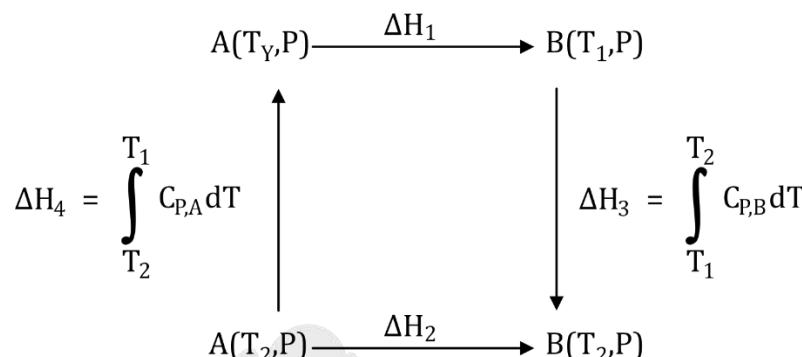


**KIRCHHOFF'S EQUATION (Variation of enthalpy with temperature) :**

The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in  $\Delta H$  with temperature is usually small compared to the value of  $\Delta H$  itself, consider a reaction  $A \rightarrow B$  at temperature  $T_1$  and pressure  $P$



Since  $H$  is state function : Change in enthalpy in cyclic process is equal to zero. To calculate enthalpy change ( $\Delta H_2$ ) at temperature  $T_2$  at constant pressure consider cyclic process shown in figure. It is clear

$\Delta H_3$  = change in enthalpy of A when temperature is raised from  $T_1$  to  $T_2$  at constant pressure.

$$\Delta H_3 = \int_{T_1}^{T_2} C_{p,B} dT$$

$\Delta H_4$  = Change in enthalpy taking 1 mole of B at constant pressure from  $T_1$  to  $T_2$

$$= \Delta H_4 = \int_{T_2}^{T_p} C_{p-A} dT$$

$$\text{now : } \Delta H_3 + \Delta H_1 + \Delta H_4 = \Delta H_2$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta H_3 + \Delta H_4$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (C_{p,B} - C_{p,A}) dT$$

$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1) \text{ If } \Delta_r C_p \text{ is independent of 'temperature'}$$

### THE SECOND LAW OF THERMODYNAMICS

**REQUIREMENT SECOND LAW:** There are two types of processes reversible process or quasi static process in which system remains in equilibrium with surrounding through out the process.

However reversible processes cannot take place on it's own - and are not natural process.

Reversible process does not lead to production of disorder.

On the other hand most of the processes taking place around us is example of irreversible process. Irreversible process also natural processes or spontaneous processes.

Example of natural processes :

(i) Water flowing down hill

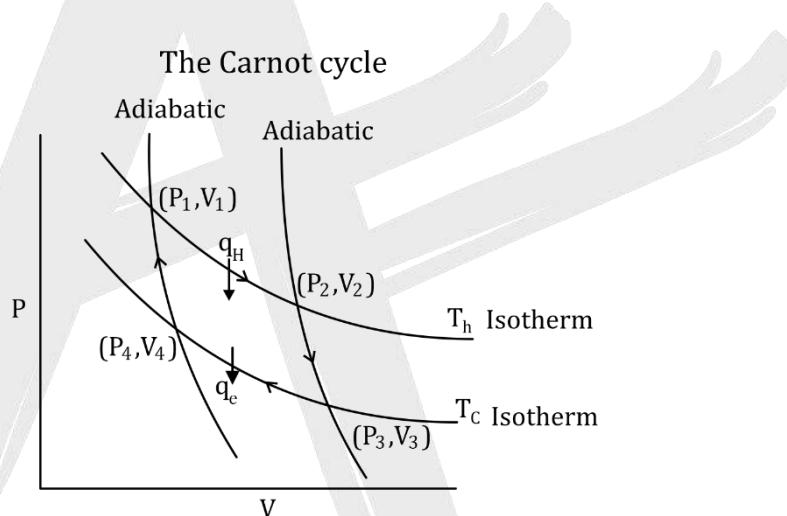
(ii) Heat flowing from hot body towards cold body on it's own

- (iii) mixing of two gases.
- (iv) Rusting of iron
- (v) Evaporation of water at room temperature.
- (vi) Formation of  $\text{NH}_3(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  gas in a closed container.
- (vii) Expansion of ideal gas in vacuum
- (viii) Burning of coal in  $\text{O}_2$

Every natural process leads to production of disorder. (During irreversible process system moves from ordered state to disordered state).

#### **EFFICIENCY OF CARNOT ENGINE :**

Carnot has devised an engine based on reversible steps. The efficiency of Carnot engine is maximum, because it is based on reversible cycle. A Carnot engine completes a cycle in four steps.



Reversible isothermal expansion from  $P_1, V_1$  to  $P_2, V_2$  at temp  $T_h$

Reversible adiabatic expansion from  $P_2, V_2, T_h$  to  $P_3, V_3, T_c$

Reversible isothermal compression from  $P_3, V_3$  to  $P_4, V_4$  at temp  $T_c$

Reversible adiabatic compression from  $P_4, V_4, T_c$  to  $P_1, V_1$  at temp  $T_h$

A carnot engine rejects minimum heat to the surrounding in its operation and maximum part of heat taken form source is converted into work. Hence efficiency of Carnot engine is given by

$$\eta = \frac{(\text{Net work done by engine in one cycle})}{\text{Net heat absorbed from source}} \times 100$$

$\eta = \frac{-w_{\text{net}}}{q_{\text{applied}}}$  where  $w_{\text{net}}$  is net work done on the engine(system) in one cycle.

$$\eta = \frac{q_H + q_C}{q_H} \times 100 \text{ (for both reversible and irreversible carnot cycle)}$$

It can be easily shown that  $-w_{\text{net}} = q_H + q_C$



$$q_H + q_c = nRT_b \ln \frac{V_2}{V_1} + nRT_c \ln \frac{V_4}{V_3}$$

$$\left\{ \begin{array}{l} T_c V_4^{\gamma-1} = T_h V_1^{\gamma-1} \\ T_c V_3^{\gamma-1} = T_h V_2^{\gamma-1} \end{array} \right\} \Rightarrow \left\{ \begin{array}{l} \frac{V_4}{V_3} = \frac{V_1}{V_2} \end{array} \right\}$$

because of reversible adiabatic process substituting these result's

$$\eta = \frac{T_h - T_c}{T_h} \times 100 \text{ (for reversible carnot cycle only)}$$

Efficiency of Carnot engine only depends upon temperature of source and sink and independent of choice of working substance.

Sum of the  $\frac{q_{rev}}{T}$  in a cyclic process is zero.

$$\text{For the Carnot cycle } \frac{q_H}{T_H} + \frac{q_C}{T_C} = 0 \Rightarrow \text{for carnot cycle } \sum \frac{q_{rev}}{T} = 0$$

The result in previous article is valid for any reversible cyclic process. It can be very easily verified.

Hence  $\oint \frac{dq_{rev}}{T} = 0 \Rightarrow$  Sum of the  $\frac{dq_{rev}}{T}$  over a cyclic path is zero.

now If  $\oint dx = 0 \Rightarrow dx$  is differential of a state function and X is state function.

$$\Rightarrow dS = \frac{dq_{rev}}{T} = \text{definite quantity}$$

$\Rightarrow S$  is a state function, known as Entropy.

### STATEMENT 2<sup>nd</sup> LAW OF THERMODYNAMICS :

It is impossible for a system to undergo cyclic process whose sole effects are the flow of heat from a heat reservoir and the performance of an equivalent amount of work by the system on surrounding. The key term in above statement is cyclic engine. If the first part of it's operation when engine do work heat is absorbed (source) and expansion on take place in second part, it must return to it's original state and to contract, it must loose heat to a cold object (sink).

In other words energy taken from source in one cycle cannot be completely converted into work. The second law of thermodynamics predicts direction of natural change. It do so with the help of state function 'S' - called entropy of system. But for predicting direction of natural change another quantity  $S_{surrounding}$  is also needed.  $S_{surrounding}$  which is called entropy of surrounding is a path dependent quantity.

$$dS_{system} = \frac{dq_{rev}}{T}$$

$$dS_{survumding} = -\frac{dq_{system}}{T}$$

Since  $S_{system}$  is state function - If a system make transition from state A to state B - by infinite paths in few of them may be reversible and other may be irreversible.  $\Delta S_{AB}$  will be same irrespective of path (A direct consequence of  $S_{system}$  being a state function).

However, If same transition from A to B is done by different irreversible path's,  $\Delta S_{\text{surrounding}}$  will be different in all processes. However if transition from A → B take place by many reversible path's,  $\Delta S_{\text{surr}}$  along each path will be same because

$$\sum_{A \rightarrow B}^{\text{path 1}} \frac{dq_{\text{rev}}}{T} = \Delta S_{\text{system}} = \sum_{A \rightarrow B}^{\text{path 2}} \frac{dq_{\text{rev}}}{T}$$

$$\Rightarrow \Delta S_{\text{surr}}(\text{path 1}) = -\Delta S_{\text{system}} = -\Delta S_{\text{surr}}(\text{path 2})$$

	$\Delta S_{\text{system}}$	$\Delta S_{\text{surrounding}}$
Reversible process	$\int_A^B \frac{dq_{\text{rev}}}{T}$	$-\int_A^B \frac{dq}{dq_{\text{rev}}}$
Irreversible process	$\int_A^B \frac{dq_{\text{rev}}}{T}$	$\int_A^B \frac{dq_{\text{irrev}}}{T} = -\left(\frac{q_{\text{irrev}}}{T}\right)_{A \rightarrow B}$

**Prediction of spontaneity of process :** If total entropy change in a process is positive the process must be spontaneous.

$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0$  for spontaneous change.

The second law of thermodynamics was developed during course of development of cyclic engines. Second law was discovered while studying efficiency of steam engines. In 1824 a french engineer Sodi carnot pointed out that for a cyclic heat engine to produce continuous mechanical works, it must exchange heat with two bodies at different temperature without a cold body to discard heat, the engine can-not function continuously.

**CLASIUS INEQUALITY:** From our experience we known if any one step in carnot engine is consciously made irreversible the efficiency of carnot engine will decrease from theoretical value

$$\eta = \frac{q_H + q_C}{q_H} = \frac{T_h - T_c}{T_h}$$

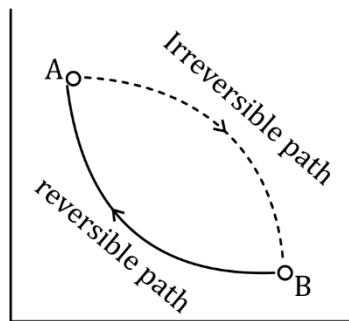
$$\Rightarrow \frac{q_H}{T_h} + \frac{q_C}{T} < 0$$

$$\Rightarrow \sum \frac{q_{\text{irr}}}{T} < 0$$

this mathematical statement is called Clasius inequality.

**Entropy change in isolated system** (isolated system = sys + surr)

Consider a system taken from state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the step is irreversible, according to Clasius inequality, sum of  $q/T$  over the cycle must be less than zero. Hence



$$\sum_{A \rightarrow B} \frac{q_{irr}}{T} + \sum_{B \rightarrow A} \frac{q_{rev}}{T} \leq 0 \Rightarrow \sum_{A \rightarrow B} \frac{q_{irr}}{T} = - \sum_{B \rightarrow A} \frac{q_{rev}}{T}$$

But  $- \sum_{B \rightarrow A} \frac{q_{rev}}{T} = \sum_{A \rightarrow B} \frac{q_{rev}}{T}$  since the process is reversible for infinitesimally small change

$$\begin{aligned} \left(\frac{dq}{T}\right)_{A \rightarrow B} &= dS_{\text{system } A \rightarrow B} \\ \Rightarrow dS_{\text{system}} &= \left(\frac{dq}{T}\right)_{A \rightarrow B} > 0 \\ \Rightarrow dS_{\text{system } A \rightarrow B} &= dS_{\text{sur } A \rightarrow B} > 0 \\ \Rightarrow \Delta S_{\text{Total isolated sys}} &> 0 \\ &\quad (\text{for an isolated system}) \\ dS_{\text{system}} &= dS_{\text{sur}} > 0 \quad (\text{for irreversible process}) \end{aligned}$$

### ENTROPY CALCULATION IN PROCESS INVOLVING IDEAL GASES :

From First law

$$\begin{aligned} dq &= dU + PdV \\ \frac{dq_{rev}}{T} &= \frac{dU}{T} + \frac{PdV}{T} \end{aligned}$$

But for ideal gas

$$\begin{aligned} \frac{dU}{T} &= \frac{nC_v dT}{T} \\ \Rightarrow dS_{\text{sys}} &= \frac{nC_v dT}{T} + \frac{nR}{V} dV \quad \{dU = nC_v dT\} \end{aligned}$$

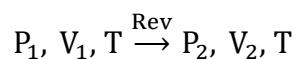
Integration gives

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \left( \frac{V_2}{V_1} \right)$$

### Isothermal process :

(a) **Reversible**

State A



$$\Delta S_{\text{system}} = nC_v/n \frac{T_2}{T_1} + nR/n \frac{V_2}{V_1}$$

Since  $T_1 = T_2$

$$\Delta S_{\text{system}} = nR/n \frac{V_2}{V_1}$$

$$\Delta S_{\text{surrounding}} = \frac{q_{\text{surrounding}}}{T} = - \frac{q_{\text{system}}}{T}$$

$$du = dq + dw \text{ (since } T_1 = T_2 \text{, So, } \Delta U = 0\text{)}$$

$$\therefore dq = -dw$$

$$\therefore q = -w \text{ as } w = -nRT/n \frac{V_2}{V_1}$$

$$q = nRT / n \frac{V_2}{V_1}$$

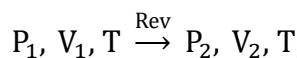
$$\therefore \Delta S_{\text{sys}} = \frac{-nRT \ell n \frac{V_2}{V_1}}{T} = -nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$= nR/n \frac{V_2}{V_1} - nR/n \frac{V_2}{V_1} = 0$$

### (b) Irreversible

State A State B



$$\Delta S_{\text{system}} = nR/n \frac{V_2}{V_1}$$

$$\Delta S_{\text{Surrounding}} = -\frac{q_{\text{system}}}{T}$$

$$q_{\text{system}} \text{ is calculated using FLOT } q_{\text{system}} = P_{\text{ext}}(V_2 - V_1)$$

$$\therefore \Delta S_{\text{surrounding}} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\Delta S_{\text{unificerse}} = nR \ell n \frac{V_2}{V_1}$$

$$= \left[ \left( nRT \ell n \frac{V_2}{V_1} \right) - P_{\text{ext}}(V_2 - V_1) \right] = [W_{\text{irrev}} - W_{\text{rev}}] > 0$$

As irreversible work of gas is more than reversible work.

**Adiabatic Proces :**

#### (a) Reversible Adiabatic

State A State B



$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$TV^{\gamma-1} = \text{constant}$$

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

$$(\Delta S)_{\text{system}} = nC_V \ln \left( \frac{V_1}{V_2} \right)^{\gamma-1} + nR \ln \frac{V_2}{V_1} = 0$$

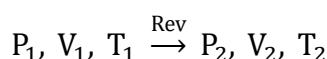
$$\Delta S_{\text{surr}} = -\frac{q_{\text{sys}}}{T} = 0 \quad (q_{\text{sys}} = 0)$$

$$\therefore \Delta S_{\text{universe}} = 0 + 0 = 0$$



## (b) Irreversible Adiabatic

State A State B



Using irreversible adiabatic process it is not possible to reach same state B which was reached by reversible adiabatic.

$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} > 0 [ (T_2)_{\text{irrev}} > (T_2)_{\text{rev}} ]$$

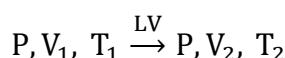
$$\Delta S_{\text{surt}} = -\frac{q_{\text{sys}}}{T} = 0 \text{ as } q = 0$$

For irreversible expansion the decrease in temperature will be lesser as work done is lesser hence, decrease in entropy due to fall in temperature will be lesser in case of irreversible expansion. Hence, net entropy would increase.

**Isobaric process :**

## (a) Reversible Isobaric

State A State B



$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rvv}}}{T} = \int_{T_1}^{T_2} \frac{-dq_{\text{sys}}}{T} = -nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} = 0$$

## (b) Irreversible Isobaric

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int \frac{nC_p dT}{T} = nC_p \varepsilon n \frac{T_2}{T_1}$$

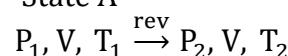
$$\Delta S_{\text{surrounding}} = \frac{-nC_p(T_2 - T_1)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$

**Isochoric Process**

## (a) Reversible Isochoric

State A



$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rvv}}}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_v n \frac{T_2}{T_1}$$

$$\Delta S_{\text{surr}} = - \int \frac{dq_{\text{rev}}}{T} = - \int_{T_1}^{T_2} \frac{nC_v dT}{T} = -nC_v n \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} = 0$$

## (b) Irreversible Isochoric

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_v dT}{T} = nC_v \ell n \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$



$$\Delta S_{\text{surrounding}} = \frac{-nC_V(T_2 - T_1)}{T_2}$$

### Entropy Calculation for phase transformations

$$\Delta S_{\text{fusion}} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{q}{T}$$

$$\text{for constant pressure } \Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus}}}{T}$$

$$\text{for constant volume } \Delta S_{\text{fus.}} = \frac{\Delta U_{\text{fusion}}}{T}$$

$$\Delta S_{\text{vap.}} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{q}{T}$$

$$\text{for constant Pressure, } \Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\text{for constant Volume, } \Delta S_{\text{vap.}} = \frac{\Delta U_{\text{vap}}}{T}$$

### Entropy Calculation solid or liquid systems:

- (a) 'Cu' block kept in open atmosphere

$$\Delta S_{\text{sys}} = \int_{T_1}^{T_2} \frac{msdT}{T} = ms \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S_{\text{surrounding}} = \int \frac{dq_{\text{surr}}}{T} = \frac{q_{\text{surr}}}{T_2}$$

$$\text{but } \Delta S_{\text{surrounding}} = -q_{\text{system}} = -ms(T_2 - T_1) = ms(T_1 - T_2)$$

$$\text{Hence, } \Delta S_{\text{surrounding}} = \frac{ms(T_1 - T_2)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \therefore \Delta S_{\text{universe}} = ms \ln \frac{T_2}{T_1} + \frac{ms_1(T_1 - T_2)}{T_2} > 0$$

- (b) Two copper block kept in contact in thermostat Two blocks are of same mass

$$\Delta S_{\text{surr}} = 0 \text{ (since no heat is lost to surrounding)}$$

$$\Delta S_{\text{system}} = \Delta S_A + \Delta S_B$$

System will reach a common temperature ( $T_f$ ) and  $T_1 > T_f > T_2$

$$\begin{aligned} \Delta S_{\text{system}} &= \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T} \\ &= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms \left[ \ell \ln \frac{T_f}{T_1} + \ell \ln \frac{T_f}{T_2} \right] \end{aligned}$$

$$\Delta S_{\text{system}} = ms \ln \frac{T_2}{T_1}$$

$$\text{Since } T_f = \frac{T_1 + T_2}{2}$$

$$\therefore \Delta S_{\text{system}} = ms \ln \frac{(T_1 + T_2)^2}{4 T_1 T_2}$$



Process	$\Delta S_{\text{sys}}_{\text{s}}$	$\Delta S_{\text{surr}}$
Isothermal reversible	$\Delta S_{\text{sys.}} = nR \ell n \frac{V_2}{V_1}$	$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$
Isothermal irreversible	$\Delta S_{\text{sys.}} = nR \ell n \frac{V_2}{V_1}$	$\Delta S_{\text{surr.}} = \frac{-q_{\text{sys}}}{T} = \frac{W_{\text{sys}}}{T}$ $= \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{5y5} = 0$	$\Delta S_{\text{surr}} = 0$
Adiabatic irreversible	$\Delta S_{5y\text{s}} = nC_P \ell n \frac{T_2}{T_1}$ $+ nR \ell n \frac{P_1}{P_2}$	$\Delta S_{\text{surr}} = 0$
Isochoric reversible	$\Delta S_{\text{sys}} = nC_V \ell n \frac{T_2}{T_1}$	$\Delta S_{\text{surr}} = -\Delta S_{\text{sys.}}$
Isochoric irreversible	$\Delta S_{5yz} = nC_V \ell n \frac{T_2}{T_1}$	$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T_{\text{surr}}}$ $= \frac{-nCC_V \cdot \Delta T}{T_{\text{surr}}}$

1. Two moles of an ideal gas is expanded isothermally and irreversibly at 27°C from volume  $V_1$  to  $7.5 V_1$  and 4.17 kJ heat is absorbed from surroundings. Determine  $\Delta S_{\text{sys}}$ ?  
(Approximate integer in Cal)

Ans.  $\Delta_{\text{sys}}S = 8\text{Cal}$

Sol.  $\Delta_{\text{sys}}S = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1}$

$$\Delta_{\text{sys}}S = nR \ln \frac{V_2}{V_1} = 2 \times 8.314 \ln 7.5 = 33.6\text{J} = 8\text{Cal}$$

2. Two mole of an ideal gas originally at a volume of 8 L. at 1000 K, is allowed to expand adiabatically until final volume is 24 L. For the gas  $C_V = 1.5R$ . Calculate values of  $\Delta S$  for the process when :

- (i) The expansion takes place reversibly.
  - (ii) The change in volume involves a free expansion.
- (Used :  $e^{1.09} = 3$  and  $1.09 \times 8.314 = 9$ )

Ans. 0.18 J/K.

Sol. (i) In case of adiabatic reversible expansion,  $dq_{rev} = 0$   $\Delta S = 0$ .

(ii) In case of free expansion (Adiabatically)

$$W = 0, q = 0, \Delta U = 0 \quad nCV_V(T_2 - T_1) = 0 \quad T_2 = T_1 \\ \Delta S = nR\ln(3) = 18J/K.$$

3. (a) One mole of an ideal gas expands isothermally and reversibly at 25°C from a volume of 10 litres to a volume of 20 litres.

(i) What is the change in entropy of the gas ?

(ii) How much work is done by the gas ?

(iii) What is  $q$  (surroundings) ?

(iv) What is the change in the entropy of the surroundings ?

(v) What is the change in the entropy of the system plus the surroundings?

(b) Also answer the questions (i) to (v) if the expansion of the gas occurs irreversibly by simply opening a stopcock and allowing the gas to rush into an evacuated bulb of 10-L volume.

Sol. (i)  $\Delta S = 2.303nR\log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76 J/K.$

(a) (ii)  $w_{rev} = 2.303nRT\log \frac{V_2}{V_1}$   
 $= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1718 J.$

(iii) For isothermal process,  $\Delta U = 0$  and heat is absorbed by the gas,

$$q_{rev} = \Delta U - W = 0 - (-1718) = 1718 J \\ \therefore q_{surr} = 1718 J. (\because \text{process is reversible}) \\ (\text{iv}) \quad \Delta S_{surr} = -\frac{1718}{298} = -5.76 J/K.$$

As entropy of the system increases by 5.76 J, the entropy of the surrounding decreases by 5.76 J, since the process is carried out reversible.

(v)  $\Delta S_{sys} + \Delta S_{surr} = 0 \dots \dots \text{for reversible process.}$

### DO YOURSELF-1

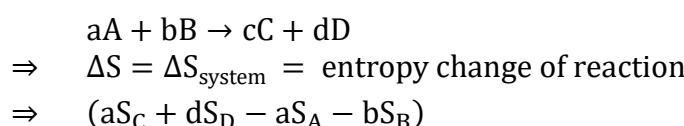
- One mole of ideal monoatomic gas was taken through isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{system}$ ,  $\Delta S_{surr}$  and  $\Delta S_{univers}$  if
  - process carried out reversibly
  - process carried out irreversibly (one step)
- Two moles of an ideal gas is expanded isothermally and irreversibly at 27°C from volume  $V_1$  to  $7.5 V_1$  and 4.17 kJ heat is absorbed from surroundings. Determine  $\Delta S_{sys}$ ? (Approximate integer in  $\text{CalK}^{-1}$ )



3. What would be the entropy change involved in thermodynamic expansion of 2 moles of a gas from a volume of 1 L to a volume of 10 L at 25°C [Given R = 8.3 J/mole – K ]
- 38.23 J/K
  - 26.76 J/K
  - 20 J/K
  - 28.23 J/K
4. An isobaric process having one mole of ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C. What would be the molar specific heat capacity ( $C_p$ ) ?
- $\frac{10}{\log_{10} 2}$  J/Kmol
  - $\frac{10}{\ln 2}$  J/Kmol
  - $\log_{10} 2$  J/Kmol
  - $10\log_{10} 2 + 8.3$  J/Kmol
5. When two mole of an ideal gas ( $C_{p,m} = \frac{5}{2}R$ ) heated from 300 K to 600 K at constant pressure. The change in entropy of gas ( $\Delta S$ ) is :
- $\frac{3}{2}R\ln 2$
  - $-\frac{3}{2}R\ln 2$
  - $5R\ln 2$
  - $\frac{5}{2}R\ln 2$
6. In previous problem calculate  $\Delta S_{\text{gas}}$  if process is carried out at constant volume :
- $5R\ln 2$
  - $\frac{3}{2}R\ln 2$
  - $3R\ln 2$
  - $-3R\ln 2$

#### Entropy change in chemical Reaction :

From application of third law absolute entropy of every compound or element can be deduced for a general chemical reaction taking place at given condition



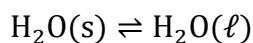
where  $S_C, S_D, S_A$  and  $S_B$  are molar entropy of substance A, B, C and D under given circumstance.



### Entropy change in phase transition :

#### Fusion :

When solid ice is heated below 273 K at external pressure of 1 atm its temperature slowly rises. At 273 K however, it starts melting into liquid without increase in temperature. The process is reversible phase transition from solid to liquid represented as :



Since process is reversible (phase transition at constant temperature and pressure are reversible phase transitions).

$$\text{Now } \Delta S_{\text{Total}} = 0 \quad (\text{since process is reversible})$$

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

$$\text{also } \Delta S_{\text{surrounding}} = \frac{-\Delta H_{\text{fusion}}}{T_f} \quad (\text{here } T_f = \text{freezing point})$$

**Vapourisation:** From your day to day experience you know that under atmospheric pressure temperature of  $\text{H}_2\text{O}(\ell)$  can not exceed 373 K. Since at 373 K liquid  $\text{H}_2\text{O}$  undergo phase transition.

$$\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$$

since  $\Delta S_{\text{Total}} = 0$

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

$$\Delta S_{\text{system}} = \Delta S_{\text{fusion}} = S_{\text{H}_2\text{O}(\text{g})} - S_{\text{H}_2\text{O}(\ell)}$$

(Process is reversible)

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

Note: Boiling point at 1 atm pressure is called normal boiling point. There can be infinite boiling points of liquid depending upon external pressure we apply on boiling vessel.

4. The enthalpy of vaporisation of liquid diethyl ether  $[(\text{C}_2\text{H}_5)_2\text{O}]$ , is 26.0 kJ mol<sup>-1</sup> at its boiling point (35.0 °C). Calculate ΔS for conversion of : (a) liquid to vapour, and (b) vapour to liquid at 35°C.

- Sol. (a)  $+84.41 \text{ J K}^{-1} \text{ mol}^{-1}$   
(b)  $-84.41 \text{ J K}^{-1} \text{ mol}^{-1}$

Sol. (a)  $\Delta S_{\text{vap.}} = \frac{\Delta H_{\text{vap.}}}{T} = \frac{26 \times 10^3}{308} = +84.41 \text{ J K}^{-1} \text{ mol}^{-1}$

(b)  $\Delta S_{\text{cond.}} = \frac{\Delta H_{\text{cond.}}}{T} = -\frac{26 \times 10^3}{308} = -84.41 \text{ J K}^{-1} \text{ mol}^{-1} \quad (\because H_{\text{cond.}} = -26 \text{ kJ})$



### ENTROPY AND CRITERIA OF SPONTANEITY OF CHEMICAL PROCESS :

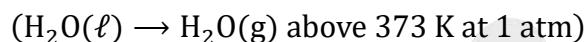
The entropy change of chemical reaction together with entropy change of surrounding determine spontaneity of a chemical process under given set of condition.

$$\Delta S_{\text{Total}} = \Delta_r S - \frac{\Delta_r H}{T}$$

If  $\Delta_r S$  = positive and very large while  $\Delta_r H$  is negative and large this means  $\Delta S_{\text{Total}} > 0$ .

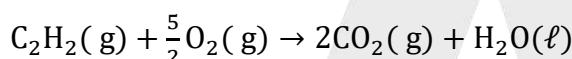
If  $\Delta_r S$  = positive but small and  $\Delta_r H$  is negative but having large value.

⇒ If  $\Delta S_{\text{Total}}$  is +ive due to large +ive value of  $\Delta_r S$ , we can say reaction is entropy driven that is increased in disorder in forward direction is the driving force of reaction which takes it in forward direction.



⇒ Sometimes reaction go completely in forward direction inspite of negative entropy change in reaction due to large -ive value of  $\Delta_r H$ . These reaction are enthalpy driven.

**Example :**

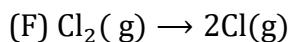
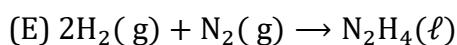


### Spontaneous and non Spontaneous

Sign of $\Delta S$	Sign of $\Delta S$	Comment	Example	$\Delta H_{298}$	$\Delta S_{298}$
-	+	spontaneous at all temperature	$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl(g)}$ $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-185 -394	14.1 3
-	-	spontaneous at low temperature	$\text{H}_2(\text{g}) + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}(\ell)$ $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$	-44 -198	-119 -187
+	+	spontaneous at high temperature	$\text{NH}_4\text{Cl(s)} \rightarrow \text{NH}_3(\text{g}) + \text{HCl(g)}$ $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO(g)}$	176 180	284 25
+	-	non spontaneous at all temperature	$3\text{O}_2 \rightarrow 2\text{O}_3$ $2\text{H}_2\text{O}(\ell) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}_2(\ell)$	286 196	-137 -126

5. Will  $\Delta S$  be positive or negative in the following processes? Discuss qualitatively

- (A)  $\text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O}(\ell)$
- (B)  $\text{H}_2\text{O}(\ell) \rightarrow \text{H}_2\text{O(g)}$
- (C)  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl(g)}$
- (D)  $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$



Sol. As we have discussed that the entropy of reaction is more if there is a change in value of  $\Delta v_g$  (the change in the stoichiometric number of gaseous species), since the entropy of gases is much larger than the entropy of the condensed phases.

- |             |                            |
|-------------|----------------------------|
| for process | (a) $\Delta S$ is +ve      |
| for process | (b) $\Delta S$ is +ve      |
| for process | (c) $\Delta S$ is zero     |
| for process | (d) $\Delta S$ is negative |
| for process | (e) $\Delta S$ is negative |
| for process | (f) $\Delta S$ is positive |

6. Predict whether the entropy change of the system in each of the following process is positive or negative.

- (A)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- (B)  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- (C)  $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g})$
- (D)  $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$
- (E)  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
- (F) Cooling of  $\text{N}_2(\text{g})$  from  $20^\circ\text{C}$  to  $-50^\circ\text{C}$

Sol. Gaseous substances generally possess more entropy than solids. So whenever the products contain more moles of a gas than the reactants, the entropy change is probably positive. And hence,  $\Delta S$  is

- (A) positive
- (B) negative
- (C) small, the sign of  $\Delta S$  is impossible to predict
- (D) negative
- (E) negative
- (F) negative

[Note : For a given substance at a given temperature,  $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$  ]

#### THIRD LAW OF THERMODYNAMICS :

Third law of thermodynamics helps in determining absolute entropy of substances. It is based on an assumption that entropy of every perfectly crystalline substance is zero at zero Kelvin. This is justified because, at absolute zero every substance is in state of lowest energy and

position of every atom or molecule is defined in solid. Hence at  $T = 0$   $S(T = 0) = 0$  Third law If we have sufficient heat capacity data (and the data on phase changes) we could write

$$S(T) = S(T = 0) + \int_0^T \frac{C_p}{T} dT$$

(If there is a phase change between 0 K and T, we would have to add the entropy of the phase change.) If  $C_p$  were constant near  $T = 0$ , we would have,

$$S(T) = S(T = 0) + C_p \ln \frac{T}{0}$$

Which is undefined. Fortunately, experimentally  $C_p \rightarrow 0$  as  $T \rightarrow 0$ . For nonmetals  $C_p$  is proportional to  $T^3$  at low temperature. For metals  $C_p$  is proportional to  $T^3$  at low temperatures but shifts over to being proportional to  $T$  at extremely low temperatures. (The latter happens when the atomic motion "freezes out" and the heat capacity is due to the motion of the conduction electrons in the metal.)

equation (i) could be used to calculate absolute entropies for substances if we know what the entropy is at absolute zero. Experimentally it appears that the entropy at absolute zero is the same for all substances. The third law of thermodynamics modifies this observation and sets  $S(T = 0) = 0$

for all elements and compounds in their most stable and perfect crystalline state at absolute zero and one atmosphere pressure. (All except for helium, which is a liquid at the lowest observable temperatures at one atmosphere.)

The advantage of this law is that it allows us to use experimental data to compute the absolute entropy of a substance. For example, suppose we want to calculate the absolute entropy of liquid water at 25°C. We would need to know the  $C_p$  of ice from 0 K to 273.15 K. We also need the heat of fusion of water at its normal melting point. With all of this data, which can be obtained partly from theory and partly from experiment, we find

$$S_{H_2O}(298.15 \text{ K}) = 0 + \int_0^{273.15} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{273.15} + \int_{273.15}^{298.15} \frac{C_p(l)}{T} dT.$$

Some substances may undergo several phase changes.

7. For a perfectly crystalline solid  $C_{p.m.} = aT^3$ , where a is constant. If  $C_{p.m.}$  is 0.42 J/K – mol at 10 K, molar entropy at 10 K is :
- (A) 0.42 J/K – mol
  - (B) 0.14 J/K – mol
  - (C) 4.2 J/K – mol
  - (D) zero



Ans. (B)

$$\text{Sol. } 0.42 = a(10)^3$$

$$S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3} [10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K - mol}$$

### GIBB'S FUNCTION :

Entropy is a universal criteria of spontaneity. This means for any process if  $\Delta S_{\text{Total}} > 0$  the process is spontaneous. Most of the chemical process take place at constant temperature and pressure. A very useful criteria of spontaneity of process at constant temperature and pressure is Gibb's function :

Gibb's function (G) is defined as

$$G = H - TS$$

Gibb's function and spontaneous process :

from 2<sup>nd</sup> law we known :

$$\frac{dq}{T} \leq dS_{\text{system}} : \text{Less than sign for if } q = q_{\text{irr}}$$

$$\Rightarrow dq \leq TdS$$

$$dq = dV + PdV$$

subsstituting value of dq from equation (iii) to equation (ii)

$$dV + PdV - TdS \leq 0$$

$$\Rightarrow d(H - TS)_{P,T} \leq 0$$

$$\therefore d(H - TS)_{P,T}^- = (dH - TdS - SdT)_{P,T}^-$$

$$= (dU + PdV + VdP - TdS - SdT)_{P,T}^- \leq 0$$

$$\Rightarrow d(H - TS)_{P,T} \leq 0$$

$$\Rightarrow d(dG)_{P,T} \leq 0$$

During course of every spontaneous process, Gibb's function decreases. If a process is allowed to run spontaneously, eventually it attain equilibrium. At equilibrium, the Gibb's function attains minimum value. No further decrease to the value of Gibb's function is possible at equilibrium.

Hence at equilibrium.  $(dG)_{T,P} = 0$ .

$\Rightarrow$  Entropy change in spontaneous process :

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$$

The sign  $>$  is for spontaneous process. A state of equilibrium in a close system is attained spontaneously.

As system approaches equilibrium from non-equilibrium state  $-S_{\text{Total}}$  keeps on increasing and at equilibrium  $S_{\text{Total}}$  attains its maximum value.

$\Rightarrow \Delta S_{\text{Total}} = 0$  at equilibrium

at this point  $S_{\text{Total}} = \text{maximum value at equilibrium in a close system}$

**SIGNIFICANCE OF GIBB'S FUNCTION :**

(a) Decrease in Gibb's function at constant temperature and pressure is related to □ Stotal (total entropy change of system and surrounding).

We know :  $\Delta G = \Delta H - T\Delta S$

(i) ; at constant T and pressure

also  $\Delta H = q_p$  at constant pressure

$q_{P_p}$  = heat absorbed by system at constant pressure.

$\Rightarrow \Delta G = q_p - T\Delta S$ .

this gives  $-\frac{\Delta G}{T} = -\frac{q_p}{T} + \Delta S$

$$-\frac{q_p}{T} + \Delta S_{\text{surrounding}}$$

$$\Rightarrow -\frac{\Delta G}{T} = (\Delta S_{\text{surrounding}} + \Delta S_{\text{system}})$$

Student might get confused in

$$\text{ex: } -\frac{q}{T} = \Delta S_{\text{surr.}}$$

ex:  $q$  = Heat absorbed by system

$-q$  = Heat absorbed by surrounding

$$\Rightarrow -\Delta G = T(\Delta S_{\text{Total}})$$

Note equation (ii) can be written as  $\Delta G = q - q_{\text{rev.}}$  for spontaneous process ( $\Delta G_{T,P} < 0$ )

$$\Rightarrow q - q_{\text{rev.}} < 0 \Rightarrow q_{\text{rev.}} > q$$

**Gibbs function and non PV work :**

Decrease in Gibb's function at constant temperature and pressure in a process gives an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electrical work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can be written as

$$dU = dq - PdV = d_{\text{wnon-PV}}$$

$-dw_{\text{non-PV}}$  = non-PV work done by the system.

$$dG = d(H - TS)$$

$$= dH - TdS - SdT$$

$$d = dU + PdV + VdP - TdS - SdT$$

$$dG = dq - PdV - w_{\text{non-PV}} + PdV + VdP - TdS - SdT$$

for a reversible change at cont. T and P



$$dG = d_{\text{rev.}} - dw_{\text{non}} + VdP - TdS - SdT$$

since  $dq_{\text{rev}} = TdS$   
 $\Rightarrow - (dG)_{T,P} = dw_{\text{non-PV}}$

Non-pV work is work done due to chemical energy transformation or due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

### Gibbs free energy change at constant temperature :

In order to derive an equation which will enable us to calculate the Gibbs free energy change of an isothermal process but with varying pressure, we may conveniently start with the equation,  
 $G = E + PV - TS$

Differentiating the above equation, we get

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

According to first law of thermodynamics,

$$\begin{aligned} dq &= dE + PdV \\ \therefore dG &= dq + VdP - TdS - SdT \end{aligned}$$

Further since  $\frac{dq}{T} = dS$ , we can replace  $dq$  by  $TdS$ .

$$\therefore dG = VdP - SdT$$

At constant temperature,  $dT = 0$

$$\begin{aligned} \therefore dG &= VdP \\ \text{or } \left(\frac{dG}{dP}\right)_T &= V \end{aligned}$$

Thus Gibb's function of every substance increases on increasing pressure, but this increase is maximum for gases, compared to solids or liquids since gases have maximum molar volume.  
On integrating equation  $dG = VdP$  for very minute changes from state 1 to 2, we have

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

In case of one mole of a perfect gas,

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

$$\Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P} = RT \ln \frac{P_2}{P_1}$$

For  $n$  moles of a perfect gas, the free energy change is

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$



**Gibbs free energy change at constant pressure From equation which is**

$$dG = VdP - SdT$$

(Only for pure substances)

when pressure is constant,  $dP = 0$

$$\therefore dG = -SdT$$

$$\text{or } \left(\frac{dG}{dT}\right)_p = -S$$

thus Gibb's function of every substance decreases with temperature, but this decrease is maximum for gases since they have maximum state of disorder. Hence on increasing temperature, gas phase gain maximum stability compared to solid or liquid phase.

Gibbs free energy change for chemical reaction :

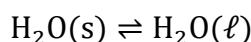
$$d(\Delta_r G) = \Delta_r V(dp) - \Delta_r S(dT)$$

at constant temperature, If  $\Delta_r V \sim \text{constant}$

$$\Rightarrow \int_1^2 d(\Delta_r C_p) = \Delta_r V \int_1^2 dp$$

$$\Rightarrow \Delta_r C_{p_2} - \Delta_r C_{p_1} = \Delta_r V(P_2 - P_1)$$

only for condensed phase : equilibrium like



Gibbs free energy change for chemical reaction :

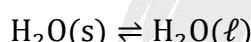
$$d(\Delta_r G) = \Delta_r V(dp) - \Delta_r S(dT)$$

at constant temperature, If  $\Delta_r V \sim \text{constant}$

$$\Rightarrow \int_1^2 d(\Delta_r C_p) = \Delta_r V \int_1^2 dp$$

$$\Rightarrow \Delta_r C_{p_2} - \Delta_r C_{p_1} = \Delta_r V(P_2 - P_1)$$

only for condensed phase : equilibrium like



### GIBBS FREE ENERGY CHANGE IN CHEMICAL REACTIONS :

Gibbs free energy changes have a direct relationship with the tendency of the system to proceed to a state of equilibrium. In view of this fact, it is desirable to have a knowledge of the free energy of chemical compounds so that the Gibbs free energy change of a possible reaction could be easily calculated. Standard free energies have been used for this case. A zero value of the Gibbs free energy is assigned to the free energies of the stable form of the elements at 25°C and 1 atm. pressure.

With this as reference point, free energies of compounds have been calculated which are called standard Gibbs free energies of formation. The difference in the Gibbs free energy of products

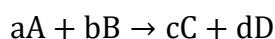


and reactants in their standard states (at 25°C and 1 bar pressure) is denoted as  $\Delta G^\circ$ . In standard enthalpy and entropy values are available,  $\Delta G^\circ$  can be written from equation as,

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

### GIBB'S FREE ENERGY IN CHEMICAL REACTIONS FROM GIBB'S FREE ENERGY OF FORMATION OF COMPOUNDS :

Consider a chemical reaction,



The standard Gibb's free energy change  $\Delta G^\circ$  can be computed on the basis discussed above (i.e., by assigning zero value to the Gibbs free energy of the stable form of elements at 25°C and 1 bar pressure). With this as reference, the standard Gibbs free energy of the products and reactants can be determined. The standard Gibbs free energy change for the overall reaction can be evaluated as :

$$\begin{aligned}\Delta G &= \Sigma G_f^\circ_{\text{(product)}} - \Sigma G_f^\circ_{\text{(reactants)}} \\ &= (cG_C^\circ + dG_D^\circ) - (aG_A^\circ + bG_B^\circ)\end{aligned}$$

A negative sign of  $\Delta G^\circ$  will show that the reaction will proceed spontaneously. note that  $\Delta G^\circ$  can be defined at any temperature, at standard pressure of 1 bar

### Reversible phase transition and Gibb's free energy change :

During reversible phase transition which occurs at transition temperatures, Gibb's function change become zero, implying the fact that these processes are reversible processes. at 373 K and 1 atm pressure  $\Delta G = 0$  for  $H_2O(l) \rightarrow H_2O(g)$  at 273 K and 1 atm pressure  $\Delta G = 0$  for  $H_2O(s) \rightarrow H_2O(l)$

Gibb's energy and equilibrium constant, an important topic taken up in chemical equilibrium. Application of Gibb's function in describing variation of vapour pressure, boiling and melting point with temperature is taken up in chemical equilibrium and liquid solutions variation of  $G/T$  with temperature, has important implication in predicting feasibility of process at different temperatures. This gives Famous Gibb's Helmholtz equation taken up in electrochemistry.

Topics of thermodynamics taken up in later chapters :

### **Application of :**

Gibb's function and non-PV work is taken in electrochemistry.

Gibb's free energy and phase equilibrium taken in liquid solution.

Gibb's function and position of equilibrium and relationship between  $\Delta G^\circ$  and  $K_{eq}$  taken up in chemical equilibrium.

Variation of  $\frac{G}{T}$  with temperature also called Gibb's helmholtz equation taken in electrochemistry.

8. Calculate the boiling point of bromine from the following data :

$\Delta H^\circ$  and  $\Delta S^\circ$  values of  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$  are 30.91 kJ/mole and 93.2 J/mol. K respectively.

Assume that  $\Delta H$  and  $\Delta S$  do not vary with temperature.

Ans. 331.6 K.

Sol. Consider the process :  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$

The b.p. of a liquid is the temperature at which the liquid and the pure gas coexist at equilibrium at 1 atm.

$$\therefore \Delta G = 0$$

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

$$\Delta H = \Delta H^\circ = 30.91 \text{ kJ}$$

$$\Delta S = \Delta S^\circ = 93.2 \text{ J/K} = 0.0932 \text{ kJ/K}$$

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

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

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

9. For a reaction  $\text{M}_2\text{O}(\text{s}) \rightarrow 2\text{M}(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$ ;  $\Delta H = 30 \text{ kJ mol}^{-1}$  and  $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$  at 1 atm. Calculate upto which temperature, the reaction would not be spontaneous.

Ans.  $T < 428.57 \text{ K}$

Sol. Given, for the change,  $\Delta H = 30 \times 10^3 \text{ J mol}^{-1}$ ,  $\Delta S = 70 \text{ JK}^{-1} \text{ mol}^{-1}$  For a non-spontaneous reaction

$$\Delta G = +\text{ve}$$

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

$\therefore \Delta H - T\Delta S$  should be + ve

$$\text{or } \Delta H > T\Delta S$$

$$\text{or } \frac{\Delta H}{\Delta S} \Rightarrow T < \frac{30 \times 10^3}{70} \Rightarrow T < 428.57 \text{ K}$$

10. Sulphur exists in more than one solid form. The stable form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs :  $s(\text{rhombic}) \rightarrow s(\text{mono clinic})$

Thermodynamic measurements reveal that at 101.325kPa and 298 K,

$$\Delta_r H = 276.144 \text{ J mol}^{-1} \text{ and } \Delta_r G = 75.312 \text{ J mol}^{-1}$$

(A) Compute  $\Delta_r S$  at 298 K

(B) Assume that  $\Delta_r H$  and  $\Delta_r S$  do not vary significantly with temperature, compute  $T_{eq}$ , the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

Ans.  $\Delta_r S = 0.674 \text{ J K}^{-1} \text{ mol}^{-1}$ , 409.7 K

Sol. (A)

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



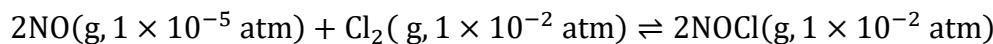
Therefore  $\Delta_r S = \frac{\Delta_r H - \Delta_r G}{T} = \frac{276.144 \text{ J mol}^{-1} - 75.312 \text{ J mol}^{-1}}{298 \text{ K}}$   
 $= 0.674 \text{ J K}^{-1} \text{ mol}^{-1}$

(B) When the rhombic sulphur is in equilibrium with monoclinic sulphur, we would have

$$\Delta_r G = 0 = \Delta_r H - T_{eq} \Delta_r S$$

$$\text{Thus } T_{eq} = \frac{\Delta_r H}{\Delta_r S} = \frac{276.144 \text{ J mol}^{-1}}{0.674 \text{ J mol}^{-1}} = 409.7 \text{ K}$$

11. Following reaction occurs at 25°C :



Calculate  $\Delta G^\circ$  [R = 8 J/moleK]

Ans. - 43.92KJ



Sol. 
$$\Delta G^\circ = -2.303RT \left( \log \frac{(1 \times 10^{-2})^2}{(1 \times 10^{-5})^2(1 \times 10^{-2})} \right) = -2.303RT \left[ \log \frac{1 \times 10^{-2}}{1 \times 10^{-10}} \right]$$
  
 $= -2.303RT[\log 1 \times 10^8] = -2.303 \times 8 \times 298 \times 8 = -43.92 \text{ KJ.}$

### DO YOURSELF-2

- Which of the following conditions regarding a chemical process ensures its spontaneity at all temperature?
  - $\Delta H > 0, \Delta S < 0$
  - $\Delta H < 0, \Delta S > 0$
  - $\Delta H < 0, \Delta S < 0$
  - $\Delta H > 0, \Delta S < 0$
- When reaction is at standard state at equilibrium, then :
  - $\Delta H^\circ = 0$
  - $\Delta S^\circ = 0$
  - equilibrium constant  $K = 0$
  - equilibrium constant  $K = 1$
- For the hypothetical reaction  $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightarrow 2\text{AB(g)}$   
 If  $\Delta_r G^\circ$  and  $\Delta_r S^\circ$  are 20 kJ/mol and  $-20 \text{ JK}^{-1} \text{ mol}^{-1}$  respectively at 200 K.  $\Delta_r C_p$  is  $20 \text{ JK}^{-1} \text{ mol}^{-1}$  then  $\Delta_r H^\circ$  at 400 K is :
  - 20 kJ/mol
  - 7.98 kJ/mol
  - 28 kJ/mol
  - 18 kJ/mol



4. Gases  $\Delta G_f^\circ$  (Cal/mole)

CO – 32.80

H<sub>2</sub>O – 54.69

CO<sub>2</sub> – 94.26

H<sub>2</sub> 0

Estimate the standard free energy change in the chemical reaction CO + H<sub>2</sub>O → CO<sub>2</sub> + H<sub>2</sub>

5. The equilibrium constant for the reaction given below is  $2.0 \times 10^{-7}$  at 300 K. Calculate the standard free energy change for the reaction;



Also, calculate the standard entropy change if  $\Delta H^\circ = 28.40 \text{ kJ mol}^{-1}$ .

6. At 1 atm and 27°C, will the vaporisation of liquid water be spontaneous ?

(Given  $\Delta H = 9710 \text{ cal}$  and  $\Delta S = 26 \text{ cal K}^{-1}$ .)



## EXERCISE # (0-I)

Carnot cycle and 2<sup>nd</sup> law of thermodynamics

1. The maximum efficiency of a heat engine operating between 100°C and 25°C is :-  
 (A) 20.11%      (B) 22.2%      (C) 25.17%      (D) 30%
2. A heat engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :-  
 (A) 0.4 Kcal      (B) 0.8 Kcal      (C) 4 Kcal      (D) 8 Kcal
3. A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at T<sub>2</sub>. A second reversible engine B absorbs, the same amount of heat as rejected by the engine A, from the reservoir at T<sub>2</sub> and rejects energy to a reservoir at 360K. If the efficiencies of engines A and B are the same then the temperature T<sub>2</sub> is :-  
 (A) 680 K      (B) 640 K      (C) 600 K      (D) 800 K

Entropy calculation and ΔS

4. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is :-  
 (A)  $\Delta S_{\text{system}} - \Delta S_{\text{surroundings}} > 0$       (B)  $\Delta S_{\text{system}} > 0$  only  
 (C)  $\Delta S_{\text{surroundings}} > 0$  only      (D)  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$
5. 2 mole of ideal gas at 27°C temperature is expanded reversibly from 2 lit. to 20 lit. Find entropy change( $R = 2 \text{ cal/mol K}$ ) :-  
 (A) 92.1      (B) 0      (C) 4      (D) 9.2
6. The entropy changes when two moles of ideal monoatomic gas are heated from 200 to 300°C reversibly and isochorically :-  
 (A)  $\frac{3}{2} R \ln\left(\frac{300}{200}\right)$       (B)  $\frac{5}{2} R \ln\left(\frac{573}{273}\right)$       (C)  $3R \ln\left(\frac{573}{473}\right)$       (D)  $\frac{3}{2} R \ln\left(\frac{573}{473}\right)$
7. When one mole of an ideal gas is compressed to half to its initial volume & simultaneously heated to twice its initial temperature. The change in entropy ( $\Delta S$ ) of gas is :  
 (A)  $C_v \ln 2$       (B)  $C_p \ln 2$       (C)  $R \ln 2$       (D)  $(C_v - R) \ln 2$
8. 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
9. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure



(1 atm) always remains constant then calculate total entropy change ( $\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ ) for given process.

- (A) 56 J/K      (B) 14 J/K      (C) 16 J/K      (D) 20 J/K

**10.** An isobaric process having one mole of ideal gas has entropy change 23.03 J/K for the temperature range 27°C to 327°C. What would be the molar specific heat capacity ( $C_v$ ) ?

- (A)  $\frac{10}{\log 2}$  J/K mol      (B)  $\frac{10}{\log 2} - 8.3$  J/K mol

- (C)  $10 \times \log 2$  J/K mol      (D)  $10 \log 2 + 8.3$  J/K mol

**11.** When two equal sized pieces of the same metal at different temperatures  $T_h$  (hot piece) and  $T_c$  (cold piece) are brought into thermal contact and isolated from it's surrounding. The total change in entropy of system is given by ?

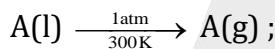
- (A)  $C \ln \frac{T_c + T_h}{2T_c}$       (B)  $C \ln \frac{T_2}{T_1}$       (C)  $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$       (D)  $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

#### Entropy change for phase change

**12.** If  $\Delta H_{\text{vaporisation}}$  of substance X(ℓ) (molar mass : 30 g/mol) is 300 J/g 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) 300 J/mol.K

**13.** For the liquid A whose normal boiling point is 300K,  $\Delta S_{\text{univ}}$  for the reaction at one atm and 300K is-



$$\Delta V_{\text{aporisation}} = 60 \text{ kJ / mol at } 1\text{atm \& } 300\text{K}$$

- (A) zero  
 (B) -2 J/mol-K  
 (C) 200 J/mol-K  
 (D) -200 J/mol-K

#### Physical significance of entropy, disorder

**14.** When two gases are mixed the entropy :-

- (A) Remains constant      (B) Decreases      (C) Increases      (D) Becomes zero

**15.** For the process,  $\text{CO}_2(s) \longrightarrow \text{CO}_2(g)$  :

- (A) Both  $\Delta H$  and  $\Delta S$  are +ve      (B)  $\Delta H$  is negative and  $\Delta S$  is +ve  
 (C)  $\Delta H$  is +ve and  $\Delta S$  is -ve      (D) Both  $\Delta H$  and  $\Delta S$  are -ve

**16.**  $\Delta S$  for the reaction ;  $\text{MgCO}_3(s) \longrightarrow \text{MgO}(s) + \text{CO}_2(g)$  will be :

- (A) 0      (B) -ve      (C) +ve      (D)  $\infty$



- 17.** Change in entropy is negative for :-  
 (A) Bromine ( $\ell$ )  $\longrightarrow$  Bromine (g)  
 (B) C(s) + H<sub>2</sub>O(g)  $\longrightarrow$  CO(g) + H<sub>2</sub>(g)  
 (C) N<sub>2</sub>(g, 10 atm, 298 K)  $\longrightarrow$  N<sub>2</sub> (g, 1 atm, 298K)  
 (D) Fe(at 400 K)  $\longrightarrow$  Fe(at 300 K)

**18.** For which reaction from the following,  $\Delta S$  will be maximum ?  
 (A) Ca(s) +  $\frac{1}{2}$ O<sub>2</sub>(g)  $\longrightarrow$  CaO(s)      (B) CaCO<sub>3</sub>(s)  $\longrightarrow$  CaO(s) + CO<sub>2</sub>(g)  
 (C) C(s) + O<sub>2</sub>(g)  $\longrightarrow$  CO<sub>2</sub> (g)      (D) N<sub>2</sub>(g) + O<sub>2</sub>(g)  $\longrightarrow$  2NO(g)

**19.** For conversion C(graphite)  $\rightarrow$  C(Diamond), the  $\Delta S$  is :-  
 (A) Zero      (B) Positive      (C) Negative      (D) Can not be predicted

**$\Delta S$  for chemical reaction**

**20.** If S<sup>0</sup> for H<sub>2</sub>, Cl<sub>2</sub> and HCl are 0.13, 0.22 and 0.19 KJ K<sup>-1</sup> mol<sup>-1</sup> respectively. The total change in standard entropy for the reaction, H<sub>2</sub> + Cl<sub>2</sub>  $\longrightarrow$  2HCl is :  
 (A) 30 JK<sup>-1</sup> mol<sup>-1</sup>      (B) 40 JK<sup>-1</sup> mol<sup>-1</sup>      (C) 60 JK<sup>-1</sup> mol<sup>-1</sup>      (D) 20 JK<sup>-1</sup> mol<sup>-1</sup>

**21.** Given  $\Delta_r S^\circ = -266$  and the listed [S<sup>0m</sup> values].  
 Calculate S<sup>0</sup> for Fe<sub>3</sub>O<sub>4</sub>(s) :  

$$4\text{Fe}_3\text{O}_4 \text{ (s)} [\dots] + \text{O}_2 \text{ (g)} [205] \longrightarrow 6\text{Fe}_2\text{O}_3 \text{ (s)} [87]$$
 (A) +111.1      (B) +122.4      (C) 145.75      (D) 248.25

**Kirchoff's equation : Variation of  $\Delta S$  and  $\Delta H$  with Temperature**

**22.** In Haber's process of manufacturing of ammonia :  

$$\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \longrightarrow 2\text{NH}_3\text{(g)} ; \Delta H_{25^\circ\text{C}}^0 = -92.2 \text{ kJ}$$

Molecule	N <sub>2</sub> (g)	H <sub>2</sub> (g)	NH <sub>3</sub> (g)
C <sub>P</sub> JK <sup>-1</sup> mol <sup>-1</sup>	29.1	28.8	35.1

 If C<sub>P</sub> is independent of temperature, then reaction at 100°C as compared to that of 25°C will be :  
 (A) More endothermic      (B) Less endothermic  
 (C) More exothermic      (D) Less exothermic

**23.** Predict the standard enthalpy of the reaction 2 NO<sub>2</sub>(g)  $\rightarrow$  N<sub>2</sub>O<sub>4</sub>(g) at 100°C. If standard enthalpy of this reaction is -57.2 kJmol<sup>-1</sup> at 25°C ? (Given C<sub>p</sub>(NO<sub>2</sub>) = 37.2 Jmol<sup>-1</sup> K<sup>-1</sup>, C<sub>p</sub>(N<sub>2</sub>O<sub>4</sub>) = 77.28 J. mol<sup>-1</sup> k<sup>-1</sup>)  
 (A) - 56.98 Jmole<sup>-1</sup>      (B) - 76.27 Jmole<sup>-1</sup>      (C) - 54.23 Jmole<sup>-1</sup>      (D) - 120 Jmole<sup>-1</sup>

**24.** Entropy change for H<sub>2</sub>O (l)  $\rightarrow$  H<sub>2</sub>O (s) at 1 atm and - 10°C, is



[Given :  $\Delta H_{\text{fusion}} (0^\circ\text{C}) = 6000 \text{ J/mol}$ ,

$$C_{p,m} (\text{H}_2\text{O}, s) = 36 \text{ J/K-mol}, C_{p,m} (\text{H}_2\text{O}, l) = 75 \text{ J/K-mol}, \ln \left( \frac{273}{263} \right) = 0.04$$

- (A)  $-23.47 \text{ J/K-mol}$
- (B)  $-20.41 \text{ J/K-mol}$
- (C)  $21 \text{ J/K-mol}$
- (D)  $20.47 \text{ J/K-mol}$

#### Change in Gibb's free energy ( $\Delta G$ )

25. Identify the correct statement for change of Gibbs energy for a system ( $\Delta G_{\text{system}}$ ) at constant temperature and pressure.
- (A) If  $\Delta G_{\text{system}} > 0$ , the process is spontaneous.
  - (B) If  $\Delta G_{\text{system}} = 0$ , the system has attained equilibrium.
  - (C) If  $\Delta G_{\text{system}} = 0$ , the system is still moving in a particular direction.
  - (D) If  $\Delta G_{\text{system}} < 0$ , the process is not spontaneous.
26. A process must be spontaneous (feasible) if
- (A) Entropy of system increases
  - (B) Energy of system decreases
  - (C) Gibbs free energy decreases
  - (D) Entropy of universe increases
27. Heat liberated for an ideal gas undergoing reversible isothermal process is 1200 cal at 300 K. What will be Gibb's free energy change for the process
- (A) 1200 cal
  - (B)  $-1200 \text{ cal}$
  - (C) 400 cal
  - (D)  $-400 \text{ cal}$
28. Which of the following extensive variable will increase during isothermal compression of an ideal gas-
- (A) U
  - (B) S
  - (C) H
  - (D) G

#### $\Delta G$ for chemical reaction

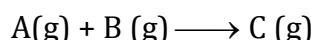
29. Which of the following pairs of a chemical reaction is certain to result in a spontaneous reaction.?
- (A) endothermic and decreasing disorder
  - (B) exothermic and increasing disorder
  - (C) endothermic and increasing disorder
  - (D) exothermic and decreasing disorder
30. For the reaction at  $25^\circ\text{C}$ ,  $\text{X}_2\text{O}_4 (l) \longrightarrow 2\text{XO}_2 (g)$
- $\Delta H = 2.1 \text{ Kcal}$  and  $\Delta S = 20 \text{ cal K}^{-1}$ . The reaction would be
- (A) spontaneous
  - (B) non-spontaneous
  - (C) at equilibrium
  - (D) unpredictable

31. For the reaction at 298 K,  $2A + B \longrightarrow C$

$\Delta H = 100$  kcal and  $\Delta S = 0.050$  kcal  $K^{-1}$ . If  $\Delta H$  and  $\Delta S$  are assumed to be constant over the temperature range, above what temperature will the reaction become spontaneous?

- (A) 1000 K      (B) 1500 K      (C) 2000 K      (D) 2500 K

32. For the reaction at 300 K

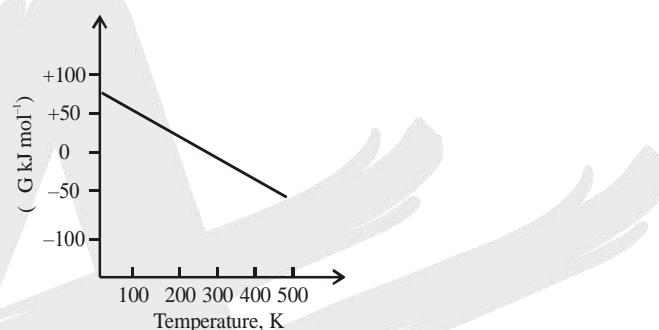


$$\Delta U = -3.0 \text{ kcal} \quad ; \quad \Delta S = -10.0 \text{ cal/K}$$

value of  $\Delta G$  is ?

- (A) -600 cal      (B) -6600 cal      (C) -6000 cal      (D) -6 cal

33. What can be concluded about the values of  $\Delta H$  and  $\Delta S$  from this graph?



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

34. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 1 atm pressure?

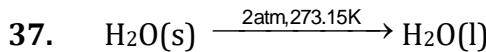
- (A) 80 cal      (B) 540 cal      (C) 620 cal      (D) zero

35. What is the free energy change ( $\Delta G$ ) when 1.0 mole of water at  $100^\circ\text{C}$  and 1 atm pressure is converted into steam at  $100^\circ\text{C}$  and 2 atm pressure?

- (A) Zero cal      (B) 540 cal      (C) 517.13 cal      (D) 510 cal

36.  $\Delta G$  for the conversion of 2 mol of  $C_6H_6(l)$  at  $80^\circ\text{C}$  (normal boiling point) to vapour at the same temperature and a pressure of 0.2 atm is

- (A) -9.44 Kcal/mol      (B) -2.27 Kcal/mol  
 (C) -1.135 Kcal/mol      (D) zero



The correct set of sign of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  respectively for the above given process is :

- (A) +, +, +      (B) +, -, +      (C) -, +, +      (D) -, -, +



38. For hypothetical reversible reaction,  $\frac{1}{2} A_2(g) + \frac{3}{2} B_2(g) \longrightarrow AB_3(g)$ ;  $\Delta H = -20\text{ KJ}$   
if standard entropies of  $A_2$ ,  $B_2$  and  $AB_3$  are 60, 40 and 50  $\text{JK}^{-1}\text{mole}^{-1}$  respectively. The above reaction will be in equilibrium at the temperature :-  
(A) 400 K      (B) 500 K      (C) 250 K      (D) 200 K
39. Standard entropy of  $X_2$ ,  $Y_2$  and  $XY_3$  are 60, 40 and 50  $\text{JK}^{-1}\text{mol}^{-1}$ , respectively. for the reaction,  
 $\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$ ,  $\Delta H = -30\text{ kJ}$  to be at equilibrium, the temperature will be :-  
(A) 1250 K      (B) 500 K      (C) 750 K      (D) 1000 K
40. Following reaction is in equilibrium at  $477^\circ\text{C}$ ,  $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$ ;  $\Delta H = -30\text{ kJ}$ .  
If standard entropy of  $N_2(g)$  and  $NH_3(g)$  are 60 and 50  $\text{J mole}^{-1}\text{K}^{-1}$  respectively then what is the standard entropy of  $H_2(g)$  at same temperature ?  
(A)  $40\text{ Jmole}^{-1}\text{K}^{-1}$       (B)  $60\text{ Jmole}^{-1}\text{K}^{-1}$       (C)  $80\text{ Jmole}^{-1}\text{K}^{-1}$       (D)  $120\text{ Jmole}^{-1}\text{K}^{-1}$

#### Variation of $\Delta G$ with temperature

41. At 298 K,  $\Delta H^\circ_{\text{combustion}}(\text{sucrose}) = -5737\text{ KJ/mol}$  &  $\Delta G^\circ_{\text{combustion}}(\text{sucrose}) = -6333\text{ KJ/mol}$ .  
Estimate additional non-PV work that is obtained by raising temperature to 310 K. Assume  $\Delta_r C_p = 0$  for this temperature change  
(A) 0      (B) 2  $\text{kJ/mol}$       (C) 24  $\text{kJ/mol}$       (D) 23.07  $\text{kJ/mol}$
42. For the hypothetical reaction,  $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$   
 $\Delta_r G$  and  $\Delta_r S$  are 20  $\text{kJ/mole}$  and  $-20\text{ JK}^{-1}\text{ mol}^{-1}$  respectively at 200 K.  
If  $\Delta_r C_p$  is  $20\text{ JK}^{-1}\text{ mol}^{-1}$  then  $\Delta_r H$  at 400 K is :-  
(A) 20  $\text{kJ/mole}$       (B) 7.98  $\text{kJ/mole}$       (C) 28  $\text{kJ/mole}$       (D) None of these

#### $\Delta G$ and non PV work

43. Combustion of sucrose is used by aerobic organisms for providing energy for the life sustaining processes. If all the "capturing" of energy from the reaction is done through electrical process (non- PV work) then calculate maximum available energy which can be captured by combustion of 3.42 gm of sucrose.

**Given :**  $\Delta H_{\text{combustion}}(\text{sucrose}) = -6000\text{ kJ mol}^{-1}$

$\Delta S_{\text{combustion}} = 180\text{ J/Kmol}$  & Body temperature is 300 K.

- (A) 60  $\text{kJ}$       (B) 59.46  $\text{kJ}$       (C) 0.54  $\text{kJ}$       (D) 60.54  $\text{kJ}$

#### Thermodynamic and equilibrium constant

44. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :-  
(A)  $-\Delta G^\circ = RT \ln K$       (B)  $\Delta G = RT \ln K$       (C)  $-\Delta G = RT \ln K$       (D)  $\Delta G^\circ = RT \ln K$

45. The value of  $\Delta G^\circ$  for a reaction in aqueous phase having  $K_c = 1$ , would be:  
 (A)  $-RT$       (B)  $-1$       (C)  $0$       (D)  $+ RT$
46. If  $\Delta G^\circ > 0$  for a reaction then :  
 (A)  $K_p > 1$   
 (B)  $K_p < 1$   
 (C) The products predominate in the equilibrium mixture  
 (D)  $K_p = 1$
47. For the reaction takes place at certain temperature  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ , if equilibrium pressure is  $X$  bar, then  $\Delta_r G^\circ$  would be :-  
 (A)  $-2 RT \ln X$       (B)  $-RT \ln (X - \ln 2)$   
 (C)  $-2 RT (\ln X - \ln 2)$       (D) None of these
48. For a reaction  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$  at equilibrium, the partial pressure of B is found to be one fourth of the partial pressure of A. The value of  $\Delta G^\circ$  of the reaction  $\text{A}(\text{g}) \rightleftharpoons \text{B}(\text{g})$  is  
 (A)  $RT \ln 4$       (B)  $-RT \ln 4$       (C)  $RT \log 4$       (D)  $-RT \log 4$

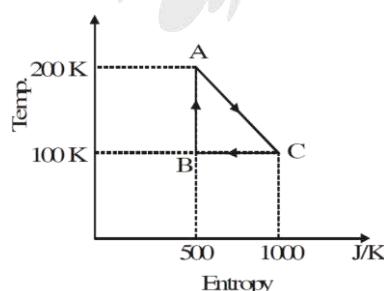
49. What is  $\Delta_r G(\text{kJ/mole})$  for synthesis of ammonia at 298 K at following sets of partial pressure :  
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) ; \Delta_r G^\circ = -33 \text{ kJ/mole}$ .

[Take  $R = 8.3 \text{ J/K mole}$ ,  $\log 2 = 0.3$  ;  $\log 3 = 0.48$ ]

Gas	$\text{N}_2$	$\text{H}_2$	$\text{NH}_3$
Pressure (atm)	1	3	0.02
(A) + 6.5	(B) - 6.5	(C) + 60.5	(D) - 60.5

### TS diagram

50. Efficiency of reversible cycle show will be



- (A) 33.33%      (B) 56%      (C) 66.6%      (D) 16.7%



## EXERCISE # (S-I)

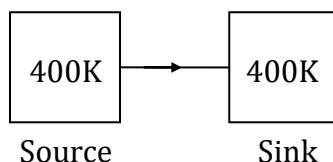
Carnot cycle and 2<sup>nd</sup> law of thermodynamics

1. A Carnot cycle has an efficiency of 40%. Its low temperature reservoir is at 70C. What is the temperature of source ?
2. A heat engine absorbs 760 kJ heat from a source at 380K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280K. State which of these represent a reversible, an irreversible and an impossible cycle.
3. The efficiency of a cannot cycle is 1/6. On decreasing the temperature of the sink by 65°C, the efficiency increases to 1/3. Calculate the temperature of source and sink.

Entropy and ΔS Calculations

4. Find the change in entropy of 1 mole of O<sub>2</sub> gas ( $C_v = 5/2 R$ ), when it is
  - (a) heated from 300 K to 400 K isobarically
  - (b) heated from 300 K to 400 K isochorically (Given :  $\ln 3 = 1.1$ )
5. 5 moles of an ideal gas is expended isothermally from 10 bar to 2 bar at 27°C against a constant external pressure of 2 bar. Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  and  $\Delta S_{univ}$ .
6. One mole of an ideal monoatomic gas (initial temperature = 127°C) is expended adiabatically and reversibly from 5 m<sup>3</sup> to 20 m<sup>3</sup>. Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  and  $\Delta S_{univ}$ .
7. One mole of an ideal monoatomic gas (initial temperature = 127°C) is expended adiabatically from 20 bar to 1 bar against a constant external pressure of 1 bar. Calculate  $\Delta S_{sys}$ ,  $\Delta S_{surr}$  and  $\Delta S_{univ}$ .
8. 2 moles of an ideal monoatomic gas undergo a reversible process for which  $P_2V = \text{constant}$ . The gas sample is made to expand from initial volume of 1L to final volume of 4L starting from initial temperature of 300K. Find the value of  $\Delta S_{sys}$  for the above process. Report your answer as 'X' where  $\Delta S_{sys} = X R \ln 2$ .
9. Consider two moles of an ideal monoatomic gas initially at 27°C and 1 atm pressure, undergoing the following reversible cycle :
  - (a) Isothermal compression to 2 atm.
  - (b) Isobaric temperature increase to 127°C.
  - (c) Return to the initial stage by the different path.
 Calculate  $\Delta S$  for each step.
10. Oxygen is heated from 300 to 600 K at a constant pressure of 1 bar. What is the increases in molar entropy ? The molar heat capacity in JK<sup>-1</sup> mol<sup>-1</sup> for the O<sub>2</sub> is (Given  $\ln 2 = 0.7$ )
 
$$C_p = 10 + 10 - 2T$$

11. 100 kJ heat is transferred from a larger heat reservoir at 400 K to another large heat reservoir at 300 K. Suppose there is no change in temperature due to exchange of heat :



Find (a)  $\Delta S_{\text{source}}$ , (b)  $\Delta S_{\text{sink}}$  and (c)  $\Delta S_{\text{total}}$ . Comment on spontaneity of process.]

12. A thermostat was maintained at 370K. For one hour 4.2 kJ of heat leaked out through thermostat insulation into a room where temperature of air was 300K. If the entropy change of the air in room is

### Entropy Change for phase change

13. One mole of NaCl(s) on melting absorbed 30 KJ of heat and its entropy is increased by  $30 \text{ JK}^{-1}$ . What is the melting point of sodium chloride ?

### $\Delta S$ for Chemical Reaction

14. Calculate the entropy of a substance at 600 K using the following data.

(i) Heat capacity of solid from 0K to normal melting point 200 K

$$C_{\text{P,m}}(\text{s}) = 0.035 \text{ T } \text{JK}^{-1}\text{mol}^{-1}.$$

(ii) Enthalpy of fusion =  $7.5 \text{ kJ mol}^{-1}$ ,

(iii) Enthalpy of vaporisation =  $30 \text{ kJ mol}^{-1}$ ,

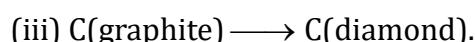
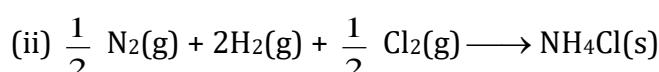
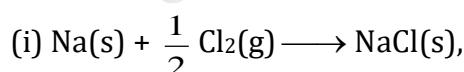
(iv) Heat capacity of liquid from 200K to normal boiling point 300K

$$C_{\text{P,m}}(\text{l}) = 60 + 0.016\text{T } \text{JK}^{-1}\text{mol}^{-1}.$$

(v) Heat capacity of gas from 300K to 600K at 1atm

$$C_{\text{P,m}}(\text{g}) = 50.0 \text{ JK}^{-1}\text{mol}^{-1}.$$

15. Calculate  $\Delta S_r^\circ$  at 298K of ;



The values of  $S^\circ (\text{JK}^{-1} \text{ mol}^{-1})$  of Na, Cl<sub>2</sub>, NaCl, NH<sub>4</sub>Cl, N<sub>2</sub>, H<sub>2</sub> diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 JK<sup>-1</sup> mol<sup>-1</sup> respectively.

16. Find  $(\Delta S)_{\text{universe}}$  (in Joule/mole/K) for a chemical reaction at 300 K given  $\Delta H^\circ_{300 \text{ K}} = 75 \text{ kJ/mol}$  ;

$$\Delta S^\circ_{300 \text{ K}} = 300 \text{ J/K}$$

**Kirchoff's equation : Variation of  $\Delta S$  and  $\Delta H$  with Temperature**

17. The standard enthalpy for the reaction  $H_2(g) + 1/2 O_2(g) \longrightarrow H_2O(l)$  is  $-285\text{ kJ}$  at  $298\text{ K}$ . Calculate the value of  $\Delta H$  at  $373\text{ K}$ . 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  $40$ ,  $30$  and  $75\text{ JK}^{-1}\text{ mol}^{-1}$ .
18. Predict the standard reaction enthalpy of  $2\text{ NO}_2(g) \rightarrow N_2O_4(g)$  at  $100^\circ\text{C}$ .  $\Delta H^\circ$  at  $25^\circ\text{C}$  is  $-57.2\text{ kJ}$ .  
 $\text{mol}^{-1} C_p(\text{NO}_2) = 37.2\text{ J mol}^{-1}\text{ K}^{-1}$   $C_p(N_2O_4) = 77.28\text{ J mol}^{-1}\text{ K}^{-1}$ .

**Change in Gibb's Free energy ( $\Delta G$ )**

19. Calculate  $\Delta G$  (in bar-L) when a definite mass of a monoatomic ideal gas at  $1\text{ bar}$  &  $27^\circ\text{C}$  is expanded adiabatically against vacuum from  $10\text{ L}$  to  $20\text{ L}$  ( $\ln 2 = 0.7$ )

 **$\Delta G$  for Chemical Reaction**

20.  $5$  mole  $H_2O(l)$  at  $373\text{ K}$  and  $1\text{ atm}$  is converted into  $H_2O(g)$  at  $373\text{ K}$  and  $5\text{ atm}$ . Calculate  $\Delta G$  for this process. [Given :  $R = 2\text{ Cal/K-mol}$ ]
21. Calculate the free energy change at  $300\text{ K}$  for the reaction;  
 $\text{Br}_2(l) + \text{Cl}_2(g) \longrightarrow 2\text{BrCl}(g)$ . For the reaction  $\Delta H^\circ = 29.3\text{ kJ}$  & the entropies of  $\text{Br}_2(l)$ ,  $\text{Cl}_2(g)$  &  $\text{BrCl}(g)$  at the  $300\text{ K}$  are  $150$ ,  $220$ ,  $240\text{ J mol}^{-1}\text{ K}^{-1}$  respectively.
22. The entropies of  $H_2(g)$  and  $H(g)$  are  $130$  and  $115\text{ J mol}^{-1}\text{ K}^{-1}$  respectively at  $298\text{ K}$ . Using the data given below calculate the bond energy of  $H_2$ (in  $\text{kJ/mol}$ ) :-  
 $H_2(g) \longrightarrow 2H(g)$  ;  $\Delta G^\circ = 406\text{ kJ/mol}$

**Variation of  $\Delta G$  with temperature**

23. A liquid freeze into a solid ( $\Delta H = -1000\text{ J/mole}$ ) at  $200\text{ K}$  and  $1\text{ atm}$ , at its normal melting point.  
(a) What is the value of  $\Delta G$  at  $200\text{ K}$ ?  
(b) What is the  $\Delta S$  value at  $200\text{ K}$ ?  
(c) Will the freezing be spontaneous at  $150\text{ K}$  and  $1\text{ atm}$ ?  
(d) What is the sign of  $\Delta G$  at  $250\text{ K}$  and  $1\text{ atm}$ ?  
Assume  $\Delta_r C_p = 0$  for this temperature change

 **$\Delta G$  and non PV work**

24. 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  $1\text{ mol}$  of glucose molecules under standard conditions at  $37^\circ\text{C}$  (blood temperature) ? The entropy change is  $+ 182.4\text{ JK}^{-1}$  for the reaction as stated.

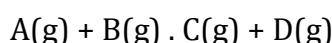
$$\Delta H_{\text{combustion [glucose]}} = -2808\text{ kJ}$$

 $\Delta G$  and equilibrium constant

25.  $\alpha$ -D Glucose undergoes mutarotation to  $\beta$ -D-Glucose in aqueous solution. If at 298K there is 60% conversion. Calculate  $\Delta G^\circ$  of the reaction.



26. For the reaction at 298 K



$$\Delta H^\circ = -29.8 \text{ kcal}; \Delta S^\circ = -0.1 \text{ kcal/K}$$

Calculate  $\Delta G^\circ$  and K.

27.  $2A(s) \longrightarrow B(g) + 2C(g) + 3D(g)$

Total pressure developed in closed container by decomposition of A at equilibrium is 12 atm at  $727^\circ\text{C}$ . Calculate  $|\Delta G^\circ|$  (in kcal), of the reaction at  $727^\circ\text{C}$  ( $R = 2 \text{ cal/mole-K}$ ,  $\ln 2 = 0.7$ ,  $\ln 3 = 1.1$ )

**Fill your answer as sum of digits (excluding decimal places) till you get the single digit answer.**

28. The equilibrium constant of the reaction  $2\text{C}_3\text{H}_6(g) \rightleftharpoons \text{C}_2\text{H}_4(g) + \text{C}_4\text{H}_8(g)$  is found to fit the expression

$$\ln K = -1.04 - 1080/T$$

Calculate the standard reaction enthalpy and entropy at 400 K.

29. Find  $\Delta G$  of the reaction in calorie at 300 K



when partial pressures of A(g) & B(g) are 100 kPa & 1000 kPa respectively

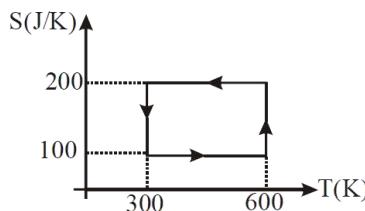
Given :  $\ln 10 = 2.3$ ;  $R = 2 \text{ cal/mol-K}$

30. For the reaction  $\text{SO}_2(g) + 1/2 \text{O}_2(g) \rightleftharpoons \text{SO}_3(g)$   $\Delta H^\circ_{298} = -98.32 \text{ kJ/mol}$ ,  $\Delta S^\circ_{298} = -95.0 \text{ J/K/mol}$ . Find the  $K_p$  for this reaction at 298 K.

31. Calculate the magnitude of standard entropy change for reaction  $X \rightleftharpoons{} Y$  if  $\Delta H^\circ = 25 \text{ KJ}$  and  $K_{eq}$  is  $10^{-7}$  at 300 K.

**TS Diagram**

32. From the given T-S diagram of a reversible Carnot engine, find



- (i) work delivered by engine in one cycle
- (ii) heat taken from the source in each cycle.
- (iii)  $\Delta S_{\text{sink}}$  in each cycle.

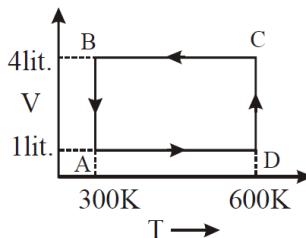




## **EXERCISE # (O-II)**

## **ONLY ONE OPTION IS CORRECT :**

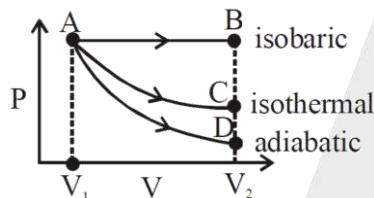
1. A heat engine that converts heat into mechanical work involving ideal monoatomic gas performing following cycle



Calculate the efficiency of the cycle (Use :  $\ln 2 = 0.7$ )

- (A) 50 %                      (B) 23.5 %                      (C) 32.5 %                      (D) 52.3%

2. Starting with same initial conditions, an ideal gas expands from volume  $V_1$  to volume  $V_2$  in three different paths AB, AC & AD as shown. Compare the entropy change during these expansions



- (A)  $\Delta S_{AB} > \Delta S_{AC} > \Delta S_{AD}$

(B)  $\Delta S_{AB} > \Delta S_{AD} > \Delta S_{AC}$

(C)  $\Delta S_{AC} > \Delta S_{AD} > \Delta S_{AB}$

(D)  $\Delta S_{AD} > \Delta S_{AC} > \Delta S_{AB}$

3. An ideal gas with the adiabatic exponent  $\gamma$  goes through a process  $P = P_0 - \alpha V$ , where  $P_0$  and  $\alpha$  are positive constants and  $V$  is the volume. At what volume will the gas entropy have the maximum value?

(A)  $\frac{\gamma P_o}{\alpha(\gamma - 1)}$       (B)  $\frac{\gamma P_o}{\alpha(\gamma + 1)}$       (C)  $\frac{\alpha P_o}{\gamma + 1}$       (D)  $\frac{\alpha P_o}{\gamma - 1}$

4. Identify the correct statement regarding entropy.

  - (A) At absolute zero temperature, the entropy of perfectly crystalline substance is +ve.
  - (B) At absolute zero temp. entropy of perfectly crystalline substance is taken to be zero.
  - (C) At 0 °C the entropy of a perfectly crystalline substance is taken to be zero.
  - (D) At absolute zero temperature, the entropy of all crystalline substances is taken to be zero.

5. The value of  $\Delta G^\circ_f$  of gaseous mercury is 31 KJ/mole. At what total external pressure mercury starts boiling at 25°C. [R = 8.3 J/K mole]

(A)  $10^{-5.44}$       (B)  $10^{-12.5}$       (C)  $10^{-6.52}$       (D)  $10^{-3.12}$

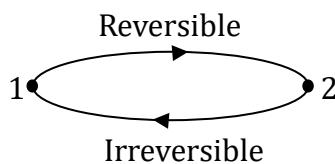


6. Statement-1 : Net heat absorbed in a cyclic process must always equal to net work done by the system in the cyclic process.  
 Statement-2 : Internal energy of system is a function of state.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.
7. Statement-1 : Entropy change in reversible adiabatic expansion of an ideal gas is zero. Because Statement-2 : The increase in entropy due to volume increase just compensate the decrease in entropy due to fall in temperature.  
 (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.  
 (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.  
 (C) Statement-1 is true, statement-2 is false.  
 (D) Statement-1 is false, statement-2 is true.

**MORE THAN ONE MAY BE CORRECT :**

8. Which of the following statements is correct:  
 (A) Reversible adiabatic process is iso-entropic process  
 (B)  $\Delta S_{\text{system}}$  for irreversible adiabatic compression is greater than zero  
 (C)  $\Delta S_{\text{system}}$  for adiabatic free expansion is zero  
 (D)  $\Delta S_{\text{surrounding}}$  for irreversible isothermal compression is greater than zero
9. Select incorrect statements -  
 (A)  $\int \frac{dq}{T}$  is always independent of path followed between two points  
 (B) Entropy of universe is conserved  
 (C) For a process in isolated system entropy either increases or remain constant  
 (D) Entropy decreases with increase in temperature at constant V

10. For the cyclic process given below, which of the following relations are **CORRECT**?



$$(A) \Delta S_{1 \rightarrow 2} = S_2 - S_1 = \int_1^2 \frac{\delta q_{rev}}{T}$$

$$(B) \Delta S_{2 \rightarrow 1} = S_1 - S_2 = \int_2^1 \frac{\delta q_{irr}}{T}$$

$$(C) \Delta S_{cycle} = \int_1^2 \frac{\delta q_{rev}}{T} + \int_2^1 \frac{\delta q_{irr}}{T} = 0$$

$$(D) \Delta S_{cycle} = 0 > \left( \int_1^2 \frac{\delta q_{rev}}{T} + \int_2^1 \frac{\delta q_{irr}}{T} \right)$$

11. The normal boiling point of a liquid 'A' is 350 K.  $\Delta H_{vap}$  at normal boiling point is 35 kJ/mole.

Pick out the correct statement(s). (Assume  $\Delta H_{vap}$  to be independent of pressure).

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

(B)  $\Delta S_{vaporisation} < 100 \text{ J/K mole}$  at 350 K and 0.5 atm

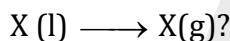
(C)  $\Delta S_{vaporisation} < 100 \text{ J/K mole}$  at 350 K and 2 atm

(D)  $\Delta S_{vaporisation} = 100 \text{ J/K mole}$  at 350 K and 2 atm

12. In isothermal ideal gas compression :

(A)  $w$  is + ve      (B)  $\Delta H$  is zero      (C)  $\Delta S_{gas}$  is + ve      (D)  $\Delta G$  is + ve

13. The normal boiling point of a liquid 'X' is 400 K. Which of the following statement is true about the process



(A) at 400 K and 1 atm pressure  $\Delta G = 0$       (B) at 400 K and 2 atm pressure  $\Delta G = + \text{ve}$

(C) at 400 K and 0.1 atm pressure  $\Delta G = - \text{ve}$       (D) at 410 K and 1 atm pressure  $\Delta G = + \text{ve}$

14. Which of the following statement (s) is/are false :

(A) When  $(\Delta G_{system})_{T,P} < 0$ ; the reaction must be exothermic

(B)  $\Delta G_{system}$  is always zero for a reversible process in a closed system

(C)  $\Delta G^\circ$  for an ideal gas is a function of temperature and pressure

(D)  $dG = VdP - SdT$  is applicable for any chemical and phase change



- 15.** Choose the correct statement (s)
- (A) Entropy of system increases when an ideal gas expanded isothermally
  - (B) All adiabatic processes are iso-entropic (or isentropic) processes
  - (C) No cyclic process is possible in which the sole result is absorption of heat from a hot reservoir and its complete conversion into work
  - (D) Two solid blocks of same material and same mass having different temperature kept in an isolated system then entropy of system must increase.
- 16.** Choose the correct statement (s)
- (A) For phase transformation of liquid water at 1 atm, 373K to water vapour at 1atm, 373K,  $\Delta G$  will be zero
  - (B)  $\Delta_r S$  for  $\frac{1}{2} N_2(g) \longrightarrow N(g)$  is positive
  - (C)  $\Delta_r H$  &  $\Delta_r S$  both are +ve for the decomposition of  $MgCO_3(s)$ .
  - (D) If  $-76.9^\circ C$  is the transition temperature for the conversion of  $P_4(s,\alpha) \rightarrow P_4(s,\beta)$  and this phase transition is spontaneous at  $T < -76.9^\circ C$  if  $\Delta_r S < 0$
- 17.** Which of the following statement(s) is/are correct :
- (A) The entropy of isolated system with P-V work only is always maximized at equilibrium
  - (B) It is possible for the entropy of close system to decrease substantially in an irreversible process.
  - (C) Entropy can be created but not destroyed.
  - (D)  $\Delta S_{\text{system}}$  is always zero for reversible process in an isolated system
- 18.** The 3<sup>rd</sup> law of thermodynamics states that entropy of pure and perfect crystalline substances is 0 at 0 K. Which of the following is not true ?
- (A) Standard molar entropy of any pure element / compound is greater than 0 at  $T > 0$  K.
  - (B) Standard molar entropy of all ions in aqueous phase is greater than 0 at  $T > 0$  K (as per thermodynamic data).
  - (C) Standard molar entropy of ions are always greater than that of  $H^+(aq)$  at any  $T > 0$  K.
  - (D) Standard molar entropy of ions may be negative (as per thermodynamic data).
- 19.** Select the correct statement(s) -
- (A)  $\Delta H_{\text{vap}}$  at equilibrium pressure & temperature is zero
  - (B)  $\Delta G_{\text{vap}}$  at equilibrium pressure & temperature is zero
  - (C)  $(\Delta S_{\text{sys}})_{\text{vap}}$  at equilibrium pressure & temperature is zero
  - (D)  $(\Delta S_{\text{univ}})_{\text{vap}}$  at equilibrium pressure & temperature is zero

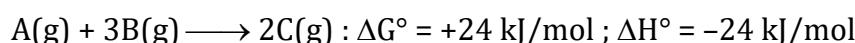


## Paragraph for Question 20 to 21

The reactions whose  $\Delta G^\circ$  are positive can not take place under standard state conditions.

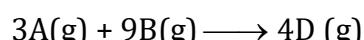
However, another reaction whose  $\Delta G^\circ$  is negative can be coupled with the former type of reaction to give overall spontaneous process.

Consider the given reactions whose  $\Delta G^\circ$  at 300 K are provided to answer following questions.



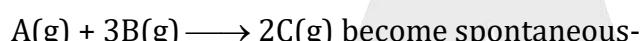
All data at 300 K temperature.

- 20.** What is  $\Delta S^\circ$  at 300 K of reaction (in J/K/mole) :



- (A) -640                    (B) -480                    (C) +640                    (D) -240

- 21.** Assuming  $\Delta H^\circ$  and  $\Delta S^\circ$  do not vary with temperature - at what temperature reaction



- (A) 6250 K                    (B) 625 K                    (C) 150 K                    (D) 1000 K

## Paragraph for 22 to 23

Thermodynamics stability is often used in chemical reactions to predict extent of reactions or to predict the preferred product in some reaction. Thermodynamically a more stable substance will be the one which has lower Gibb's free energy. In various cases it might be decided on the basis of enthalpy, however that may not always be true. The thermodynamic data therefore can be used for predicting stability among isotopes & to decide the possible transformation. Based on this information & the data given below, answer the questions that follow.

<b>Data:</b>	$\Delta H_f^\circ$ of Sn <sub>(white)</sub> = 0	$\Delta H_f^\circ$ of Sn <sub>(gray)</sub> = -2.1 kJ/mole
	$S^\circ$ of Sn <sub>(white)</sub> = 52 J/K-mole	$S^\circ$ of Sn <sub>(gray)</sub> = 44 J/K-mole

All above data at 300 K.

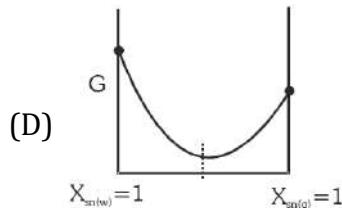
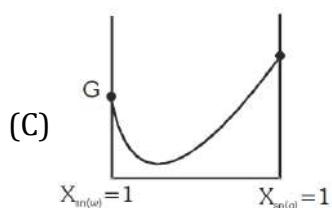
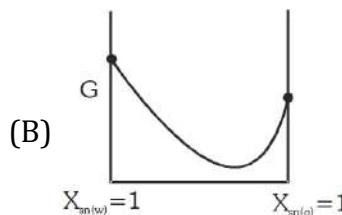
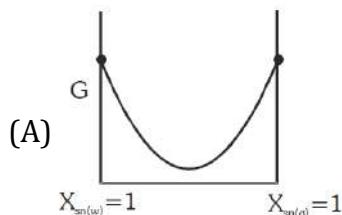
Density of Sn<sub>(w)</sub> = 7.36 g/ml

Density of Sn<sub>(g)</sub> = 5.769 gm/ml

One such transformation is 'tin pest' an allotropic transformation of the element white tin to gray results in brittleness of tin objects at low temperatures.



22. Which of the following graph is correct for the allotropic transition  $\text{Sn}_{(\text{white})} \rightarrow \text{Sn}_{(\text{gray})}$  at 1 bar & 300 K.



23. Choose correct option -

- (A) both forms exist at all temperature
- (B) There will be a contraction in volume as temperature is reduced.
- (C) At 200 K, only gray tin exists.
- (D) At 300 K, only white tin exists.

#### MATCH THE COLUMN :

24. Column-I

- (A) Reversible adiabatic compression
- (B) Reversible vaporisation
- (C) Adiabatic free expansion of ideal gas in vacuum
- (D) Dissociation of  $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Column-II

- (P)  $\Delta S_{\text{system}} > 0$
- (Q)  $\Delta S_{\text{system}} < 0$
- (R)  $\Delta S_{\text{surrounding}} < 0$
- (S)  $\Delta S_{\text{surrounding}} = 0$

25. Column-I

- (Related to process)**
- (A) Fusion at melting point
  - (B) Vapourisation at boiling point
  - (C) Condensation at triple point
  - (D) Melting at normal boiling point

Column-II

- (Related to system)**
- (P)  $\Delta G = 0$
  - (Q)  $\Delta G < 0$
  - (R)  $\Delta S > 0$
  - (S)  $\Delta H \approx \Delta U$



26. Match the column :

**Column-I**

(P)  $(P) - (\Delta G)_{T,P}$

(Q) Work done in irreversible isothermal ideal gas expansion

(R)  $\Delta G$  for reversible isothermal expansion of an ideal gas.

(S)  $\Delta S_{\text{gas}}$  for isothermal expansion of an ideal gas.

**Column-II**

(1)  $nRT \ln \frac{P_2}{P_1}$

(2) non-PV work done by system

(3)  $-nR \ln \frac{P_2}{P_1}$

(4)  $-P_{\text{ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$

**Code:**

	P	Q	R	S
(A)	2	4	1	3
(B)	4	2	3	1
(C)	3	1	2	4
(D)	2	3	1	4

27. Match the Column :

**Column-I**



**Column-II**

(1)  $\Delta_r S > 0$

(2)  $\Delta_r G > 0$

(3)  $\Delta_r H < 0$

(4)  $\Delta_r U > 0$

**Code:**

	P	Q	R	S
(A)	2	4	1	3
(B)	4	2	3	1
(C)	2	1	3	4
(D)	4	3	1	2



## EXERCISE # (S-II)

## INTEGER

1. A reversible cyclic process involves 6 steps. In step-1, 3 system absorb 500 J, 800 J of heat from a heat reservoir at temperature 250K & 200K respectively. Step 2, 4, 6, are adiabatic such that the temperature of one reservoir changes to that of next. Total work done by the system in whole cycle is 700 J. Find the temperature during step 5 if it exchange heat from a reservoir at temperature  $T_5$
2. 1 mole of ideal monoatomic gas is heated by supplying 5 kJ heat from a reservoir maintained at 400 K from 300 K to 400 K. In the process volume of gas increased from 1 L to 10 L. Find  $\Delta S_{\text{total}}$  (in J/K · mol) in the process

Use :  $\ln \left( \frac{4}{3} \right) = 0.3$ ,  $\ln 10 = 2.3$ ,  $R = 8.3 \text{ J/K-mol}$  and  $\ln x = 2.3 \log x$

3. One mole of ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate  $\Delta S_{\text{system}}$ ,  $\Delta S_{\text{surr}}$ , and  $\Delta S_{\text{total}}$  in
  - when the process carried out reversibly
  - when the process carried out irreversibly (one step)
4. Heat capacity of a solid A(s), given to be  $aT^3$  in vicinity of absolute zero. Taking heat capacity to be a  $T^3$  from 0 K to 10 K, b from 10 K to normal M.P. at 150 K and c from 150 K to 200 K, find the absolute entropy of A (l) at 200 K.

Given;  $a = 0.5 \times 10^{-3} \text{ J/(K mole)}$

$b = 15 \text{ J/(K mole)}$

$c = 20 \text{ J/(K mole)}$

$\Delta H_{\text{fusion}} = + 30 \text{ kJ/mole}$

5. Fixed amount of an ideal mono atomic gas contained in a sealed rigid vessel ( $V = 24.6 \text{ litre}$ ) at 1.0 bar is heated reversibly from  $27^\circ\text{C}$  to  $127^\circ\text{C}$ . Determine change in Gibb's energy (in Joule) if entropy of gas  $S = 10 + 10^{-2} T \text{ (J/K)}$
6. The enthalpy change for vapourisation of liquid 'A' at 200 K and 1 atm is 22 kJ/mol. Find out  $\Delta S_{\text{vapourisation}}$  for liquid 'A' at 200 K? The normal Boiling point of liquid 'A' is 300 K?

$A(l) [200 \text{ K } 1 \text{ atm}] \rightarrow A(g) [200 \text{ K } 1 \text{ atm}] \quad \Delta S_{\text{vap}} = ?$

Given:  $C_{p,m}(A(g)) = 30 \text{ J/mol K}$

$C_{p,m}(A(l)) = 40 \text{ J/mol K}$

Use :  $\ln(3/2) = 0.405$



7. At 300 K,  $\Delta H^\circ_{\text{combustion}}(\text{sucrose}) = -5000 \text{ KJ/mol}$  &  $\Delta G^\circ_{\text{combustion}}(\text{sucrose}) = -6000 \text{ KJ/mol}$ . Estimate additional non-PV work that is obtained by raising temperature to 309 K. Assume  $\Delta_r C_p = 0$  for this temperature change.
8. The  $K_p$  for reaction  $A + B \rightleftharpoons C + D$  is 1.34 at  $60^\circ\text{C}$  and 6.64 at  $100^\circ\text{C}$ . Determine the standard free energy change of this reaction at each temperature and  $\Delta H^\circ$  for the reaction over this range of temperature ?
9. Calculate the equilibrium pressure (in Pascal) for the conversion of graphite to diamond at  $25^\circ\text{C}$ . The densities of graphite and diamond may be taken to be 2.20 and 3.40 g/cc respectively independent of pressure.  
Given :  $\Delta G^\circ (\text{C (graphite)} \rightarrow \text{C(diamond)}) = 2900 \text{ J/mol}$ .
10. Select the conditions which represent the criteria for spontaneity of a process in a closed system, from the following given conditions.

<b>Serial Number</b>	<b>conditions</b>
1.	$(dG)_{P,T} > 0$
2.	$(\Delta S)_{\text{universe}} > 0$
3.	$(dU)_{S,V} > 0$
4.	$(dH)_{S,P} < 0$
5.	$(dS)_{U,V} < 0$
6.	$(dS)_{H,P} > 0$

(Answer by adding the serial numbers of the correct conditions.)



## EXERCISE (JEE-MAIN)

1. The standard entropy change for the reaction  $4\text{Fe(s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Fe}_2\text{O}_3\text{(s)}$  is  $-550\text{JK}^{-1}$  at 298 K. [JEE Main, 2022]

[Given : The standard enthalpy change for the reaction is  $-165\text{ kJ mol}^{-1}$ . The temperature in K at which the reaction attains equilibrium is . (Nearest Integer)]

2. Given below are two statements: One is labelled as Assertion A and the other is labelled as Reason R

Assertion A : The reduction of a metal oxide is easier if the metal formed is in liquid state than solid state.

Reason R : The value of  $\Delta G^\Theta$  becomes more on negative side as entropy is higher in liquid state than solid state.

In the light of the above statements. Choose the most appropriate answer from the options given below

- (A) Both A and R are correct and R is the correct explanation of A  
 (B) Both A and R are correct but R is NOT the correct explanation of A  
 (C) A is correct but R is not correct  
 (D) A is not correct but R is correct

3. Which of the following relation is not correct? [JEE Main, 2022]

- (A)  $\Delta H = \Delta U - P\Delta V$   
 (B)  $\Delta U = q + W$   
 (C)  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0$   
 (D)  $\Delta G = \Delta H - T\Delta S$

4. For combustion of one mole of magnesium in an open container at 300 K and 1 bar pressure,  $\Delta cH^\Theta = -601.70\text{ kJ mol}^{-1}$ , the magnitude of change in internal energy for the reaction is \_\_\_\_ kJ. (Nearest integer)

(Given :  $R = 8.3\text{ J K}^{-1}\text{ mol}^{-1}$ ) [JEE Main, 2022]

5. For the reaction  $2\text{NO}_2\text{(g)} \rightleftharpoons \text{N}_2\text{O}_4\text{(g)}$ , when  $\Delta S = -176.0\text{JK}^{-1}$  and  $\Delta H = -57.8\text{ kJ mol}^{-1}$ , the magnitude of  $\Delta G$  at 298 K for the reaction is  $\text{kJmol}^{-1}$ . (Nearest integer) [JEE Main, 2021]

6. For a chemical reaction  $A + B \rightleftharpoons C + D$  ( $\Delta_r H^\Theta = 80\text{ kJ mol}^{-1}$ ) the entropy change  $\Delta_r S^\Theta$  depends on the temperature T (in K) as  $\Delta_r S^\Theta = 2T(J\text{ K}^{-1}\text{ mol}^{-1})$   
 Minimum temperature at which it will become spontaneous is K. [JEE Main, 2021]

7. For water  $\Delta_{\text{vap}} H = 41\text{ kJ mol}^{-1}$  at 373 K and 1 bar pressure. Assuming that water vapour is an ideal gas that occupies a much larger volume than liquid water, the internal energy change during evaporation of water is \_\_\_\_  $\text{kJ mol}^{-1}$  [Use :  $R = 8.3\text{ J mol}^{-1}\text{ K}^{-1}$ ]

[JEE Main, August 2021]

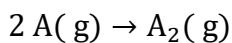
8. Select the correct option :

- (1) Entropy is function of temperature and also entropy change is function of temperature.  
 (2) Entropy is a function of temperature & entropy change is not a function of temperature.



- (3) Entropy is not a function of temperature & entropy change is a function of temperature.  
 (4) Both entropy & entropy change are not a function of temperature. [Jee Main, 2020]

9. For a dimerization reaction, [Jee Main, 2020]



at 298 K,  $\Delta U^\circ = -20 \text{ kJ mol}^{-1}$ ,  $\Delta S^\circ = -30 \text{ JK}^{-1} \text{ mol}^{-1}$ , then the  $\Delta G^\circ$  will be J.

10. For the reaction;  $A(l) \rightarrow 2B(g)$   $\Delta U = 2.1 \text{ kcal}$ ,  $\Delta S = 20 \text{ cal K}^{-1}$  at 300 K. Hence  $\Delta G$  in kcal is \_\_\_\_\_: [Jee Main, 2020]
11. For one mole of an ideal gas, which of these statements must be true? [Jee Main, 2020]
- (A) U and H each depends only on temperature
  - (B) Compressibility factor z is not equal to 1
  - (C)  $C_{P,m} - C_{V,m} = R$
  - (D)  $dU = C_V dT$  for any process
- |                      |                      |
|----------------------|----------------------|
| (1) (A) and (C)      | (2) (B), (C) and (D) |
| (3) (A), (C) and (D) | (4) (C) and (D)      |

12. A process will be spontaneous at all temperatures if: [JEE-MAIN 2019 (April)]
- |                                       |                                       |
|---------------------------------------|---------------------------------------|
| (1) $\Delta H < 0$ and $\Delta S > 0$ | (2) $\Delta H > 0$ and $\Delta S < 0$ |
| (3) $\Delta H > 0$ and $\Delta S > 0$ | (4) $\Delta H < 0$ and $\Delta S < 0$ |
13. Enthalpy of sublimation of iodine is 24 cal g<sup>-1</sup> at 200°C. If specific heat of I<sub>2</sub>(s) and I<sub>2</sub>(vap) are 0.055 and 0.031 cal g<sup>-1</sup> K<sup>-1</sup> respectively, then enthalpy of sublimation of iodine at 250°C in cal g<sup>-1</sup> is: [JEE-MAIN 2019 (April)]
- |          |          |          |         |
|----------|----------|----------|---------|
| (1) 2.85 | (2) 22.8 | (3) 11.4 | (4) 5.7 |
|----------|----------|----------|---------|
14. The INCORRECT match in the following is: [JEE-MAIN 2019 (April)]
- |                              |                              |                              |                              |
|------------------------------|------------------------------|------------------------------|------------------------------|
| (1) $\Delta G^0 > 0$ , K < 1 | (2) $\Delta G^0 < 0$ , K < 1 | (3) $\Delta G^0 < 0$ , K > 1 | (4) $\Delta G^0 = 0$ , K = 1 |
|------------------------------|------------------------------|------------------------------|------------------------------|
15. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is : (Specific heat of water liquid and water vapour are 4.2 kJ K<sup>-1</sup> kg<sup>-1</sup> and 2.0 kJ K<sup>-1</sup> kg<sup>-1</sup>; heat of liquid fusion and vapourisation of water are 334 kJ kg<sup>-1</sup> and 2491 kJ kg<sup>-1</sup>; respectively). ( $\log 273 = 2.436$ ,  $\log 373 = 2.572$ ,  $\log 383 = 2.583$ ) [JEE-MAIN 2019 (Jan)]
- |  |  |  |  |
|--|--|--|--|
| (1) 7.90 kJ kg <sup>-1</sup> K <sup>-1</sup> | (2) 8.49 kJ kg <sup>-1</sup> K <sup>-1</sup> | (3) 9.26 kJ kg <sup>-1</sup> K <sup>-1</sup> | (4) 2.64 kJ kg <sup>-1</sup> K <sup>-1</sup> |
|--|--|--|--|



16. A process has  $\Delta H = 200 \text{ J mol}^{-1}$  and  $\Delta S = 40 \text{ JK}^{-1} \text{ mol}^{-1}$ . Out of the values given below, choose the minimum temperature above which the process will be spontaneous:

[JEE-MAIN 2019 (Jan)]

- (1) 12K      (2) 20K      (3) 4K      (4) 5K

17. The process with negative entropy change is:

[JEE-MAIN 2019 (Jan)]

- (1) Dissolution of iodine in water  
 (2) Synthesis of ammonia from N<sub>2</sub> and H<sub>2</sub>  
 (3) Sublimation of dry ice  
 (4) Dissolution of CaSO<sub>4</sub>(s) to CaO(s) and SO<sub>3</sub>(g)

18. Two blocks of the same metal having same mass and at temperature T<sub>1</sub> and T<sub>2</sub>, respectively, are brought in contact with each other and allowed to attain thermal equilibrium at constant pressure. The change in entropy, ΔS, for this process is :

[JEE-MAIN 2019 (Jan)]

- (1)  $2C_p \ln \left[ \frac{(T_1 + T_2)^{\frac{1}{2}}}{T_1 T_2} \right]$   
 (2)  $C_p \ln \left[ \frac{(T_1 + T_2)^2}{4 T_1 T_2} \right]$   
 (3)  $2C_p \ln \left( \frac{T_1 + T_2}{4 T_1 T_2} \right)$   
 (4)  $2C_p \ln \left[ \frac{T_1 + T_2}{2 T_1 T_2} \right]$

19. For the chemical reaction X  $\rightleftharpoons$  Y, the standard reaction Gibbs energy depends on

temperature T (in K) as :  $\Delta_r G^\circ \text{ (in kJ mol}^{-1}\text{)} = 120 - \frac{3}{8} T$

The major component of the reaction mixture at T is :

[JEE-MAIN 2019 (Jan)]

- (1) Y if T = 280 K      (2) X if T = 315 K      (3) Y if T = 300 K      (4) X if T = 350 K

20. The reaction,



$\Delta_r H^\circ = + 491.1 \text{ kJ mol}^{-1}$  and  $\Delta_r S^\circ = 198.0 \text{ JK}^{-1} \text{ mol}^{-1}$ , is not feasible at 298 K. Temperature above which reaction will be feasible is :-

[JEE-MAIN 2019 (Jan)]

- (1) 2040.5 K      (2) 1890.0 K      (3) 2480.3 K      (4) 2380.5 K

21. For the equilibrium,  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ , the value of  $\Delta G^\circ$  at 298 K is approximately :

[JEE-MAIN 2019 (Jan)]

- (1) -80 kJ mol<sup>-1</sup>      (2) -100 kJ mol<sup>-1</sup>      (3) 80 kJ mol<sup>-1</sup>      (4) 100 kJ mol<sup>-1</sup>

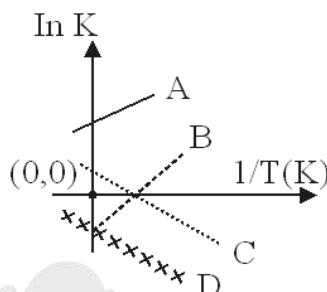
22. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by  $\Delta_r G^\circ = A - Bt$

[JEE-MAIN 2019 (Jan)]

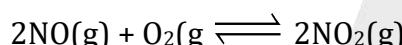
Where A and B are non-zero constants. Which of the following is TRUE about this reaction ?

- (1) Exothermic if  $B < 0$   
 (2) Endothermic if  $A > 0$   
 (3) Exothermic if  $A > 0$  and  $B < 0$   
 (4) Endothermic if  $A < 0$  and  $B > 0$

23. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ? (JEE MAIN - 2018)



- (1) A and D      (2) A and B      (3) B and C      (4) C and D
24. The following reaction is performed at 298 K. (JEE MAIN - 2015)



The standard free energy of formation of  $\text{NO(g)}$  is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of  $\text{NO}_2\text{(g)}$  at 298 K? ( $K_P = 1.6 \times 10^{12}$ )

- (1)  $86600 + R(298) \ln(1.6 \times 10^{12})$   
 (2)  $86600 - \frac{\ln(1.6 \times 10^{12})}{R(298)}$   
 (3)  $0.5[2 \times 86,600 - R(298) \ln(1.6 \times 10^{12})]$     (4)  $R(298) \ln(1.6 \times 10^{12}) - 86600$

25. The molar heat capacity ( $C_p$ ) of  $\text{CD}_2\text{O}$  is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of  $\text{CD}_2\text{O}$  vapour from 1000 K to 100 K at constant pressure will be  
 (D = deuterium, at. mass = 2u) (JEE MAIN -(online) 2014)
- (1) -23.03 cal deg $^{-1}$     (2) 2.303 cal deg $^{-1}$     (3) 23.03 cal deg $^{-1}$     (4) -2.303 cal deg $^{-1}$

26. The entropy ( $S^\circ$ ) of the following substances are : (JEE MAIN -(online) 2014)

$\text{CH}_4\text{(g)}$  186.2 J K $^{-1}$  mol $^{-1}$

$\text{O}_2\text{(g)}$  205.0 J K $^{-1}$  mol $^{-1}$

$\text{CO}_2\text{(g)}$  213.6 J K $^{-1}$  mol $^{-1}$

$\text{H}_2\text{O(l)}$  69.9 J K $^{-1}$  mol $^{-1}$

The entropy change ( $\Delta S^\circ$ ) for the reaction



- (1) -312.5 JK $^{-1}$  mol $^{-1}$   
 (2) -37.6 JK $^{-1}$  mol $^{-1}$   
 (3) -108.1 JK $^{-1}$  mol $^{-1}$   
 (4) -242.8 JK $^{-1}$  mol $^{-1}$



**27.** The incorrect expression among the following is :-

(AIEEE - 2012)

(1)  $K = e^{-\Delta G^\circ/RT}$

(2)  $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

(3) In isothermal process,  $W_{\text{reversible}} = -nRT \ln \frac{V_f}{V_i}$

(4)  $\ln K = \frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}}$

**28.** The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm<sup>3</sup> to a volume of 100 dm<sup>3</sup> at 27°C is :-

(AIEEE - 2011)

- (1) 32.3 J mol<sup>-1</sup> K<sup>-1</sup> (2) 42.3 J mol<sup>-1</sup> K<sup>-1</sup> (3) 38.3 J mol<sup>-1</sup> K<sup>-1</sup> (4) 35.8 J mol<sup>-1</sup> K<sup>-1</sup>

**29.** For a particular reversible reaction at temperature T,  $\Delta H$  and  $\Delta S$  were found to be both +ve. If  $T_e$  is the temperature at equilibrium, then reaction would be spontaneous when:-

(AIEEE - 2010)

- (1)  $T = T_e$  (2)  $T_e > T$  (3)  $T > T_e$  (4)  $T_e$  is 5 times T

**30.** In conversion of lime-stone to lime,  $\text{CaCO}_3(s) \longrightarrow \text{CaO}(s) + \text{CO}_2(g)$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are +179.1 kJ mol<sup>-1</sup> and 160.2 J/K respectively at 298 K and 1 bar. Assuming that  $\Delta H^\circ$  and  $\Delta S^\circ$  do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :-

(AIEEE - 2007)

- (1) 1008 K (2) 1200 K (3) 845 K (4) 1118 K

**31.** Identify the correct statement regarding a spontaneous process :-

(AIEEE - 2007)

- (1) For a spontaneous process in an isolated system, the change in entropy is positive  
 (2) Endothermic processes are never spontaneous  
 (3) Exothermic processes are always spontaneous  
 (4) Lowering of energy in the reaction process is the only criterion for spontaneity

**32.** In a 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:-

(AIEEE - 2003)

- (1)  $(dS)_{V,E} = 0, (dG)_{T,P} = 0$  (2)  $(dS)_{V,E} = 0, (dG)_{T,P} > 0$   
 (3)  $(dS)_{V,E} < 0, (dG)_{T,P} < 0$  (4)  $(dS)_{V,E} > 0, (dG)_{T,P} < 0$

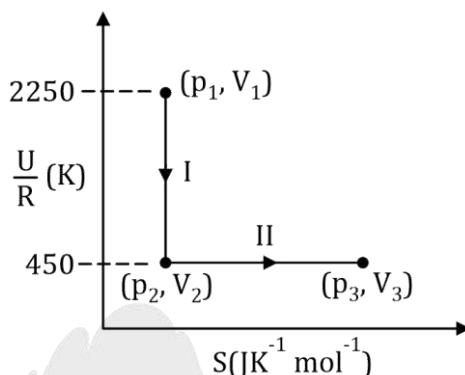
**33.** The correct relationship between free energy change in a reaction and the corresponding equilibrium constant  $K_c$  is :-

(AIEEE - 2003)

- (1)  $\Delta G^\circ = RT \ln K_c$  (2)  $-\Delta G^\circ = RT \ln K_c$   
 (3)  $\Delta G = RT \ln K_c$  (4)  $-\Delta G = RT \ln K_c$

## EXERCISE # (JEE-ADVANCED)

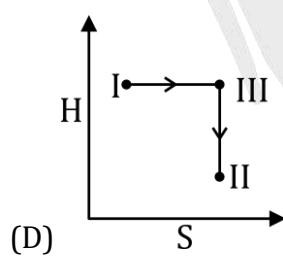
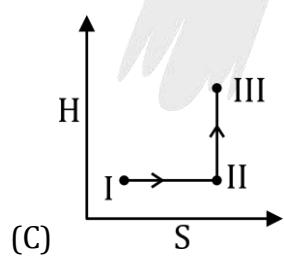
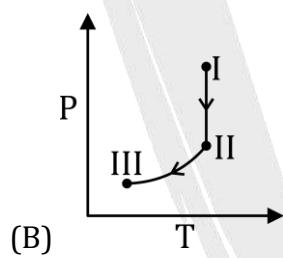
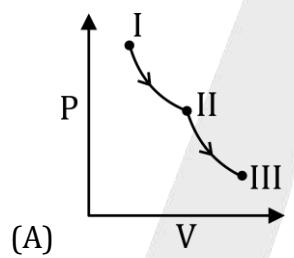
1. One mole of an ideal gas at 900 K, undergoes two reversible processes, I followed by II, as shown below. If the work done by the gas in the two processes are the same, the value of  $\ln \frac{V_3}{V_2}$  is \_\_\_\_\_. [JEE Adv. 2021]



(U: internal energy, S: entropy, p: pressure, V: volume, R: gas constant)

(Given: molar heat capacity at constant volume, C of the gas is  $5/2R$ )

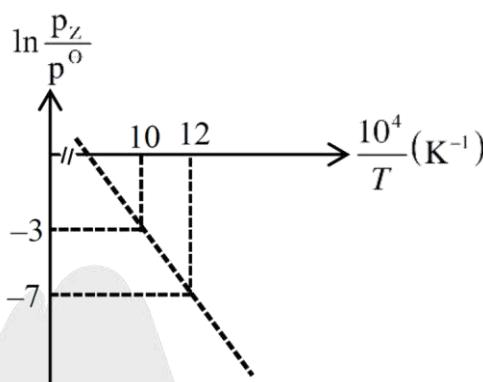
2. An ideal gas undergoes a reversible isothermal expansion from the state I to state II followed by a reversible adiabatic expansion from state II to state III. The correct plot(s) representing the changes from the state I to state III is(are) (p: pressure, V: volume, T: temperature, H: enthalpy, S: entropy) [JEE Adv. 2021]



## Question stem for Question Nos. 3 and 4

For the reaction  $X(s) \rightleftharpoons Y(s) + Z(g)$ , the plot of  $\ln \frac{p_z}{p^\ominus}$  versus  $\frac{10^4}{T}$  is given below (in solid line),

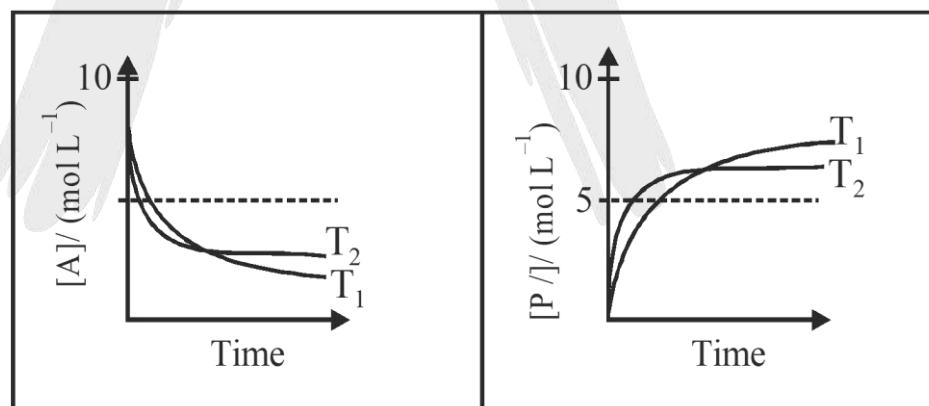
where  $p_z$  is the pressure (in bar) of the gas Z at temperature T and  $P = 1$  bar. [JEE Adv. 2021]



(Given,  $\frac{d(\ln K)}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^\ominus}{R}$ , where the equilibrium constant,  $K = \frac{p_z}{p^\ominus}$  and the gas constant,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

3. The value of standard enthalpy,  $\Delta H^\ominus$  (in  $\text{kJ mol}^{-1}$ ) for the reaction is \_\_\_\_.
4. The value of  $\Delta S^\ominus$  (in  $\text{J K}^{-1} \text{ mol}^{-1}$ ) for the given reaction, at 1000 K is \_\_\_\_.
5. For a reaction,  $A \rightleftharpoons P$ , the plots of  $[A]$  and  $[P]$  with time at temperatures  $T_1$  and  $T_2$  are given below.

[JEE ADV. 2018]



If  $T_2 > T_1$ , the correct statement(s) is (are)

(Assume  $\Delta H^\ominus$  and  $\Delta S^\ominus$  are independent of temperature and ratio of  $\ln K$  at  $T_1$  to  $\ln K$  at  $T_2$  is

greater than  $\frac{T_2}{T_1}$ . Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)



- (A)  $\Delta H^\theta < 0, \Delta S^\theta < 0$       (B)  $\Delta G^\theta < 0, \Delta H^\theta > 0$   
 (C)  $\Delta G^\theta < 0, \Delta S^\theta < 0$       (D)  $\Delta G^\theta < 0, \Delta S^\theta > 0$
6. The surface of copper gets tarnished by the formation of copper oxide.  $N_2$  gas was passed to prevent the oxide formation during heating of copper at 1250 K. However, the  $N_2$  gas contains 1 mole % of water vapour as impurity. The water vapour oxidises copper as per the reaction given below:
- [JEE ADV. 2018]
- $$2\text{Cu(s)} + \text{H}_2\text{O(g)} \longrightarrow \text{Cu}_2\text{O(s)} + \text{H}_2\text{(g)}$$
- $p_{H_2}$  is the minimum partial pressure of  $H_2$  (in bar) needed to prevent the oxidation at 1250 K.
- The value of  $\ln p_{H_2}$  is \_\_\_\_.
- (Given: total pressure = 1 bar, R (universal gas constant) =  $8 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $\ln(10) = 2.3$ . Cu(s) and Cu<sub>2</sub>O(s) are mutually immiscible.)
- At 1250 K:  $2\text{Cu(s)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{Cu}_2\text{O(s)}$ ;  $\Delta G^\theta = -78,000 \text{ J mol}^{-1}$
- $\text{H}_2\text{(g)} + \frac{1}{2}\text{O}_2\text{(g)} \longrightarrow \text{H}_2\text{O(g)}$ ;  $\Delta G^\theta = -1,78,000 \text{ J mol}^{-1}$ ; G is the Gibbs energy)
7. Consider the following reversible reaction,
- $$\text{A(g)} + \text{B(g)} \rightleftharpoons \text{AB(g)}$$
- The activation energy of the backward reaction exceeds that of the forward reaction by  $2RT$  (in  $\text{J mol}^{-1}$ ). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of  $\Delta G^\theta$  (in  $\text{J mol}^{-1}$ ) for the reaction at 300 K is \_\_\_\_.
- (Given;  $\ln(2) = 0.7$ ,  $RT = 2500 \text{ J mol}^{-1}$  at 300 K and G is the Gibbs energy)      [JEE ADV. 2018]
8. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 are
- $$\Delta_f G^\theta [\text{C(graphite)}] = 0 \text{ kJ mol}^{-1}$$
- $$\Delta_f G^\theta [\text{C(diamond)}] = 2.9 \text{ kJ mol}^{-1}$$
- The standard state means that the pressure should be 1 bar, and substance should be pure at a given temperature. The conversion of graphic [C(graphite)] to diamond [C(diamond)] reduces its volume by  $2 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ . If C(graphite) is converted to C(diamond) isothermally at T = 298 K, the pressure at which C(graphite) is in equilibrium with C(diamond), is
- [Useful information :  $1\text{J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ ;  $1 \text{ Pa} = 1 \text{ kg m}^{-1} \text{ s}^{-2}$ ;  $1 \text{ bar} = 10^5 \text{ Pa}$ ]      [JEE ADV. 2017]
- (A) 29001 bar      (B) 58001 bar      (C) 14501 bar      (D) 1450 bar
9. For a reaction taking place in a container in equilibrium with its surroundings, the effect of temperature on its equilibrium constant K in terms of change in entropy is described by



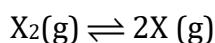
[JEE ADV. 2017]

- (A) with increase in temperature, the value of K for exothermic reaction decreases because the favourable change in entropy of the surroundings decreases
- (B) With increases in temperature, the value of K for endothermic reaction increases because the entropy change of the system is negative
- (C) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surrounding decreases
- (D) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

**Paragraph-10-11**

Thermal decomposition of gaseous  $X_2$  to gaseous X at 298 K takes place according to the following equation:

[JEE(Advanced) 2016]



The standard reaction Gibbs energy,  $\Delta G^\circ$ , of this reaction is positive. At the start of the reaction, there is one mole of  $X_2$  and no X. As the reaction proceeds the number of moles of X formed is given by  $\beta$ . Thus,  $\beta_{\text{equilibrium}}$  is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given:  $R = 0.083 \text{ L bar K}^{-1} \text{ mol}^{-1}$ )

- 10.** The equilibrium constant  $K_p$  for this reaction at 298 K, in terms of  $\beta_{\text{equilibrium}}$ , is

$$(A) \frac{8\beta_{\text{equilibrium}}^2}{2-\beta_{\text{equilibrium}}} \quad (B) \frac{8\beta_{\text{equilibrium}}^2}{4-\beta_{\text{equilibrium}}^2} \quad (C) \frac{4\beta_{\text{equilibrium}}^2}{2-\beta_{\text{equilibrium}}} \quad (D) \frac{4\beta_{\text{equilibrium}}^2}{4-\beta_{\text{equilibrium}}^2}$$

- 11.** The INCORRECT statement among the following, for this reaction, is

- (A) Decrease in the total pressure will result in formation of more moles of gaseous X
- (B) At the start of the reaction, dissociation of gaseous  $X_2$  takes place spontaneously
- (C)  $\beta_{\text{equilibrium}} = 0.7$
- (D)  $K_c < 1$

- 12.** One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings ( $\Delta S_{\text{surr}}$ ) in  $\text{J K}^{-1}$  is

[JEE(Advanced) 2016]

(1 L atm = 101.3 J)

- (A) 5.763      (B) 1.013      (C) -1.013      (D) -5.763



13. Match the thermodynamic processes given under Column I with the expressions given under Column II.

[JEE(Advanced) 2015]

**Column I**

- (A) Freezing of water at 273 K and 1 atm
- (B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions
- (C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container
- (D) Reversible heating of  $\text{H}_2(\text{g})$  at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm

**Column II**

- (P)  $q = 0$
- (Q)  $w = 0$
- (R)  $\Delta S_{\text{sys}} < 0$
- (S)  $\Delta U = 0$
- (T)  $\Delta G = 0$

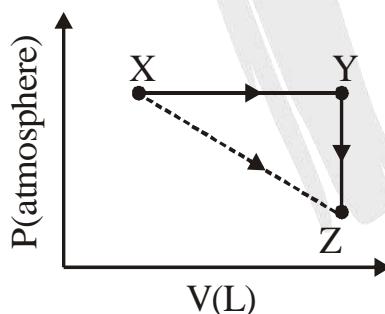
14. For the process,  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$

at  $T = 100^\circ\text{C}$  and 1 atmosphere pressure, the correct choice is:

[JEE(Advanced) 2014]

- (A)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} > 0$
- (B)  $\Delta S_{\text{system}} > 0$  and  $\Delta S_{\text{surroundings}} < 0$
- (C)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} > 0$
- (D)  $\Delta S_{\text{system}} < 0$  and  $\Delta S_{\text{surroundings}} < 0$

15. For an ideal gas, consider only P-V work in going from an initial state X to the final state Z. The final state Z can be reached by either of the two paths shown in the figure. Which of the following choice(s) is (are) correct? [Take  $\Delta S$  as change in entropy and w as work done] [JEE 2012]



- (A)  $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$
- (B)  $W_{x \rightarrow z} = W_{x \rightarrow y} + W_{y \rightarrow z}$
- (C)  $W_{x \rightarrow y \rightarrow z} = W_{x \rightarrow y}$
- (D)  $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

16. Match the transformations in Column-I with appropriate option in Column-II [JEE 2011]

**Column-I**

- (A)  $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$
- (B)  $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- (C)  $2\text{H}\bullet \rightarrow \text{H}_2(\text{g})$

**Column-II**

- (P) phase transition
- (Q) allotropic change
- (R)  $\Delta H$  is positive



- |   |                            |
|---|----------------------------|
| (D) $P_{(\text{white, solid})} \rightarrow P_{(\text{red, solid})}$ | (S) $\Delta S$ is positive |
|   | (T) $\Delta S$ is negative |

**17.** Statement-1 : For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. [JEE 2008]

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

**18.** Statement-1 : There is a natural asymmetry between converting work to heat and converting heat to work. [JEE 2008]

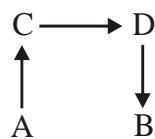
Statement-2 : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

- (A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.
- (B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.
- (C) Statement-1 is true, statement-2 is false.
- (D) Statement-1 is false, statement-2 is true.

**19.** For the process  $\text{H}_2\text{O(l)} (1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O(g)} (1 \text{ bar}, 373 \text{ K})$ , the correct set of thermodynamic parameters is :- [JEE 2007]

- |  |  |
|--|--|
| (A) $\Delta G = 0, \Delta S = + \text{ve}$ | (B) $\Delta G = 0, \Delta S = - \text{ve}$           |
| (C) $\Delta G = + \text{ve}, \Delta S = 0$ | (D) $\Delta G = - \text{ve}, \Delta S = + \text{ve}$ |

**20.** A process  $A \rightarrow B$  is difficult to occur directly instead it takes place in three successive steps.



$$\Delta S (A \rightarrow C) = 50 \text{ e.u.}$$

$$\Delta S (C \rightarrow D) = 30 \text{ e.u.}$$

$$\Delta S (B \rightarrow D) = 20 \text{ e.u.}$$

Where e.u. is entropy unit.

Then the entropy change for the process  $\Delta S (A \rightarrow B)$  is :-

[JEE 2006]



- (A) + 100 e.u.      (B) - 60 e.u.      (C) - 100 e.u.      (D) + 60 e.u.

21. The enthalpy of vapourization of a liquid is  $30 \text{ kJ mol}^{-1}$  and entropy of vapourization is  $75 \text{ J mol}^{-1} \text{ K}^{-1}$ . The boiling point of the liquid at 1 atm is :- [JEE 2004]

- (A) 250 K      (B) 400 K      (C) 450 K      (D) 600 K

22.  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  [JEE 2004]

This reaction is carried out at 298 K and 20 bar. 5 mol each of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$  are taken initially.

Given :  $(\Delta G_f^0)_{\text{N}_2\text{O}_4} = 100 \text{ kJ mol}^{-1}$ ;  $(\Delta G_f^0)_{\text{NO}_2} = 50 \text{ kJ mol}^{-1}$

(i) Find  $\Delta G$  for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium.

23. Show that the reaction  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$  at 300 K is spontaneous and exothermic, when the standard entropy is  $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . The standard Gibbs free energies of formation for  $\text{CO}_2$  and  $\text{CO}$  are  $-394.4$  and  $-137.2 \text{ kJ mol}^{-1}$ , respectively. [JEE 2001]

24. When 1-pentyne (A) is treated with 4N alcoholic KOH at  $175^\circ\text{C}$ , it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne (A), 95.2% 2-pentyne(B) & 3.5% of 1, 2-pentadiene (C). [JEE 2001]

The equilibrium was maintained at  $175^\circ\text{C}$ . Calculate  $\Delta G^\circ$  for the following equilibria.



From the calculated value of  $\Delta G_1^\circ$  &  $\Delta G_2^\circ$  indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C.



## **ANSWER KEY**

## **EXERCISE # (0-I)**

1. (A) 2. (B) 3. (C) 4. (D) 5. (D) 6. (C) 7. (D)  
8. (D) 9. (C) 10. (B) 11. (D) 12. (C) 13. (A) 14. (C)  
15. (A) 16. (C) 17. (D) 18. (B) 19. (C) 20. (A) 21. (C)  
22. (C) 23. (A) 24. (B) 25. (B) 26. (D) 27. (A) 28. (D)  
29. (B) 30. (A) 31. (C) 32. (A) 33. (A) 34. (D) 35. (C)  
36. (B) 37. (C) 38. (B) 39. (C) 40. (A) 41. (C) 42. (A)  
43. (D) 44. (A) 45. (C) 46. (B) 47. (C) 48. (A) 49. (D)  
50. (A)

## **EXERCISE # (S-I)**



## EXERCISE # (O-II)

1. (C)      2. (A)      3. (B)      4. (B)      5. (A)  
 6. (A)      7. (A)      8. (A,B,D)      9. (A,B,D)      10. (A,D)  
 11. (A,C)      12. (A,B,D)      13. (A,B,C)      14. (A,B,C,D)  
 15. (A,C,D)      16. (A,B,C,D)      17. (A,B,C,D)      18. (B,C)  
 19. (B,D)      20. (A)      21. (C)      22. (C)      23. (A)  
 24. ((A)→S; (B)→P,R; (C)→P,S; (D)→P,R)  
 25. ((A)→P,S,R; (B)→P,R; (C)→P; (D)→Q,R,S)  
 26. (A)      27. (C)

## EXERCISE # (S-II)

1. (100)      2. (10.352)  
 3. (i) Rev. Process  $\Delta S_{\text{syst}} = \frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = -\frac{3}{2} R \ln 10$   
 (ii) Irr Process  $\Delta S_{\text{sys}} = \frac{3}{2} R \ln 10$ ;  $\Delta S_{\text{surr}} = \frac{3}{2} R (0, 9)$ ;  $\Delta S_{\text{total}} = \frac{3}{2} R (1.403)$   
 4. ( $S_T = 246.586 \text{ J / (mole. K)}$ )      5. (-530 J)      6. (74.05 J/K)  
 7. (30 kJ/mole)  
 8. (-810 J/mol; -5872 J/mol and 41.3 kJ/mol)      9. ( $P_2 = 1.50 \times 10^9 \text{ Pa}$ )  
 10. (12)

## EXERCISE # (JEE-MAIN)

1. 300      2. A      3. A      4. (600)      5. (5)      6. (200)  
 7. (38 kJ/mol)      8. (A)      9. (-13537.57)      10. (2.70 Kcal/mol)  
 11. (C)      12. (A)      13. (B)      14. (B)      15. (C)      16. (D)      17. (B)  
 18. (B)      19. (B)      20. (C)      21. (C)      22. (C)      23. (B)      24. (C)  
 25. (A)      26. (D)      27. (D)      28. (C)      29. (C)      30. (D)      31. (A)  
 32. (D)      33. (B)



## EXERCISE (JEE-ADVANCED)

1. (10) 2. (A,B,D) 3. (166.28) 4. (141.34)  
5. (A,C) 6. (14.6) 7. (8500) 8. (C) 9. (A,C)  
10. (B) 11. (C) 12. (C)  
13. (((A)→R,T (B)→P,Q,S (C)→P,Q,S (D)→P,Q,S,T))  
14. (B) 15. (AC) 16. ((A)→P,R,S ; (B)→R,S ; (C)→T ; (D)→P,Q,T)  
17. (D) 18. (A) 19. (A) 20. (D) 21. (B)  
22. (i)  $5.705 \times 10^3 \text{ J mol}^{-1}$   
(ii) Since initial gibbs free energy change of the reaction is positive, so the reverse reaction will take place  
23. ( $\Delta H^\circ = -285.4 \text{ kJ/mol}$ ,  $\Delta G^\circ = -257.2 \text{ kJ/mol}$ )  
24. (15991 K,  $\text{mol}^{-1}$ , 12304 J  $\text{mol}^{-1}$ ; B > C > A)



**SOLUTION**  
**EXERCISE # (O-I)**

1.  $H = 1 - \frac{T_2}{T_1} = 1 - \frac{298}{373}$

2.  $H = 1 - \frac{T_2}{T_1} = 1 - \frac{|W|}{q}$

$$1 - \frac{300}{500} = \frac{|W|}{2}$$

$$|W| = 0.8 \text{ kcal}$$

3.  $H = 1 - \frac{T_2}{1000} = 1 - \frac{360}{T_2}$

$$T_2 = 600 \text{ K}$$

5.  $\Delta S = nR \ln \frac{V_2}{V_1}$  for isothermal process

6.  $\Delta S = nC_V \ln \frac{V_2}{V_1}$  for isochoric process

7. Initial state  $\xrightarrow{(P,V,T)} \text{Final state } \left(\frac{V}{2}, 2T\right)$

$$\Delta S = nC_V \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)$$

8. Initial pressure (P) =  $\frac{nRT}{V} = \frac{2 \times 0.0821 \times 243.6}{20} = 2 \text{ atm}$

Final pressure (P) = 1 atm

$$\Delta S = nR \ln \left( \frac{P_1}{P_2} \right) = 2 \times 2 \times \ln \left( \frac{2}{1} \right) \\ = 2.77 \text{ Cal/K}$$

9. Initial state  $\xrightarrow[2 \text{ atm}]{\text{isothermal expansion}} \text{Final state } 1 \text{ atm}$

$$\text{Heat transfer (q)} = -w = +P_{\text{ex}} + \left[ \frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$$

$$= 1 \left[ \frac{10 \times 0.821 \times 300}{1} - \frac{10 \times 0.821 \times 300}{2} \right]$$



$$\Delta S_{\text{sys}} = nR \ln \left( \frac{P_1}{P_2} \right) = 10 \times 8.3 \times \ln \left( \frac{2}{1} \right)$$

$$= 57.33 \text{ J/K}$$

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{sys}}}{T} = \frac{-5 \times 0.821 \times 300 \times 100}{300}$$

$$= -41.05 \text{ J/K}$$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr.}} = 16 \text{ J/K}$$

**10.** For isobaric process

$$\Delta S = nC_p \ln \left( \frac{T_2}{T_1} \right)$$

$$23.03 = 1 \times C_p \ln \left( \frac{600}{300} \right)$$

$$C_p = \frac{23.3}{\ln 2} = 33.23 \text{ J}$$

$$C_v = C_p - R$$

**11.** Final temperature of both blocks =  $\frac{T_h + T_c}{2}$

$$\therefore \Delta S = \Delta S_I + \Delta S_{II}$$

$$= C \ln \left( \frac{T_h + T_c}{2T_h} \right) + \ln \left( \frac{T_h + T_c}{2T_c} \right)$$

$$= C \ln \left( \frac{T_h + T_c}{2T_h T_c} \right)^2$$

**12.**  $\Delta S = \frac{\Delta H}{T} = \frac{-300 \times 30}{300} = -30 \text{ J/K-mole}$

**13.** Phase transition is a constant pressure and constant temperature reversible process i.e, reversible isobaric & isothermal process

**14.** Due to mixing of gases randomness increases

**15.**  $\Delta H +$  positive and  $\Delta S +$  positive

**16.**  $\Delta S +$  positive

**20.**  $\Delta S_{\text{reaction}} = \sum S_{\text{product}} - \sum S_{\text{reactant}}$

$$= (2 \times 0.19) - (0.13 + 0.22)$$

$$= 0.03 \text{ kJ/K-mole}$$

**21.**  $\Delta S_{\text{reaction}} = \sum S_{\text{product}} - \sum S_{\text{reactant}}$



22.  $\Delta H_{T_2} = \Delta H_{T_1} + (\Delta C_p)_{\text{reaction}} [T_2 - T_1]$

23.  $\Delta H_{T_2} = \Delta H_{T_1} + (\Delta C_p)_{\text{reaction}} [T_2 - T_1]$

24.  $\Delta S = 75 \ln(273/263)$   
 $+ 36 \ln(263/273) - 6000/273$   
 $= -20.41 \text{ J/K-mol}$

29.  $\Delta H < 0 \text{ & } \Delta S > 0$

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

$$= 2.1 - \frac{298 \times 20}{1000}$$

$$= -3.86 \text{ kCal}$$

$\therefore$  reaction is spontaneous

31. For spontaneous process

$$\Delta G = \Delta H - T\Delta S < 0$$

$$T > \frac{\Delta H}{\Delta S}$$

32.  $\Delta H = \Delta U + \Delta n g RT$

$$= -3 \times 1000 + (-1) \times 2 \times 300$$

$$= -3600 \text{ Cal.}$$

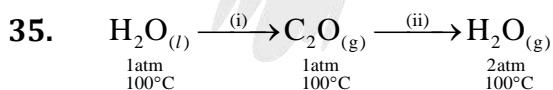
$$\Delta G = \Delta H - T\Delta S$$

$$= -3600 - 300 \times (-10)$$

$$= -600 \text{ Cal.}$$

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

34.  $\Delta G = 0$

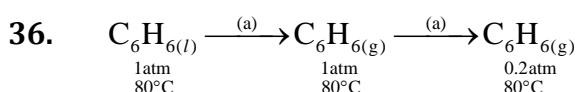


$$\Delta G_{(\text{i})} = 0$$

$$\Delta G_{(\text{ii})} = nRT \ln \left( \frac{P_2}{P_1} \right)$$

$$= 1 \times 2 \times 298 + 80 \ln \left( \frac{0.2}{1} \right)$$

$$= -2270 \text{ cal}$$





$$\Delta G_{(a)} = 0$$

$$\begin{aligned}\Delta G_{(b)} &= nRT \ln\left(\frac{P_2}{P_1}\right) \\ &= 2 \times 2 \times (273 + 80) \ln\left(\frac{0.2}{1}\right) \\ &= -2270 \text{ cal}\end{aligned}$$

**37.** Normal B.P. of water is 100°C

$$\text{38. } T = \frac{\Delta H}{\Delta S}$$

**39.** At equilibrium

$$\Delta G = 0 = \Delta H - T\Delta S$$

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

**40.** At equilibrium

$$\Delta S = \frac{\Delta H}{T} = \frac{-30 \times 1000}{750} = -40 \text{ J/K-mole}$$

$$\Delta S_{\text{reaction}} = \sum S_{\text{product}} - \sum S_{\text{reactant}}$$

$$\text{41. } \Delta G_{298K} = \Delta H_{298K} - 298 \times \Delta S_{298K}$$

$$\Delta G_{298K} = \frac{-5737 + 6333}{298} \text{ kJ/K-mole}$$

$$= 2 \text{ kJ/K-mole}$$

$$\Delta G_{310K} = \Delta H_{310K} - 310 \times \Delta S_{310K}$$

$$\Delta G_{310K} = -5737 - 310 \times 2$$

$$= -6357 \text{ kJ}$$

$$\text{Addition non-PV work} = |\Delta G_{310K} - \Delta G_{298K}|$$

$$= 24 \text{ kJ}$$

$$\text{42. } \Delta G_{200K} = \Delta H_{200K} - 200 \times \Delta S_{200K}$$

$$20 = \Delta H - \frac{200 \times (-20)}{1000}$$

$$\Delta H = 16 \text{ kJ}$$

$$\Delta H_{400K} = \Delta H_{200K} + (\Delta C_p) [400 - 200]$$

$$= 16 + \frac{20 \times 200}{1000}$$

$$= 20 \text{ kJ/mole}$$



**43.** Maximum non-PV work =  $|\Delta G_R|$

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

$$\Rightarrow \Delta G = -6000 - \frac{300 \times 180}{100} \text{ (for mole)}$$

$$\Rightarrow \Delta G = -6054 \text{ kJ}$$

$\Rightarrow |\Delta G|$  for 0.01 moles of sucrose

$$\Rightarrow 60.54 \text{ kJ ; option (D)}$$

**46.**  $\Delta G^\circ = -RT \ln K$

**47.**  $K_p = -p_{NH_3} \times p_{H_2S}$

$$= \left( \frac{X}{2} \right) \left( \frac{X}{2} \right)$$

$$= \left( \frac{X}{2} \right)^2$$

$$\Delta G^\circ = -RT \ln K_p$$

**48.**  $K = \frac{P_B}{P_A} = \frac{1}{4}$

$$\Delta G^\circ = -RT \ln K$$

$$= -RT \ln \left( \frac{1}{4} \right)$$

$$= RT \ln (4)$$

**49.**  $\Delta G = \Delta G^\circ + RT \ln \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3}$

$$\Delta G = -33000 + 8.314 \times 2.303 \log \frac{(0.02)}{1 \times 3^3} = -60.5 \text{ kJ/mole}$$

### EXERCISE # (S-I)

$$1. \quad \eta = 1 - \frac{T_2}{T_1} = \frac{400}{100}$$

$$1 - \frac{(273+7)}{T_1} = 0.4$$

$$T_1 = 466.67 \text{ K or } 193.67^\circ\text{C}$$

$$2. \quad \eta_{rev.} = 1 - \frac{T_2}{T_1} = 1 + \frac{q_2}{q_1}$$



$$\eta_{\text{rev.}} = 1 + \frac{q_2}{q_1}$$

$$\eta_{\text{irr}} < \eta_{\text{rev.}}$$

3. Let source temperature is  $T_1$  & sink temperature is  $T_2$

$$\therefore \eta = 1 - \frac{T_2}{T_1} = \frac{1}{6}$$

$$\therefore \frac{T_2}{T_1} = \frac{5}{6}$$

On decreasing sink temperature by  $65^\circ\text{C}$

$$\eta = 1 - \left( \frac{T_2 - 65}{T_1} \right) = \frac{1}{3}$$

$$1 - \frac{T_2}{T_1} + \frac{65}{T_1} = \frac{1}{3}$$

$$\therefore T_1 = 65 \times 6 = 390 \text{ K or } 117^\circ\text{C}$$

$$T_2 = \frac{5}{6} \times 390 = 325 \text{ K or } 52^\circ\text{C}$$

4. (a)  $\because \Delta S = n C_p \ln \left( \frac{T_2}{T_1} \right) \dots \text{(for isobaric process)}$

$$= 1 \times \frac{7}{2} R \ln \left( \frac{400}{300} \right)$$

$$= \frac{7}{2} R (0.286)$$

- (b)  $\because \Delta S = n C_v \ln \left( \frac{T_2}{T_1} \right) \dots \text{(for isochoric process)}$

$$= 1 \times \frac{5}{2} R \ln \left( \frac{400}{300} \right)$$

$$= 1 \times \frac{5}{2} R (0.286)$$

5.  $\Delta S_{\text{sys.}} = n R \ln \left( \frac{P_1}{P_2} \right) \quad \text{(for isothermal process)}$

$$= 5 \times R \ln \left( \frac{10}{2} \right)$$

$$= 5 \times 8.314 \times \ln 5$$



$$= 66.92 \text{ J/K}$$

For irreversible isothermal process

$$q_{\text{sys}} = -w = + P_{\text{ext}} [V_2 - V_1]$$

$$= 2 \left[ \frac{5 \times R \times 300}{2} - \frac{5 \times R \times 300}{10} \right]$$

$$= 1200 \text{ R} = 1200 \times 8.314 \text{ J}$$

$$\therefore \Delta S_{\text{surr.}} = -\frac{q_{\text{sys}}}{T} = -\frac{1200 \times 8.314}{300} = -33.256 \text{ J/K}$$

$$\therefore \Delta S_T = \Delta S_{\text{sys}} + \Delta S_{\text{surr.}}$$

$$= 33.66 \text{ J/K}$$

6.  $\Delta S_{\text{sys}} = nR \ln \left( \frac{V_2}{V_1} \right) \dots \text{(for isothermal process)}$

$$= 1 \times 8.314 \times \ln \left( \frac{20}{5} \right)$$

$$= 11.53 \text{ J/K}$$

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys}} = -11.53 \quad \text{(for rev. process)}$$

$$\Delta S_T = 0$$

7. For adiabatic irr. process

$$\Delta U = w_{\text{irr.}} \& q = 0$$

$$nC_V (T_2 - T_1) = -P_{\text{ext}} \left[ \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right]$$

$$1 \times \frac{3}{2} R [T_2 - 400] = -1 \left[ \frac{1 \times R \times T_2}{2} - \frac{1 \times R \times 400}{20} \right]$$

$$\frac{3}{2} T_2 - 600 = -T_2 + 20$$

$$\frac{5}{2} T_2 = 620$$

$$T_2 = 248 \text{ K}$$

$$\Delta S_{\text{sys}} = nC_p \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{P_1}{P_2} \right)$$

$$= 1 \times \frac{5}{2} \times R \times \ln \left( \frac{248}{400} \right) + 1 \times R \times \ln \left( \frac{20}{1} \right)$$

$$= 15.63 \text{ J/K}$$

$$\Delta S_{\text{surr.}} = 0$$

$$\Delta S_T = 15.63 \text{ J/K}$$

## 8. For polytrophic

$$P^2V = C$$

$$\text{or} \quad PV^{\frac{1}{2}} = C$$

$$\text{polytropic index} = \frac{1}{2}$$

$$\therefore V^{\frac{1}{2}-1} T = C$$

$$V_1^{-0.5} T_1 = V_2^{-0.5} T_2$$

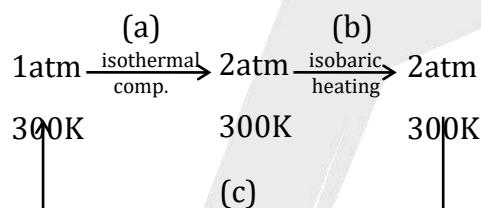
$$1^{-0.5} \times 300 = 4^{-0.5} \times T_2$$

$$T_2 = 600 \text{ K}$$

$$\therefore \Delta S_{\text{sys}} = n C_v \ln \left( \frac{T_2}{T_1} \right) + nR \ln \left( \frac{V_2}{V_1} \right)$$

$$= 2 \times \frac{3}{2} \times R \ln \left( \frac{600}{300} \right) + 2 \times R \times \ln \left( \frac{4}{1} \right)$$

$$= 7R \ln 2$$



9.

$$\Delta S_{(a)} = nR \ln\left(\frac{P_1}{P_2}\right)$$

$$= 2 \times R \times \ln \left( \frac{1}{2} \right) = -11.52 \text{ J/K}$$

$$\Delta S_{(b)} = nC_p \ln \left( \frac{T_2}{T_1} \right)$$

$$= 2 \times \frac{5}{2} R \ln \left( \frac{400}{300} \right) = 11.96 \text{ J/K}$$

$$\Delta S_{(c)} = -[\Delta S_{(a)} + \Delta S_{(b)}]$$

$$= -0.44 \text{ J/K}$$

$$10. \quad \Delta S = \int \frac{q}{T}$$



$$= \int \frac{nC_p dT}{T} \quad (\text{for isobaric process})$$

$$= \int_{300}^{600} \frac{1 \times (10 + 10^{-2} T) dt}{T}$$

$$= 10 \text{ K/J}$$

11. (a)  $\Delta S_{\text{source}} = \frac{q}{T} = -\frac{100 \times 10^3}{400} = -250 \text{ J/K}$

(b)  $\Delta S_{\text{sink}} = \frac{q}{T} = \frac{100 \times 10^3}{300} = 333.33 \text{ J/K}$

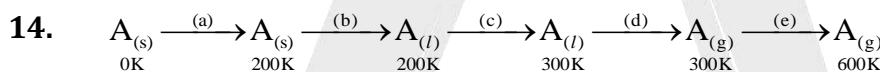
(c)  $\Delta S_T = \Delta S_{\text{source}} + \Delta S_{\text{sink}}$   
 $= 83.33 \text{ J/K}$

12.  $\Delta S_{\text{room}} = \frac{q}{T} = \frac{4.2 \times 1000}{300} \text{ J/K}$   
 $= 14 \text{ J/K}$

13. For melting at melting point

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

$$T = \frac{30 \times 10^3}{30} = 1000 \text{ K}$$



$$\Delta S_{\text{sys}} = \Delta S_{(a)} + \Delta S_{(b)} + \Delta S_{(c)} + \Delta S_{(d)} + \Delta S_{(e)}$$

$$= \int_0^{200} \frac{nC_p dT}{T} + \frac{\Delta H_{\text{fus.}}}{\text{M.P.}} + \int_{200}^{300} \frac{nC_p dT}{T} + \frac{\Delta H_{\text{vap.}}}{\text{B.P.}} + nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$= 205.08 \text{ J/K - mole}$$

15.  $\Delta S_{\text{rxn}} = \sum S_{\text{product}} - \sum S_{\text{Reactant}}$

(i)  $\Delta S_{\text{rxn}} = 72 - \left[ 5 + \frac{223}{2} \right]$

$$= -90.5 \text{ J/K - mole}$$

(ii)  $\Delta S_{\text{rxn}} = S_{\text{NH}_4\text{Cl}} - \left( \frac{S_{\text{N}_2}}{2} + 2 \times S_{\text{H}_2} + \frac{S_{\text{Cl}_2}}{2} \right)$

$$= -374.5 \text{ J/K - mole}$$

(iii)  $\Delta S_{\text{rxn}} = S_{\text{diamond}} - S_{\text{graphite}}$   
 $= -3.26 \text{ J/K - mole}$



16.  $\Delta S_{\text{sys}} = 300$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T} = \frac{-75 \times 1000}{300} = -250$$

$$\Delta S_T = 300 - 250$$

$$= 50 \text{ J/K}$$

17.  $\Delta H_{T_2} = \Delta H_{T_1} + (\Delta C_p)_{\text{rxn}} (T_2 - T_1)$

$$= -283.5 \text{ KJ}$$

18.  $\Delta H_{T_2} = \Delta H_{T_1} + (\Delta C_p)_{\text{rxn}} (T_2 - T_1)$

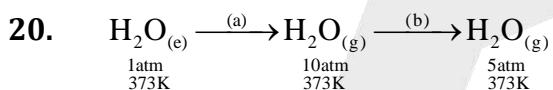
19. For isothermal process :

$$\Delta G = nRT \ln \left( \frac{V_1}{V_2} \right)$$

$$= P_1 V_1 \ln \left( \frac{V_1}{V_2} \right)$$

$$= 1 \times 10 \times \ln \left( \frac{10}{20} \right)$$

$$= 7 \text{ bar. lt}$$



$$\Delta G_{(\text{a})} = 0 \quad (\because \text{process is rev. place change})$$

$$\Delta G_{(\text{b})} = nRT \ln \left( \frac{P_2}{P_1} \right)$$

$$= 5 \times 2 \times 373 \times \ln \left( \frac{5}{1} \right)$$

$$= 3730 \ln(5)$$

21.  $\Delta S_{\text{rxn}} = \sum S_{\text{product}} - \sum S_{\text{Reactant}}$

$$= (2 \times 240) - (150 + 220)$$

$$= 110 \text{ J/K - mole}$$

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

$$= 29.3 - \frac{300 \times 110}{1000}$$

$$= -3.7 \text{ KJ/mole}$$

22.  $\Delta S_{\text{rxn}} = 2 \times 115 - 130$



$$= 100 \text{ J/K - mole}$$

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

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

$$= 406 + \frac{298 \times 100}{1000}$$

$$= 436 \text{ kJ/mole}$$

23. (i)  $\text{L} \rightleftharpoons \text{S}$  :  $\Delta H = -1000 \text{ Joule. mole}$  at

$T = 200 \text{ K}$  and  $P = 1 \text{ atm}$ . At normal melting point, this transformation is reversible – Hence

$\Delta G = 0$  Ans.

$$(ii) \Delta S = -\frac{\Delta H}{T} = \frac{-1000}{200} = -5 \text{ J/mole. K}$$

$$(iii) \Delta S_{\text{total}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

Assuming that  $\Delta S$  and  $\Delta H$  do not vary temperature

$$\Delta S_{\text{total}} = -5 \text{ J/mole. K} + \left( \frac{\Delta H}{T} \right)$$

$$= -5 + \frac{1000}{150} = +1.66 \text{ J/mole.K}$$

process is spontaneous

$$(iv) \Delta G = -T\Delta S_{\text{total}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

$$= -5 + \left( \frac{\Delta H}{T} \right)$$

$$= -5 + \frac{1000}{150} = -1 \text{ J/mole. K}$$

$$\Rightarrow \Delta G = -(250)(-1) = +250 \text{ J/mole. K}$$

The process is non-spontaneous at 250 K

24.  $W_{\text{non-PV}} = \Delta G = \Delta H - T\Delta S$

$$= -2808 - \frac{310 \times 182.4}{1000}$$

$$= -2864.5 \text{ kJ}$$

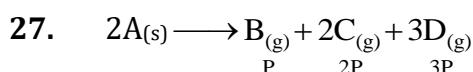
25.  $\therefore \Delta G^\circ = -RT \ln K$

$$= -\frac{8.314 \times 298}{1000} \times \ln \left( \frac{0.6}{0.4} \right)$$

$$= -1.005 \text{ kJ/mole}$$

26.  $\therefore \Delta G^\circ = -RT \ln K = 0$

$$\therefore K = 1$$



$$\text{Total pressure} = P + 2P + 3P = 12$$

$$\therefore P = 2$$

$$K_p = P_B \times P_C^2 \times P_D^3$$

$$= 2 \times 4^2 \times 6^3$$

$$\Delta G^\circ = -RT \ln K_p$$

$$= -17.8 \text{ Kcal}$$

28.  $\because DG^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$

$$\therefore \ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

On comparing

$$\Delta H^\circ = 1080 \times R$$

$$\Delta G^\circ = -1.04 \times R$$

29.  $2 \times 3 \ln \frac{(10 \times 10 / 1)}{10}$

$$600 \ln 10$$

$$= 600 \times 2.3$$

$$= 1380 \text{ cal}$$

30.  $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$

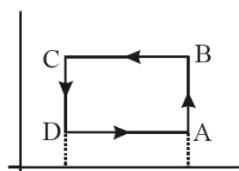
$$K = 1.862 \times 10^{12}$$

31.  $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$

$$-8.314 \times 300 \times \ln(10^{-7}) = 25 \times 1000 - 300 \Delta S$$

$$\therefore \Delta S = -51 \text{ kJ/K}$$

32. (i)  $W_{AB} = -nRT \ln \frac{V_2}{V_1}$



$$\Delta S = \frac{q_{ues}}{T} = -\frac{W_{AB}}{T}$$

$$\Rightarrow -W_{AB} = T\Delta S = 600 \times 100$$



- $W_{BC} = -nC_V(T_1 - T_2)$
- $W_{CD} = T\Delta S = 300 \times (-100)$
- $W_{DA} = -nC_V(T_2 - T_1)$

Net work delivered during one cycle

$$= -W_{AB} - W_{BC} - W_{CD} - W_{DA}$$

$$= 300 \times 100 = 30 \text{ kJ}$$

Note: Net work done = area of the rectangle

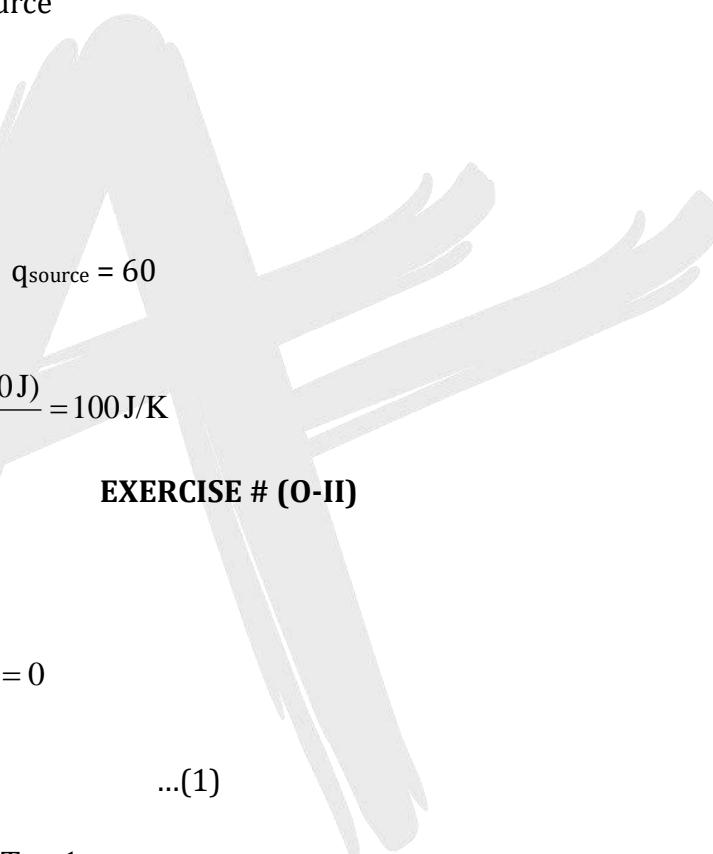
$$(ii) \frac{W_{\text{net}}}{T} = \eta \text{ and } \eta = \frac{600 - 300}{600} = \frac{1}{2}$$

$\Rightarrow q =$  heat taken from the source

$$= \frac{-W_{\text{net}}}{1/2} = \frac{30 \text{ kJ}}{1/2} = +60 \text{ kJ}$$

$$(iii) \Delta S_{\text{sink}} = -\frac{q_{\text{sink}}}{T}$$

$$\text{also } (q_{\text{source}} + q_{\text{sink}}) = 30$$



$$q_{\text{source}} = 60$$

$$\Rightarrow q_{\text{sink}} = -30 \text{ kJ}$$

$$\Rightarrow \Delta S_{\text{sink}} = -\frac{q_{\text{sink}}}{T} = \frac{-(30000 \text{ J})}{100} = 100 \text{ J/K}$$

### EXERCISE # (O-II)

3.  $dS = \frac{n \cdot C_{V,m} \cdot dT + P \cdot dV}{T}$

For maximum entropy,  $\frac{dS}{dV} = 0$

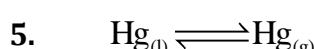
or,  $n \cdot C_{V,m} \frac{dT}{dV} + P = 0 \quad \dots(1)$

Now,  $P = \frac{RT}{V} = P_0 - \alpha V \Rightarrow \frac{dT}{dV} = \frac{1}{R}(P_0 - 2\alpha V)$

From (1) and (2),  $\dots(2)$

$$1 \times \frac{R}{\gamma - 1} \times \frac{1}{R}(P_0 - 2\alpha V) + (P_0 - \alpha V) = 0$$

$$\therefore V = \frac{\gamma \cdot P_0}{\alpha(\gamma + 1)}$$



$$K_p = V \cdot P_{\text{Hg}_{(g)}}$$

$$\Delta G^\circ = -RT \ln K_p$$



$$31 \times 1000 = -8.3 \times 298 \times \ln K_p$$

$$\ln K_p = -\frac{31 \times 1000}{8.3 \times 298}$$

$$\log K_p = -\frac{31 \times 1000}{8.3 \times 298 \times 2.303} = -5.44$$

$$K_p = 10^{-5.44} = V.P.$$

For boiling ! V.P. = External pressure =  $10^{-5.44}$  bar.

8. Free expansion is also called isothermal adiabatic expansion.

9. (a)  $\int \frac{q_{irr}}{T} \neq \Delta S$

(d)  $\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right)$  for isochoric process

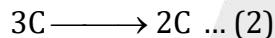
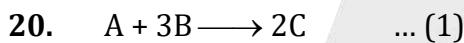
11.  $\Delta S_{T_2, P_2} = \Delta S_{T_1, P_1} + (\Delta G)_{\text{reaction}} \ln\left(\frac{T_2}{T_1}\right) + \Delta n g R \ln\left(\frac{P_1}{P_2}\right)$

14. (C)  $\Delta G^\circ$  depends only on temperature.

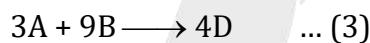
(D)



17. Entropy of isolated system is maximized at equilibrium.



On  $3 \times (1) + 2 \times (2)$



$$\begin{aligned} \Delta G_3 &= 3\Delta G_1 + 2\Delta G_2 \\ &= (3 \times 24) + 2(-60) \\ &= -48 \text{ kJ/mole} \end{aligned}$$

$$\begin{aligned} \Delta H_3 &= 3\Delta H_1 + 2\Delta H_2 \\ &= 3(-24) + 2(-84) \\ &= -240 \text{ kJ/mole} \end{aligned}$$

$$\Delta G_3 = \Delta H_3 + T\Delta S_3$$

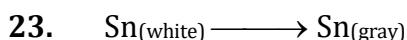
$$-48 = -240 - 300 \times \Delta S_3$$

$$\Delta S_3 = -0.64 \text{ kJ/K-mole}$$

21.  $T = \frac{\Delta H_1}{\Delta S_1} = \frac{\Delta H_1}{\left( \frac{\Delta H_1 - \Delta G_1}{300} \right)}$



$$= \frac{-24 \times 300}{-(24+24)} = 150\text{K}$$



$$\Delta H^\ominus = -2.1 - 0 = -2.1 \text{ kJ}$$

$$\Delta S^\ominus = 44 - 52 = -8 \text{ J / K}$$

$$\Delta G^\ominus = -2.1 + \frac{8 \times 300}{1000}$$

$$= -2.1 + 2.4 = 0.3 \text{ kJ}$$

$\therefore \text{Sn}(\text{gray})$  is thermodynamically less stable.

$\therefore G$  of  $\text{Sn}(\text{white})$  will be less.

Also on decreasing temperature,  $\text{Sn}(\text{white})$  converts to  $\text{Sn}(\text{gray})$  which makes it more brittle and expansion will be observed.

### EXERCISE (S-II)

1. Let heat involved in step 5 is  $Q_5$

$$q_{\text{total}} = -W_{\text{total}}$$

$$500 + 800 + Q_5 = 700$$

$$Q_5 = -600 \text{ J}$$

Since  $\Delta S_{\text{total}} = 0$

$$\frac{500}{200} + \frac{800}{200} - \frac{600}{T_5} = 0$$

$$2 + 4 - 6 = 0.$$

$$T_5 = 100 \text{ K}$$

2.  $\Delta S_{\text{system}} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1};$

$$\Delta S_{\text{surr}} = \frac{-q}{400}$$

$$\Delta S_{\text{total}} = -\frac{5000}{400} + \frac{3}{2} \times (8.3) \times \ln \frac{4}{3} + (8.3)(2.3)$$

$$\Delta S_{\text{total}} = +10.352 \text{ J/K-mol}$$

3. (i) For reversible process

$$\Delta S_{\text{sys}} = nC_v \ln \left( \frac{T_2}{T_1} \right)$$

$$= 1 \times \frac{3}{2} \times R \times \ln \left( \frac{1000}{100} \right)$$



$$= \frac{3}{2} R \ln 10$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = -\frac{3}{2} R \ln(10)$$

$$\Delta S_T = 0$$

(ii) For irreversible isochoric process

$$\Delta S_{\text{sys}} = nC_v \ln \left( \frac{T_2}{T_1} \right) = 1 \times \frac{3}{2} \times R \times \ln \left( \frac{1000}{100} \right)$$

$$= \frac{3}{2} \times R \times \ln (10)$$

$$\therefore q_{\text{sys}} = \Delta U = nC_v (1000 - 100)$$

$$= 1 \times \frac{3}{2} R \times 900$$

$$\therefore \Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{q_{\text{sys}}}{T} = \frac{-\frac{3}{2} \times R \times 900}{1000}$$

$$= -\frac{3}{2} \times R \times 0.9$$

$$\Delta S_T = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

4.  $S_T - S_{0 \text{ K}}$

$$= \int_{0 \text{ K}}^{10 \text{ K}} \frac{C(s).dT}{T} + \int_{10 \text{ K}}^{150 \text{ K}} \frac{C(s).dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{150}^{200} \frac{C(l).dT}{T}$$

$$S_T = \int_{0 \text{ K}}^{10 \text{ K}} \frac{aT^3.dt}{T} + \int_{10}^{150} \frac{b.dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_M} + \int_{150}^{200} \frac{C.dt}{T}$$

$$S_T = \frac{0.5}{3} + 15 \times \ln(15) + 200 + 20 \ln \frac{4}{3}$$

$$S_T = 0.166 + 40.62 + 200 + 5.8$$

$$S_T = 246.586 \text{ J / (mole. K)}$$

5. At constant volume

$$dG = -sdT$$

$$\Delta G = - \int_{300}^{400} sdT$$

$$= \int_{300}^{400} (10 + 10^{-2}T) dT$$



$$= -530 \text{ J}$$

6.  $\Delta H_{300} - \Delta H_{200} = (-10)(100) \text{ Joule}$   
 $\Rightarrow \Delta H_{300} = 2200 - 1000 = + 21000 \text{ Joule}$   
 $\Rightarrow \Delta H_{300} = + 21 \text{ kJ/mol}$
- $$\Delta S_{300} = \frac{21000}{300} = 70 \text{ J/K - mol}$$
- $$\Delta S_{300} - \Delta S_{200} = (-10) \ln (3/2)$$
- $$\Rightarrow \Delta S_{200} = 70 + 10 \ln (3/2) = 74.05 \text{ J/K}$$

**Steps is Marking :**

$$\Delta H_{\text{vap}, 300K} = 21,000 \text{ Joule}$$

$$\Delta S_{\text{vap}, 300K} = \frac{21000}{300} = + 70 \text{ J/K mole}$$

$$\Delta S_{200} = \Delta S_{300} = + 10 \ln \frac{300}{200}$$

$$\Delta S_{\text{vapourisation}, 200K, 1\text{atm}} = 74.05 \text{ J /K mole}$$

7. At 300 K :  $\Delta G = \Delta H - T\Delta S$

$$\begin{aligned}\Delta S &= \frac{\Delta H - \Delta G}{T} \\ &= \frac{-5000 + 6000}{300} = \frac{1000}{300} \text{ RJ/K}\end{aligned}$$

- At 309 K :  $\Delta G = \Delta H - T\Delta S$

$$= -5000 - 309 \times \frac{1000}{300} = 30 \text{ kJ}$$

8.  $\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]$

$$\ln\left(\frac{6.64}{1.34}\right) = \frac{\Delta H}{8.314} \left[ \frac{1}{333} - \frac{1}{373} \right]$$

$$\Delta H = 41.3 \text{ kJ/mole}$$

$$\Delta G^\circ = -RT \ln K$$

$$= -8.314 \times 333 \ln (1.34)$$

$$= -810 \text{ J/mole}$$

$$\Delta G^\circ = -RT \ln K$$

$$= -8.314 \times 373 \times \ln (6.64)$$

$$= -5872 \text{ J/K}$$



9.  $\Delta G_2 - \Delta G_1 = \Delta V [P_2 - P_1]$

$$\Delta V = 12 \times \left[ \frac{1}{3.4} - \frac{1}{2.2} \right] \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$\Delta V = -\frac{14.4}{3.4 \times 2.2} \times 10^{-6} \Rightarrow -1.925 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

Let  $P_2$  is equilibrium pressure;  $\Delta G_2 = 0$ ;  $P_2 = 1 \text{ bar} = 10^5 \text{ Pa}$

$$0 - \Delta G_1 = -1.925 \times 10^{-6} [P_2 - 1]$$

$$2900 = 1925 \times 10^{-6} [P_2 - 1]$$

$$P_2 = \frac{2900}{1.925 \times 10^{-6}} + P_1$$

$$\Rightarrow 1506.5 \times 10^6 + 10^5$$

$$P_2 = 1.50 \times 10^9 \text{ Pa} \quad \text{Ans.}$$

10.  $2 + 4 + 6 = 12$

### EXERCISE (JEE-MAIN)

1.  $\Delta G = \Delta H - T\Delta S = 0$  at equilibrium

$$\Rightarrow -165 \times 103 - T \times (-505) = 0$$

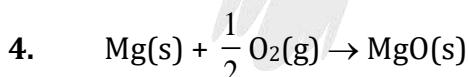
$$\Rightarrow T = 300 \text{ K}$$

The answer is 300

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

$\because$  Entropy of liquid is more than solid

$\therefore$  on melting the entropy increases and  $\Delta G$  becomes more negative and hence it becomes easier to reduce metal



$$\Delta H = \Delta U + \Delta n g RT$$

$$- 601.70 \times 10^3 = \Delta U - \frac{1}{2} \times 8.3 \times 300$$

$$- 601.70 \text{ kJ} = \Delta U + 1.245 \text{ kJ}$$

$$\Delta U = - 600.455 \text{ kJ}$$

Ans. 600



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

$$\Delta G = 57.8 - \frac{298(-176)}{1000}$$

$$\Delta G = -5.352 \text{ kJ/mole}$$

| Nearest integer value | = 5

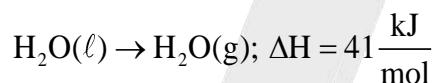
6.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

To make the process spontaneous

$$\begin{aligned}\Delta G^\circ &< 0 \\ \Delta H^\circ - T\Delta S^\circ &< 0 \\ T &> \frac{\Delta H^\circ}{\Delta S^\circ} \\ T &> \frac{80000}{2T} \\ 2T^2 &> 80000 \\ T^2 &> 40000 \\ T &> 200\end{aligned}$$

The minimum temperature to make it spontaneous is 200 K

7. Given equation is



$$\Rightarrow \text{Formation the relation : } \Delta H = \Delta U + \Delta n_g RT$$

$$\Rightarrow 41 \frac{\text{kJ}}{\text{mol}} = \Delta U + (1) \times \frac{8.3}{1000} \times 373$$

$$\Rightarrow \Delta U = 41 - 3.0959$$

$$= 38 \text{ kJ/mol}$$

8.

$$\begin{aligned}(1) \quad \Delta S &= \int \frac{dq}{T} \\ S_T &= \int_0^T \frac{n c dT}{T}\end{aligned}$$

9.  $2 \text{ A(g)} \rightarrow \text{A}_2(\text{g})$

$$\Delta U^\circ = -20 \text{ kJ/mol and } \Delta S^\circ = -30 \text{ J/Kmol}$$

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

$$= -20000 - 1 \times 8.314 \times 298$$

$$= -22477.57$$

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

$$= -22477.57 + 298 \times 30$$

$$= -13537.57$$



10.  $A(t) \rightarrow 2 B(g)$

$$\Delta U = 2.1 \text{ Kcal}, \Delta S = 20 \text{ cal K}^{-1} \text{ at } 300 \text{ K}$$

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

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

$$\Delta G = \Delta U + \Delta n_g RT - T\Delta S$$

$$= 2.1 + \frac{2 \times 2 \times 300}{1000} - \frac{300 \times 20}{1000}$$

$$(R = 2 \text{ cal K}^{-1} \text{ mol}^{-1})$$

$$= 2.1 + 1.2 - 6 = -2.70 \text{ Kcal/mol}$$

11. For ideal Gas

$$U = f(T), H = f(T)$$

$$Z = 1$$

$$C_p - C_v = R$$

$$dU = C_v dT$$

12. For the process to be spontaneous

$$\Delta G = \Delta H - T\Delta S < 0$$

13.  $I_{2(s)} \rightarrow I_{2(g)}$  :  $\Delta H_{200^\circ\text{C}} = 24 \text{ Cal/grm.}$

$$\Delta H_{250^\circ\text{C}} = \Delta H_{200^\circ\text{C}} + (\Delta C_p)_{rxn} [T_2 - T_1]$$

14.  $\Delta G^\circ = -RT \ln k$

$$16. \quad T = \frac{\Delta H}{\Delta S} = \frac{200}{40} = 5 \text{ K}$$

$$19. \quad \Delta G^\circ = 120 - \frac{3}{8}T = RT \ln k$$

$$\Delta G^\circ = 0 = 120 - \frac{3}{8}T \quad \text{Then } K = 1$$

$$\therefore T = 320 \text{ K}$$

$$\text{If } T > 320 \text{ K then } K > 1 \quad \text{So} \quad y > x$$

$$\text{If } T < 320 \text{ K then } K < 1 \quad \text{So} \quad x < y.$$



20.  $T = \frac{\Delta H}{\Delta S} = \frac{491.1 \times 1000}{198} = 2480.3 \text{ K}$

21.  $\Delta G^\circ = -RT \ln k_w$

$$= \frac{-8.314 \times 258 \times \ln 10^{-14}}{1000}$$

23.  $\Delta G^\circ = -RT \ln k = \Delta H^\circ - T\Delta S^\circ$

$$\ln k = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{R} \left( \frac{1}{T} \right)$$

$$\text{Slop} = \left( -\frac{\Delta H^\circ}{R} \right)$$

24.  $\Delta G^\circ_{\text{rxn}} = -RT \ln k_p = 2 \times \Delta G^0_{f_{\text{NO}_2}} - 2 \Delta G^0_{f_{\text{NO}}}$

$$\Delta G^0_{f_{\text{NO}_2}} = \frac{1}{2} [2 \times 86600 - R \times 298 \ln(1.6 \times 10^{12})]$$

25.  $\Delta S = n c_p \ln \left( \frac{T_2}{T_1} \right)$

$$= 1 \times 10 \times \ln \left( \frac{1000}{100} \right)$$

$$= 10 \times 2.303 \times 1$$

$$= 23.03 \text{ Cal/K}$$

26.  $\Delta S_{\text{rxn}} = \sum S_{\text{Product}} - \sum S_{\text{Reactant}}$

28.  $\Delta S = nR \ln \frac{V_2}{V_1}$

30.  $T = \frac{\Delta H^\circ}{\Delta S^\circ}$



## EXERCISE # (JEE-ADVANCED)

1. Process I is adiabatic reversible

Process II is a reversible isothermal process

Process I – (Adiabatic Reversible)

$$\Delta U / R = 450 - 2250$$

$$\Delta U = -1800 R$$

$$W_I = \Delta U = -1800R$$

Process II – (Reversible Isothermal Process)

$$T_1 = 900 \text{ K}$$

Calculation of  $T_2$  after the reversible adiabatic process

$$-1800R = nC_v(T_2 - T_1)$$

$$-1800R = 1 \times 5/2 R(T_2 - 900)$$

$$T_2 = 180 \text{ K}$$

$$W_{II} = -nRT_2 \ln \frac{v_3}{v_2} = W$$

$$-1 \times R \times 180 \ln \frac{v_3}{v_2} = -1800R$$

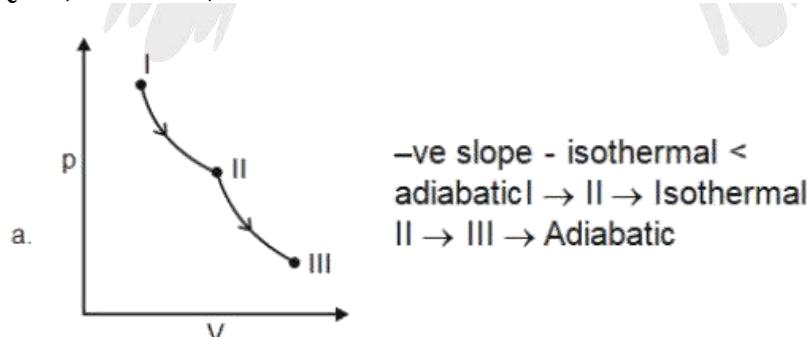
$$\ln \frac{v_3}{v_2} = 10$$

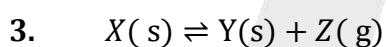
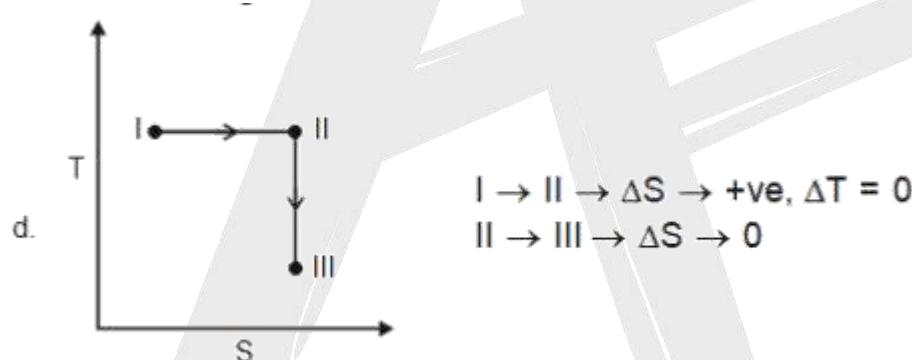
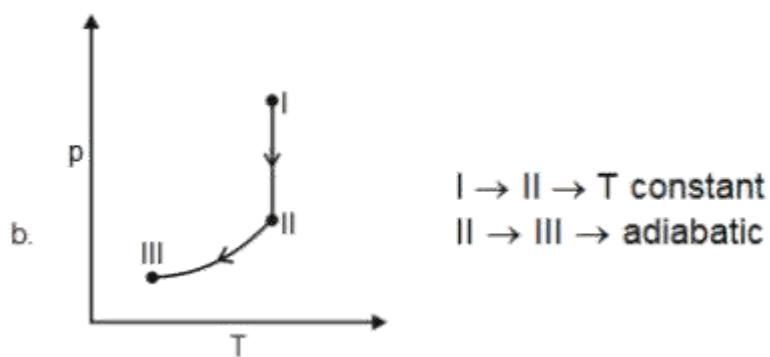
2.  $I \rightarrow II \rightarrow$  reversible, isothermal expansion,

$T \rightarrow$  constant,  $\Delta V \rightarrow +ve, \Delta S \rightarrow +ve \Delta H \Rightarrow 0$

$II \rightarrow III \rightarrow$  Reversible, adiabatic expansion

$$Q = 0, \Delta V \rightarrow +ve, \Delta S \rightarrow 0$$





Given  $K = \frac{p_z}{p^\theta}$

$$\ln K = \ln A - \frac{\Delta H^\circ}{RT}$$

$$\Rightarrow \ln \frac{p_z}{p^\theta} = \ln A - \frac{\Delta H}{RT}$$

Slope of  $\ln \frac{p_z}{p^\theta}$  vs  $\frac{1}{T}$  is  $\frac{d[\ln(\frac{p_z}{p^\theta})]}{d(\frac{1}{T})} = \frac{-\Delta H^\circ}{R}$

From the graph, we have  $\frac{-\Delta H^\circ}{R} = -2 \times 10^4$

$$\Rightarrow \Delta H^\circ = 2 \times 10^4 \times 8.314 \text{ J}$$

$$\Delta H^\circ = 166.28 \text{ kJ mol}^{-1}$$



4.  $-RT\ln K = \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\ln K = H^\circ / RT + S^\circ / R$$

$$\Delta S^\circ / R = 17$$

$$\Delta S^\circ = 17R$$

$$= 141.338 \text{ J K}^{-1}$$

5. ∵ With increase in temperature yield of reaction decreases

$$\therefore \Delta H < 0$$

$$\therefore \frac{\ln K_1}{\ln K_2} > \frac{T_2}{T_1}$$

$$T_1 \ln K_1 > T_2 \ln K_2$$

On multiplying R in both side

$$RT_1 \ln K_1 > RT_2 \ln K_2$$

$$-RT_2 \ln K_2 > -RT_1 \ln K_1$$

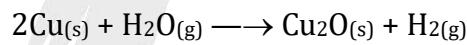
$$\Delta G_2^\circ > \Delta G_1^\circ$$

$$\Delta H^\circ - T_2 \Delta S^\circ > \Delta H^\circ - T_1 \Delta S^\circ$$

$$\therefore \Delta S^\circ(T_1 - T_2) > 0$$

$$\therefore \Delta S^\circ < 0$$

6. For the reaction



$$\Delta G^\circ = -78000 + 178000$$

$$= 10^5 \text{ J/mole}$$

$$\therefore \Delta G^\circ = RT \ln K_p = 10^5$$

$$\ln K_p = \frac{-10^5}{8 \times 1250} = -10$$

∴ For above reaction

$$K_p = \frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} = \frac{p_{\text{H}_2}}{1 \times \frac{1}{100}} = 100 p_{\text{H}_2}$$



$$\therefore \ln K_p = \ln 100 p_{H_2} = -10$$

$$\ln p_{H_2} = -10 - 2 \times 2.3$$

$$\ln p_{H_2} = -14.6$$

7. Given :

$$E_{ab} = E_{af} + 2RT$$

$$A_f = 4 A_b$$

$$\therefore K = \frac{k_f}{k_b} = \frac{A_f e^{-E_{af}/RT}}{A_b e^{-E_{ab}/RT}}$$

$$= 4 e^{-\frac{(E_{af} - E_{ab})}{RT}}$$

$$K = 4 e^{+2}$$

$$\therefore \Delta G^\circ = -RT \ln K$$

$$= -RT \ln(4e^{+2})$$

$$= -2500 [\ln 4 + 2]$$

$$= -2500 [2 \times 0.7 + 2]$$

$$= 2500 \times 3.4 \text{ J/mole}$$

$$= 8500 \text{ J/mole}$$

8. C(graphite)  $\rightarrow$  C(Diamond)

$$\Delta G_{rxn}^\circ = 2.9 - 0 \text{ kJ/mole} = -(P-1) \times [-2 \times 10^{-6}] \times 10^5$$

$$P - 1 = \frac{29000}{062} = 14500$$

$$P = 14501 \text{ bar.}$$

14.  $\therefore$  Process is endothermic

$$\therefore \Delta S_{sys} > 0$$

$$\& \Delta S_{surr} < 0$$

19. Process is reversible at given condition

$$\therefore \Delta G = 0$$

$\therefore$  Process is endothermic

$$\therefore \Delta S > 0$$



$$\begin{aligned}
 20. \quad \therefore \Delta S_{A \rightarrow B} &= \Delta S_{A \rightarrow C} + \Delta S_{C \rightarrow D} + \Delta S_{D \rightarrow B} \\
 &= 50 + 30 + (-20) \\
 &= 60
 \end{aligned}$$

$$21. \quad B.P. = \frac{\Delta H}{\Delta S} = \frac{30 \times 1000}{75} = 400 \text{ K}$$

$$\begin{aligned}
 22. \quad \Delta G_{rxn}^{\circ} &= 2 \times \Delta G_{f_{NO_2}}^{\circ} - \Delta G_{f_{N_2O_4}}^{\circ} \\
 &= 2 \times 50 - 100 = 0
 \end{aligned}$$

$$Q_p = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{10^2}{10} = 10$$

$$\begin{aligned}
 \therefore \Delta G &= \Delta G^{\circ} + RT \ln Q_p \\
 &= 0 + 8.314 \times 298 \ln 10 \\
 &= 5.705 \times 10^3 \text{ J/mole}
 \end{aligned}$$

$$\begin{aligned}
 23. \quad \Delta G_{rxn}^{\circ} &= \Delta G_{fCO_2}^{\circ} - \Delta G_{fCO}^{\circ} \\
 &= -394.4 + 137.2 \\
 &= -257.2 \text{ kJ/mole}
 \end{aligned}$$

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

$$\begin{aligned}
 \therefore \Delta H^{\circ} &= \Delta G^{\circ} + T\Delta S^{\circ} \\
 &= -257.2 + 300 \times (-0.094) \\
 &= -285.4 \text{ kJ/mole}
 \end{aligned}$$

$$\Delta G_1^{\circ} = -RT \ln K$$

$$\begin{aligned}
 &= -RT \ln \frac{[A]}{[B]} \\
 &= -8.314 \times 448 \times \ln \frac{1.3}{55.2} \\
 &= +15991 \text{ J/mole}
 \end{aligned}$$

$$\Delta G_2^{\circ} = -RT \ln K$$

$$\begin{aligned}
 &= -RT \ln \frac{[C]}{[B]} \\
 &= -8.314 \times 448 \times \ln \frac{3.5}{55.2} \\
 &= -12304 \text{ J/mole}
 \end{aligned}$$