + 3H_2(g) → N_2H_4(l) + H_2O(l)$	-317 kJ
$4NH_3(g) + O_2(g) → 2N_2H_4(l) + 2H_2O(l)$	286 kJ
$H_2(g) + 1/2O_2(g)→H_2O(l)$	-385kJ

(A) -620.5   (B) -622.75

(C) 1167.5   (D) +622.75

Q.2 Find $\Delta_r U°$ for the reaction $4HCl(g) + O_2(g) → 2Cl_2 + 2H_2O(g)$ at 300 K. Assume all gases are ideal.

Given: $H_2(g) + Cl_2(g)→2HCl(g)$

$\Delta_r H°_{300} = -184.5$ kJ/mole

$2H_2(g) + O_2(g)→2H_2O(g)$
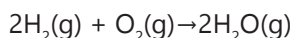
$\Delta_r H°_{300} = -483$ kJ/mole (Use R = 8.3 J/mole)

(A) 111.5 kJ/mole   (B) -109.01kJ/mole

(C) -111.5 kJ/mole   (D) None of these

Q.3 The enthalpy changes at the following reactions at 27°C are

$Na(s) + 1/2Cl_2(g) → NaCl(s)$

$\Delta_r H = -411$ kJmol

$H_2 (g) + S(s) + 2O_2 (g) → H_2SO_4 (l)$

$\Delta_r H = -811$ kJ/mol

$2Na(s) + S(s) + 2O_2 (g) → Na_2SO_4(s)$

$\Delta_r H = -1382$ kJ/mol

$1/2H_2 (g) + 1/2Cl_2(g) →HCl(g)$
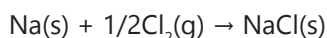
$\Delta_r H = -92$ kJ/mol;   R = 8.3 J/K-mol

From these data, the heat change of reaction at constant volume (in kJ/mol) at 27C for the purpose

$2NaCl(s) + H_2SO_4 (l)\rightleftharpoons Na_2SO_4 (s) + 2HCl(g)$ is
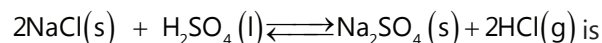
(A) 67   (B) 62.02   (C) 71.98   (D) None

Q.4 For the reaction at 300K A(g) + B(g) → C(g)

$\Delta E = -3.0$ kcal ; $\Delta S = -10.0$ cal/K; value of G is?

(A) -600 cal   (B) -6600 cal

(C) -6000 cal   (D) None

Q.5 What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°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 kJ/mol at 300 K. The enthalpy of vaporisation for liquid X and X_4 are respectively 30 kJ/mol and 72 kJ/mol respectively. ΔS for tetramerization of X in liquid phase is -125 J/Kmol at 300 K, what is the ΔG at 300 K for tetramirization of X in liquid phase?

(A) -52 kJ/mol   (B) -89.5 kJ/mol

(C) -14.5 kJ/mol   (D) None of these

Q.7 Standard entropy of X_2 Y_2 and XY_3 are 60, 40 and 50 JK^{-1}mol^{-1}, respectively. For the reaction
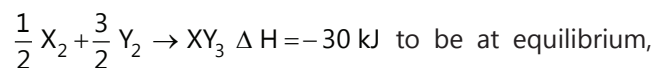
$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$ $\Delta H = -30$ kJ to be at equilibrium,

the temperature will be

(A) 1250 K   (B) 500 K   (C) 750 K   (D) 1000 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 contract into thermal contact and isolated from its surrounding. The total change in entropy of system is given by

(A) $C \ln \dfrac{T_c + T_h}{2T_c}$ (B) $C \ln \dfrac{T_2}{T_1}$

(C) $C \ln \dfrac{(T_{c-} + T_h)^2}{2T_h.T_c}$ (D) $C \ln \dfrac{(T_{c-} + T_h)^2}{4T_h.T_c}$

Q.9 Two moles of an ideal gas (C_m = 312 R) is subjected to following change of state.

A(500 K, 5.0 bar) $\longrightarrow$ B $\longrightarrow$ C (250 K, 1.0 bar)
Reversible isothermal expansion   Isochoric cooling   Single stage adiabatic compression
(3 bar) D $\longleftarrow$
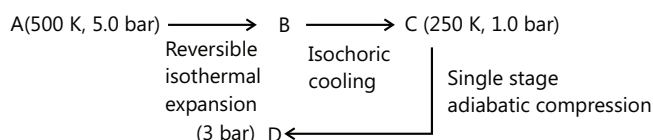
The correct statement is 1 are:

(A) The pressure at B is 2.0 bar

(B) The temperature at D is 450 K

(C) $\Delta H_{CD} = 1000$ R

(D) $\Delta U_{BC} = 375$ R

Multiple Correct Choice Type

Q.10 From the following data at 25^{0}C

Reaction	$\Delta_r H^0$ kJ/mol
$\frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \rightarrow OH(g)$	42

Reaction	$\Delta_r H^0$ kJ/mol
$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$	-242
$H_2(g) \rightarrow 2H(g)$	436
$O_2(g) \rightarrow 2O(g)$	495

Which of the following statement(s) is/ are correct:

(A) $\Delta_r H^0$ for the reaction H_2O (g) $\rightarrow$ 2H (g) + O (g) is 925.5 kJ/mol

(B) $\Delta_r H^0$ for the reaction OH (g) $\rightarrow$ H (g) + O(g) is 502 kJ/mol

(C) Enthalpy of formation of H (g) is -218 kJ/mol

(D) Enthalpy of formation of OH (g) is 42 kJ/mol

Q.11 Which is the following is true?

(A) For the reaction $CaCO_3$ (calcite) $\rightarrow CaCO_3$ (aragonite)

Given: $\Delta_f G^0_{298}$ (calcite) = -1128.8 kJ/mol, $\Delta_f G^0_{298}$ (calcite) = -1127.75 kJ/mol,

Then calcite forms in thermodynamically more stable at standard conditions.

(B) For the reaction,

(a) C (diamond) +2H$_2$ (g) $\rightarrow H_4$ (g) ΔH_1

(b) C (g) + 4H (g) $\rightarrow CH_4$ (g) ΔH_2
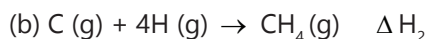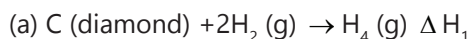
Then more heat is evolved in reaction (b)

(C) $\Delta_f H^0$ (I$_2$, g) = $\Delta_{sub} H$ [I$_2$, s] at 25^{0}C
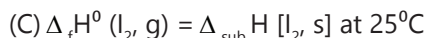
(D) For the exothermic reaction

2 Ag (s) +11O$_2$(g) $\rightarrow$ 2Ag$_2$O(s) at 298 K.
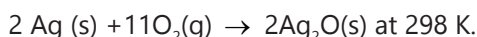
   $\Delta H < \Delta U$

Q.12 Which of the following statement (s) is /are true?

(A) When $(\Delta_{system})_{TP} < 0$; the reaction must be exothermic

(B) $\Delta 1_f H^0$ (S, monoclinic) $\neq 0$

(C) If dissociation enthalpy of CH_4 (g) is 1656 kJ/mol and C_2H_6 (g) is 2812 kJ/mole, then value of C-C bond enthalpy will be 328 kJ/mole

(D) If H$^+$(aq) + OH (aq) $\rightarrow H_2$O(l)

$\Delta_r H^0$= -56 kJ/mol

$\Delta_f H^0$(H$_2$O, g) = -242 kJ/mole; Enthalpy of vaporization of liquid water = 44 kJ/mol then $\Delta_f H^0$(H$_2$O, g) = -142 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
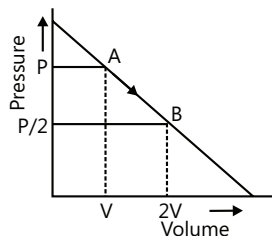
Select the correct statement(s) among the following

(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. ΔH_{vap} at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume ΔH_{vap} to be independent of pressure).

(A) $\Delta S_{vaporisation} > 100$ J/Kmole at 350 K and 0.5 atm

(B) $\Delta S_{vaporisation} > 100$ J/Kmole at 350 K and 0.5 atm

(C) $\Delta S_{vaporisation} > 100$ J/Kmole at 350 K and 2 atm

(D) $\Delta S_{vaporisation} > 100$ 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) $W_{adiabatic} > W_{isothermal}$ 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) ΔS_r and ΔH_r both are +ve for the decomposition of Mg $C_3(s)$

Q.17 If one mole monoatomic ideal gas was taken through process AB as shown in figure, then select correct option(s).
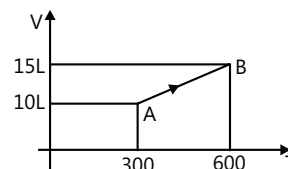
(A) W_{AB} = -2496.52J

(B) q_{AB} = 5237.82 J

(C) H_{AB}=3741.3 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

$$T \left(\frac{C_{pm}}{R} \right) P = constant$$

Q.19 Which of the following is true for reversible adiabatic process involving an ideal gas?

(A) Gas with higher Y has high magnitude of slope in a P (y-axis) vs T (x-axis) curve

(B) Gas with higher Y has high magnitude of slope in a V (y-axis) vs T (x-axis) curve

(C) Gas with higher Y has high magnitude of slope in a P (y-axis) vs V (x-axis) curve

(D) Gas with higher Y has high magnitude of slope in a P (y-axis) vs V (x-axis) curve

Q.20 100 ml 0.5 N H_2SO_4 (strong acid) is neutralised with 200 ml 0.2M NH_4OH in a constant pressure Calorimeter which results in temperature rise of 1.4°C. If heat capacity of Calorimeter content is 1.5 kJ/°C. Which statement is /are correct

Given:

$HCl + NaOH \rightarrow NaCl + H_2O + 57$ kJ

$CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O + 48.1$ kJ
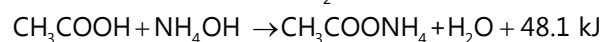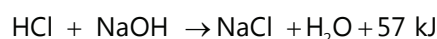
(A) Enthalpy of neutralisation of HCl v/s NH_4OH is -52.5 kJ/mol

(B) Enthalpy of dissociation (ionization) of NH_4OH is 4.5 kJ/mol

(C) Enthalpy of dissociation of CH_3COOH is 4.6 kJ/mol

(D) ΔH For $2H_2O(l) \rightarrow 2H(aq.) + 2OH^-$ is 114 kJ

Q.21 Which of the following does not represent ΔH formation of the product.

(A) $\frac{1}{2}H_2(g) + (aq) \rightarrow H^+(aq)$

(B) $\frac{2}{3}O_3(g) \rightarrow O_2(g)\ e^-$

(C) $NH_4^+(g) + Cl^-(g) \rightarrow NH_4Cl(s)$

(D) $P_4(black) + 5O_2(g) \rightarrow P_4O_{10}(s)$

(E) Reaction representing $\Delta H_{combustion}$ of $C\,(graphite)$

Q.22 Which of the following statements is /are false?

(A) ΔS for $\frac{2}{3}N_2$ (g) $\times$ N (g) is positive

(B) ΔG_{system} is always zero for a reversible process in a closed system

(C) ΔG^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) ΔH is zero

(C) ΔS_{gas} is +ve   (D) ΔG is +ve

Q.24 A piston cylinder device initially contains 0.2 m³ neon (assume ideal) at 200 kPa insideat T_1^0C. 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_2^0C ensures a constant temperature inside. Select correct statement(s) for given process
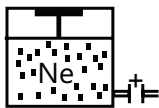
(A) ΔU must be zero   (B) ΔU cannot be zero

(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: S_8 (s) + O_2(g) $\rightarrow$ SO_2(g), represents complete combustion of S_8(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 –

13.7kCal/mol. If the enthalpy of neutralization of oxalic acid $(H_2C_2O_4)$ by a strong base in -25.4 kCal/mol, then the enthalpy changes (ΔH) of the process

$H_2C_2O_4 \rightarrow 2H^+ + C_2O_4^{2-}$ is 11.7 kCal/mol.

Statement-II: $H_2C_2O_4$ 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 K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes $(1/8)^{th}$ of initial volume.

Frictionless adiabatic piston

The gas in section 'A' is heated reversible

22.4L   22.4L

A   B

Adiabatic wall

Initial state
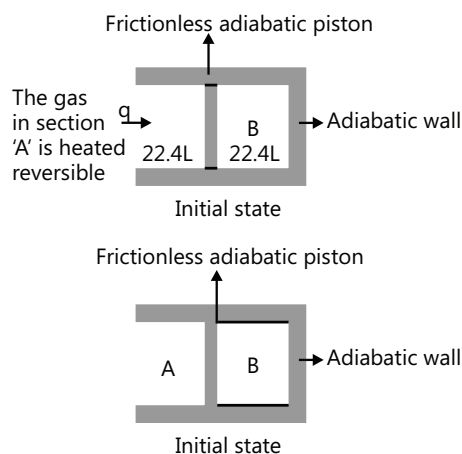
Given: R = 2 cal/mol-K, C_{vm} of monoatomic gas = $\frac{3}{2}$ R, At 1 atm & 0^0C ideal gas occupy 22.4 liter.

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 H_2O (l) at 353 K is 532 mm Hg. The external pressure on H_2O (l) taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (=0.9 kg) of H_2O (l) at 33 K is increased to 1 atm. Temperature remained constant. Now, heat is supplied keeping pressure constant till 0.45 L of H_2O (l) (=0.45 kg) is evaporated to form H_2O (g) at 373 K. carefully observe the diagrams provided and form given data, answer the following questions

Given:

Specific heat of H_2O = 4.2J/gm^{0}C

Use H_{vap} at 373 K and 1 atm =+40 kJ/mol

     1L atm = 100 Joule

     1 atm = 760 mm Hg

        R = 8 Joule/mole K

(Assume internal energy of liquid to be dependent only on temperature).
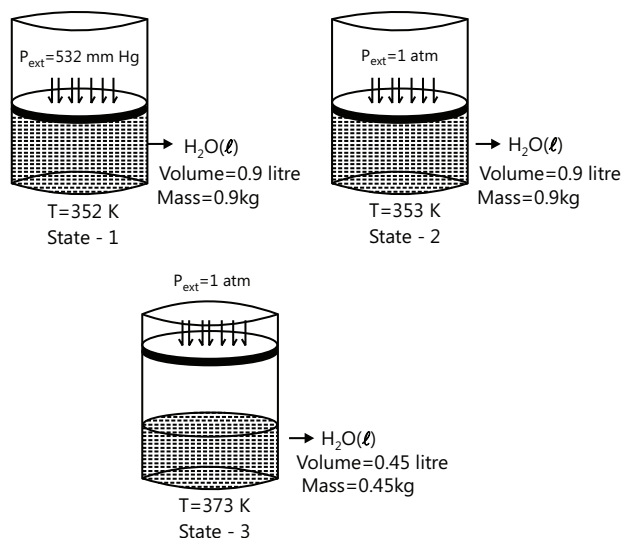
Q.32 ΔH When system is taken from state 1 to state 2 (Joule)?

(A) Zero   (B) 0.27   (C) 27   (D) 90

Q.33 Total change in ΔU 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
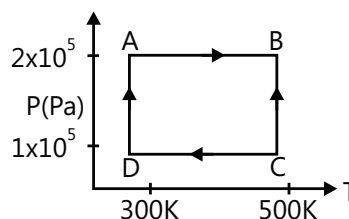
Q.36 Assuming the gas to be ideal the work done by the gas in taking it from A to B is

(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) $W = \int_{V_2}^{V_1} P_{ext}\, dV$

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) $\Delta S_{system} > 0$
(B) Reversible vaporisation	(q) $\Delta S_{system} < 0$
(C) Free expansion of ideal gas in vacuum	(r) $\Delta S_{surrounding} < 0$
(D) Dissociation of $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	(s) $\Delta S_{surrounding} = 0$

Previous Years' Questions

Q.1 The species which by definition has zero standard molar enthalpy of formation at 298 K is **(2010)**

(A) $Br_2(g)$ (B) $Cl_2(g)$ (C) $H_2O(g)$ (D) $CH_4(g)$

Q.2 The value of $\log_{10} K$ for a reaction $A \rightleftharpoons B$ is (Given: $\Delta_r H^\circ_{298K} = -54.07$ kJ mol^{-1},

$\Delta_r S^\circ_{298K} = 10$ JK^{-1} and R=8.314 JK^{-1} mol^{-1}; 2.303 × 8.314 × 298 = 5705) **(2007, 3M)**

(A) 5   (B) 10   (C) 95   (D) 100

Q.3 For the process H_2O (l) (1 bar, 373 K) → H_2O (G) (1 bar, 373 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

C   →   D
↑   ↓
A   B
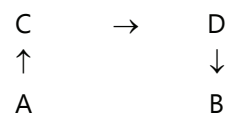
Given that $\Delta S_{(A \to C)} = 50$ eu

$\Delta S_{(C \to D)} = 30$ eu

$\Delta S_{(D \to B)} = 20$ eu

where eu is entropy unit. Then $\Delta S_{(A \to B)}$ 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) $\dfrac{4R}{2}$ (B) $\dfrac{3R}{2}$ (C) $\dfrac{5R}{2}$ (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 increases from 298.0 K to 298.45 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in mol^{-1} is **(2009)**

Q.9 For the reaction, $2CO + O_2 \rightarrow 2CO_2$; ΔH= -560 kJ. Two moles of CO and one mole of O_2 are taken in a container of volume 1 L. They completely form two moles of 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 ΔU 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 ΔH and ΔU. **(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 ration $\dfrac{W_d}{W_s}$ is **(2010)**
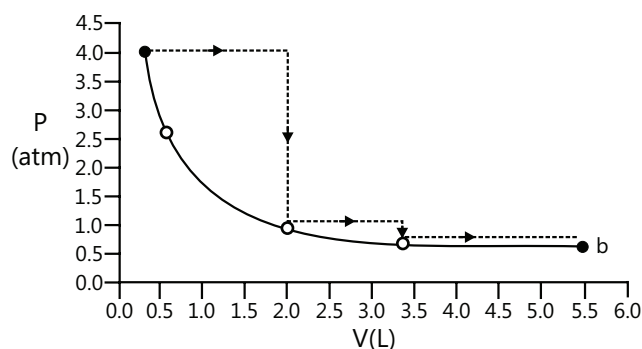
Read the following questions and answer as per the direction given below:

(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) $CO_2(s) \rightarrow CO_2(g)$	(p) Phase transition
(B) $CaCO_2(s) \rightarrow CaO(s) + CO_2(g)$	(q) Allotropic change
(C) $2H \rightarrow H_2(g)$	(r) ΔH is positive
(D) $P_{(white, solid)} \rightarrow P_{(red, solid)}$	(s) ΔS is positive
	(t) ΔS is negative

Q.16. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 250C are –400 kJ/mol, –300 kJ/mol and –1300 kJ/mol, respectively. The standard enthalpy of combustion per gram of glucose at 25^0C is *(2013)*

(A) +2900 kJ (B) – 2900 kJ

(C) –16.11 kJ (D) +16.11 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)*
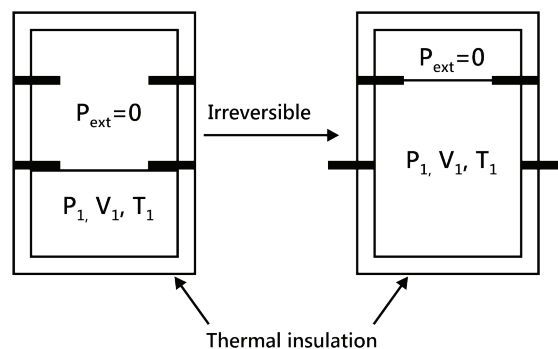
(A) q = 0 (B) $T_2 = T_1$
(C) $P_2V_2 = P_1V_1$ (D) $P_2V_2^\gamma = P_1V_1^\gamma$

Q.18 For the process $H_2O(l) \rightarrow H_2O(g)$ at T = 100°C and 1 atmosphere, the correct choice is *(2015)*

(A) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} > 0$

(B) $\Delta S_{system} > 0$ and $\Delta S_{surrounding} < 0$

(C) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} > 0$

(D) $\Delta S_{system} < 0$ and $\Delta S_{surrounding} < 0$

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 (ΔS_{surr}) in 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 J; w=20 J; Δ=-45J

Q.3 (a) 0.47 gm, (b) 0.47 kg

Q.4 -10 J

Q.5 q=177.9kJ, W = 2.5 kJ; ΔE=175.4kJ

Q.6 0.3024 kJ

Q.7 ΔE= 75.11 kJ

Q.8 ΔE = 0.993 Kcal, ΔH = 1 Kcal

Q.9 ΔH = 12168 calories; ΔE = 11623 calories

Q.10 ΔE = 27.91 kJ mol^{-1}, t = 514 sec.

Q.11 W_{in} = 9353.25 W_{in} =+17288.47 K, ΔU = ΔH = 0

Q.12 W= -3.988 kJ

Q.13 4.59 kJ

Q.14 q = 0; w = ΔU = 4.12 kJ; ΔH = 5.37 kJ V_f=11.8 dm^2, P= 5.21 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 K; T = 2436.0 K,

(b) ΔE = 0; q = W= +3262.88 cal

Q.17 (a) AC, (b) 170 J, (c) 10 J

Q.18 ΔH_{373} (H_2O (l)) = -284.11 kJ

Q.19 (a) 13.064 KJ mol^{-1}, (b) 10.587 kJ mol^{-1}

Q.20 T = 1059 K

Q.21 21.18 JK^{-1} Mol^{-1}

Q.22 (i) -90.5

(ii) -374.5

(iii) -3.26 (all in J mol^{-1} K^{-1})

Q.23 196.66°C

Q.24 205.08 JK^{-1} mol^{-1}

Q.25 -2864.5 KJ

Q.26 436 kJ mol

Q.27 Heat produced = -15549.7 kcal

Q.28 ΔH_1 = 0.96 kcal, ΔH_2 = 1.74 kcal

Q.29 Bond energy = 34 kcal/mol ; ΔH = 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^{-1}

Q.7   2.95 kCal

Q.8   -1410 Cal

Q.9   9.82 mol % CH_4

Q.10 **-**31.5 kJ mole

Q.11 -352 kJ mol^{-1}

Q.12 -669.7 kJ mole^{-1}

Q.13 (a) T_2 = 395.8; V_2=16.24L; W_{rev}=1194.72J.

       (b) $V_{1/2}$=17.24 L $T_{1/2}$=420K

       W_{rev}=1496.52J.

Q.14 w=P^0V^0; qCA= $-\dfrac{5}{2}$ P°V° ; qAB=3 3 P°V° ;

       qBC $-\dfrac{1}{2}$ P°V° T_{max}= $=\dfrac{25}{8}\left(\dfrac{P°V°}{R}\right)$

Q.15 (i) ΔS_{gas} = ΔS_{surr} and ΔS_{total}= 0,

       (ii) ΔS_{total}=2.808 JK^{-1}

       (iii) ΔS_{total}=9.134 JK^{-1}

Q.16 74.05 J/K

Q.17 (i) Rev. Process ΔS_{sys} $=\dfrac{3}{2}$R in 10 ;

       ΔS_{surr}= $-\dfrac{3}{2}$R In 10;

       (ii) In process ΔS_{sys} $=-\dfrac{3}{2}$R R In 10 ; ΔS_{surr}=$-\dfrac{3}{2}$R (0.9)

       ΔS_{total}=$-\dfrac{3}{2}$R (1.403)

Q.18 $\Delta G = 5.59$ kJ mol^{-1}

Q.19 (i) $\Delta S_{sys} = 0$; $\Delta S = 0$ and $\Delta S_{total} = 0$;

(ii) $\Delta S_{total} = \Delta S_{sys} = 0.957$ JK^{-1}

(iii) $\Delta S_{sys} = \Delta S_{total} = 3.81$ JK^{-1}

Q.20 24kJ/mol

Q.21 Heat released = 11.16 Kcal per mol of initial mixture.

Q.22 1: 3

Q.23 (a) 92.435g (b) 93.715g

Q.24 404.18K

Q.25 0.9345 k cal g^{-1}, 3.94 k Cal cm^{-3}

Q.26 292 kCalmol

Q.27 -718 kJmol

Q.28 (i) 13 times, (ii) 21.54 sec

Q.29 EB-H-B=455 kJmole

Q.30 -11420 cal

Exercise 2

Single Correct Chioce 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 Chioce 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 → p, r, s; B → q, s; C → q, s; D → s   **Q.40** A → s; B → p, r ; C → p, s; D → p, r

Previous Years' Questions

Q.1 B   **Q.2** C   **Q.3** A   **Q.4** B   **Q.5** A   **Q.6** A,B

Q.7 A, D, C   **Q.8** 9   **Q.9** -563 KJ   **Q.10** 9900   **Q.11** 2   **Q.12** B

Q.13 D   **Q.14** B   **Q.15** A → p, r, s ; B → r, s ; C → t; D → p, q, t   **Q.16** C

Q.17 C   **Q.18** B   **Q.19** C

Solutions

JEE Main/Boards

Exercise 1

Sol 1: (i) H_2O (g) → $H_2O(\ell)$

Volume of system ↓es

$W = -P\Delta V$

∴W +ve

(ii) $H_2O(s)$ → $H_2O(g)$

V system ↓es

$W = -P\Delta V$

$\Delta V > 0$, ∴ W –ve

(iii) $H_2O(s)$ → H_2O (l)

V↓es, $W = -\Delta V$, $\Delta V < 0$

∴ W +ve

(iv) $CaCO_3$ → $CaO(s)$ + $CO_2(s)$

V↑ es,

∴ $\Delta V > 0$ ∴ W < 0

Sol 2: Q = –65 J

W = 20J

(Contraction work done system)

$\Delta E = Q + W$

= 20 – 65 = – 45 J

Sol 3: $H_{combustion}$ = –2808 kJ/mol

(i) Energy × Eff = Change in potential energy.

∴ $\dfrac{\text{Mass of glucose}}{180} \times 2808 \times 10^3 \times \dfrac{25}{100}$

= 62.25 × 3 × 9.8

= 0.47 kg

Sol 4: $W = -P\Delta V$

= – 1 × (1.1 – 1)

= –0.1 atm

= –0.1 × 10^5 × 10^{-3}J = –10J

Sol 5: $\underset{\text{34.2 ml}}{CaCO_3} \longrightarrow \underset{\text{16.9 ml}}{CaO} + \underset{\text{24.4 L}}{CO_2}$

Q = +177.9 kJ

$W = -P\Delta V$

= – 1 × (24.4+16.9×10^{-3}–34.2 × 10^{-3})

= –1 × (24.4 – 17.3 × 10^{-3})

= –2438.27

∴ Q + W = ΔE

177.9 × 10^3 –2438.27=ΔE

∴ ΔE = 175.462 kJ

Sol 6: $W = -P\Delta V$

= –1.5(50–50–50)×10^{-3}

= –1.5 × –50 ×10^{-3} × 10^5 × 10^{-3}

W = 15 = 0.0075

H = −0.31

$\Delta V = \Delta H - \Delta(PV)$

$\Delta V = -0.31$ kJ + 0.15 kJ = 0.3025

Sol 7: ΔH_{vap} = 40.66 kJ/mol

ΔH_{gas} = 2 × 40.66 kJ

PV = nRT

1 × V = 2× 0.0821 × 373

V = 61.2466 L

$\Delta PV = 1(\Delta V) = 1(V_g - V_L)$

2 moles ∴ Mass of H_2O = 36g

d = 1 gm/cm³

∴ V = 36 cm³ = 36×10⁻³L

∴ $\Delta V = \dfrac{(61.2466 - 36 \times 10^{-3}) \times 10^2}{1000}$

$V_L << V_g \ \Delta V = V_g$

$\Delta V = \Delta H - \Delta PV$

= 81.32 − 6.125 = 75.1216

Sol 8: Q = 1 Kcal

P = 1 atm

$W = -\int PdV = -\int dV = -P\Delta V$

= − 1(1.5 − 1.2) × 10⁵ × 10⁻³ J

$= \dfrac{0.3 \times 10^2}{1000}$ kJ = 0.03 kJ

4.18 J = 1 cal

∴ $1J = \dfrac{1}{4.18}$ cal

∴ 0.03 kJ = −7.18 × 10⁻³ kcal

$\Delta E = Q + W$

= 1 − 7.8 × 10⁻³

= 0.993 kcal

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

= $\Delta E + P\Delta V$

= 0.993 + 7.8 × 10⁻³

= 1 k Cal

Sol 9: $V_{vapour} = \dfrac{nRT}{P} = \dfrac{1 \times 0.0821 \times 273}{4.6 / 760}$

= 3703.07 L

$\Delta H = \Delta H_{fusion} + \Delta H_{vap} + H$

0°C → 0°C

ice   water

$\Delta H = nCp\Delta T$

$\Delta T = 0$, ∴ $\Delta H_{process} = 0$

ΔH_{total} = (80 + 596) × 18 = 12168 cal

$\Delta E = \Delta H - (\Delta PV)$

= $\Delta H - P\Delta V$

= $12168 - \dfrac{4.6}{760} \times 3703.07$

= 12168 − 536.20

= 11623 cal

Sol 10: ΔH_{vap} = 30.84 kJ/mol

$V_{vap} = \dfrac{1 \times 0.0821 \times 353}{1}$

= 28.9 L

$W = -P\Delta V = +PV_{vap}$

= +0.0821 × 353 = 2.89 kJ

$\Delta E = \Delta H - \Delta PV$

= +30.84 − 2.89

= 27.91 kJ/mol

We know VIT = Q

$Q + W = \Delta E$

∴ $Q = \Delta E - W$

= $\Delta E + \Delta PV = \Delta H$

∴ 12 × 0.5 × t = 30.84 × 10³ × $\dfrac{7.8}{78}$

t = 514 sec.

Sol 11: p_i = 4 atm p_t = 1 atm

Const. external pressure of 1 atm.

$4V_i$ = 5 × 0.082 × 300

∴ V_i = 30.79

$V_t = 4 V_i$ = 123.16

$\Delta V = nC_v\Delta T$

$\Delta T = 0 \Rightarrow \Delta V = 0$

$\Delta H = nC_p\Delta T = 0$

$W_{rev} = \int -PdV = -\int \dfrac{nRT}{V}dV = -nRT \lambda n \ V_2/V_1$

= $-nRT \ln 4 = -5 \times 8.314 \times 300 \ln 4 = -17228.47$ J

$W_{air} = -P\Delta V = -P\Delta V = -1(123.16 - 30.79) \times 10^{-5} \times 10^3$

$= 9353.25$ J

Sol 12: $5 \times V_i = 1 \times V_f$ $\quad \therefore \dfrac{V_f}{V_i} = 5$

$w = -\int PdV = -\int \dfrac{nRT}{V}dV = -nRT \, \lambda n \, \dfrac{V_f}{V_i}$

$= -1 \times 8.314 \times 298 \times \lambda n \, 5 = -3.988$ kJ

Sol 13: $P(V_m - b) = RT$

$P = \dfrac{RT}{V_m - b}$

$w = -\int PdV = \dfrac{\dfrac{-RT}{V}dV}{\dfrac{V}{n} - b} = \int_{V_i}^{V_f} \dfrac{RT}{V - nb} dV$

$= -nRT \, \ell n\left(\dfrac{V_f - nb}{V_i - nb}\right)$

$= -2 \times 8.314 \times 300 \times \ell n\left(\dfrac{0.6 - 2 \times 0.1}{1.2 - 2 \times 0.1}\right)$

$= \dfrac{600}{1000} \times 8.314 \, \ell n\left(\dfrac{1.2 - 0.2}{0.6 - 0.2}\right)$ kJ

$= 0.6 \times 8.314 \, \ell n\left(\dfrac{1}{0.4}\right) = 4.59$ kJ

Sol 14: $2 \times V = 200 \times 3 \times 0.0821$

$V = 8.21 \times 3 \quad V_i = 24.63$L

$V^{r-1} = $ Constant

$\dfrac{T_i}{T_f} = \left(\dfrac{V_f}{V_i}\right)^{r-1}$

$\dfrac{200}{250} = \left(\dfrac{V_f}{24.63}\right)^{r-1}$

$C_v = 27.5$

$C_p = V_c + R = 27 + 8.314$

$r = \dfrac{C_p}{C_V} = \dfrac{27.5 + 8.314}{27.5} = 1.302$

$\left(\dfrac{200}{250}\right)^{\frac{1}{0.31}} = \dfrac{V_f}{24.63}$

$V_f = 11.79$ L $V_f = 11.8$ dm^2

$\Delta V = n\ell\Delta T = 3 \times 27.5 \times 50 = 4215 = 9.12$ KJ

$q = 0$ (idealistic process)

$\therefore \Delta V = W = 4.12$ kJ

$\Delta H = nC_p \Delta T = 3 \times 50 \times 35.81 = 5.37$ kJ

$\dfrac{P_f V_f}{T_f} = \dfrac{P_i V_i}{T_i}$

$\therefore P_f = \dfrac{2 \times 24.63 \times 256}{200 \times 11.8}$; $P_f = 5.21$ atm

Sol 15:
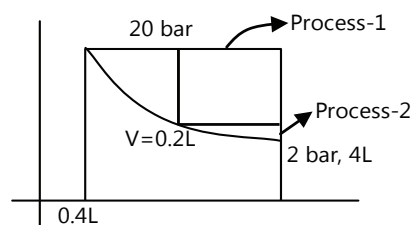
$V_f = \dfrac{2 \times 4}{20} = 0.4$

Process 1

$W = -nRT \ln\dfrac{V_f}{V_i} = PV \, \ln(V_f / V_i)$

$= -2 \times 8.314 \times \ln\left(\dfrac{0.4}{4}\right) \times T$

$W_{rev} = 18.424$ bar L

(ii) Single stage compression

$w = -P\Delta V = -20 \times (0.4 - 4)$

$= 3.6 \times 20 = 72$ 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 $C_V = \dfrac{3R}{2}$, $r = \dfrac{5}{3}$

$n = 1$ mole

$P_1 V_1 = nRT_1$

$2 \times 10 = 1 \times 0.0821 \, T_1$

$\therefore T_1 = 243.60$ K

In step (BC)

W = 0

Volume const.

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \quad \frac{20}{2} = \frac{T_2}{243.60}$$

$\therefore T_2 = 2436$ K

W = 0 as dV = 0   q = $\Delta V = nC_V \Delta T$

$$= \frac{3}{2}R \times 2 \times (-2436 + 243.6)$$

$= 3 \times 8.314 \times 2192.4$

$= -54682.841$ J

In process A – B

W = – PdV

= – PΔV

= – 20 × (10-1)

= – 180 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 = ΔV – W

$$= \frac{54682.841}{4.18} + \frac{18000}{4.18} = 17388.24 \text{ J}$$

In process (CA)

$\Delta T = 0 \Rightarrow \Delta V = 0$

$$Q = W = -\int PdV = +PV \ln\frac{V_i}{V_f}$$

$$= +20 \times 1 \times \lambda n\left(\frac{20}{1}\right) = \frac{59.914 \times 100}{4.18}$$

$$W_{total} = \frac{5991.46}{4.17} - \frac{18000}{4.17} = -3262 \text{ cal.}$$

Sol 17:
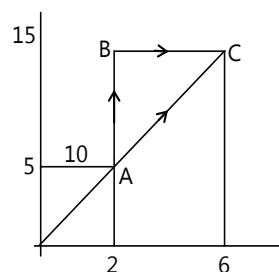
Work done is area under the PV curve

∴ Work done under A–C curve is least.

$Q_{AC} = 200$ J

$$W_{AC} = -\int PdV$$

$$\left(P = \frac{5}{2}V\right) \text{ along AC}$$

$$W_{AC} = -\int_2^6 \frac{5}{2}VdV$$

$$W_{AC} = -\frac{5}{4}V^2 \Big|_2^6$$

$$= \frac{-5}{4}\left(6^2 - 4\right) = \frac{-5}{4} \times 4(9-1)$$

$= -5 \times 8 = -40$

V = Q + W

$V_C - V_A = 200 - 40$

$V_C = 10 + 200 - 40$

$V_C = 170$ J

From A–B

W = 0 as ΔV = 0

∴Q = ΔV = 10 J

Sol 18: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O \,(\ell)$
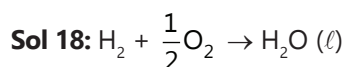
$\Delta H_{reac} = -285.76$

$$\Delta H_{(373)} = \Delta H_{298} + \int_{298}^{373} nC_p\Delta T$$

$$\Delta H_{373} = -285.76 + \int 75.312 - 38.83 - \frac{29.16}{2}$$

$$= -285.76 \times 10^3 + 21.902 \text{ T } \Big|_{298}^{375}$$

$= -285.76 \times 10^3 + 21.902 \times 75$

$\Delta H_{373} = -284.11$ kJ

Sol 19: ΔH = nCpΔT

$10^5 \times V = 8.314 \times 298$;

$V = 24.77$ l, $T_f = 2T = 596$;

$V_f = 2V = 24.77 \times 2 = 49.54$;

$$\Delta H = n\int Cp\Delta V = \int CpdT ;$$

$$= \int_{298}^{596} (22.34 + 4.81 \times 10^{-3}\,T)dT$$

$$= 22.34T + \frac{48.1}{2} \times 10^{-3}\,T^2$$

$$= 22.34 \times 298 + \frac{48.1}{2} \times 10^{-3}\,(596^2 - 298^2)$$

$$= 6657.32 + 6407.21$$

$$\Delta H = 13.064$$

$$\Delta V = \Delta H - \Delta PV = H - P\Delta V$$

$$= 13.064 - \frac{10^5 \times 24.77}{1000} \times 10^{-3}$$

$$= 13.064 - 2.477 = 10.587$$

Sol 20: Q = 30.5 kJ

$$\Delta S = 28.8$$

$$\Delta S = \frac{Q_{rev}}{T}$$

$$28.8 = \frac{30.5 \times 10^3}{T} \qquad \therefore T = 1059K$$

Sol 21: $T_1 = 300$; $T_2 = 600$, P = 1 bar

$$\Delta S = \int n\frac{Cp}{T}\frac{dT}{T_1} + nR\,\ln\frac{P_2}{P_1}$$

$$\Delta S = \int n\frac{Cp\,dT}{T}$$

$$= \int \frac{n \times 25.5 + 13.6 \times 10^{-3} - 42.5 \times 10^{-7}\,T^2}{T}$$

$$\Delta S = 25.5\,\ln\frac{T_2}{T_1} + 13.6 \times 10^{-3}\,T\Big|_{300}^{600}$$
$$- 42.5 \times 10^{-7}\,(T_2{}^2 - T_1{}^2)$$

$$= 25.5\,\ln 2 + 13.6 \times 10^{-3} \times 300$$
$$- 42.5 \times 10^{-7}\,(600^2 - 300^2)$$

$$= 17.67 + 4.08 - 0.1475$$

$$= 21.18\ J\ K^{-1}\ mol^{-1}$$

Sol 22: $2Na + Cl_2 \rightarrow 2NaCl$

$$\Delta S = 2 \times S_{NaCl} - S_{Cl_2} - 2 \times S_{Na}$$

$$= 2 \times 72 - 223 - 2 \times 51$$

$$\Delta S = -181/2 = -90.5$$

$$N_2 + 4H_2 + Cl_2 \rightarrow 2NH_4Cl$$
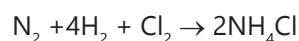
$$\Delta S = \left(2 \times S_{NH_4Cl} - S_{Cl_2} - S_{V_2} - 4S_{H_2}\right)/2$$

$$= 2 \times 95 - 223 - 192 - 4 \times 131$$

$$= -749/2 = -374.5$$

$$C_{graphite} - C_{diamond}$$

$$\Delta S = S_{diamond} - S_{graphite}$$

$$= 2.43 - 5.69 = -3.26$$

Sol 23: Efficiency = 40%

$$0.4 = 1 - \frac{T_L}{T_H}$$

$$\frac{T_L}{T_H} = 0.6$$

$$\frac{273 + 7}{T_H} = 0.6$$

$$\therefore T_H = \frac{280}{0.6} = 466.6\ K = 193.66°C$$

Sol 24:

$$\int_0^{600} S = \int_0^{200} S + \frac{H_{fus}}{T} + \frac{T_{vap}}{T} + \int_{200}^{300} S + \int_{300}^{600} S$$

$$S_{600} = \int_0^{200} \frac{dT^{0.034T}}{T} + \frac{7.5 \times 10^3}{200} + \int_{200}^{300} \frac{60 + 0.016T}{T}$$

$$+ \frac{30 \times 10^3}{300} + \int_{300}^{600} \frac{50.dT}{T}$$

$$= 7 + 0.035\,(200-0) + 37.5 + 60\,\lambda n\left(\frac{300}{200}\right)$$

$$+ 0.016(300-200) + \frac{30000}{600} + 50\,\lambda n\left(\frac{600}{300}\right)$$

$$= 37.5\,T + 24.328 + 1.6 + 34.657 + 100 = 205.08J$$

Sol 25: $\Delta H_{combush} = -2808$

$$\Delta S = 182.4$$

$$T = 37° = 310\ K$$

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

$$= \left(-2808 - \frac{310 \times 182.4}{1000}\right)KJ$$

$$\Delta G = -2864.5$$

Sol 26: $H_2 \rightarrow 2H$ S^0 130.6 114.6

$\Delta S^\circ = 2 \times 114.6 - 130.6 = 98.6$

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

$406.62 \times 10^3 = \Delta H^\circ - 298 \times 98.6$

$\Delta H^\circ = \left(406.62 + \dfrac{298 \times 98.6}{1000}\right) KJ$

$\Delta H^\circ = 436$ KJ/mol H_2

Sol 27: $C_8H_{18} + 8.5\ O_2 \longrightarrow 8\ CO + 9\ H_2O(g)$
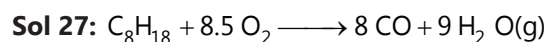
$V = 3.785 \times 10^3$ ml

$d = 0.702$ g/ml

$\therefore$ Mass $= 0.7025 \times 3.785 \times 10^3$ g $= 2658.9625$

Moles $= \dfrac{2658.9625}{114} = 23.33$ moles

given

$C_8H_{18} + 12.5\ O_2 \rightarrow 8\ CO + 9H_2O(\ell)$
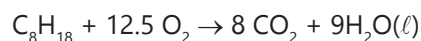
$\Delta H = -130.27$

$\Delta H_{comb} = -n\Delta H_{f\ reactant} - n\Delta H_{f\ product}$

$-1302.7 = \Delta H_f C_8H_{18} + 12.5$

$\times\ O_2 - 8 \times \Delta H CO_2 - 9 \times \Delta H_f H_2O$

$\therefore \Delta H_f\ C_8H_{18} = 13027 + 8 \times (-94.05) + 9 \times (-68.32)$

$\dfrac{\Delta H_{reactant}}{mol\ C_8H_{18}} = 8\ \Delta H_f\ (O) + 9 + \Delta H_{H_2O(g)} - 8.9 \times \Delta H_{f\ O_2}$

$-\Delta\ \Delta H_{f\ C_8H_{18}} + 64.58$

$= 8 \times (-26.41) + 9 \times (-57.79) - 666.80$

$\therefore \Delta H$ for given conditions $=$

$\Delta H_{reac} \times 23.33$

$= -666.80 \times 23.32 = -15549.7$

Sol 28: cis–2–butene $\rightarrow$ trans–2–butene $\Delta H < 0$

cis–2–butene = trans-2-butene $- \Delta H_2$

 $+\ 6\ O_2$

trans–2-butene $\rightarrow 4CO + 4H_2O$

Trans $\Delta H^\circ_{cumb} = \underbrace{4\Delta H_{CO_2} + 4\Delta H_{H_2O}}_{\Delta H} + \Delta H_f C_4H_8$
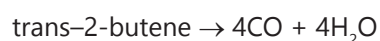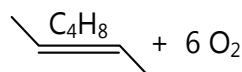
trans

$\Delta H^\circ_{comb} = 4\Delta H_{CO_2} + 4\Delta H_{H_2O} - \Delta H_{f_{C_4H_8}}$

1–butene Cis

$\Delta H_{f_{trans-2}} = \Delta H' + 649.8$ Kcal

$\Delta H_{f_{1-butene}} = \Delta H' + 647.1$ Kcal

$\Delta H_1 = \Delta H_{f_{trans}} - \Delta H_{f_{cis}}$

$\Delta H_2 = \Delta H_{f_{buten}} - \Delta H_{f_{cis}}$

$\Delta H_1 - \Delta H_2 = \Delta H_{f_{trans}} - \Delta H_{f_{cis}}$

$= 649.8 - 647.1$

$\Delta H_1 - \Delta H_2 = 2.7$

$\Delta H_1 + 5\Delta H_2 = 0$

$\Delta H_1 - \Delta H_2 = -2.7$

$\Delta H_1 + \dfrac{9}{4}\Delta H_1 = -2.7$

$\Delta H_1 = -0.964$ kcal

$\Delta H_2 = \dfrac{9}{5} \times 0.964$ kcal

$= 1.74$ kcal

Sol 29: $Xe \rightarrow Xe^+ + e^-$ $\Delta H = 279$

$F + e^- \rightarrow F^-$ $\Delta H = -85$ kcal/mol

$F_2 \rightarrow 2F$ $\Delta H = 38$ kcal/mol

$\left.\begin{array}{l} Xe \rightarrow Xe^+ + e^- \\ F_2 \rightarrow 2F \\ 2F + e^- \rightarrow F + F^- \end{array}\right\}$ Add ΔH
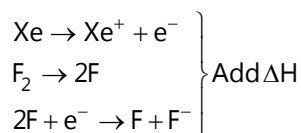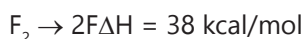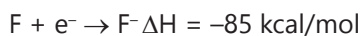
$\Delta H = -4 \times$ B.E.$_{Xe-F}$

$-\Delta H_{ion} - \Delta H_{+gain\ enthalpy} - \Delta H_{Bond\ energy}$

$292 = -4 \times x + 297 + 85 + 38$

$x = \dfrac{292 - 279 + 85 + 38}{4} = 34$

Sol 30: Combustion of ethane:

$CH_3 - CH_3 + \dfrac{7}{2}O_2 \rightarrow 2CO_2 + 3H_2O$
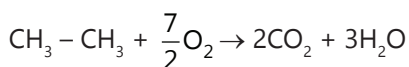
$\Delta H^\circ_{comb} = E_{C-C} + 6E_{C-H}$

$+ \dfrac{7}{2} E_{O=O} - 2\Delta H_{f_{CO_2}} - 3\Delta H^\circ_{H_2O}$

$-1559.8 = E_{C-C} + 6E_{C-H} + \dfrac{7}{2}(498.34) - 2(-39.5) - 3(-285.8)$

$E_{C-C} + 6E_{C-H} = -1460.01$ ...(i)

Combustion of Ethene:

$CH_2 = CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
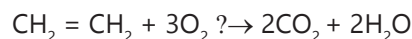
$\Delta H^o_{Comb} = E_{C=C} + 4E_{C-H}$

$+ E_{O=O} - 2H_{fCO_2} - 2\Delta H^o_{fH_2O}$

$-1410.9 = E_{C=C} + 4E_{C-H}$

$+ 3(498.34) - 2(-393.5) - 2(-285.8)$

$E_{C=C} + 4E_{C-H} = -1274.48$ ....(ii)

Combustion of Acetylene:

$CH \equiv CH + 5/2\ O_2 \rightarrow 2CO_2 + H_2O$
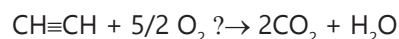
$\Delta H^o_{comb} = E_{C \equiv C} + 2E_{C-H} + 2E_{C-H}$

$+ 5/2E_{O=O} - 2\Delta H_{fCO_2} - 2\Delta H_{fH_2O}$

$-1299.7 = E_{C \equiv C} + 2E_{C-H}$

$+ 5/2(498.34) - 2(-393.5) - 2(-285.8)$

$E_{C \equiv C} + 2E_{C-H} = -1412.45$ .....(iii)

Combustion of Acetaldehyde:

$$\begin{matrix} & O \\ & \parallel \end{matrix}$$
$CH_3 - C - H + 5/2\ O_2 \rightarrow 2CO_2 + 2H_2O$
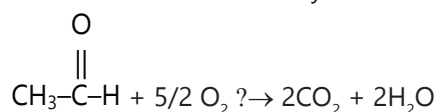
$\Delta H^o_{comb} = E_{C-C} + E_{C=O} + 4E_{C-H}$

$+ 5/2\ E_{o=o} - 2\Delta H_{fCO_2} - 2\Delta H_{fH_2O}$

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) $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

$\Delta H = -25$

$-25 = 4 \times C - H + 4Cl$

$- Cl - 3 \times CH - 1C - Cl - 1\ H - Cl$

$-25 = 4x + y - 3x - 84 - 103$

$y - x = 162$

$x = \dfrac{9}{5}\ y$

$\dfrac{9}{5}\ x + \dfrac{1}{5}\ x = 162$

$\dfrac{14}{5}\ y = 162$

$y = 57.75$ k cal

Sol 3: (C) $Au(OH)_3 + HAuCl_4$

$\rightarrow HAuCl_4 + 3\ H_2O$
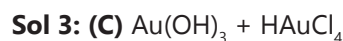
$36.8 + x \times -28 = 0.44$

$x(36.8 - 28) = 0.44$

$x = 0.05$

Sol 4: (B)

$H_2 + 1/2\ O_2 \longrightarrow H_2 O(l)$

$H_2O(g)$
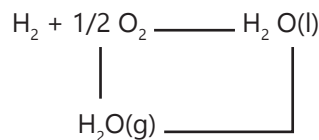
$\Delta H_{comb} = BE\ (H - 11) + \frac{1}{2}\ B.E\ (O = O - 2 \times B.E\ (OH)$

B.E. (vap)

$= x_1 + x/2 - 2 \times x_3 - x_4$

Sol 5: (C)

$C(graphite) \longrightarrow C(diameter)$
$\quad\quad\ \downarrow +O_2 \quad\quad\quad\quad \downarrow +O_2$
$\quad\quad\ CO_2 \quad\quad\quad\quad\quad CO_2$

$\Delta H = 1.9$ kJ

$C(graphite) + O_2 \rightarrow CO_2$

$\Delta H = \Delta H_f CO_2$
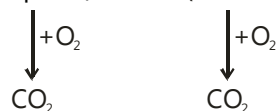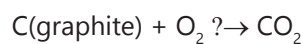
$C(graphite) + O_2 \Delta H \longrightarrow CO_2$
$\quad\quad \downarrow \quad\quad\quad\quad\quad\quad\ \uparrow$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\ CO_2$
$C\ graphite + O_2 \longrightarrow$
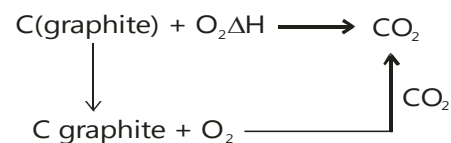
$\Rightarrow \Delta H' = \Delta H_{fCO_2} + \Delta H_{c-c\ graphite}$

$\Delta H' = \Delta H_f - 1.9$

Sol 6: (A) $NH_3 + 3 Cl_2 \rightarrow NCl_3 + 3HCl = -\Delta H_1$

$N_2 + 3H_2 \rightarrow 2NH_3 = \Delta H_2$

$H_2 + Cl_2 \rightarrow 2HCl = \Delta H_3$
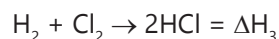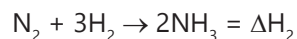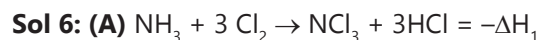
$-\Delta H_1 = 3\Delta H_f \, HCl + \Delta H_{fNCl_3} - \Delta H_f \, NO_3$

$\therefore \Delta H_{fNCl_3} = \dfrac{\Delta H_2}{2} - \dfrac{3\Delta H_3}{2} - \Delta H_1$

Sol 7: (B)

$$C_2H_5OH \begin{array}{l} \xrightarrow{\ \ 1\ \ } C_2H4 \ 8/9 \ \ +H_2O \ \ \Delta H°=45.54 \\ \\ \xrightarrow{\ \ 2\ \ } CH_3CHO \ \ \ H_2 \ \ \ \Delta H°=68.91 \end{array}$$
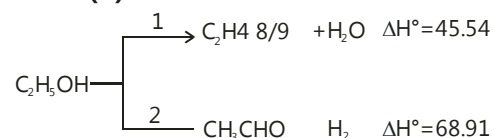
Molar ratio of $C_2 H_4$ to $CH_3 CHO$ = 8: 1

$\therefore$ Enthalpy per unit

$8x \, t \, x = 0$

$\therefore x = 1/9$

$\therefore \Delta H = \dfrac{1}{9} \times 45.54_4 \cdot \dfrac{8\times 68.91}{9} = 48.137$

Sol 8: (C) $E_1 = 1 - \dfrac{T_2}{1000}$

$E_1 = 1 - \dfrac{360}{T_2}$

$\therefore 1 - \dfrac{T_2}{1000} = 1 - \dfrac{360}{T_2}$

$\therefore (T_2)^2 = 360 \times 1000$

$T_2 = 600$

Sol 9: (C) Isochoric $\therefore V_1 = V_2$

$\Delta S = nC_v \ln \dfrac{T_2}{T_1} = nR \ln \dfrac{V_2}{V_1}$

$\therefore \Delta S = 2 \times \dfrac{3R}{2} \ln \left(\dfrac{300 + 273}{200 + 273} \right)$

$= 3R \ln \left(\dfrac{573}{473} \right)$

Sol 10: (C) $\Delta G = \Delta dP = \int \dfrac{nRT}{P} dP$

$= nRT \ln \dfrac{P_2}{P_1} = 517.13$

Sol 11: (A)
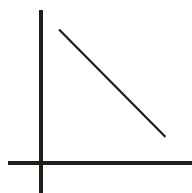
$\Delta G = \Delta H - T\Delta S$

$y = \Delta H - x \, \Delta S$

Slope is $-ve$

$\therefore \Delta S < 0$

$\therefore \Delta S > 0$ and intercept > 0

$\therefore \Delta H > 0$

Sol 12: (C) ΔH_{vap} = 300/g at T = 300 k

$= 300 \times 30$ J/mol

ΔS mole $= \dfrac{\Delta H_{moles}}{T} = \dfrac{300 \times 30}{300} = 30$ J/mol

Sol 13: (D) $P \times 20 = 2 \times 0.0821 \times 243.6$ k

P_i = 2 atm P_f = 1 atm

$\Delta S = -4R \ln \dfrac{P_2}{P_1}$

$= 2 \times \dfrac{8.314}{4.19} \ln 2 = 2.77$

Previous Years' Questions

Sol 1: (C) $H_2O_{(l)} \xrightarrow{\text{vaporization}} H_2O_{(g)}$
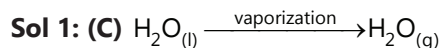
$\Delta n_g = 1 - 0 = 1$

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

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

$= 41 - 8.3 \times 10^{-3} \times 373 = 37.9$ 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, ΔG must be negative. According to the equation -

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

If ΔH and ΔS both are positive, than term T. ΔS will be

greater than ΔH at high temperature and consequently ΔG will be negative at high temperature.

Sol 6: (B) $dS = \dfrac{dQ_{rev}}{T}$; $T = \dfrac{30 \times 10^3}{75}$; $T = 400$ K

Sol 7: (A) $C_2H_6 + \dfrac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$ substitute the values.

Sol 8: (B) $H_2(g) + \dfrac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286.20$ kJ
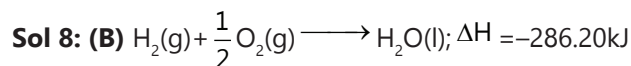
$\Delta H_r = \Delta H_f(H_2O, l) - \Delta H_f(H_2, g) - \dfrac{1}{2}\Delta H_f(O_2, g)$

$-286.20 = \Delta H_f(H_2O(l))$

So, $\Delta H_f(H_2O, l) = -286.20$

$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$; $\Delta H = 57.32$ kJ

$\Delta H_r = \Delta H_f^o(H^+, aq)\ \Delta H_f^o(OH^-, aq) - \Delta H_f^o(H_2O, l)$

$57.32 = 0 + \Delta H_f^o(OH^-, aq) - (-286.20)$

$\Delta H_f^o(OH^-, aq) = 57.32 - 286.20 = -228.88$ kJ

Sol 9: (D) Standard molar heat enthalpy (H^o) of a compound is equal to its standard heat of formation from most stable states of initial components.

Sol 10: (A) $\Delta H = \dfrac{240}{2} - 349 - 381$

$= 120 - 349 - 381 = -610$ kJ/mol

Sol 11: (B) $XY \longrightarrow X_{(g)} + Y_{(g)}$; $\Delta H = +a$ kJ/mole ...(i)

$X_2 \longrightarrow 2X$; $\Delta H = +a$ kJ/mole ... (ii)

$Y_2 \longrightarrow 2Y$; $\Delta H = +0.5a$ kJ/mole ... (iii)

$\dfrac{1}{2} \times$ (ii) $+ \dfrac{1}{2} \times$ (iii) $-$ (i), gives

$\dfrac{1}{2}X_2 + \dfrac{1}{2}Y_2 \longrightarrow XY$;
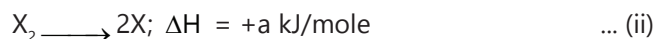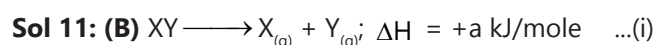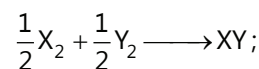
$\Delta H = \left(+\dfrac{a}{2} + \dfrac{0.5}{2}a - a\right)$ kJ / mole

$+\dfrac{a}{2} + \dfrac{0.5a}{2} - a = -200$; $a = 800$

Sol 12: (D)

$2C(s) + H_2(g) \longrightarrow C_2H_2(g)\ \Delta H = 225$ KJ/mol

$\downarrow \qquad \downarrow \qquad \qquad \uparrow\ -(2\varepsilon_{C-H} + \varepsilon_{C \equiv C})$

$2C(g) + 2H(g) \longrightarrow$
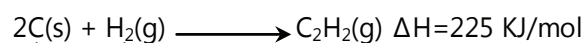
$\therefore \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{C \equiv C} = +225$

$\therefore \varepsilon_{C \equiv C} = 1740 - 700 - 225 = +815$ 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, $q = -w$; $\Delta u = 0$

$q = +208$ J

$w = -208$ J(expansion work)

Sol 17: (A) $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$
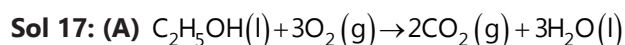
Bomb calorimeter gives ΔU of the reaction

So, as per question

$\Delta U = -1364.47$ kJ mol^{-1}

$\Delta n_g = -1$

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

$= -1364.47 - \dfrac{1 \times 8.314 \times 298}{1000}$

$= -1366.93$ kJ mol^{-1}

Sol 18: (D)

$2\Delta G_{f(NO_2)}^0 - \left[2\Delta G_{f(NO)}^0 + \Delta G_{f(O_2)}^0\right] = \Delta G_r^0 = -RT \ell n K_p$

$2\Delta G_{f(NO_2)}^0 - \left[2 \times 86,600 + 0\right] = -RT \ell n K_p$

$2\Delta G_{f(NO_2)}^0 = 0.5\left[2 \times 86,600 - R(298)\ell n(1.6 \times 10^{12})\right]$

Sol 19: (C) $C(S) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5$ kJ / mol

$CO(g) + \dfrac{1}{2}O_2(g) \rightarrow CO_2(g)$; $\Delta H = -283.5$ kJ / mol
$C(S) + \dfrac{1}{2}O_2(g) \rightarrow CO(g)$; $\Delta H = -393.5 + 283.5$ kJ / mol
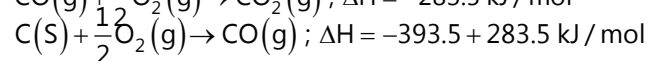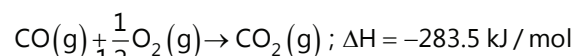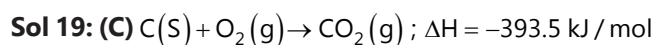
$= -110$ kJ / mol

JEE Advanced/Boards

Exercise 1

Sol 1: $2 C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
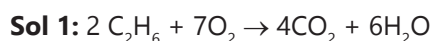
$\Delta H_{comb} = \Delta H$ for reactants $- \Delta H_f$ products

$3120 = 2 \times \Delta H_f (C_2 H_6)- 4 \times \Delta H$

$+ CO_2 - 6 \Delta HH_2O$

$\therefore \Delta H_f (C_2 H_6)= \dfrac{3120 - 4 \times 395 - 6 \times 286}{2} = 88$ KJ

Sol 2: $\Delta H_f (Cs_2)$

$C + O_2 \rightarrow CO_2 \ \Delta H_{comb.} = -393.3$

$S + O_2 \rightarrow SO_2 \ \Delta H_{comb.} = 293.72$

$CS_2 + 2O_2 \rightarrow CO_2 + 2SO_2 \ \Delta H_{comb.}$

$= -1108.76$

$\therefore C + S_2 \rightarrow CS_2$
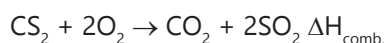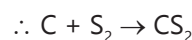
$-\Delta H_3 + \Delta H_1 + 2\Delta H_2$

$= 1108.76 - 393.3 - 2 \times 293.72$

$\Delta H = 128.02$

Sol 3: $Fe_2O_3 + 3C \rightarrow 2F_e + 3CO$

$FeO + C \rightarrow Fe(s) + CO$

$C(g) + O_2 \rightarrow CO_2$

$CO + \frac{1}{2} O_2 \rightarrow CO_2$

$Fe(s) + \frac{1}{2} O_2 \rightarrow FeO$

$Fe + CO \rightarrow FeO + C \ \Delta H = -155.8$

$C + O_2 \rightarrow CO_2 ; \Delta H = -393.51$

$CO_2 \rightarrow CO + \frac{1}{2} O_2; \Delta H = + 282.98$

$Fe+CO+C+O_2+CO_2 \rightarrow FeO+C+CO_2 +CO +H_2O_2+Fe+$

$\frac{1}{2}O_2 = FeO$
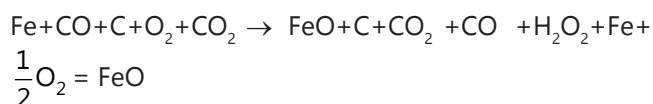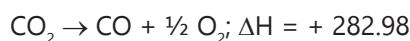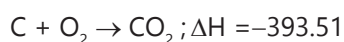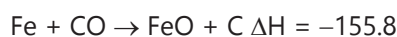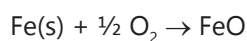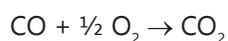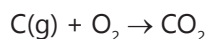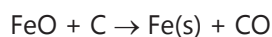
$\therefore \Delta H_f = -155.8 - 393.51 + 282.98 = -266.33$

$2Fe + 3/2 O_2 \rightarrow Fe_2O_3$

$2Fe + 3CO \rightarrow Fe_2O_3 + 3C \ \Delta H = -492.6$

$3C + 3O_2 \rightarrow 3CO_2 \ \Delta H = -3 \times 393.51$

$3CO_2 \rightarrow 3CO + 3/2 O_2 \ \Delta x = +3 \times 282.8$

$\therefore$ Here $2Fe + 3/2 O_2 \rightarrow Fe_2O_3$
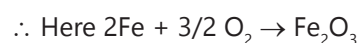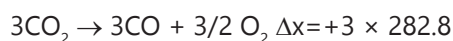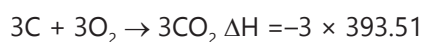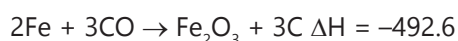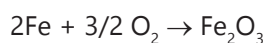
$\Delta H_2 = -492.6 - 3 \times 393.51 + 3 \times 282.98$

$= -824.2$

Sol 4:
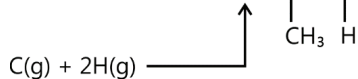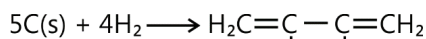
ΔH atom

$= \Delta H_{C(S) \rightarrow C(B)} + \Sigma BE_{(Reactants)} - \Sigma BE_{(products)}$

$\Delta H_{formation}$

$= 5 \times 171 + [4 \times 104 - 2 \times 83 - 2 \times 147 - 8 \times 98.8]$

$= 20.6$ K cal

Sol 5: $C_2 H_4 (g) + H_2 (g) \rightarrow C_2 H_6 (g)$
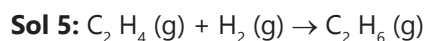
$\Delta H_{reaction} = \Sigma BE_{reactants} - \Sigma BE_{products}$

$= 1 \times C = C + 4 \times C{-}H - 1 \times C - E + 6 \times (-H)$

$= 1 \times C = C - 1 \times C{-}C = 2 \times C{-}4$

$= 606.68 + 431.79 - 336 - 81 - 2 \times 410.87$

$= -120.08$

Sol 6:
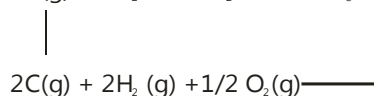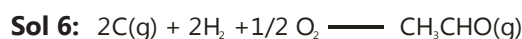
$\therefore \Delta H_f = 2 \times \Delta H_{sub} + \Sigma BE_{reactants} - \Sigma BE_{products} = 2 \times 718.4$

$+ \left[2 \times 435.8 + \dfrac{495}{2} - 4 \times 413.4 - 728.0 - 347.0 \right]$

$= -192.73$

Sol 7:
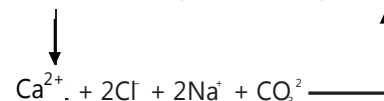
$\Delta H_{reac.} = -288.5 + 129.80 + 1261.65$

$= 2.98k$ cal

Sol 8: NaOH + HCl $\rightarrow$ NaCl (Strong acid–base)

$\therefore \Delta H^0 = -1368$ cal

ΔH NH$_4$OH + HCl $\rightarrow$ NH$_4$Cl + H$_2$O
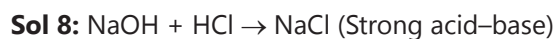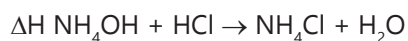
$\therefore \Delta H' = \Delta H - 1\Delta H_{diss} -12270$

= $-13680 + \Delta H_{diss}$

$\therefore \Delta H_{diss} = 1410$

Sol 9: $CH_4(g)+O_2(g)$ at T= 298 k $P=\dfrac{740}{766}$ atm

v = 1 L

$CH_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
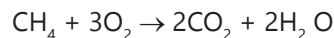
PV = nRT

$\dfrac{740}{760} \times 1 = n \times 0.0821 \times 298$

$\therefore n_E = 0.04$

$\Delta H_{rec} = 1260 \times 0.667$

$0.667 \times 1260 = n_{C_{H_4}} \times \Delta H_{co}$

$340 = n_{C_{H_4}} \times 215 \times 10^3$

$n_{C_{H_4}} = 0.0039$

$\therefore n_{C_{H_4}} = \dfrac{0.0039}{0.04} \times 100 = 9.82\%$

Sol 10: $HA + NaOH \rightarrow NaA + H_2O$

$\qquad \downarrow \qquad \downarrow$

$\qquad 400\times0.2 \ \ 100 \times 0.8$

$V_t = 400 + 100 = 500 \ cm^3$

$n = 1 \ g/cm^3$

$\therefore \Delta H = \dfrac{-500 \times 4.2 \times \Delta T}{1000} = -31.5 \ KJ$

Sol 11:

$Na(s) + 1/2 \ F_2 \longrightarrow NaF \longleftarrow$

$Na(g) \ + \ 4F \qquad\qquad Na^+ + F^{-1}$

$Na^+ \ \ - \ F^-$
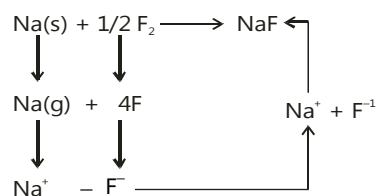
$\therefore \Delta H_f = \Delta H_{sap} + \dfrac{\Delta BE}{2} + I.E. \ \Delta H_{EG} + L.E.$

$-57 = 101 + \dfrac{160}{2} + 494 + \Delta H_{EG} \ 894$

$\Delta H_{EG} = -352$

Sol 12:

$CH_3OH + 3/2 \ O_2 \longrightarrow CO_2 + 2H_2O$

$\qquad \downarrow \qquad\qquad\qquad\qquad \downarrow$

$CH_3O(g) + 3/2 \ O_2 \longrightarrow CO_2 (g) + 2 \times H_2O(g)$
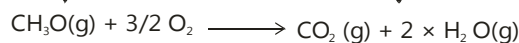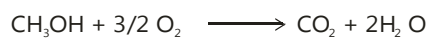
Resonance eng of $CO_2 + 43$

$\therefore \Delta H_{cob} = +35.5+$

$\Sigma BE_{react} - \Sigma B.E._{products} -40.0 \times 2$

$= 35.5 + 3/2 \times 494 + 351.5 + 464.5 + 3 \times 414 - 2 \times 711 - 143 - 2 \times 40.6 - 464.5 = -669.7$

Sol 13: (A) $C_V = 3R/2r = 5/3$

$P_i = 1$ atm; $P_f = 2$ atm

$T_i = 300$ k

$1 \times V = 300 \times 1 \times 0.082$

$V_i = 24.63$

$1 \times (24.63)^r = 2 \times V_i^r$

$\therefore W_{adiabatic} = \int -PdV = -\int \dfrac{CdV}{V^{1-r}} = 1194.72 \ J$

$P^{1-r}T^r = $ Const.

$P_f^{\ 1-\frac{5}{3}}T_f^{\ \frac{5}{3}} = P_i^{\ -\frac{2}{3}}T_f^{\ 3}p_f$

$2^{-2300}\left(\dfrac{T}{300}\right)^5 = 1$

$\dfrac{T}{300} = 4^{\frac{1}{5}}$

$T = 4^{1/5} \times 300$

$T_f = 395.85$

(B) $1 \times V_1 = 1 \times R \times T_1 = 300 \ R$

$P.V = nRT$

$nC_V \Delta T = -P_2(V_2 - V_1)$

$2 \times V_f = 1 \times R \times T_f$

$1 \times \dfrac{3R}{2}(T_2 - T_1) = -2(V_2 - V_1)$

$\dfrac{3R}{2}(T_2 - 300) = T_f \times R + 2 V_1$

$\dfrac{3R}{2}(T_2 - 300) = -T_f \times R + 2 \times 300 \ R$

$\dfrac{3T}{2} - 450 = -T_f \ 1 + 600$

$\dfrac{5T}{2} = 1050$

$T_f = \dfrac{2100}{5}$

$V_f = 420\,k$

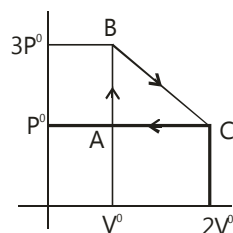$T_f = \dfrac{R \times 420}{2} = 210\,R = 17.24$

$\therefore W = -2\,(V_2 - V_1) = -2\,(210\,R - 300\,R)$

$= 180\,R = 1496.525\,J$

Sol 14: $C_v = 3R/2 \quad n = 1$

Work done by gas = Area under P – V curve

= Area of $\triangle ABC$

$= \dfrac{1}{2} \times (3P^0 - P^0) \times (2V^0 - V_0)$

$= \dfrac{-2P^0 V^0}{2} = -P_0 V_0$

$\Delta V_{cycle} = 0$

$\therefore w_{d1} = Q_{process} = P_0 V_0$

$W_{AB} = 0 \quad Q_{AB} = \Delta V_{AB} = nC_v \Delta T$

$= \dfrac{3R\Delta T}{2} = \dfrac{3}{2}\,\Delta PV$

$= \dfrac{3}{2} \times (3P_0 V_0 - 2P_0 V_0) = 3P_0 V_0$

$W_{AC} = P_0 \times (V_0 - 2V_0) = P_0 V_0$

$\Delta V_{AC} = NC_v \Delta T = \dfrac{3}{2}\,\Delta P_0 V_0$

$\dfrac{3}{2}\,P_0\,(V_0 - 2V_0) = -\dfrac{3}{2}\,P_0 V_0$

$\therefore Q = \Delta U - W$

$= -3/2\,P_0 v_0 - P_0 V_0$

$-5/2\,P_0 V_0$

$Q_{AB} + Q_{BC} + Q_{CA} = Q_{plou} = P_0 V_0$

$-5/2\,P_0 V_0 + 3P_0 V_0 + Q_{BC} = P_0 V_0$

$\therefore Q_{BC} = \dfrac{P_0 V_0}{2}$

at B temp $= \dfrac{3P_0 V_0}{R}$

at $\triangle$ temp $= \dfrac{P_0 V_0}{R}$

at B temp $= \dfrac{2P_0 V_0}{R}$

from B – C

P – V curve is

$P = mV + C$

$(3P_0 = m V_0 + C) \times 2$

$P_0 = 2mV_0 + C$

$5P_0 = C$

$3P_0 = m V_0 + 5P_0$

$\therefore m = \dfrac{-2P_0}{V_0}$

$\therefore P = \dfrac{-2P_0}{V_0}\,V + 5P_0$

$\left(5P_0 - \dfrac{2P_0}{V_0}V\right) V = RT$

$T = R\left(5P_0 V - \dfrac{2P_0}{V_0}V^2\right)$

$\dfrac{2T}{dV} = 0 \text{ at } 5P_0 - \dfrac{4P_0}{V_0}\,V = 0$

$\therefore V_0 = 5/4\,V$

$T = R\,[5\,P_0 \times 5/4\,V_0 - 2\,\dfrac{P_0}{V_0} \times \dfrac{25}{16}\,V_0]$

$T_{max} = R\left(\dfrac{25}{4} - \dfrac{25}{8}\right) P_0\,V_0 = \dfrac{25}{8}\,\dfrac{P_0 V_0}{R}$

Sol 15: (i) $\Delta S_{gas} = nC_v \ln \dfrac{T_2}{T_1} + nR \ln \dfrac{V_2}{V_1}$

$\Delta S_{gas} = R \times \ln 3 = 9.13$

Reverse $\therefore \Delta S_{gas} = -\Delta S_{surr.} \therefore \Delta S_{total} = 0$

$\Delta S_{surr.} = -\dfrac{Q_{rev}}{T}$

$9.134 = \dfrac{-Q_{rev}}{298}$

$\therefore Q_{rev} = 2775.572$

$\therefore Q_{avg} = -2775.572 + 836.8$

$\therefore \Delta S_{total} = 9.134 + \dfrac{-2775.572}{278} + \dfrac{836.8}{298}$

$= \dfrac{836.8}{298} = 2.808\,J/k$

(iii) In case of free expansion Q = 0

$\therefore \Delta S_{surr.} = 0$

$\therefore \Delta S_{system} = \Delta S_{total} = 9.134$ J

Sol 16: Ag(ℓ) $\to$ Ag

$\Delta H_{avg} = 22$ Kj

$\Delta S_{300} = \dfrac{\Delta T}{T} = \dfrac{22 \times 10^3}{300} = \dfrac{220}{3}$ J

$\displaystyle\int_{300}^{200} \Delta S = \int \dfrac{nC_p}{T} - nR\, dP$

$\because P_2 = P_1 = 100$

$\Delta S_{200} \dfrac{-220}{3} = C_p \ln \dfrac{T_2}{T_1} - C_p(\ell) \ln \dfrac{T_2}{T_1}$

$\Delta S_{-200/3} = (30 - 40) \ln \left(\dfrac{200}{300}\right)$

$\Delta S = \dfrac{220}{3} + 10 \ln (3/2)$

$= 22/3 + 10 \times 0.405 = 74.05$ J/k

V = constant

Sol 17: $\Delta S_{sys} = nC_V \ln T_2/T_1$

$= 1 \times \dfrac{3R}{2} \ln (1000/10)$

$= \dfrac{3R}{2} \ln 10$

$\therefore \Delta S_{total} = 0$

$\therefore \Delta S_{surr.} = \Delta S_{system} = -3/2 k\ln (10)$

(ii) Irreversible Process

$\Delta S_{system} = -3/2\, R \ln (10)$

W + Q = ΔU

W = 0 as dV = 0 $\therefore$ Q = ΔU = $nC_V \Delta T$

$= \dfrac{3R}{2} \times 900$

$\therefore \Delta S_{total} = \dfrac{3R}{2} (0.9 - \lambda n 10)$

$= -\dfrac{3R}{2} \times 1.403$

Sol 18:

H_2O (1L, 1 atm, 323k) $\to H_2O$ (g, 1 atm, 323 k)
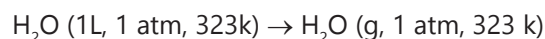
ΔH_{vap} H at 373 = 40.639 = 2.1

$\Delta H_{373} = 40.639 \times 10^3$ J

$\Delta H_{323} = 38.54$ KJ

$\Delta S_{373} = \dfrac{\Delta H_{vap}}{373} = \dfrac{40639}{373} = 108.95$ J

$\displaystyle\int_{373}^{323} = \int_{373}^{323} \dfrac{nC_p dT}{T}$

$= (33.305 - 75.312) \ln (T_2/T_1)$

$= -42.00 \ln (373/325)$

$\Delta S_{323} = 108.95 - 6.04$

$= 102.349$

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

$= 38.54 - \dfrac{102.349 \times 323}{1000} = 5.54$ kJ/mol

Sol 19: Adiabatic expansion

$\therefore$ P = 0 $\therefore \Delta S_{surr} = 0$

$\therefore \Delta S_{total} = \Delta S_{system}$

(i) Case:I: Reversible process,

$\therefore \Delta S_{system} = \Delta S_{total} = 0$

(ii) Case–II: Irreversible P_{ext}

= 262.65 KPa

ΔS_{system}

Neon $\to$ monoatomic

$C_V = 3R/2$ r = 5/3

$P^{1-r} = $ const.

$P \propto T^{r/r-1}$

$\dfrac{P_2}{P_1} = \left(\dfrac{T_2}{T_1}\right)^{r/r-1}$

$\dfrac{202.65}{506.65} \left(\dfrac{T_2}{473}\right)^{\left(\frac{5/3}{2/3}\right)}$

$\therefore T_f = 327.85$

$V_{ex} = 20.26$ J
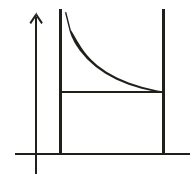
PV = nRT

$n \times \dfrac{3R}{2} \Delta T = -P_{ext} (V_2 - V_1)$

$$n \times \frac{3R}{2} \Delta T = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right)$$

$\therefore$ w = nC_p ln T_2/T_1 – nP ln (P_2/P_1)

= –2.85 + 3.81 = 0.957 KJ

(iii) In case of free expansion

$\therefore$ ΔS = –ne λn (P_2/P_1)

$= \frac{-10}{20} \times 8.314\ \lambda n \left(\frac{202.65}{506.625}\right)$ = 3.81 J/k

Sol 20: $\Delta_r C_p$ = 0

$\therefore$ ΔH^0_{298} = ΔH^0_{373}

ΔS°_{298} = ΔH°_{373}

P–V work = $T\Delta 3^\circ$

$\therefore$ –6333 = –5737 – 298 $\rightarrow$ ΔS°

ΔS° = 2

Additional non-PV work

= (310 –298)× 2 = 24 kJ/mol

Sol 21: $\Delta H_{f\ FeO}$ = –65 k

$\Delta H_{f\ Fe2\ O3}$ = –197 k Cal

$FeO + Fe_2 O_3$

2   1

initially

$2FeO\ \frac{3}{2}O_2 \rightarrow Fe_2O_3$
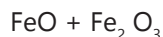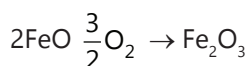
2–2x 1+ x

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 $Fe_2 O_3$

$\Delta H = \frac{\Delta H_{fFeO_3}}{2} - \Delta H_{FeO}$

= –197/2 + 65 = –33.5

$\therefore$ ΔH/mole = –11.167

Sol 22: ΔH_{diss} (H_A) = –6900 + 13400

ΔH_{diss} (H_B) = –2900 + 13400

x – 6900 + (1 – x) x – 2900 = –3900

69 × x + (1 – x) × 29 = 39

40 x = 10

n = 0.25%

$\therefore$ 25% is given to HA and 75% to HB

Sol 23: $HgO \rightarrow Hg + \frac{1}{2}O_2$
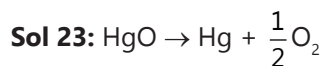
At constant pressure

$\therefore$ ΔH = 41.84

$\therefore$ 41.84 = $\frac{m}{200.6}$ × 90.8

$\therefore$ m = 92.435

(b) Δv = 41.84

$\Delta H = \Delta U + \Delta PT$

= $\Delta U + \Delta nRT$

= $\Delta U + \frac{m}{2 \times 200.6}$ × 8 × 314 × 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 g

Sol 24: $Fe_2O_3 + 3H_2 \rightarrow 2\ Fe + 3H_2\ O(\ell)$

ΔH°_{298} = –35.1
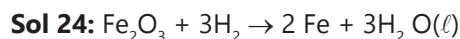
ΔH°_{max} = –265

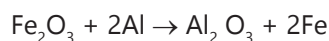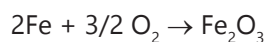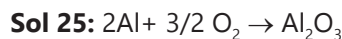$\int_{298}^{T} \Delta H = n(\Delta CP_{Products} - \Delta C_{rad})\ \Delta T = 0$

$\Delta H_T - \Delta H_{298}$ (2 × 25.5 + 3 × 75.3

– 104.5 –3 × 28.9) [T – 28]

$-26 + 35.1 = \frac{85.7}{10^3}$ (T_{-298})

$\frac{9100}{85.7}$ = T–298

T_f = 404.18 K

Sol 25: $2Al + 3/2\ O_2 \rightarrow Al_2O_3$

$2Fe + 3/2\ O_2 \rightarrow Fe_2O_3$

$Fe_2O_3 + 2Al \rightarrow Al_2 O_3 + 2Fe$

$\Delta H°_f = \Delta Hf_{Al_2O_3} - \Delta H_{fe_2O_3} = -399 + 199 = -200$ k cal/mol

2 mole of mixture

∴ Mole of Fe_2O_3 and ½ mole of Al_2

∴ Mass of Fe_2O_3 = 160

Mass of Al = 27 × 2 = 54

∴ Mass total = 214

∴ ΔH/mol = −200

$\Delta H/g = \dfrac{-200}{2 \times 214} = 0.9345$ g

Mole mix mass 2 mole of Al = 54 (g)

d = 2.7 g/cc

∴ $V_1 = \dfrac{54}{2.7} = 20$
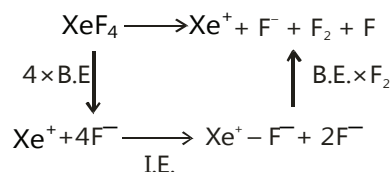
$V_2(Fe_2O_3) = \dfrac{160}{5.2} = 30.77$

V_{total} = 50.77 cc

∴ $\Delta H = \dfrac{-200}{50.77} = 3.94$ k cal

Sol 26:

$XeF_4 \longrightarrow Xe^+ + F^- + F_2 + F$

$4 \times B.E$ ↓   ↑ $B.E. \times F_2$

$Xe^+ + 4F^- \longrightarrow Xe^+ - F^- + 2F^-$
          I.E.

$+\Delta H_{EQ}$ = electron affinity = −85

= 4 × 34 + 279−85 − 38 = 292 k cal/mol

Sol 27: $N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta°H = -46 \times 2$

$\Delta H°_f = -46$

$NH_3 + 1/2 H_2 + 1/2 Cl_2 \longrightarrow NH_4Cl$

$\Delta H_{reac.}$ $\Delta°H_f$ $-\Delta°H_f NH_3$

      NH_4Cl $B.H_2$ Lattice energy

NH_3 H   u $\xrightarrow[1.E]{}$ $H^+ + Cl$

         $+\Delta H_{E.S}$
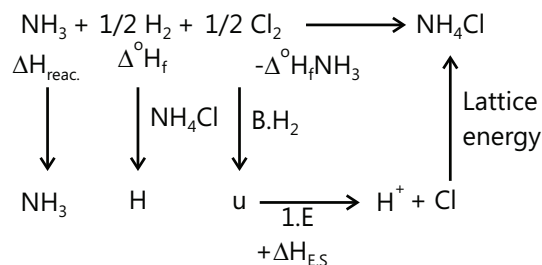
∴ $\Delta H_{rea} = \dfrac{B.EH_2}{2} + \dfrac{B.E.Cl}{2}$

$+ I.E.H_2 + \Delta H_{E.G Cl}$ + Lattice + Protein gain

$-314 + 46 = \dfrac{218}{2} + \dfrac{124}{2} + 1310$

− 348 + proton gain − 683

∴ Proton gain = −718 kJ/mol

Sol 28: $10^{-3} \times 1.2 \times 1 = 0.0820 \times 273 \times x$

∴ $n_t = 0.5 \times 10^{-3}$

CO (will at) = ?

$CO + H_2O_2 = CO_2$; $\Delta H = -280$ KJ

∴ $n_{CO} + 280 \times 10^3 = 7$

∴ $n_{CO} = \dfrac{7}{280} \times 10^{-3} = 2.5 \times 10^{-5}$

Proportion by volume

$\Rightarrow \dfrac{n_{CO}}{n_t} = \dfrac{2.5 \times 10^{-5}}{5 \times 10^{-3}} = 0.05$

$\dfrac{n_{CO}}{n_{CO_t}} = 0.001$ % y

$10^{-5} = 0.05 \times (1/2)$

After each cycle

$n_{CO_t} = \dfrac{1}{2} n_{CO}$

∴ $\dfrac{n_{CO}}{n_{CO_t}} = \dfrac{1}{2} \ell n$

$2 \times 10^{-4} = (0.5)^n$

∴ n = 13

13 × x + 80 = 6 × 60

$x = \dfrac{360 - 80}{13}$

x = 21.54 sec

Sol 29:

$B(s) + 3/2 H_2(g) \longrightarrow BH_3$

↓   ↓   ↑

B(g)   3/2H $\longrightarrow$

2B $+3H_2 \longrightarrow B_2$

│   │   ↑

2B(s)   6H
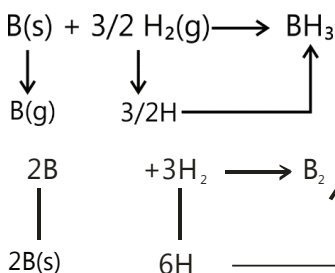
$\Delta H°_f = \Delta H B + 3/2 \Delta H_6 H - 3 \times B.E. (B - H)$

$100 = 565 + 436 \times 3/2 - 3 \times x$

∴ X = 373 H − = a
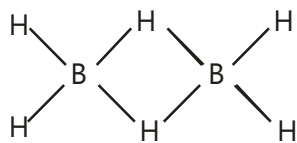
3 – centre, 2 – electron bond

$\Delta H^o_{f\,B_2H_6} - 36 = 2 \times 565 + 436 \times 3 - 4 \times x$

Sol 30: $CHCl_2 - COOH$ by NaOH = 12850

HCl by NaOH is 13680

NH_4OH by HCl is 12270

$CH\,Cl_2\,COOH + NaOH$

$\rightarrow CHCl_2\,COONa + H_2O$

$NH_4OH + HCl \rightarrow NH_4\,Cl + H_2O$

$NaOH + HCl \rightarrow NaCl + H_2 + (2) - (3)$ gives

$CHCl_2 + NH_4OH \rightarrow CH\,Cl_2\,COONa + NH_4\,Cl$

$\therefore \Delta H_{reac} = -12830 - 12270 + 413680 = -11420$

ΔH_{diss} of $CH\,C\lambda_2\,COOH = 13680 - 12830 = 850$

$\Delta H_{diss}\,NH_4\,OH = 13680 - 12270 = 1410$

Exercise 2

Single Correct Choice Type

Sol 1 : (A) $N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\,H_2O\,(\ell)$

a $\rightarrow$ (1) $2NH_3 + 3N_2O \rightarrow 4N_2 + 3H_2O$

b $\rightarrow$ (2) $N_2O + 3H_2 \rightarrow N_2H_4 + H_2O$

c $\rightarrow$ (3) $4NH_3 + O_2 \rightarrow 2N_2H_4(\ell) + 2H_2O(\ell)$

d $\rightarrow$ (4) $H_2 + \frac{1}{2}\,O_2\,(r) \rightarrow 2N_2H_4(\ell) + 2H_2O$

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

$c = 1 - \dfrac{8}{9} = -\dfrac{1}{8}$

$b - \dfrac{2}{8} = -1$

$b = -1 + \dfrac{1}{4} = -\dfrac{3}{4}$

$\therefore \Delta H = \dfrac{1011}{4} + \dfrac{1}{8}$

$\times 286 - \dfrac{285 \times 9}{4} + \dfrac{317 \times 3}{4}$

$\Delta H = -620.5$

Sol 2: (C) $HCl + O_2 \rightarrow 2\,Cl_2 + 2H_2O$

$\Delta H_{reac.} = -2 \times \Delta H_1 + \Delta H_2$

$= 2 \times 184.5 + 483 = 114$

$\Delta H = \Delta V + \Delta ng$

$-114 = \Delta V + -1 \times 8.3 \times 300$

$\Delta V = -1115.5$

Sol 3: (B) $\Delta H_{reac.} = \Delta H_f + Na_2SO_4 + 2\Delta H\,HCl$

$-2\,\Delta H_f\,NaCl - \Delta H_f\,H_2SO_4$

$= -1382 - 2 \times 92 + 2 \times 441 + 811$

$\Delta V = \Delta H - ngRT = 62.02$

$\Delta H = -67$

Sol 4: (A) A(g) + B(g) $\rightarrow$ C

$\Delta E = -3\,k\,Cal$

$\Delta H = \Delta E + \Delta_{ng}R$

$= -3 - \dfrac{1 \times 1.987 \times 300}{1000}$
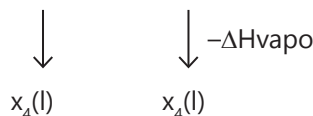
$\Delta H = -3.60$

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

$= -3.5 + \dfrac{300 \times -10}{1000}$ 0.6 k cal $\Rightarrow$ 600 cal

Sol 5: (D) $\Delta S = \dfrac{\Delta H_{vap}}{T}$

$\therefore T\Delta S - \Delta H = -\Delta G = 0$

$\therefore \Delta G = 0$

Sol 6: (C)

$4x(g) \longrightarrow x_4(g)$

$x_4(l) \qquad x_4(l)$

$\Delta S = -125\,J/k$

$-100 \times 4 = -4 \times 30 - 32 + 4x$

$\Theta x = 52$

$\Delta G = \Delta H - 1\Delta S$

$= -52 - \left(\dfrac{-125 \times 300}{1000} \right)$

$= -52 + \dfrac{123 \times 3}{10}$

$\Delta H = -14.5$

Sol 7: (C) $\dfrac{1}{2} x_2 + \dfrac{3}{2} y_2 ? \to xy_3 \ \Delta H = -30$

Reactive at equals

$\therefore \Delta G = 0$

$\therefore \Delta H - T\Delta S = 0$

$\Delta H = T\Delta S$

$\Delta S = \left(50 - \dfrac{3}{2} \times 40 - \dfrac{60}{2} \right)$

$-30 \times 10^3 = T \times (50 - 60 - 30)$

$T = \dfrac{30 \times 10^3}{40}$

$T = 750$ K

Sol 8: (D)

(Sizes here mass is equal)

$n \times C_P (T_f - T_H) + n \times C_P (T_f - T_C) = 0$

$\therefore 2 T_f = T_H + T_C$

$T_f = \dfrac{T_H + T_C}{2}$

$\therefore \Delta S = C \ln \dfrac{T_2}{T_1}) H + C \ln \dfrac{T_2}{T_1} \lambda n$

$= C \ln \left[\dfrac{T_f}{T_H} \right] + C \ln \dfrac{T_f}{T_H}$

$= C \ln \left[\dfrac{(T_H + T_C)^2}{T_H T_C} \right]$

Sol 9: (A) $(V = 3/2\ R)$

A(500k, 5 bar) ———— B (500k, P)
reversible
isothermal
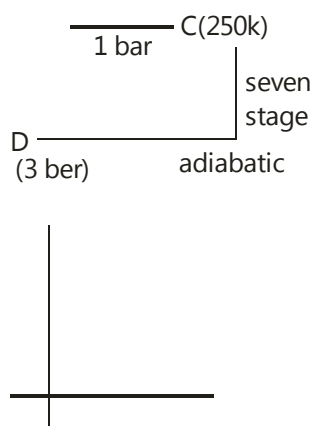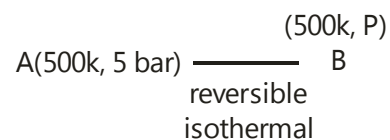
$10^5 \times 5 \times V = 80314 \times 2 \times 500 \times 100$

$V_i = 8.31$

$4 \times 2 \times 10^{-3} \ m^3$

$V_i = 16.628$ L

$\dfrac{P}{1} = \dfrac{500}{250}$

$\therefore P_B = 2$ bar

$P_V = \dfrac{3}{2} R, \ \dfrac{1}{r} = \dfrac{C_v}{C_p} = \dfrac{3R/2}{3R/2 + R} = \dfrac{3}{5}$

$r = 5/3$

$PV^r =$ Const.

$P \left(\dfrac{T}{P} \right)^r =$ const.

$P^{1-r} T^r =$ const.

$3^{1-5/3} T^{5/3} = 1^{1-5/3} \times (25)^{5/3}$

$\therefore \dfrac{T}{250} = 3^{2/5} \left(\dfrac{T}{250} \right)^{5/3} = 3^{2/5}$
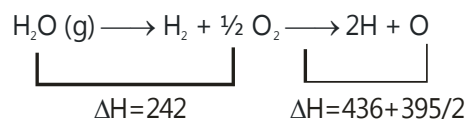
$T_f = 387.9$

$\Delta V_{BC} = HC_V \Delta T$

$= \dfrac{2 \times 3R}{2} (250 - 500)$

$= 3R \times 250 = 0750$ R

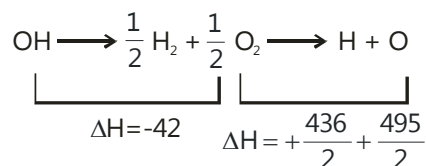$\Delta H_{CA} = nC_P \Delta T = 2 \times 5 \dfrac{R}{2} (357.90 - 250)$

Multiple Correct Choice Type

Sol 10: (A, D) $H_2O (g) \to 2H(g) + O(g)$

$H_2O (g) \longrightarrow H_2 + \frac{1}{2} O_2 \longrightarrow 2H + O$

$\Delta H = 242 \qquad \Delta H = 436 + 395/2$

$\therefore \Delta H_{total} = 242 + 436 + \dfrac{495}{2} = 925.5$

$OH \longrightarrow \dfrac{1}{2} H_2 + \dfrac{1}{2} O_2 \longrightarrow H + O$

$\Delta H = -42 \qquad \Delta H = +\dfrac{436}{2} + \dfrac{495}{2}$

$\therefore \Delta H_{total} = -42 + \dfrac{436 + 495}{2} = 423.5$

ΔH formation of $H = \dfrac{436}{2} = 218$

$\Delta H_f \, OH = 42 - 0 - 0 = 42$

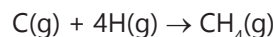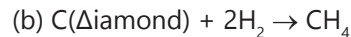**Sol 11: (A, B, C, D)** $CaCO_3$ (Calvin $\to$ $CaCO_3$/area)

$\Delta_f G^0 \, (CalC) = -1128.8$

$\Delta G^0 f = -1127.75$

$\Delta G^0_{avg} > \Delta G^0_f \, (CalC)$

$\therefore$ Cal is more stable

(b) $C(\Delta iamond) + 2H_2 \to CH_4$

$C(g) + 4H(g) \to CH_4(g)$

More heat is evolved volume in case (b)

as C diamond $\to$ C(gas) $\Delta H > 0$

(c) $\Delta_f H^0 \, I_2(g) = \Delta_{surr.} H \, I_2(s)$ at 25° C

(d) $2Ag(s) = 112O_2 \, (g) \to \Delta_{nges}$

$= -ve + 1 \times RT$

$\therefore \Delta V > \Delta H$

Sol 12: (B, C) (A) $(\Delta G_{system}) < 0$ then react must be is fare

$\Delta H - T\Delta S < 0$

$\Delta H > 0$

(B) $\Delta_f H^0$ (S, Momenta k) $\neq 0$ true

$BE_{CH_4} = 1654$

$BE_{CH} = \dfrac{1654}{4}$

$BE_{(C-C)} = B._{C2H6} - 6 \times B_{CH})$

$28.2 - \dfrac{6 \times 1658}{4}$

$= 2812 - 2482 = 328$

(Δ) $H^0 + \Delta H^- \to H_2O(\ell)$

$\Delta H = -56$ KJ

$H_2 \, (g) + O_2 \, (l) \to \Delta H_f \, (H_2O)$
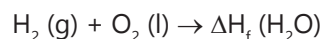
$H_{vep} = 44$ Kj cm

$\therefore \Delta H_f \, (H_2O, \ell) = -44 - 242$

$= -286$

$-56 = -286 \, \Delta H \, (OH^-)$

$286 - 56 = \Delta H \, (OH^-)$; $Hf(OH^-) = 230$

Sol 13: (A, B, D)
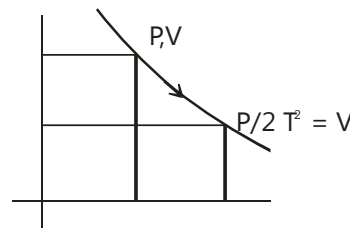
$P = mV + C$

$\dfrac{P}{2} \, 2m \, V + C$

$mV = \dfrac{P}{2}$

$\therefore m = \dfrac{-P}{2V}$

$Process = \dfrac{-P}{2V}$ volume $+ \dfrac{3P}{2}$

$sw = -PdV$

$= \left(\dfrac{-P}{2V} x + \dfrac{3P}{2} \right) dV = -\dfrac{P}{fV^0} V^2 + \dfrac{3P}{2} \Big|_V^{2V}$

$= \dfrac{-P}{4V} (4V^0 - V^0) + \dfrac{3P}{2} \times V$

$= -\dfrac{3}{4} PV + \dfrac{3}{2} PV = \dfrac{3}{4} PV$

$PV \, \lambda n \, 2$

$\lambda n \, 2 < ¾ \therefore$ work done is higher

$-\dfrac{2}{2V} x^2 + \dfrac{3}{2} PX = nRY$

Parabolic bott

$T = \dfrac{3PX}{2} - \dfrac{Px^2}{2V}$

$\dfrac{\delta T}{\delta x} = \dfrac{3P}{2} - \dfrac{Px}{V}$

$x = 3/2 \, V$

$\dfrac{\delta^2 T}{\delta x^2} = -P$

T atomic max at 3/2 V

$$V_{atm} = \frac{2V}{P}\left(\frac{3}{2}P - pressure\right)$$

$$\frac{2V}{P}\left(\frac{3P}{2} - pressure\right) Pressure = T$$

Sol 14: (A, C) Normal boiling point = 350 K

ΔH_{vap} = 3TKJ

at $\Delta S = \dfrac{350 \times 10^3}{350}$ = 100 J

(i) ΔS at 1 atm 350 k = 100 J

at 0.5 350

$P < P_{vap}$ CHO mol

$\Delta S > \Delta Svap > 100$

(ii) as at 2 at 350 k

as $P > P_{vap}$

$S < S$ val

Sol 15: (A, C, D) In adiabatic explained

w < 0,

Q = 0

$\therefore \Delta V = w$

$\Delta V < 0$

$w_{rev} < \Delta_{ice}$

$\therefore \Delta V_{rev} < \Delta_{avg}$
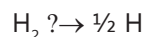
$\Delta T_{rev} < \Delta T_{ice}$

$\therefore T_{f\,rev} < T_{f\,ice}$

(ii) K.E = 3/2 nRT dependent on temperature if T is constant then KE is constant for adiabatic expansion of gas

$nC_V \Delta T = w < 0$

$H_2\ ? \to \frac{1}{2} H$

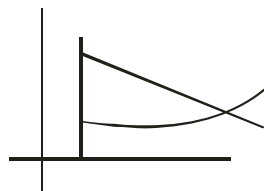$\Delta S > 0$, STV as no. of molecules hence no. of molecules.

Sol 16: (A, C, D) At any common row on the p–v curve

$P(V)^r$

PV = C 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

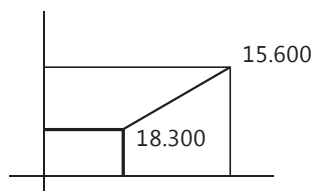Slope of adiabatic C is more negative theorem slope of isothermal

Adiabatic curve is above isothermal curve

Hence area under adiabatic curve > area under isothermal curve

Hence $w_{adiabatic} > w_{isothermal}$

$\delta = \dfrac{C_P}{C_v}$ not necessarily constant

Sol 17: (B, D)

$\Delta H_{AB} = nC_p\Delta T$

$= 1 \times \dfrac{5R}{2} \times 300 = 6235.5$ J

$\Delta S = nC_V \ln \dfrac{T_2}{T_1} - \ln R \ln \dfrac{V_2}{V_1}$

$= \dfrac{3R}{2} \ln 2 + R\ln\left(\dfrac{15}{10}\right)$

$\therefore \Delta S > 0$

V = mT + C

10 = 300 m + C

15 = 600 m + C

$m = \dfrac{5}{300}$

$10 = \dfrac{5}{300} \times 100 + C$

C = 5

$V = \dfrac{T}{300} + 5$

$PV = R (V - 5) \times 60$

$P = R \left(60 - \dfrac{300}{V} \right)$

$w = \left(\dfrac{300}{V} - 60 \right)$

$= (300 \ln V - 60 V) R = -1488.88J$

$\Delta V = nC_V \Delta T$

$= 1 \times \dfrac{3R}{2} \times 300 = 3746.3$

$q = -w + Q$

$= 1491.8 + 3746.3 = 5237.82$

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 $T^r p^{1-r} = 0$

$T^{\frac{CP}{CV}} \cdot T^{\frac{-e}{CV}} = 0$

$T^{\frac{CP}{R}} P^{-1}$ const.

$P = \dfrac{RT}{V_V - b} - \dfrac{a}{V^2}$

$w = - \int_{V_1}^{V_2} PdV$

$= -RT \ln \left[\left(\dfrac{V_2 - b}{V_1 - b} \right) - a \left(\dfrac{1}{V_2} - \dfrac{1}{V_1} \right) \right]$

Sol 19: (C, D) $P V^r = $ const.

$\therefore P^{1-r} T^r = $ const.

$V^{1+r} T^{-1} = $ const.

$PT^{\frac{r}{1-r}} = w$

$P = G \times T$

$\dfrac{rP}{rT} = \dfrac{r-1}{r}$

$\dfrac{rP}{rT} = \dfrac{r}{r_1} PT^{-r} = 1 + \dfrac{1}{r-1} PT^{-r}$

$\therefore \dfrac{rP}{rT} > 0$

$v^0 = \cos T^{\frac{1}{1+r} - 1}$

$\dfrac{rV}{rT} = \dfrac{1}{1+r}$ $GT = \dfrac{-r}{1+r}$

as r is $\dfrac{rV}{rT} = \dfrac{1}{1+r}$ $VT^{-r} > 0$

$P = CV^{-r}$

$\dfrac{rP}{rV} = -rCV^{-r}$

Sol 20: (A, B, D) $H_2SO_4 + 2(NH_4)OH \rightarrow (NH_4)_2 SO_4 + 2H_2O$

$\Delta H_{reac.} = 2 \times \Delta H_{dissociation}$ of $(NH_4)_2$ OH $\times$ moles of NH_4OH $+ 2 \times$ moles of dissociation of H_2O

Given $-1.5 \times 1.4 = -0.05 \times 57 \times 2 + 2 \times 0.2 \Delta H_{diss.}$

$3.6 = 2 \times 0.2 \times 0.2 \times \Delta H$

$\therefore \Delta H_{diss} = 4.5$ KJ

ΔH_{reac} (HCl − NaOH) $= -57 + 4.5 = -52.5$

$\Delta H(CH_3COOH - NH_4 OH) = -48.1$

$-48.1 = -57 + 4.5 + \Delta H_{diss} CH_3 COOH$

$\therefore H_{diss} CH_3 COOH = 4.4$ KJ

ΔH for $2H_2 O$ (l) $\rightarrow 2H^+ + 2OH^-$

$= 2 \times 57 = 114$

Sol 21: (A, B, C, D) Only (g) $+ O_2 \rightarrow CO_2$

Replacement ΔH_f of product

Sol 22: (B, C, D) ΔS for ½ $H_2 \rightarrow N$ is + ve true

as no. of molecules yes, entropy increase

ΔG_{system} is O for reversible process act standard conditions

ΔG^0 i real $= VdP - sdT$

Function of P,V,T not just P and T at equilibrium ΔG is moles

Nothing fixed about ΔS

Sol 23: (A, B, D) In isothermal gas cylinder,

(A) w + ve dV < 0 = w = −PdV

$\therefore$ w + ve

(B) $\Delta H = \Delta U = 0$ as $\Delta T = 0$

(C) $\Delta S = R \ln \dfrac{V_2}{V_1}$, $= V_2 > V_1$

$\therefore \Delta S$ − ve

(D) $\Delta G = - T\Delta S > 0$ as $\Delta S < 0$

Sol 24: (B, C, D) 0.2 m³ Ne at 200 kP at T_i

V_f = ½ VB_i = 0.1 m³

Temperature constant inside as gas volume < and pressure is constant to maintain temperature to maintain air temperature
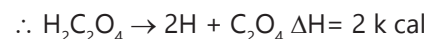
q may be +ve or – ve

$\Delta V \neq 0$ as Δ nRT $\neq 0$

Assertion Reasoning Type

Sol 25: (D) HCl + NaOH = −13.7

∴ ΔH_{rest} 0 × Alkali = −25%

ΔH_{diss} = +2 × 13.7 − 25% = 2

∴ $H_2C_2O_4 \rightarrow 2H + C_2O_4$ ΔH= 2 k cal

Sol 26: (D) $\Delta H = nC_p \Delta T$

(For ideal gas, ΔH is a function of compressor alone)

Sol 27: (D) Q = 0

w = ΔV

and w < 0, ∴ ΔU < 0

No comments can be made about temperature T might not increase

Sol 28: (D) $\frac{1}{8}$ S_8 (s) + O_2 (g) ?→ SO_2 (g)

S − (−2 × 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

$V_f = \frac{V}{8}$ $V_i = PV^r$ = 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 atm

In container A, V_f = 22.4 + $\frac{7}{8}$ × 22.5

= $\frac{15}{8}$ × 22.4

$V_f = \frac{15}{8} V_i$

P_f = 8 atm

Sol 30: (A) $\dfrac{\frac{15}{8} \times 22.4}{T_f} = \dfrac{1 \times 22.4}{2+.3}$

$C_f = \dfrac{273 \times 5}{8}$ 4= 1638

Sol 31: (B) $\Delta H_A = nC_p\Delta T = 1 \times \dfrac{5 \times 8.34}{2} \times$ (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 kg

$\Delta H = \Delta U + \Delta pV$

Dependent only on temperature

∴ $\Delta H = \Delta pV$ = (1–0.7) × 0.9 L

= 0.3 × 0.9 L = 0.3 × 0.9 × 100 J= 27 J

Sol 33: (C) From 1 to 3

$\Delta U = \Delta$ (nCT)

ΔmCT = 0.9 × C × (373 − 353) + $\dfrac{0.4 \times 40}{18}$ = 1075.6

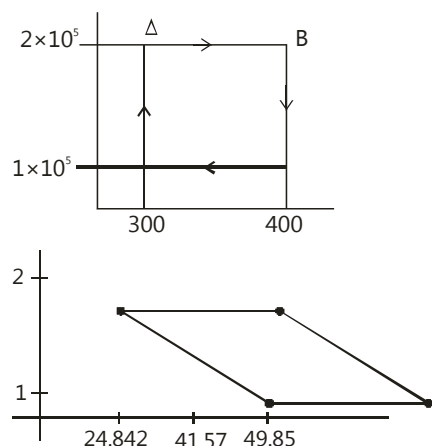**Sol 34: (B)** ΔH = 1.8 × 4.2 + $\dfrac{450}{18}$ × 80 = 1075.6

Sol 35: (B) Work done in 1 to 3

w_{1-2} = 0 as ΔU = 0

$w_{2-3} = P_{ext}$ dU = $\dfrac{0.45 \times 10^3}{18} \times \dfrac{0.0821 \times 373}{1000}$

w_2 (10 KJ)

Paragraph 3:

Sol 36: (C) w A–B –w = $PC\Delta v = nR\Delta T$

$= 2 \times 10^5 \times T$

$= 2 \times 8.314 \times 200 = 400\ R$

Sol 37: (B) Work done$= -nRT \ln \dfrac{V_2}{V_1}$

$= -nRT \ln \dfrac{P_2}{P_1} = 2R \times 300 \ln\left(\dfrac{1}{2}\right)$

$= +600\ R \times \ln 2 = +414\ R$

Sol 38: (B)

Net work done in cycle

$\Rightarrow$ ln A – B = $P\Delta V = nR\Delta T$

$2R \times (500 - 300)$

B–C = $-nRT \ln \dfrac{P_2}{P_1} = 2R \times 500 \ln\left(\dfrac{1}{2}\right)$

$= -2R\ 500 \ln 2$

C–D = $P\Delta V$ – nRT = $2 \times R\ (300 - 500)$

D–A = $-2R \times 300 \ln (1/2) = 2R \times 300\ \lambda n\ 2$

$\therefore$ Total mole = 2 R (500 – 300) –2R 500 λn 2

$= 2R\ (500 - 300) + 2 \times 300\ \lambda n\ 2$

$= 2R\ (300 - 500)$ ln

$= 420\ R \ln 2$

$= 276\ R$

Match the Columns

Sol 39: A $\rightarrow$ p, r, s; B $\rightarrow$ q, s; C $\rightarrow$ q, s; D $\rightarrow$ s

(i) Reversible isothermal

$P = -nRT \ln \dfrac{V_2}{V_1} = 2.303\ nRT \log \dfrac{P_2}{P_1}$

(p, r)

(ii) Reversible adiabatic =

w = $\Delta U = nC_V\ (T_2 - T_1)$

qs

(iii) Irreversible adiabatic = $nC_V\ \Delta T = -P_{ex}\ dV$

(iv) Irreversible isothermal w = $-\int P_{ex} dV$

Sol 40: A $\rightarrow$ s; B $\rightarrow$ p, r; C $\rightarrow$ p, s; D $\rightarrow$ p, r

Irreversible adiabatic compression

(A) Q = 0, $\therefore \Delta S_{surr} = 0$, $\Delta S_{system} = 0$

(B) Reversible vap

$\Delta S_{system} > 0$

as gaseous

Reversible, process $\therefore \Delta S_{total} = 0$

$\therefore \Delta S_{surr} < 0$

(C) free expansion of ideal gas

Q = w = 0

$\therefore \Delta S_{surr.} = 0$

Expansion $\therefore \Delta S_{system} > 0$

(Δ) diss. of $CaCO_3$ (S) $\rightarrow$ CaO(s) + CO_2(g)

$\Delta S_{system} > 0$

$\Delta S_{system} + \Delta S_{surr} = 0$

$\therefore \Delta S_{surr} < 0$

Previous Years' Questions

Sol 1: (B) Elements in its standard state have zero enthalpy of formation. Cl_2 is gas at room-temperature, ΔH_f^o of Cl_2(g) is zero.

Sol 2: (C) $\Delta G^o = \Delta H^o - T\Delta S^o$

$= -54.07 \times 10^3 J - 298 \times 10 J = -57.05 \times 10^3\ J$

Also, $\Delta G^o = -2.303\ RT \log K$

$\Rightarrow \log K = \dfrac{-\Delta G^o}{2.303\ RT} = \dfrac{57.05 \times 10^3}{5705} = 10$

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:

$$\Delta S_{A \to B} = \Delta S_{A \to C} + \Delta S_{C \to D} + \Delta S_{D \to B}$$

= 50 eu + 30 eu + (–20 eu) = 60 eu

Sol 5: (A) Given, $\dfrac{P}{V} = 1 \Rightarrow p = V$

Also from first law: $dq = C_v dT + p dV$

For one mole of an ideal gas: $pV = RT$

$\Rightarrow pdV + Vdp = RdT$

From (i) $pdV = Vdp$

Substituting in Eq. (ii) gives

$2pdV = RdT$

$\Rightarrow pdV = \dfrac{R}{2}dT \Rightarrow dq = C_v dT + \dfrac{R}{2}dT$

$\Rightarrow \displaystyle\int \dfrac{dq}{dT} = C_v + \dfrac{R}{2} = \dfrac{3}{2}R + \dfrac{R}{2} = 2R$

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 = 0.45K

q = heat-capacity × ΔT = 2.5 × 0.45 = 1.125 kJ

$\Rightarrow$ Heat produced per mol = $\dfrac{1.125}{3.5}$ × 28 = 9 kJ

Sol 9: $\Delta H = \Delta U + \Delta(pV) = \Delta U + V\Delta p$

$\Rightarrow \Delta U = \Delta H - V\Delta p$

= –560 – 1× 30 × 0.1 = –563 kJ

Sol 10: $\Delta U = q + W$

For adiabatic process, q = 0, hence $\Delta U = W$

$W = -p(\Delta V) = -p(V_2 - V_1)$

$\Rightarrow \Delta U = -100 (99 - 100) = 100$ bar mL

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

where, $\Delta pV = p_2 V_2 - p_1 V_1$

$\Rightarrow \Delta H = 100 + (100 \times 99 - 1 \times 100) = 9900$ bar mL

Sol 11: Work-done along dased path:

$$|-W| = \sum p\Delta V = 4 \times 1.5 + 1 \times 1 + \dfrac{2}{3} \times 2.5 = 8.65 \text{ L atm}$$

Work-done along solid path: $-W = nRT \ln \dfrac{V_2}{V_1}$

$= p_1 V_1 \ln \dfrac{V_2}{V_1} = 2 \times 2.3 \log \dfrac{5.5}{0.5}$

$= 2 \times 2.3 \log 11 = 4.79$

$\Rightarrow \dfrac{W_d}{W_s} = \dfrac{8.65}{4.79} = 1.80 \approx 2$

Sol 12: (B) Statement-I is true.

$dq = dE + p_{ext}dV = 0$

$\Delta T = 0 \therefore dE = 0; p_{ext} = 0 \therefore p_{ext}dV = 0$

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 Gibb's 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 → p, r, s; B → r, s; C → t; D → p, q, t

1. (A) $CO_2(s) \longrightarrow CO_2(g)$

It is just a phase transition (sublimation) as no chemical change has occurred. Sublimation is always endothermic. Product is gas, more disordered, hence ΔS is positive

(B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

It is a chemical decomposition, not a phase change. Thermal decomposition occur at the expense of energy, hence endothermic. Product contain a gaseous species, hence, $\Delta S > 0$.

(C) $2H \longrightarrow H_2(g)$
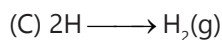
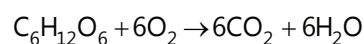A new H–H covalent bond is being formed, hence $\Delta H < 0$.

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

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

$$\Delta H_{combustion} = \left(6 \times \Delta H_f CO_2 + 6 \times \Delta H_f H_2O\right)$$
$$-\Delta H_f C_6H_{12}O_6$$

$$= \left(6 \times -400 + 6 \times -300\right) - \left(-1300\right)$$

= -2900 kJ/mol

= -2900/180 kJ/g

= -16.11 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

$$\Delta E = 0$$

So, $T_1 = T_2$

Also, $P_1\ P_1 = P_2\ P_2$

Sol 18: (B) At 100°C and 1 atmosphere pressure

$H_2O(\ell) \rightleftharpoons H_2O(g)$ is at equilibrium. For equilibrium

$\Delta S_{total} = 0$ and $\Delta S_{system} + \Delta S_{surrounding} = 0$

$\therefore \Delta S_{system} > 0$ and $\Delta S_{surrounding} < 0$

Sol 19: (C) $\Delta E = q + w$

$0 = q - P_{ext}\ \Delta V$

$q = P_{ext}\ \Delta V = 3$ atm $(2-1)L = 3$ atm L

$= \left(3 \times 101.3\right)$ Joule

$$\Delta S_{surr} = -\frac{q}{T} = \frac{3 \times 101.3}{300} = -1.013 \text{ Joule/K}$$