THERMODYNAMICS-02

1. LIMITATION OF FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics can evaluate the value of ΔU and ΔH (i.e. energy difference between two states), but can not predict the feasibility of a process. Many processes can take place on their own and many others require an external force to carry out the process. The first law is clueless about why some processes happens on their own and why some others do not.

❖ **Importance of Second law :**

What is the driving force for a process which takes system from one state to other on it's own? Why such processes (***called spontaneous process***) take place at all? Answers to these questions are given by second law.

2. SPONTANEOUS PROCESS

A spontaneous process is the one which takes place on its own & can drive some other process as well. However, in some cases, initiation may be required.

Ex :

(i) Mixing of two gases.

(ii) Cooling of a hot object by transferring heat to surrounding.

(iii) Water flowing down the hill.

(iv) Rusting of iron.

(v) Burning of coal, coke, hydrocarbons.

(vi) Volcanic eruptions.

The synonyms of spontaneous processes are **natural processes** and irreversible processes.

It is a common observation that natural processes occur with finite rate. All spontaneous processes take place due to a finite driving force (which can be temperature difference, height difference, potential energy difference, etc.). Also the change brought about by a spontaneous process can not be restored without making some effort (which brings about permanent change in surrounding). Hence it is quite natural to call these processes as irreversible processes.

Ex :

When water flows from a dam, a part of the potential energy is converted into electrical energy and a part is converted into kinetic energy. The kinetic energy part is lost as heat energy. This loss of extra work is the permanent change in universe, because this heat energy lost cannot be completely converted back into P.E. of water.

3. Disorder :

The term 'disorder' is related to randomness. Any macroscopic property of a system is an average of large number of microscopic forces which are random in nature. Greater the randomness associated with microscopic forces, greater is the uncertainty about exact microscopic description of a macroscopic state and greater will be the disorder associated with the macroscopic state.

As a rule :

(i) Greater the number of molecules in which a given energy is distributed, greater is the disorder.

(ii) Greater the spread of given number of molecules with given energy in space, greater will be the disorder.

4. SECOND LAW OF THERMODYNAMICS

The entropy of the universe increases in course of every spontaneous process. The entropy of system is a state function. The change in entropy of a system is given by -

$dS = \frac{dq_{rev}}{T}$ where ; dq_{rev} = heat exchanged by system in a very small step (reversibly).

4.1 Entropy :

Entropy is a measure of disorder. The entropy is a state function and a basic quantity directly defined by second law. In every spontaneous process, entropy of universe increases.

There are three types of entropy changes :

(i) ΔS_{System} : Entropy change of system

(ii) $\Delta S_{Surrounding}$: Entropy change of surrounding

(iii) ΔS_{Total} : Entropy change of universe

$$\Delta S_{system} + \Delta S_{surrounding} = \Delta S_{universe} = \Delta S_{total} = \Delta S_{isolated}$$

Normally, ΔS means entropy change of system.

4.2 Second law in terms of entropy of universe :

For any spontaneous process (irreversible process) -

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

During a reversible process -

$$\Delta S_{universe} = 0$$

Thus during irreversible process, entropy of universe increases while during reversible process, entropy of universe remains constant.

4.3 Physical significance of quantity $\frac{dq_{rev}}{T}$:

dq_{rev} = heat absorbed by the system, T = absolute temperature at which heat is absorbed. Suppose, similar quantity of heat is absorbed at two different temperatures T_1 and T_2 ($T_2 >> T_1$). When heat is supplied at high temperature, the % age increase in kinetic energy is less compared to heat supplied at low temperature. Hence, disorder will increase by greater value, when heat is supplied at lower temperature.

4.4 Determining '$\Delta S_{surr.}$' for irreversible processes :

The change in entropy is given by : $\frac{\text{heat absorbed by an entity}}{\text{Exact temperature at which heat is absorbed}}$

The irreversible processes are fast and uncontrolled. The exact temperature of system during exchange of heat cannot be known. Hence, reversible path is needed to evaluate the entropy of system. Along reversible path, the heat exchange and exact temperature both are known.

Surrounding is generally a big entity and heat absorbed by surrounding is comparatively very small as compared to its size. Hence, internal equilibrium of surrounding is not disturbed during exchange of heat.

$\therefore$ Actual heat exchange of system is reversible heat exchange of surroundings

$\therefore$ $(q_{rev})_{surr} = -q_{irr}$ [$\mathbf{q_{irr}}$ **=** Actual heat gained by system in a irreversible process.]

Hence, exact temperature and heat exchange both are known as far as surrounding is concerned even for an irreversible process.

$\therefore$ **For irreverisble process :** $\Delta S_{surr} = \frac{-q_{irr}}{T}$

	ΔS_{system}	$\Delta S_{surrounding}$
(i)	**For reversible process :** $\Delta S_{system} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$	**For reversible process :** $\Delta S_{surr} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T} = -\Delta S_{system}$
(ii)	**For irreversible process :** $\Delta S_{system} = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$ [Where ; dq_{rev} = heat gained by system for imaginary reversible path between same states]	**For irreversible process :** $\Delta S_{surr} = -\frac{q_{irr}}{T}$
(iii)	Always evaluated along reversible path (for both reversible and irreversible process)	For reversible process, ΔS_{surr} is evaluated along reversible path, while for irreversible process, irreversible heat is used to calculate ΔS_{surr}.
(iv)	Since no actual process is reversible, ΔS_{system} is always evaluated by hypothetical path.	For hypothetical process, ΔS_{surr} is evaluated by hypothetical heat, while for real irreversible process, it is evaluated by heat exchanged in irreversible process.

5. SECOND LAW (IN TERMS OF ENGINE)

(i) No cyclic engine is possible whose only effect is complete conversion of heat into work without making any change in surrounding on its own.

(ii) Heat can not flow from cold body to hot body on it's own without external intervention.

(iii) Complete conversion of heat (taken from a single source) into work is not possible in a cyclic process while complete conversion of work into heat is possible in a cyclic process. Thus, heat and work are not equivalent from the view point of II law.

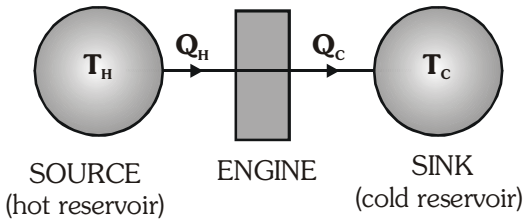
All above statements can be easily justified by realising that heat is a disordered form of energy while work is an ordered form of energy.

Complete conversion of **[Heat ⟶ Work]** on it's own without any external assistance means **[Disorder ⟶ Order]** on it's own - which is impossible.

5.1 Heat engine :

A heat engine is a device which can work continuously and cyclically without any external help absorbing heat from a source and rejecting a part of heat into sink. The net heat absorbed by engine (heat absorbed from source – heat given out to sink) is converted into work.

⇒ Heat engine must work in cycles , otherwise it can not work continuously.



Q_H = Heat gained by engine per cycle

Q_C = Heat rejected by engine per cycle

Efficiency of engine : $\eta = \frac{Q_H - Q_C}{Q_H} = \frac{w_{by}}{Q_H}$

W_{by} = Work done by engine per cycle.

During operation of heat engine, heat is transferred from source (high temperature reservoir) to sink (low temperature reservoir) thus degrading the quality of energy. Note that net energy of universe remains conserved, but it's quality is degraded (i.e. more disordered energy) when heat engine runs spontaneously.

5.2 CARNOT ENGINE

A carnot engine (a hypothetical engine) runs in reversible manner. Thus during expansion (work producing process) maximum work is done. However during compression (work requiring process) minimum work need to be done. Thus no engine can be more efficient than carnot engine.

The carnot engine works in following steps. (Assume ideal gas as working material).

(i) Reversible isothermal expansion $(P_1,V_1,T_2 \rightarrow P_2,V_2,T_2)$

(ii) Reversible adiabatic expansion $(P_2,V_2,T_2 \rightarrow P_3,V_3,T_1)$

(iii) Reversible isothermal compression $(P_3,V_3,T_1 \rightarrow P_4,V_4,T_1)$

(iv) Reversible adiabatic compression $(P_3,V_3,T_1 \rightarrow P_1,V_4,T_2)$

Now: $Q_{NET} = -w_{NET}$ **.....(i)**

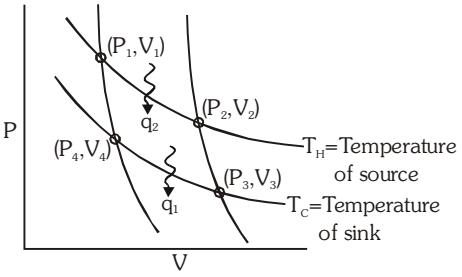
$w_{NET} = w_{12} + w_{23} + w_{34} + w_{41}$ **.....(ii)**

$w_{12} = -nRT_H \ln\left(\frac{V_2}{V_1}\right)$ **.....(iii)**

$w_{23} = nC_V(T_C - T_H)$ **.....(iv)**

$w_{34} = -nRT_C \ln\left(\frac{V_4}{V_3}\right)$ **.....(v)**

$w_{41} = -nC_V(T_H - T_C)$ **.....(vi)**



Also since process 2 – 3 and 4 – 1 are reversible adiabatic process.

$T_H V_2^{\gamma-1} = T_C V_3^{\gamma-1}$ **.....(vii)** for process 2 – 3

$T_C V_1^{\gamma-1} = T_H V_4^{\gamma-1}$ **.....(viii)** for process 1 – 4

from above equations

$\left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right)$ **.....(ix)**

Substituting the value of $\left(\frac{V_4}{V_3}\right)$ in eq.(v) and adding w in individual step.

$$w_{NET} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) + nC_V(T_C - T_H) - nRT_C \ln\left(\frac{V_4}{V_3}\right) - nC_V(T_C - T_H)$$

$$w_{NET} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) - nRT_C \ln\left(\frac{V_1}{V_2}\right)$$

$$w_{NET} = -nR\,[T_C - T_H] \ln\left(\frac{V_2}{V_1}\right)$$

$\Rightarrow$ Efficiency $\eta = -\frac{w_{NET}}{q_2}$

$$\eta = -\frac{nR\ln\left(\frac{V_2}{V_1}\right)[T_H - T_C]}{nRT_H \ln\left(\frac{V_2}{V_1}\right)}$$

$\therefore \quad \eta = \frac{T_H - T_C}{T_H}$

Thus efficiency of carnot engine depends only upon temperature of source and sink.

Note : If working substance is changed (eg. ideal gas by real gas) efficiency of carnot engine remains unaffeced.

EXERCISE-1

1. 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 or an impossible cycle.

2. 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) None

3. A carnot 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

4. An ideal gas heat engine operates in carnot's cycle between 227ºC and 127ºC. It absorbs 6×10^4 cal of heat at high temperature. Amount of heat converted to work is :

(A) 2.4×10^4 cal (B) 4.8×10^4 cal (C) 1.2×10^4 cal (D) 6.0×10^4 cal

6. ENTROPY CHANGE OF AN IDEAL GAS

From definition of entropy of system -

$$dS_{system} = \frac{dq_{rev}}{T} \qquad \text{.....(i)}$$

from first law, $dq_{rev.} = dU + PdV$

For a reversible change involving an ideal gas -

$$dq_{rev} = nC_{V,m}.dT + \frac{nRT}{V}.dV \qquad \text{.....(ii)}$$

$$\Rightarrow \quad \int_1^2 \frac{dq_{rev}}{T} = \int_1^2 \frac{nC_{V,m}dT}{T} + \int_{V_1}^{V_2} nR\frac{dV}{V}$$

$$\Delta S_{system} = nC_{v,m} \ln\frac{T_2}{T_1} + nR\ell n\left(\frac{V_2}{V_1}\right) = nC_{p,m} \ln\frac{T_2}{T_1} - nR.\ln\frac{P_2}{P_1}$$

Note : This formula is applicable to all ideal gas process.

6.1 Ideal gas processes :

(i) For isothermal change :

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T} = \frac{1}{T}\int_1^2 dq_{rev} \qquad (\because T = \text{constant})$$

$$\Rightarrow \quad \Delta S = \frac{q_{rev}}{T} = nR\ell n\frac{V_2}{V_1} \qquad \left[\because q_{rev} = nRT\ln\left(\frac{V_2}{V_1}\right)\right]$$

(ii) For isochoric change :

$$\Delta S = \int\frac{dq_v}{T} = \int_1^2 \frac{nC_{V,m}dT}{T} = nC_{V,m}\int_1^2\frac{dT}{T} \qquad [\because\ dq_v = nC_{V,m}.dT]$$

$$\Rightarrow \quad \Delta S = nC_{V,m}\ell n\frac{T_2}{T_1}$$

(iii) For isobaric change :

$$\Delta S = \int\frac{dq_P}{T} = \int_1^2 \frac{nC_{P,m}.dT}{T} = nC_{P,m}\int_1^2\frac{dT}{T} \qquad [\because\ dq_P = nC_{P,m}dT]$$

$$\Rightarrow \quad \Delta S = nC_{P,m}\ell n\left(\frac{T_2}{T_1}\right)$$

(iv) Reversible adiabatic process :

$q_{rev} = 0$

$$\Rightarrow \quad \Delta S = \underbrace{nC_V \ln\frac{T_2}{T_1}}_{\substack{\text{entropy change due to}\\ \text{change in temperature}}} + \underbrace{nR\ln\frac{V_2}{V_1}}_{\substack{\text{entropy change due to}\\ \text{change in volume}}} = 0$$

(a) During reversible adiabatic expansion :

$$T_2 < T_1 \text{ and } V_2 > V_1$$

$\Rightarrow$ Sign of two terms are opposite and magnitudes are same because for reversible adiabatic process -

$$nC_{V,m} \ln\frac{T_2}{T_1} = -nR\ln\frac{V_2}{V_1}$$

$\Rightarrow$ +ive and –ive term cancel out each other and hence, $\Delta S = 0$

Thus, decrease in entropy during expansion due to decrease in temperature is exactly cancelled out by increase in entropy due to increase in volume of system in reversible adiabatic expansion.

(b) During reversible adiabatic compression :

$$T_2 > T_1 \text{ and } V_2 < V_1$$

$$\Rightarrow \quad \Delta S_{Total} = \underbrace{nC_{V,m}\ln\frac{T_2}{T_1}}_{+ive} + \underbrace{nR\ln\frac{V_2}{V_1}}_{?\,ive} = 0$$

Thus, increase in entropy due to increase in temperature is compensated by decrease in entropy due to decrease in volume of system in reversible adiabatic compression.

Hence, $\Delta S = 0$ for reversible adiabatic compression.

(v) Irreversible adiabatic process :

Since process is irreversible, $\Delta S_{Total} > 0$.

$\Rightarrow \quad \Delta S_{system} + \Delta S_{surr} > 0$

$\because \quad \Delta S_{surr} = 0$

$\because \quad \Delta S_{system} > 0$

The physical interpretation is -

(a) During irreversible adiabatic compression, large quantity of heat is produced while decrease is volume is less.

Thus, increase in entropy due to rise in temperature exceeds the decrease in entropy due to decrease in volume. Hence net entropy change is positive.

(b) During irreversible adiabatic expansion, due to sudden decrease in external pressure, the system remains less challenged during expansion. Hence system do less work-resulting in lesser decrease in temperature.

The increase in volume of system is relatively larger (because system was less challenged)

Thus increase in entropy due to increase in volume exceeds decrease in entropy due to decrease in temperature. The net change in entropy is positive in both processes $\Delta S_{surr.} = 0$ ($\because$ no heat is exchanged with surrounding) and $\Delta S_{total} > 0$.

(vi) Free expansion of an ideal gas against vacuum :

Free expansion of an ideal gas is an example of irreversible adiabatic as well as irrversible isothermal process.

During free expansion, the $P_{ext.} = 0$. Hence, the ideal gas is not challenged at all during expansion. The kinetic energy of ideal gas remains constant. Hence, no temperature difference is created during expansion between system and surrounding.

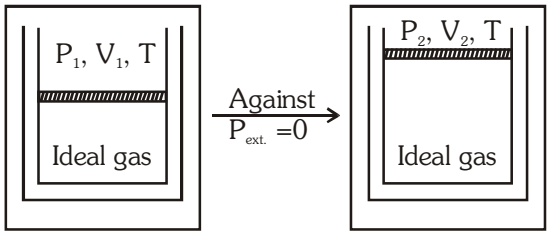
$\because$ $\Delta T = 0$, the heat absorbed during the process = 0

Since, $V_f > V_i$ and T = constant, $\Delta S_{system} > 0$

The free expansion is an example where $q_{actual} = 0$, still $\Delta S_{system} > 0$.

This is reasonable, because : $\Delta S_{system} = \int \frac{dq_{rev.}}{T}$

This, example clearly shows that even if q_{actual} between two states is zero, this does not means that $\int_1^2 \frac{dq_{rev.}}{T}$ between two states is zero. This outlines the importance of reversible path and $q_{rev.}$ in calculation of entropy of system.



$q_{irr} = 0$; $w_{irr} = 0$

$$\Delta S_{system} = \int_1^2 \frac{dq_{rev.}}{T} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{surr.} = \frac{-q_{irr}}{T} = 0$$

$$\Delta S_{total.} = nR \ln \frac{V_2}{V_1} > 0$$

ENTROPY CALCULATION

Process	$\Delta S_{Sys.}$	$\Delta S_{Surr.}$
Isothermal reversible	$\Delta S_{Sys.} = nR\ell n\frac{V_2}{V_1}$	$\Delta S_{Surr.} = -\Delta S_{Sys.}$
Isothermal irreversible	$\Delta S_{Sys.} = nR\ell n\frac{V_2}{V_1}$	$\Delta S_{Surr.} = \frac{-q_{Sys}}{T} = \frac{W_{Sys}}{T} = \frac{-P_{ext}(V_2 - V_1)}{T}$
Adiabatic reversible	$\Delta S_{Sys.} = 0$	$\Delta S_{Surr.} = 0$
Adiabatic irreversible	$\Delta S_{Sys.} = nC_{P,m}\,\ell n\frac{T_2}{T_1} + nR\ell n\frac{P_1}{P_2}$	$\Delta S_{Surr.} = 0$
Isochoric reversible	$\Delta S_{Sys.} = nC_{V,m}\ell n\frac{T_2}{T_1}$	$\Delta S_{Surr.} = -\Delta S_{Sys.}$
Isochoric irreversible	$\Delta S_{Sys.} = nC_{V,m}\ell n\frac{T_2}{T_1}$	$\Delta S_{Surr.} = \frac{-q_{sys}}{T_{surr}} = \frac{-nC_{V,m}\Delta T}{T_{final}}$

Ex.1 ***Three moles of an ideal gas is expanded isothermally from 2L to 10L , at 27°C. Calculate ΔS_{sys} and ΔS_{surr} and $\Delta S_{univ.,}$ if the process is preformed.***

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 1 atm

(iii) As free expansion

Sol: ***(i)*** $\Delta S_{univ.} = 0,\ \Delta S_{surr.} = -\Delta S_{sys.}$

and $\Delta S_{sys} = nR\ell n\frac{V_2}{V_1} = 3R.\ell n\frac{10}{2} = 40.14\ J/K$

(ii) $\Delta S_{sys} = 40.14\ J/K$

$\Delta S_{surr.} = -\frac{P_{ext.}(V_2 - V_1)}{T} = -\frac{1\times(10-2)\times 101.3}{300} = -2.7\ J/K$

and $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 37.44\ J/K$

(iii) $\Delta S_{sys} = 40.14\ J/K$

$\Delta S_{surr.} = 0 \qquad as\ P_{ext} = 0$

and $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 40.14\ J/K$

Ex.2. Two moles of an ideal monoatomic gas is expanded adiabatically from 10L, 27ºC to 80L. Calculate ΔS_{sys}, ΔS_{surr} and ΔS_{univ} , if the process is performed.

(i) Reversibly

(ii) Irreversibly, against a constant external pressure of 0.1 atm.

(iii) As free expansion

Sol.: $\Delta S_{surr} = 0$ *for all*

(i) $\Delta S_{sys} = \Delta S_{surr} = \Delta S_{univ} = 0$

(ii) $n \cdot C_{v,m} \cdot (T_2 - T_1) = -P_{ext}(V_2 - V_1)$

$$or \quad 2 \times \frac{3}{2} \times 0.0821 \times (T_2 - 300) = -0.1 \times (80 - 10) \Rightarrow T_2 = 271.58\ K$$

$$Now, \quad \Delta S_{sys} = n \cdot C_{v,m} \cdot \ell n \frac{T_2}{T_1} + nR \cdot \ell n \frac{V_2}{V_1}$$

$$= 2 \times \frac{3}{2} R \times \ell n \frac{271.58}{300} \times 2 \times R \times \ell n \frac{80}{10} = 32.90\ J/K$$

$$and\ \Delta S_{univ} = \Delta S_{sys}$$

(iii) $T_1 = T_2 \Rightarrow \Delta S_{sys} = nR \cdot \ell n \frac{V_2}{V_1} = 2 \times R \times \ell n \frac{80}{10} = 34.58\ J/K$

6.2 Entropy change of solids and liquids upon heating :

$$\Delta S = \int \frac{dq_{rev}}{T} = \int \frac{mS.dT}{T} = mS.\ell n \frac{T_2}{T_1}$$ [S = specific heat of solid/ liquid]

For molar change in entropy, m = M(g/mole) ; where M = molar mass.

Note, for solids and liquids ($MS \cong C_P \cong C_V$)

Ex.3 Two blocks of equal masses and heat capacity but at different temperatures are taken in an adiabatic vessel. Show that total change in entropy when both attain thermal equilibrium is always positive.

Sol. Let the temperature of hot body be T_H, temperature of cold body be T_C & the final temperature be T_F.

Now, net heat exchanged by two bodies must be zero.

$\Rightarrow \quad m.S\,(T_F - T_H) + mS\,(T_F - T_C) = 0$

$$\Rightarrow \quad T_F = \frac{T_H + T_C}{2}$$

Since both bodies are of finite mass, entropy of both bodies are evaluated by reversible paths.

$$\Delta S_{Hot} = \int_{T_H}^{T_F} mS.\frac{dT}{T} = mS.\ell n \frac{T_F}{T_H}$$

$$\Delta S_{Cold} = \int_{T_C}^{T_F} mS.\frac{dT}{T} = mS.\ell n \frac{T_F}{T_C}$$

$$\Rightarrow \quad \Delta S_{total} = (mS)\,\ell n\left(\frac{T_F^2}{T_H T_C}\right)$$

$$\Rightarrow \quad T_H^2 + T_C^2 + 2T_H T_C - 4T_H T_C = (T_H - T_C)^2 > 0$$

$$\Rightarrow \quad (T_H + T_C)^2 > 4T_H T_C$$

$$\Rightarrow \quad \Delta S_{total} > 0$$

6.3 Reversible phase transitions : Reversible phase transitions are always isothermal & isobaric.

$$\Delta S_{system,\ P,T} = \frac{q_{rev.}}{T} = \frac{\Delta H_{P,T}}{T_{Transition}}$$

$$\Delta S_{surr} = \frac{-\Delta H_{P,T}}{T_{Transition}}$$

$$\Delta S_{total} = 0$$

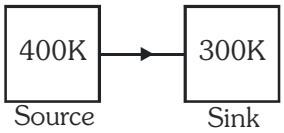
Thus, $\mathbf{\Delta S_{vaporisation}}$ **at boiling point** $= \mathbf{\frac{\Delta H_{vaporisation}}{T_{vaporisation}}}$

$\mathbf{\Delta S_{fusion}}$ **at melting point** $= \mathbf{\frac{\Delta H_{fusion}}{T_{fusion}}}$

$\mathbf{\Delta S_{sublimation}}$ **at sublimation point** $= \mathbf{\frac{\Delta H_{sub\,lim\,ation}}{T_{sub\,lim\,ation}}}$

$$\mathbf{\Delta S_{allotropic\ modification} = \frac{\Delta H_{allotropic\ modification}}{T_{transition}}}$$

Ex.4 ***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 ΔS_{source}, ΔS_{sink} and ΔS_{total}. Comment on spontaneity of process.

Ans. **(i)** $\Delta S_{source} = \frac{\text{heat absorbed by source}}{\text{Temperature of source}}$

$$\Delta S_{source} = \frac{-100kJ}{400} = -250J/K$$

(ii) $\Delta S_{sink} = \frac{\text{heat absorbed by sink}}{\text{Temperature of sink}}$

$$= \frac{+100000\,J}{300} = 333.33\,J/K$$

(iii) $\Delta S_{Total} = \Delta S_{source} + \Delta S_{sink} = +83.33$ J/K

Ex.5 ***Trouton's rule states that the ratio of the molar heat of vaporisation of a liquid to its normal boiling point is approximately the same for all liquids,*** $\frac{\Delta H_{vap}}{T_{bp}} = 88\ JK^{-1}\ mol^{-1} = \Delta S_{vap.}$

Which of the following liquids do not follow Trouton's rule : NH_3, C_6H_6, CCl_4, $CHCl_3$, Hg. Explain.

Ans. **NH_3, due to H-bonding : $\Delta S_{vap} > 88$ J/K-mol**

EXERCISE-2

5. Identify the correct statement regarding a sponateous process :- **[AIEEE-2007]**

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

(B) Endothermic processes are never spontaneous

(C) Exothermic processes are always spontaneous

(D) Lowering of energy in the reaction process is the only criterion for spontaneity

6. Find the change in entropy (in cal/k) of 1 mole of O_2 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, ln2 = 0.7)**

7. One mole of NaCl(s) on melting as it's melting point absorbed 32.76 kJ of heat and its entropy is increased by 30 JK^{-1}. What is the melting point of sodium chloride ?

8. The entropy change when two moles of ideal monoatomic gas is heated from 200°C 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) $\frac{3}{2}R\ln\left(\frac{573}{473}\right)$

9. Predict the sign entropy change for the following processes:

(A) $O_2(g) \rightarrow 2O(g)$

(B) $2O_3(g) \rightarrow 3O_2(g)$

(C) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

(D) $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

(E) $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$

(F) $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

10. 5 mole of an ideal gas expands reversibly from a volume of 8 dm^3 to 80dm^3 at a constant temperature of 27°C. The change in entropy is :–

(A) 41.57 JK^{-1} (B) – 95.73 JK^{-1} (C) 95.73 JK^{-1} (D) – 41.57 JK^{-1}

11. ΔS for the reaction ; $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$ will be :

(A) 0 (B) –ve (C) +ve (D) ∞

12. Change in entropy is negative for :-

(A) Bromine (ℓ) $\longrightarrow$ Bromine (g)

(B) $C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$

(C) (C) N_2(g, 10 atm, 298 K) $\longrightarrow$ N_2 (g, 1 atm, 298K)

(D) Fe(at 400 K) $\longrightarrow$ Fe(at 300 K)

13. For which reaction from the following, ΔS will be maximum ?

(A) $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)$

(B) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

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

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

14. When two gases are mixed the entropy :–

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

15. For the process, $CO_2(s) \longrightarrow CO_2(g)$:

(A) Both ΔH and ΔS are +ve (B) ΔH is –ve and ΔS is +ve

(C) ΔH is +ve and ΔS is –ve (D) Both ΔH and ΔS are –ve

7. THIRD LAW OF THERMODYNAMICS

''At absolute zero, the entropy of a perfectly crytalline substance is zero'', which means that at absolute zero, every crystalline solid is in a state of perfect order and its entropy should be zero. By virtue of the third law, the absolute value of entropy (unlike absolute value of enthalpy) for any pure substance can be calculated at room temperature.

$$S_T - S_{0K} = \int_0^T \frac{q_{rev}}{T}$$

Since $S_{0K} = 0$

$$S_T = \int_0^T \frac{q_{rev}}{T}$$

The variation of entropy of a substance with temperature is given by graph :

At 1, entropy of substance is zero.

- **from 1-2 ;** The temperature of solid increases upon heating -

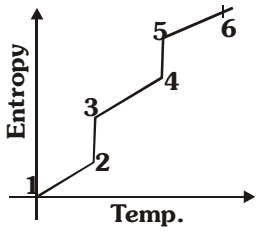
$$\Rightarrow \quad S_2 - S_1 = \int \frac{C_{P,solid}}{T} dT \qquad \text{.....(i)}$$

- **from 2-3 ;** The temperature remains constant during phase transition

$$\Rightarrow \quad S_3 - S_2 = \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} \qquad \text{.....(ii)}$$

- **from 3-4 ;** The temperature of liquid increases

$$\Rightarrow \quad S_4 - S_3 = \int_{T_3}^{T_4} \frac{C_{P,liquid} \cdot dT}{T} \qquad \text{.....(iii)}$$



Change in entropy of a pure substance with temperature at constant pressure.

- **from 4-5 ;** Reversible vaporisation takes place at constant temperature -

$$\Rightarrow \quad S_5 - S_4 = \Delta S_{vap.} = \frac{\Delta H_{vap.}}{T_b} \qquad \text{.....(iv)}$$

- **from 5-6 ;** The gas is heated -

$$\Rightarrow \quad S_6 - S_5 = \int_{T_5}^{T_6} \frac{C_{P,gas}.dT}{T} \qquad \text{.....(v)}$$

$$\Delta S_{1-6} = (S_2 - S_1) + (S_3 - S_2) + (S_4 - S_3) + (S_5 - S_4) + (S_6 - S_5) = S_6 - S_1 \qquad [\because S_1 = 0]$$

$\because$ S_6 = absolute entropy at 6.

$$= \int_{T_1}^{T_2} \frac{C_{P,Solid}dT}{T} + \frac{\Delta H_{fusion}}{T_f} + \int_{T_3}^{T_4} \frac{C_{P,liquid}dT}{T} + \frac{\Delta H_{vap}}{T_b} + \int_{T_5}^{T_6} \frac{C_{P,gas}dT}{T}$$

- **Comment :** Absolute entropy of a substance can be calculated using third law by reversible path.

7.1 Standard absolute molar entropy :

It is the entropy in one mole of substance at standard temperature at 1 bar.

It is calculated assuming that substance is heated isobarically and reversibly at 1 bar from 0 K to standard temperature.

7.2 Comparing absolute entropies of substance :

(i) The absolute entropies of substance follow the order,

$$S(g) >> S(l) > S(s)$$

(ii) Entropy increases when solid and liquid is dissolved into solvent,

e.g.	$CH_3OH(l)$	S° = 127 J/K-mole
	$CH_3OH(aq)$	S° = 132.3 J/K-mole
	NaCl(s)	S° = 72.4 J/K-mole
	NaCl(aq.)	S° = 115.4 J/K-mole

(iii) The entropy of dissolved gas is less than pure gas.

e.g.	HCl(g)	S° = 186.7 J/K-mole
	HCl(aq)	S° = 55.2 J/K-mole

(iv) Entropy rises with increasing mass, (if other factors are similar).

e.g.	$F_2(g)$	S° = 203 J/K-mole
	$Cl_2(g)$	S° = 223 J/K-mole
	$Br_2(g)$	S° = 245 J/K-mole

(v) Entropy is lower in covalently bonded solids, with strong directional bonds, than in solids with partial metallic character.

e.g.	C(diamond)	S° = 2.44 J/K-mole
	C(graphite)	S° = 5.69 J/K-mole
	Sn(gray)	S° = 44.8 J/K-mole
	Sn(white)	S° = 51.5 J/K-mole

(vi) Entropy increases with increasing softness and with weakness of bonds between atoms.

e.g.	C(diamond)	Be(s)	$S_1O_2(s)$	Pb(s)	Hg(*l*)
	2.44	9.54	41.8	64.9	77.4
	diamond	hard metal	quartz	soft metal	liquid

(vii) Entropy increases with chemical complexity

Sub.	NaCl	$MgCl_2$	$AlCl_3$
	72.4	89.5	167

For $CuSO_4.nH_2O$

n = 0	n = 1	n = 3	n = 5
S° = 113	150	225	305

Note : Above data is given in SI unit.

7.3 Entropy change ($\Delta_r S$) of a chemical reaction :

The change in entropy when reactants turn into products according to a balanced chemical reaction with specified physical state of each reactant and product is called entropy of reaction.

- **Consider a reaction :**

$$aA(m) + bB(n) \xrightarrow{T,P} cC(o) + dD(p)$$

where m, n, o, p are physical states at temperature T and pressure P.

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

$$\Delta_r S = cS_C + dS_D - aS_A - bS_B$$

S_A, S_B, S_C and S_D are absolute molar entropies at temperature T and pressure P **(from third law)**

So, $\Delta_r S$ is evaluated from table of data of third law entropies of various substances.

7.4 $\Delta S_{Surrounding}$ for chemical reaction :

$\mathbf{\Delta_r H} = q_P$ = heat absorbed by the system during chemical reaction.

$\Rightarrow$ $\mathbf{-\Delta_r H} = -q_P = q_{surr}$ = heat absorbed by the surrounding.

Now,

$$\boxed{\Delta S_{Surr} = \frac{q_{surr}}{T} = -\frac{\Delta_r H}{T}}$$

If $\Delta_r H$ = –ive (exothermic) heat is lost by the system and gained by the surrounding. Hence, ΔS_{surr} increases.

If $\Delta_r H$ = +ive (endothermic process), entropy of surrounding decreases.

$\because$ $\Delta S_{surr} = -\frac{\Delta_r H}{T} = -ive$

- We can not comment on entropy change of system from knowledge of $\Delta_r H$. The entropy change of system ($\Delta_r S$) is estimated by third law.

7.5 Driving force of a spontaneous chemical process :

The driving force of a spontaneous chemical process is increase in entropy of universe.

In simple terms, negative value of $\Delta_r H$ and positive value of $\Delta_r S$ favours the chemical process.

If $\Delta_r H$ is positive, the enthalpy factor don't support the forward process. Under these conditions, $\Delta_r S$ should be sufficiently positive to drive the reaction in forward direction. If $\Delta_r H$ is +ive and $\Delta_r S$ is –ive, under a given situation, the process become non-spontaneous because both factors tends to decrease the entropy of the universe.

7.6 Prediction the sign of $\Delta_r S$ by inspecting a balanced chemical reaction.

(i) If more no. of gaseous moles are present on product side, $\Delta_r S$ will be +ive (since gas is more disordered than solid or liquid).

(ii) If solid $\longrightarrow$ liquid

solid $\longrightarrow$ gas

liquid $\longrightarrow$ gas

then, $\Delta_r S$ = +ive.

(iii) If a molecule is undergoing cyclisation, it's rotational modes of motion are replaced by vibrational modes of motion.

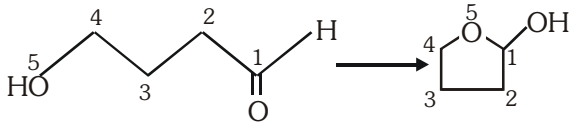
Since quantum energy separation of rotational motion is closely spaced compared to vibrational energy state, rotational energy is more disordered. Hence, $\Delta_r S$ = –ive.

- **Example :**

$HCOOH(g) \longrightarrow H_2(g) + CO_2(g)$; Δn_g = +ive $\Rightarrow \Delta_r S$ = +ive

$H_2O(\ell) \longrightarrow H_2O(g)$; $\Delta_r S$ = +ive

$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(g)$; Δn_g = +ive $\Rightarrow \Delta_r S$ = +ive



; $\Delta_r S$ = –ive

7.7 Table for spontanity of chemical process and sign of $\Delta_r H$, $\Delta_r S$ and dependence on temperature.

Sign of ΔH	Sign of ΔS	Comment	Example	ΔH°_{298}	ΔS°_{298}
–	+	Spontaneous at all temperature	$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	–185	14.1
			$C(s) + O_2(g) \rightarrow CO_2(g)$	–394	3
–	–	Spontaneous at low temperature	$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(\ell)$	–44	–119
			$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	–198	–187
+	+	Spontaneous at high temperature	$NH_4Cl(s) \rightarrow NH_3(g) + HCl(g)$	176	284
			$N_2(g) + O_2(g) \rightarrow 2NO(g)$	180	25
+	–	Non spontaneous at all temperature	$3O_2 \rightarrow 2O_3$	286	–137
			$2H_2O(\ell) + O_2(g) \rightarrow 2H_2O_2(\ell)$	196	–126

7.8 State of equilibrium :

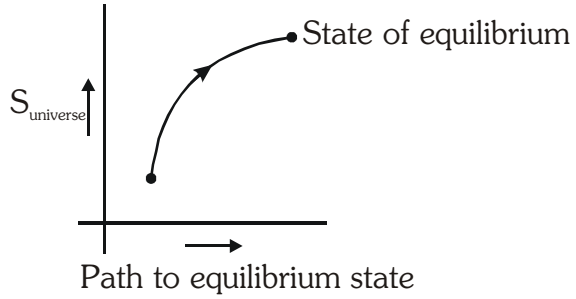
A system at equilibrium is a stable system. Hence, it's state variables become constant (do not vary with time) at equilibrium.

If a system is in non-equilibrium state, it moves spontaneously in the direction of equilibrium (because the equilibrium state is stable). During the spontaneous movement towards equilibrium, the entropy of universe increases.

As the system gets closer to equilibrium state, the driving force to attain equilibrium become small and so does the increase in disorder of universe. At equilibrium, the driving force to move ahead finishes and entropy of the universe can not increase further.

In nutshell, when a system attains equilibrium, it's capacity to increase the disorder of universe is lost.

- At equilibrium, the entropy of universe is maximum.



8. GIBB'S FUNCTION

Gibb's function 'G' is defined as $G = H - TS$.

Since 'G' is a combination of state variables (a compound state variable), it is a state function. The dimension of Gibb's function is the dimension of energy. 'G' is an extensive quantity.

Gibb's function provide a very useful criteria for spontanity of a process taking place at constant temperature and pressure (isobaric, isothermal process).

The entropy of universe is also a very useful criteria of spontanity, but it is based on properties of system as well as surrounding.

The Gibb's function provides criteria for spontaneity based only on the properties of system.

$$\mathbf{\Delta G = \Delta H - \Delta(TS)}$$

$$\mathbf{\Delta G = \Delta H - T\Delta S} \qquad \textbf{(Isothermal process)}$$

Ex.6 The thermodynamic stability of a substance is dependent upon the value of Gibb's function. Explain the stability of solid at low temperature and stability of gas at very high temperature.

Sol. Any stable state tries to minimise it's enthalpy while maximising its entropy.

For solids - $G_{solid} = H_{solid} - TS_{solid}$ (at certain T & P)

For liquids - $G_{liquid} = H_{liquid} - TS_{liquid}$ (at certain T & P)

For gas - $G_{gas} = H_{gas} - TS_{gas}$ (at certain T & P)

At any given T and P, $H_{solid} < H_{liquid} < H_{gas}$

and $S_{solid} < S_{liquid} < S_{gas}$

At very low temperature, TS term contributes very little towards Gibb's function. Hence -

$G_{solid} < G_{liquid} < G_{gas}$ (at very low temperature).

This explains why solids are most stable at low temperature.

At very high temperature, TS term is very important. Since S_{gas} is large, for gas TS term becomes very large at large temperature. Hence -

$\Rightarrow$ $G_{solid} > G_{liquid} > G_{gas}$ (at very high temperature). Thus, gaseous state is most stable at high temperature.

Hence, the low enthalpies of solid are responsible for stability of solid at low temperature, while high entropy of gas is responsible for stability of gas at high temperature.

8.1 $\Delta G_{T,P}$ and $\Delta S_{universe}$

Decrease in Gibb's function at constant temperature and pressure is related to ΔS_{total} (total entropy change of system and surrounding).

$-\Delta G = T(\Delta S_{total})$

At constant P, T

if $\Delta G < 0 \Rightarrow$ spontaneous process

if $\Delta G > 0 \Rightarrow$ non-spontaneous process

if $\Delta G = 0 \Rightarrow$ reversible process

At constant P, T, Gibbs energy of a system spontaneously decreases.

EXERCISE-3

16. Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature) ? The entropy change is + 210 JK^{-1} for the reaction as stated.

$\Delta H_{combustion\ [glucose]} = -2808$ kJ / mol.

17. 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

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

(A) 1250 K (B) 500 K (C) 750 K (D) 1000 K

19. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, then reaction would be spontaneous when :-

[AIEEE-2010]

(A) $T = T_e$ (B) $T_e > T$ (C) $T > T_e$ (D) T_e is 5 times T

20. For a reaction at 25°C, enthalpy change (ΔH) and entropy change (ΔS) are -11.7×10^3 J mol^{-1} and -105 J mol^{-1} K^{-1} respectively. The reaction is :

(A) Spontaneous (B) Non spontaneous

(C) At equilibrium (D) Can't say anything

21. Identify the correct statement for change of Gibbs energy for a system at constant temperature and pressure.

(A) If $\Delta G_{system} > 0$, the process is spontaneous.

(B) If $\Delta G_{system} = 0$, the system has attained equilibrium.

(C) If $\Delta G_{system} = 0$, the system is still moving in a particular direction.

(D) If $\Delta G_{system} < 0$, the process is non spontaneous.

22. In conversion of lime-stone to lime, $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

the values of $\Delta H°$ and $\Delta S°$ are +179.1 kJ mol^{-1} and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is :- **[AIEEE-2007]**

(A) 1008 K (B) 1200 K (C) 845 K (D) 1118 K

8.2 CALCULATE ΔG FOR VARIOUS PROCESSES

(i) Ideal gas subjected to isothermal compression or expansion :

For isothermal process :

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

For ideal gas, $\Delta H = nC_{P,m}\Delta T = 0$ (As $\Delta T = 0$, for isothermal change)

& $\Delta S = nR \ln \frac{V_2}{V_1}$ (for isothermal change)

$\therefore$ $\Delta G = -nRT \ln \frac{V_2}{V_1}$

Hence, during isothermal expansion Gibb's function decreases while during isothermal compression Gibb's function increases.

(ii) Isothermal and isobaric phase transitions :

At transition temperature, the stability (or Gibb's functions) of two phases are equal. Hence, there is no driving force for conversion of one phase into other. This means phase transitions are examples of reversible processes at transition temperature.

Now, for reversible, isothermal and isobaric change, $\Delta G = 0$

$\Rightarrow$ $\Delta G = 0$, for phase transitions at transition temperature.

Thus, $\Delta G_{vap} = 0$ at boiling point :

$\Rightarrow$ $\Delta H_{vap} = T_b \Delta S_{vap}$

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

Also, $\Delta G_{fusion} = 0$ at melting point :

$\Rightarrow$ $\Delta H_{fusion} = T_f \Delta S_{fusion}$

$T_f = \frac{\Delta H_{fusion}}{\Delta S_{fusion}}$

Ex.7 The enthalpy of vaporization of a liquid is 30 kJ mol^{-1} and entropy of vaporization is 75J mol^{-1} K^{-1}. The boiling point of the liquid at 1 atm is :

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

Ans. [B]

Sol. $T = \frac{\Delta H_{vap}}{\Delta S_{vap}} = \frac{30 \times 10^3}{75} = 400K$

Ex.8 At what minimum temperature would a given reaction become spontaneous if ΔH = +119 kJ and ΔS = +263 J/K?

(A) 452 K ***(B) 2210 K*** ***(C) 382 K*** ***(D) 2.21 K***

Ans. [A]

Sol. $T = \frac{\Delta H}{\Delta S} = \frac{119 \times 10^3}{263} = 452.47K$

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iii. $\Delta_r G$ for a chemical reaction.

Consider a reaction :

$$aA + bB \xrightarrow{T,P} cC + dD$$

The change in Gibb's function for a chemical reaction is change in ΔG when reactants react according to a given balanced chemical reaction with specified physical state of each reactant and product at given temperature and pressure.

$\Delta_r G = cG_C + dG_D - aG_A - bG_B$ .....(i)

Where G_A, G_B, G_C and G_D are molar Gibb's function of A,B,C and D respectively at given T and P.

also,
$$\left.\begin{aligned} G_A &= H_A - TS_A \\ G_B &= H_B - TS_B \\ G_C &= H_C - TS_C \\ G_D &= H_D - TS_D \end{aligned}\right\} \quad \text{.....(ii)}$$

Substituting (ii) in (i)

$\Delta_r G = (cH_C + dH_D - aH_A - bH_B) - T(cS_C + dS_D - aS_A - bS_B)$

$\Rightarrow \quad \boxed{\Delta_r G = \Delta_r H - T\Delta_r S}$

$(\Delta H_r)_{T,P}$	$(\Delta S_r)_{T,P}$	(ΔG_r)	**Remarks**
– ve	+ ve	Always –ve	Reaction is spontaneous
+ ve	– ve	Always +ve	Reaction non-spontaneous
+ ve	+ ve	At low temperature, ΔG = + ve	Non-spontaneous
		At high temperature, ΔG = – ve	Spontaneous
– ve	– ve	At low temperature, – ve	Spontaneous
– ve	– ve	At high temperature, + ve	Non spontaneous

(iv) Gibb's functions of pure substances :

Consider a pure substance having a Gibb's function as follows :

$G = H - TS = U + PV - TS$

Let, the pressure and temperature are varied by infinitesimally small value :

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

As, $dU = dq - PdV$ and $TdS = dq$ [Assume only PV- work and reversible process.]

$dG = VdP - SdT$

(a) If pressure is varied keeping temperature constant -

$$dG = VdP \Rightarrow \left(\frac{dG}{dP}\right)_T = V$$

The physical significance of above relation is when pressure over a substance is increased, it's Gibb's function increases & the increase is proportional to molar volume. Since molar volume of gas, liquid and solid are in order, as follows :

$$\mathbf{V_{Gas} > V_{Liquid} > V_{Solid}}$$

Hence, Gibb's function of gases increases most rapidly on increasing pressure.

That's why, gas phase becomes unstable at high pressure.

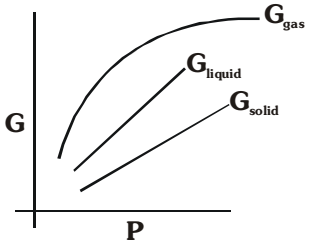


Fig : Variation of Gibb's function of pure substance with pressure at constant temperature.

(b) If temperature is changed keeping pressure constant -

$$dG = -SdT \Rightarrow \left(\frac{dG}{dT}\right)_P = -S$$

Since entropy of pure substances are always positive, the slope of G vs T curve is negative. Also since,

$$\mathbf{S_{gas} > S_{liquid} > S_{solid}}$$

$\Rightarrow$ the slope is more negative for gas.

Thus, on increasing temperature, the Gibb's function of pure substances decreases, but this decrement is maximum for gaseous phase. Thus, gas phase acquire stability on increasing temperature.

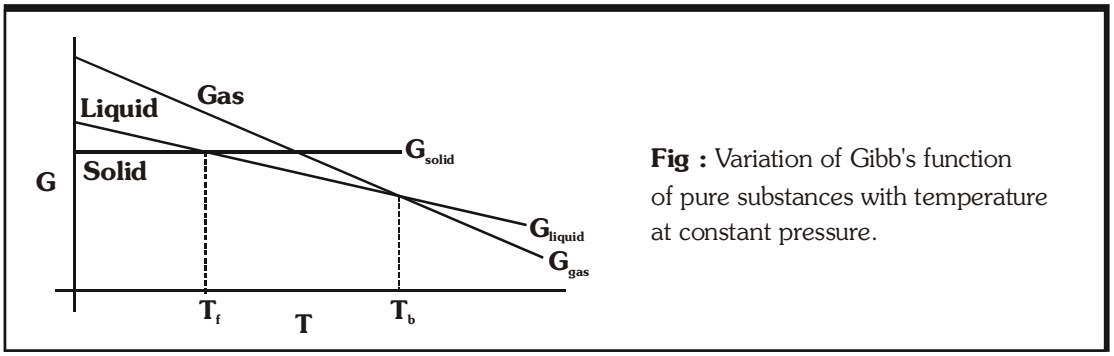


Fig : Variation of Gibb's function of pure substances with temperature at constant pressure.

Ex. 9. *Calculate ΔG_m for the following process:*

(i) *H_2O (ℓ, 100ºC, 1 atm) $\longrightarrow$ H_2O (g, 100ºC, 1 atm)*

(ii) *H_2O (ℓ, 100ºC, 1 atm) $\longrightarrow$ H_2O (g, 100ºC, 0.5 atm)*

Sol. : ***(i)*** *$\Delta G = 0$ (Equilibrium condition)*

(ii) *H_2O (ℓ, 100ºC, 1atm) $\xrightarrow{1}$ H_2O (g, 100ºC, 1 atm) $\xrightarrow{2}$ H_2O (g, 100ºC, 0.5 atm)*

$$\Delta G_1 = 0$$

$$\Delta G_2 = nRT \cdot \ell n \frac{P_2}{P_1} = 1 \times R \times 373 \times \ell n \frac{0.5}{1} = -2149.5\ J$$

$\therefore$ $\Delta G = \Delta G_1 + \Delta G_2 = -2149.5\ J$

8.3 APPLICATION OF GIBB'S ENERGY (AS MEASURE OF NON-PV WORK)

For a pure substance

$$dG = d(H - TS) = dH - TdS - SdT$$

also $dH = dU + PdV + VdP$

also $dU = dq - PdV - w_{non\text{-}PV}$

($w_{non\text{-}PV}$ = non-PV work done by system)

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

for a reversible change at constant T and P.

$dq = TdS$; and SdT and VdP term vanishes.

$\Rightarrow$ $dG = TdS - w_{non\text{-}PV} - TdS$

$(dG)_{T,P} = - w_{non\text{-}PV}$

$\Rightarrow$ $\boxed{-(dG)_{T,P} = w_{non-PV}}$

Thus decrease in Gibb's function at constant temperature and pressure is equal to maximum non-PV work obtainable from system.

9. Chemical equilibrium :

The state of chemical equilibrium is characterised by constant value of temperature, pressure and composition of a closed system. The state of equilibrium represent most stable state acquired by chemical system under given conditions.

The characteristics of state of equilibrium are :

(i) The equilibrium is attained in closed system.

(ii) At equilibrium, the chemical system is at minimum value of Gibb's function possible under given conditions.

(iii) A state of equilibrium is attained spontaneously.

(iv) At equilibrium, the rate of change of Gibb's function with progress of reaction under given conditions becomes zero $\Rightarrow \Delta_r G = 0$.

(v) At state of equilibrium, the total Gibb's function of products becomes equal to total Gibb's function of reactants.

9.1 EQUILIBRIUM CONSTANT

Gas phase reactions :

Consider a reaction :

$$\mathbf{aA(g) + bB(g) \longrightarrow cC(g) + dD(g)}$$

Now molar Gibb's functions of A, B, C and D are given by :

$$G_A = G^\circ_A + RT\ln\left(\frac{P_A}{P_0}\right)$$

$$G_B = G°_B + RT\ln\left(\frac{P_B}{P_0}\right)$$

$$G_C = G°_C + RT\ln\left(\frac{P_C}{P_0}\right)$$

$$G_D = G°_D + RT\ln\left(\frac{P_D}{P_0}\right)$$

Now, $\Delta_r G = cG_C + dG_D - aG_A - bG_B$

Substituting value of G_A, G_B, G_C and G_D in above equation :

$$\Delta_r G = (cG°_C + dG°_D - bG°_B - aG°_A) + RT\ln\left[\frac{\left(\frac{P_C}{P_0}\right)^c\left(\frac{P_D}{P_0}\right)^d}{\left(\frac{P_A}{P_0}\right)^a\left(\frac{P_B}{P_0}\right)^b}\right]$$

$$\mathbf{\Delta_r G = \Delta_r G° + RT \ln Q}$$

Where , $Q = \left(\frac{P_C^c.P_D^d}{P_A^a.P_B^b}\right)\left(\frac{1}{P_0}\right)^{(c+d-a-b)}$

At equilibrium, $\Delta_r G = 0$ and $Q = K_P = \left(\frac{P_C^c.P_D^d}{P_A^a.P_B^b}\right)\left(\frac{1}{P_0}\right)^{\Delta n_g}$

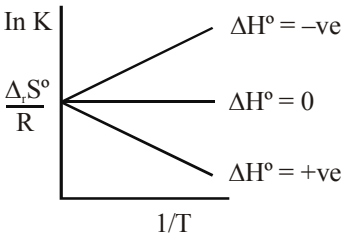
$$\mathbf{\Delta_r G° = -RT\ln K_P}$$

Note : Q contains partial pressures at that moment but K_P contain partial pressures at equilibrium.

10. RELATIONSHIP BETWEEN, ΔGº AND EQUILIBRIUM CONSTANT

$\Delta G° = -RT\ln Keq$

$\Delta H° - T\Delta S° = -RT\ln Keq$



$$\ln K_{eq} = \frac{-\Delta_r H°}{RT} + \frac{\Delta_r S°}{R}$$

$$\ln K_1 = \frac{\Delta_r S°}{R} - \frac{\Delta_r H°}{RT_1}$$

$$\ln K_2 = \frac{\Delta_r S°}{R} - \frac{\Delta_r H°}{RT_2}$$

[where K_1 & K_2 are values of K_p at temperature T_1K & T_2K respectively]

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H°}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$ (Van't Hoff's equation)

EXERCISE-4

23. 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:-

(A) $(dS)_{V, E} = 0, (dG)_{T, P} = 0$

(B) $(dS)_{V, E} = 0, (dG)_{T, P} > 0$ **[AIEEE-2003]**

(C) $(dS)_{V, E} < 0, (dG)_{T, P} < 0$

(D) $(dS)_{V, E} > 0, (dG)_{T, P} < 0$

24. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is :- **[AIEEE-2003]**

(A) $\Delta G° = RT\ \ell nK_C$ (B) $-\Delta G° = RT\ \ell nK_C$

(C) $\Delta G = RT\ \ell nK_C$ (D) $-\Delta G = RT\ \ell nK_C$

25. For the reaction at 298 K

$A(g) + B(g) \rightleftharpoons C(g) + D(g)$

$\Delta H° = -29.8$kcal; $\Delta S° = -0.1$ kcal/K

Calculate $\Delta G°$ and K.

26. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K is :-

(A) $-\Delta G° = RT \ln K$ (B) $\Delta G = RT \ln K$

(C) $-\Delta G = RT \ln K$ (D) $\Delta G° = RT \ln K$

ANSWER KEY

EXERCISE-1

1. **Ans. (i) irreversible, (ii) reversible, (iii) impossible**

2. **Ans.(A)** **3.** **Ans.(B)** **4.** **Ans.(C)**

EXERCISE-2

5. **Ans.(A)**

6. **Ans. (a) 2.1 cal/K , (b) 1.5 cal/K** **7.** **Ans 819ºC**

8. **Ans.(C)**

9. **Ans.**

(A) (+ive) **(B) (+ive)** **(C) $\approx$ 0** **(D) (+ive)**

(E) (+ive) **(F) (–ive)**

10. **Ans.(C)** **11.** **Ans.(C)** **12.** **Ans.(D)** **13.** **Ans.(B)**

14. **Ans.(C)** **15.** **Ans.(A)**

EXERCISE-3

16. **Ans. –2873.1 kJ** **17.** **Ans. (B)** **18.** **Ans.(C)** **19.** **Ans.(C)**

20. **Ans.(B)** **21.** **Ans.(B)** **22.** **Ans.(D)**

EXERCISE-4

23. **Ans.(D)** **24.** **Ans.(B)** **25.** **Ans.$\Delta G^\circ = 0$; K = 1**

26. **Ans.(A)**

MISCELLANEOUS SOLVED QUESTION

1. When 1-pentyne(A) is treated with 4N alcoholic KOH at 175°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). The equilibrium was maintained at 175°C. Calculate $\Delta G°$ for the following equilibria.

$B \rightleftharpoons A \qquad \Delta G_1° = ?$

$B \rightleftharpoons C \qquad \Delta G_2° = ?$

From the calculated value of $\Delta G_1°$ & $\Delta G_2°$ indicate the order of stability of A, B & C. Write a reasonable reaction mechanism sharing all intermediate leading to A, B & C. **[JEE 2001]**

2. Show that the reaction $CO(g) + ½\ O_2(g) \longrightarrow CO_2(g)$ at 300 K is spontaneous and exothermic, when the standard entropy is – 0.094 kJ mol^{-1} K^{-1}. The standard Gibbs free energies of formation for CO_2 and CO are –394.4 and –137.2 kJ mol^{-1}, respectively. **[JEE 2001]**

3. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

This reaction is carried out at 298 K and 20 bar. 5 mol each of N_2O_4 and NO_2 are taken initially.

Given : $(\Delta G_f^0)_{N_2O_4} = 100 kJ\ mol^{-1}; (\Delta G_f^0)_{NO_2} = 50 kJ\, mol^{-1}$

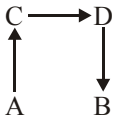
(i) Find ΔG for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium. **[JEE 2004]**

4. The enthalpy of vapourization of a liquid is 30 kJ mol^{-1} and entropy of vapourization is 75 J mol^{-1} 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

5. A process A ⟶ B is difficult to occur directly instead it takes place in three successive steps.



ΔS (A ⟶ C) = 50 e.u. **[JEE 2006]**

ΔS (C ⟶ D) = 30 e.u.

ΔS (B ⟶ D) = 20 e.u.

Where e.u. is entropy unit.

Then the entropy change for the process ΔS (A ⟶ B) is :-

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

6. For the process H_2O (l) (1 bar, 373 K) ⟶ H_2O(g) (1 bar, 373 K), the correct set of thermodynamic parameters is :- **[JEE 2007]**

(A) $\Delta G = 0, \Delta S = +$ ve (B) $\Delta G = 0, \Delta S = -$ ve

(C) $\Delta G = +$ ve, $\Delta S = 0$ (D) $\Delta G = -$ ve, $\Delta S = +$ve

7. **Statement-1 :** There is a natural asymmetry between converting work to heat and converting heat to work.

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.

[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.

8. **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.

EXERCISE (S-I)

❑ Carnot Cycle

1. The efficiency of a carnot 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. **TD0001**

2. A carnot cycle has an efficiency of 40%. Its low temperature reservoir is at 9°C. What is the temperature of source ? **TD0002**

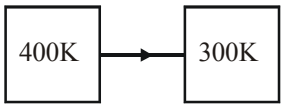
3. A diatomic ideal gas is expanded isothermally to 32 times of it's initial volume then it is cooled to restore to initial entropy at constant volume. Calculate ratio of intial temperature to final temperature **TD0003**

4. One mole of an ideal monoatomic gas was taken through reversible isochoric heating from 100 K to 1000 K. Calculate ΔS_{system}, ΔS_{surr} and ΔS_{total}

(i) when the process is carried out reversibly

(ii) when the process is carried out irreversibly (one step) **TD0004**

5. 100 kJ heat is transferred from a large 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 and combinedly source and sink form isolated sytem.



Find (a)ΔS_{source}, (b) ΔS_{sink} and (c) ΔS_{total}. Also comment on spontaneity of process. **TD0005**

6. A system of 100 kg mass undergoes a process in which its specific entropy increases from 0.3 $kJkg^{-1}K^{-1}$ to $0.4kJkg^{-1}K^{-1}$. At the same time, the entropy of the surrounding decreases from 80 kJK^{-1} to 75 kJK^{-1}. Find the $(\Delta S)_{universe}$ in kJK^{-1}. **TD0006**

7. Calculate $(\Delta S)_{universe}$ (in cal/K) when 1kg water at 300K is brought into contact with a heat reservoir at 600K. Specific heat capacity of water is 1cal/gm-°C. Assume no change in physical state of water.

(ln2 = 0.7) **TD0007**

8. 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 ΔS_{total} (in J/K -mol) in the process

Use : $\ln\left(\frac{4}{3}\right) = 0.3$, ln 10 = 2.3, R = 8.3 J/K-mol and ln x = 2.3 log x **TD0008**

9. Calculate $\Delta S_r°$ at 298K of

(i) $Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow NaCl(s)$, **TD0009**

(ii) $\frac{1}{2}N_2(g) + 2H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow NH_4Cl(s)$ **TD0010**

(iii) $C(graphite) \longrightarrow C(diamond)$. **TD0011**

The values of S° of Na, Cl_2, NaCl, NH_4Cl, N_2, H_2 diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 JK^{-1} mol^{-1} respectively.

10. Idenfity the susbtance in each of the following pairs of samples that has the higher entropy?

(A) $Br_2(l)$ or $Br_2(g)$ (B) $C_2H_6(g)$ or $C_3H_8(g)$

(C) MgO(s) or NaCl(s) (D) KOH(s) or KOH(aq) **TD0012**

❑ **Gibb's Function**

11. Calculate the ΔG^o change at 300 K for the reaction ;

$Br_2(\ell) + Cl_2(g) \longrightarrow 2BrCl(g)$. For the reaction $\Delta H° = 29.3$ kJ & the standard entropies of $Br_2(\ell)$, $Cl_2(g)$ & BrCl(g) at the 300 K are 150, 220, 240 J $mol^{-1}K^{-1}$ respectively. **TD0013**

12. The standard entropies of $H_2(g)$ and H(g) are 130 and 115 J $mol^{-1}K^{-1}$ respectively at 300K. Using the data given below calculate the bond energy of H_2(in kJ/mol) :-

$H_2(g) \longrightarrow 2H(g)$; $\Delta G° = 406$ kJ/mol **TD0014**

13. 5 mole $H_2O(\ell)$ at 373K and 1 atm is converted into $H_2O(g)$ at 373K and 5 atm. Calculate ΔG for this process. [Given : R = 2Cal/K-mol, ln 5 = 1.6] **TD0015**

14. Calculate ΔG (in bar-L) when a definite mass of a monoatomic ideal gas at 1 bar & 27°C is expanded adiabatically against vacuum from 10 L to 20 L (ln2 = 0.7) **TD0016**

15. Find $(\Delta S)_{universe}$ (in Joule/mole/K) at 1 bar for a chemical reaction at 300 K if $\Delta H^o_{300\ K} = 75$ kJ / mol $\Delta S^o_{300\ K} = 300$ J/K **TD0017**

16. A liquid freezes into a solid ($\Delta H = -1000$ J/mole) at 200 K and 1 atm, (it's normal melting point).

(i) What is the value of ΔG at 200 K ?

(ii) What is the ΔS value at 200 K ?

(iii) Will the freezing be spontaneous at 150 K and 1 atm ? Calculate $\Delta S_{total.}$

(iv) What is the value of ΔG at 250 K and 1 atm ?

(And it is assumed that ΔS and ΔH do not depend on temperature) **TD0018**

❑ **Thermodynamic and equilibrium constant**

17. α-D Glucose undergoes mutarotation to β-D-Glucose in aqueous solution. If at 300K there is 60% conversion. Calculate $\Delta G°$ of the reaction. (ln2 = 0.7, ln 3 = 1.1)

α-D-Glucose $\rightleftharpoons$ β-D-Glucose **TD0019**

18. The equilibrium constant of the reaction $2C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

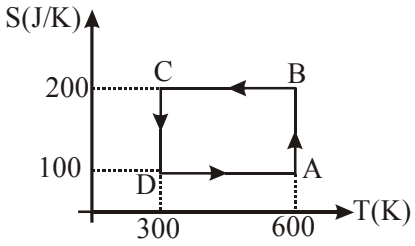
$$\ln K = -1.04 - \frac{1088K}{T}$$

Calculate the standard reaction enthalpy and entropy at 400 K. **TD0020**

19. For the reaction $SO_2(g) + 1/2\ O_2(g) \rightleftharpoons SO_3(g)$; $\Delta H°_{300} = -95$ kJ/mole, $\Delta S°_{300} = -95.0$ J/K mole. Find the value of ln k_p for this reaction at 300 K. **TD0021**

EXERCISE (S-II)

1. From the given T-S diagram of a reversible carnot engine, find



(i) work delivered by engine in one cycle **TD0022**

(ii) heat taken from the source in each cycle. **TD0023**

(iii) ΔS_{sink} in each cycle. **TD0023**

2. At 300 K, $\Delta H^\circ_{combustion}$ (sucrose) = – 5000 KJ/mol & $\Delta G^\circ_{combustion}$(sucrose) = –6000 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. **TD0024**

3. The K_P for reaction A + B $\rightleftharpoons$ C + D is 2.0 at 27°C and 8.0 at 127°C. Determine the standard free energy change of this reaction at each temperature and ΔH° for the reaction over this range of temperature (ln2 = 0.7) ? **TD0025**

4. 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 ($\Delta S_{system} + \Delta S_{surrounding}$) for given process. **TD0026**

5. For a reaction :

$2A(s) + B(g) \longrightarrow 3C(l)$,

standard entropy change of reaction is –2 kJ/mol-K and standard enthalpy of combustion of A(s), B(g) and C(*l*) are –100, –60 –285 kJ/mol respectively, then find the maximum useful work that can be obtained at 27°C and 1 bar pressure from the reaction (in kJ/mol). **TD0032**

6. $2A(s) \rightleftharpoons B(g) + 2C(g) + 3D(g)$

Total pressure developed in a closed container by decomposition of A at equilibrium is 12 bar at 727ºC. Calculate $|\Delta G^\circ|$ (in kcal) of the reaction at 727°C. (R = 2 cal/mole-K, ln 2 = 0.7, ln3 = 1.1) **TD0028**

7. Find ΔG(J/mol) for the reaction at 300kPa & 27ºC when all gases are in stoichiometric ratio of moles. $N_2O_4(g) \rightarrow 2NO_2(g)$ [ln2 = 0.7]

Given : $\Delta G_f^\circ(N_2O_4) = 100 kJ/mol$

$\Delta G_f^\circ(NO_2) = 50 kJ/mol$

R = 8 J/mol-K **TD0029**

8. 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 $JK^{-1}\ mol^{-1}$) for the O_2 is (Given : $\ell n2 = 0.7$)

$C_{P,m} = 10 + 10^{-2}T$ **TD0030**

9. Calculate the molar entropy of a substance at 600 K and 1 bar using the following data.

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

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

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

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

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

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

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

$C_{P,m}(g) = 50.0\ JK^{-1}mol^{-1}$. **TD0031**

EXERCISE (O-I)

1. A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at T_2. A second reversible engine B (based on carnot cycle) absorbs the same amount of heat as rejected by the engine A, from the reservoir at T_2 and rejects energy to a reservoir at 360K. If the efficiencies of engines A and B are the same then the temperature T_2 is :-

(A) 680 K (B) 640 K (C) 600 K (D) 670 K **TD0033**

2. Which of the following is incorrect for a closed system in which an irreversible process is occuring?

(A) $Q_{sys} + Q_{surr} = 0$ (B) $W_{sys} + W_{surr} = 0$

(C) $\Delta U_{sys} + \Delta U_{surr} = 0$ (D) $\Delta S_{sys} + \Delta S_{surr} = 0$ **TD0034**

3. For conversion C(graphite) $\rightarrow$ C(Diamond), the ΔS is :-

(A) Zero (B) Positive

(C) Negative (D) Can not be predicted **TD0035**

4. Considering entropy (S) as a thermodynamic parameter, the criteria for the spontaneity of any process is :-

(A) $\Delta S_{system} - \Delta S_{surroundings} > 0$ (B) $\Delta S_{system} > 0$ only

(C) $\Delta S_{surroundings} > 0$ only (D) $\Delta S_{system} + \Delta S_{surroundings} > 0$ **TD0036**

5. If $\Delta H_{vaporisation}$ 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) –10 J/mol.K **TD0037**

6. For 1 mole of an ideal monoatomic gas on moving from one state to other, the temperature is doubled but pressure becomes $\sqrt{2}$ times. Then entropy change in the process will be (R = 2 Cal/mol-K)

(A) R ln 2 (B) 2R ln 2 (C) 3R ln 2 (D) $\frac{R}{2} ln 2$ **TD0038**

7. If S^0 for H_2, Cl_2 and HCl are 0.13, 0.22 and 0.19 kJ K^{-1} mol^{-1} respectively. The total change in standard entropy for the reaction, $H_2 + Cl_2 \longrightarrow 2HCl$ is : **TD0039**

(A) 30 JK^{-1} mol^{-1} (B) 40 JK^{-1} mol^{-1} (C) 60 JK^{-1} mol^{-1} (D) 20 JK^{-1} mol^{-1}

8. 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 **TD0040**

9. Identify the correct statement regarding entropy.

(A) At absolute zero, the entropy of perfectly crystalline substance is taken to be +ve

(B) At absolute zero, 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.

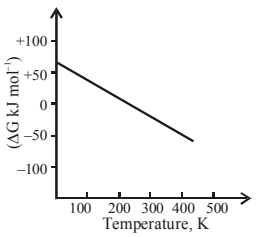
(D) At absolute zero, the entropy of all crystalline substances is taken to be zero. **TD0041**

10. In which of the following reactions do you expect to have a decrease in entropy?

(A) $Fe(s) \longrightarrow Fe(l)$ (B) $2\,Fe(s) + 3/2\,O_2(g) \longrightarrow Fe_2O_3(s)$

(C) $HF(l) \longrightarrow HF(g)$ (D) $2\,H_2O_2(l) \longrightarrow 2\,H_2O(l) + O_2(g)$ **TD0042**

11. What can be concluded about the values of ΔH and ΔS from this graph?



(A) $\Delta H > 0$, $\Delta S > 0$

(B) $\Delta H > 0$, $\Delta S < 0$

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

(D) $\Delta H < 0$, $\Delta S < 0$ **TD0043**

12. For the reaction at 300 K

$$A(g) + B(g) \longrightarrow C(g)$$

$\Delta U = -3.0$ kcal ; $\Delta S = -10.0$ cal/K

value of ΔG is ?

(A) –600 cal (B) –6600 cal (C) –6000 cal (D) none **TD0044**

13. For the reaction that taking place at certain temperature $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$, if equilibrium pressure is X bar, then $\Delta_r G°$ would be :-

(A) – 2 RT ln X (B) – RT (ln X – ln2)

(C) – 2 RT (ln X–ln 2) (D) – 0.5 RT (ln X–ln 2) **TD0045**

14. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure ?

(A) 80 cal (B) 540 cal (C) 620 cal (D) zero **TD0046**

15. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure ?

(A) Zero (B) 540 cal (C) 517.13 cal (D) 510 cal **TD0047**

16. If $\Delta G° > 0$ for a gaseous reaction then :

(A) $K_P > 1$

(B) $K_P < 1$

(C) The products predominate in the equilibrium mixture

(D) Mole of product must be less than mole of reactant **TD0048**

17. 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 cal (C) 400 cal (D) –400 cal **TD0049**

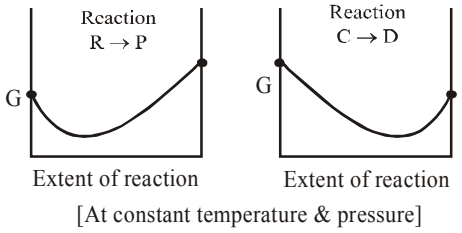
18. With the help of given curves select the correct statement.

(A) C will partially convert into D.

(B) R will not convert into P

(C) R will be completely converted into P.

(D) C will be completely converted in D. **TD0050**



[At constant temperature & pressure]

19. Evaluate $\Delta S°$ for the reaction below at 25°C.

$$CH_4(g) + 2Cl_2(g) \rightarrow CCl_4(\ell) + 2H_2(g)$$

Given :	$CH_4(g)$	$Cl_2(g)$	$CCl_4(l)$	$H_2(g)$
$\Delta H°_f$ (kJ/mol)	–74.81	0	–135.4	0
$\Delta G°_f$ (kJ/mol)	–50.75	0	–65.27	0

(A) –360 J/K (B) –66.9 J/K (C) –155 J/K (D) – 487 J/K **TD0051**

20. All of the following have $\Delta G°_f = 0$, except :-

(A) $O_2(g)$ (B) $Br_2(g)$ (C) $H_2(g)$ (D) Ca(s) **TD0052**

EXERCISE (O-II)

***Single correct* :**

1. 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 ? Suppose heat capacity of each piece is C. **TD0053**

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

2. 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 **TD0054**

3. For the hypothetical reaction , $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$, Δ_rG and Δ_rS are 20 kJ/mole and –20 $JK^{-1}\,mol^{-1}$ respectively at 200 K. If Δ_rC_p is 20 $JK^{-1}\,mol^{-1}$ then Δ_rH at 400 K is :-

(A) 20 kJ/mole (B) 7.98 kJ/mole (C) 28 kJ/mole (D) 16 kJ/mole **TD0055**

4. 1 mole of ice at 0ºC is converted in steam at 100ºC then calculated ΔS, in the process. enthalpy of vapourisation and fusion are 540 cal gm^{-1} and 80 cal gm^{-1} respectively. Use the average heat capacity of liquid water as 1cal gm^{-1} degree.

(A) $18\left(\frac{80}{373}+\frac{540}{373}+ln\frac{373}{273}\right)$ (B) $18\left(\frac{80}{273}+\frac{540}{373}+ln\frac{373}{273}\right)$

(C) $18\left(\frac{80}{273}+\frac{540}{373}+ln\frac{273}{373}\right)$ (D) $18\left(\frac{80}{273}+\frac{540}{373}+100\right)$ **TD0056**

5. The value of ΔG_f° of gaseous mercury is 38 kJ/mole. At what total external pressure mercury start boiling at 27°C. (R.ln10 = 19 J/K-mol)

(A) $10^{-6.67}$ (B) $10^{-1.67}$ (C) $10^{-13.33}$ (D) $10^{-3.33}$ **TD0057**

6. If molar internal energy for a gas in a closed rigid vessel given by

$$U = a + bT + cT^2$$

find the entropy change (in J/K) at constant volume when 1 mol of gas are heated from 200 K to 400K.

[Given : a = 20 J/mol; b = 10 J/K-mol; c = 2×10^{-2} J/K^2-mol] (*ln* 2 = 0.7)

(A) 15 (B) 30 (C) 60 (D) 9.78 **TD0058**

7. Statement -1 : When process H_2O (s) $\rightleftharpoons$ H_2O (*l*), reaches equiilibrium in a closed system at constant temperature and pressure, Gibb's function of H_2O (s) & H_2O (*l*) become same.

Statement - 2 : For reversible phase change at constant temperature & pressure, change in Gibb's free energy will be zero.

(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. **TD0059**

8. Statement- 1 : Absolute entropy of an ion in aqueous solution at 298 K may be negative.

Statement -2 : Absolute entropy at 298 K of any substance can never be negative.

(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. **TD0060**

9. **Statement-1 :** Net heat absorbed in a cyclic process must be 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. **TD0061**

10. **Statement-1 :** Entropy change in reversible adiabatic expansion of an ideal gas is zero.

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. **TD0062**

MORE THAN ONE MAY BE CORRECT :

11. Select the correct statement(s).

(A) In a reversible process, ΔG is always zero in a closed system.

(B) In a reversible process, ΔS_{univ} is always zero in a closed system.

(C) In a reversible process, ΔS_{sys} is always zero in a closed system.

(D) In a reversible process, ΔS_{sys} is always zero in an isolated system. **TD0063**

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

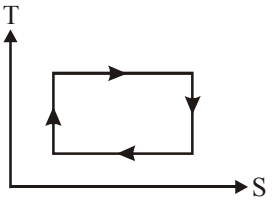
(A) The quantities E, H and G have the same dimension

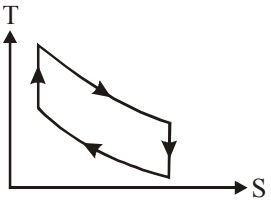
(B) Gibb's free energy of 10 gm ice at 0° C and 1.0 atm is less than the Gibb's free energy of 10 gm water at 0° C and 1 atm.

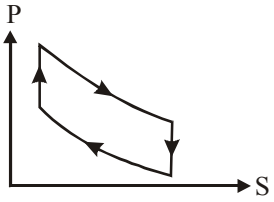
(C) $\Delta S_{sys} = 0$ for every adiabatic process in a closed system.

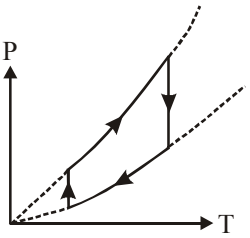
(D) For every reversible process in a closed system, $\Delta S_{sys} = \frac{\Delta H_{sys}}{T}$ **TD0064**

13. Which of the following represents the carnot cycle-

(A) 

(B) 

(C) 

(D) 

TD0065

14. The normal boiling point of a liquid 'A' is 350 K. ΔH_{vap} at normal boiling point is 35 kJ/mole. Pick out the correct statement(s). (Assume ΔH_{vap} to be independent of pressure).

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

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

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

(D) $\Delta S_{vaporisation} = 100$ J/K mole at 350 K and 2 atm TD0066

15. In isothermal ideal gas compression :

(A) w is + ve (B) ΔH is zero (C) ΔS_{gas} is + ve (D) ΔG is + ve TD0067

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

(A) $\Delta_r S$ for $\frac{1}{2}N_2(g) \longrightarrow N(g)$ is positive

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

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

(D) Entropy of a closed system is always maximized at equilibrium TD0068

17. Which of the following processes are spontaneous ?

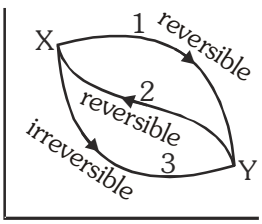
(A) Burning of fossil fuel

(B) Decomposition of water into H_2 and O_2 gas at room temperature

(C) Spreading of perfume in a room

(D) Diffusion of gas from high pressure to low pressure TD0069

18. Suppose a system make a transition from state X to state Y.



Given : $\Delta S_{XY} = 10$ J/K

(A) The state Y is more disordered than state X.

(B) ΔS_{XY} for path 1 and 3 is same.

(C) $\Delta S_{YX} = -10$ J/K

(D) The transition $X \rightarrow Y$ must be spontaneous. TD0070

19. In which of the following processes involving an ideal gas, entropy of system remains constant?

(A) Reversible isothermal expansion

(B) Irreversible adiabatic expansion

(C) Reversible adiabatic expansion

(D) Free expansion **TD0071**

20. In which of the following process involving ideal gas, entropy of surrounding remains constant ?

(A) Reversible isobaric heating

(B) Reversible adiabatic expansion

(C) Irreversible adiabatic compression

(D) Free expansion **TD0072**

Paragraph for Question 21 to 22

The reactions whose ΔG° are positive can not take place under standard state conditions. However another reaction whose ΔG° is negative can be coupled with the former type of reaction to give overall spontaneous process.

Consider the given reactions whose ΔG° at 300 K are provided to answer following questions.

$A(g) + 3B(g) \longrightarrow 2C(g)$: $\Delta G^\circ = +24$ kJ/mol ; $\Delta H^\circ = -24$ kJ/mol

$3C(g) \longrightarrow 2D(g)$: $\Delta G^\circ = -60$ kJ/mol ; $\Delta H^\circ = -84$ kJ/mol

All data at 300 K temperature.

21. What is ΔS° at 300 K of reaction (in J/Kmole) :

$3A(g) + 9B(g) \longrightarrow 4D(g)$

(A) –640 (B) –480 (C) +640 (D) –240 **TD0073**

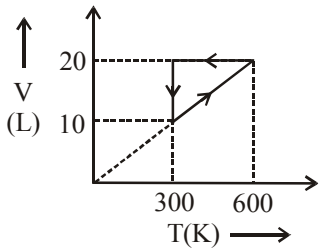
22. Assuming ΔH° and ΔS° do not vary with temperature. At what minimum temperature reaction

$A(g) + 3B(g) \longrightarrow 2C(g)$ become spontaneous-

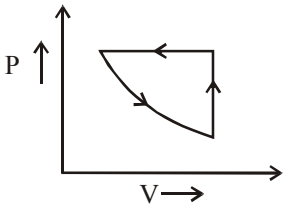
(A) 6250 K (B) 625 K (C) 150 K (D) 1000 K **TD0074**

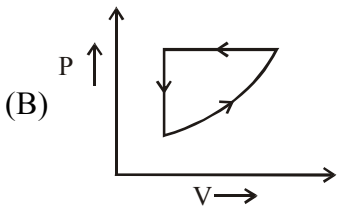
Paragraph for Q.23 to Q.24

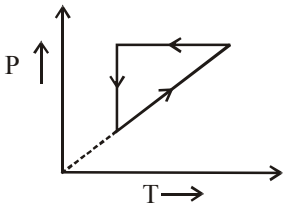
One mol of ideal monoatomic gas undergo the state change as shown in the following graph
(ln 2 = 0.7)

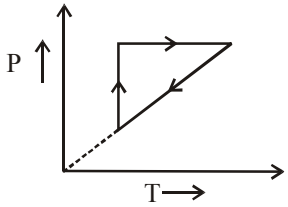


23. Correct graph for the process in paragraph is -

(A) 

(B) 

(C) 

(D) 

TD0075

24. Efficiency of the cycle will be -

(A) 50% (B) 25 % (C) 13.63 % (D) 12 % **TD0076**

MATCH THE LIST :

25. Match the Column :

	Column-I		**Column-II**
(P)	H_2O (ℓ, 1 atm, 363 K) $\rightarrow H_2O$ (g, 1 atm, 363 K)	(1)	$\Delta_r S > 0$
(Q)	H_2O (s, 1 atm, 373 K) $\rightarrow H_2O$ (g, 1 atm, 373 K)	(2)	$\Delta_r G > 0$
(R)	H_2O (ℓ, 1 atm, 273 K) $\rightarrow H_2O$ (s, 1 atm, 273 K)	(3)	$\Delta_r H < 0$
(S)	H_2O (s, 1 atm, 353 K) $\rightarrow H_2O$ (ℓ, 1 atm, 353 K)	(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

TD0080

MATCH THE COLUMN :

26.

Column–I	**Column-II**
(A) Reversible adiabatic compression	(P) $\Delta S_{system} > 0$
(B) Reversible vaporisation	(Q) $\Delta S_{system} < 0$
(C) Adiabatic free expansion of ideal gas in vacuum	(R) $\Delta S_{surroundig} < 0$
(D) Dissociation of $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$	(S) $\Delta S_{surrounding} = 0$

TD0081

27.

Column-I **(Related to process)**	**Column-II** **(Related to system)**
(A) Fusion at melting point	(P) $\Delta G = 0$
(B) Vapourisation at boiling point	(Q) $\Delta G < 0$
(C) Condensation at triple point	(R) $\Delta S > 0$
(D) Melting at normal boiling point	(S) $\Delta H \simeq \Delta U$

TD0082

EXERCISE (J-MAIN)

1. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is :- **[AIEEE-2011]**

(1) 32.3 J mol^{-1} K^{-1} (2) 42.3 J mol^{-1} K^{-1}

(3) 38.3 J mol^{-1} K^{-1} (4) 35.8 J mol^{-1} K^{-1} **TD0083**

2. The incorrect expression among the following is :- **[AIEEE-2012]**

(1) $K = e^{-\Delta G°/RT}$

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

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

(4) $\ln K = \frac{\Delta H° - T\Delta S°}{RT}$ **TD0084**

3. The entropy (S°) of the following substances are : **[JEE-MAINS-(online) 2014]**

CH_4 (g) 186.2 J K^{-1} mol^{-1}

O_2 (g) 205.0 J K^{-1} mol^{-1}

CO_2 (g) 213.6 J K^{-1} mol^{-1}

H_2O (l) 69.9 J K^{-1} mol^{-1}

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

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O$ (ℓ) is:- **TD0085**

(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}

4. The molar heat capacity (C_p) of CD_2O is 10 cals at 1000 K. The change in entropy associated with cooling of 32 g of CD_2O vapour from 1000 K to 100 K at constant pressure will be (D = deuterium, at. mass = 2u) **[JEE-MAINS-(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} **TD0086**

5 $\Delta_f G°$ at 500 K for substance 'S' in liquid state and gaseous state are + 100.7 kcal mol^{-1} and + 103 kcal mol^{-1}, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to : (R = 2 cal K^{-1} mol^{-1}) - **[JEE-MAINS-(online) 2018]**

(1) 0.1 atm (2) 10 atm (3) 100 atm (4) 1 atm **TD0087**

6. For which of the following processes, ΔS is negative? **[JEE-MAINS-(online) 2018]**

(1) C(diamond) $\rightarrow$ C(graphite) (2) N_2(g, 273 K) $\rightarrow$ N_2(g, 300K)

(3) $H_2(g) \rightarrow 2H(g)$ (4) N_2(g, 1 atm) $\rightarrow$ N_2(g, 5 atm) **TD0088**

7. At 320 K, a gas A_2 is 20% dissociated to A(g). The standard free energy change at 320 K and 1 atm in J mol^{-1} is approximately : **[JEE-MAINS-(online) 2018]**

(R = 8.314 JK^{-1} mol^{-1}; ℓn 2 = 0.693; ℓn 3 = 1.098)

(1) 4281 (2) 4763 (3) 2068 (4) 1844 **TD0089**

8. Two blocks of the same metal having same mass and at temperature T_1 and T_2, 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-MAINS-(online) 2019]**

(1) $2C_P \ln\left(\frac{T_1+T_2}{4T_1T_2}\right)$ (2) $2C_P \ln\left[\frac{(T_1+T_2)^{\frac{1}{2}}}{T_1T_2}\right]$ (3) $C_P \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right]$ (4) $2C_P \ln\left[\frac{T_1+T_2}{2T_1T_2}\right]$ **TD0090**

9. For the chemical reaction $X \rightleftharpoons Y$, the standard reaction Gibbs energy depends on temperature T (in K) as : **[JEE-MAINS-(online) 2019]**

$$\Delta_r G^o \text{ (in kJ mol}^{-1}) = 120 - \frac{3}{8}T$$

The major component of the reaction mixture at T is :

(1) X if T = 315 K (2) X if T = 350 K (3) Y if T = 300 K (4) Y if T = 280 K **TD0091**

10. For the equilibrium, **[JEE-MAINS-(online) 2019]**

$2H_2O \rightleftharpoons H_3O^+ + OH^-$, the value of ΔG^o at 298 K is approximately :- **TD0092**

(1) –80 kJ mol^{-1} (2) –100 kJ mol^{-1} (3) 100 kJ mol^{-1} (4) 80 kJ mol^{-1}

11. The standard reaction Gibbs energy for a chemical reaction at an absolute temperature T is given by

$$\Delta_r G^o = A - BT$$

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

(1) Exothermic if B < 0 **[JEE-MAINS-(online) 2019]**

(2) Exothermic if A > 0 and B < 0

(3) Endothermic if A < 0 and B > 0

(4) Endothermic if A > 0 **TD0093**

12. The reaction, $MgO(s) + C(s) \rightarrow Mg(S) + CO(g)$, for which $\Delta_r H^o = +491.1$ kJ mol^{-1} and $\Delta_r S^o = 198.0$ JK^{-1} mol^{-1}, is not feasible at 298 K. Temperature above which reaction will be feasible is :-

[JEE-MAINS-(online) 2019]

(1) 1890.0 K (2) 2480.3 K (3) 2040.5 K (4) 2380.5 K **TD0094**

13. A process has $\Delta H = 200$ Jmol^{-1} and

$\Delta S = 40$ JK^{-1}mol^{-1}. Out of the values given below, choose the minimum temperature above which the process will be spontaneous : **[JEE-MAINS-(online) 2019]**

(1) 5 K (2) 4 K (3) 20 K (4) 12 K **TD0095**

14. The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is : **[JEE-MAINS-(online) 2019]**

(Specific heat of water liquid and water vapour are 4.2 kJ K^{-1} kg^{-1} and 2.0 kJ K^{-1} kg^{-1} ; heat of liquid fusion and vapourisation of water are 344 kJ kg^{-1} and 2491 kJ kg^{-1}, respectively).

(log 273 = 2.436, log 373 = 2.572, log 383 = 2.583)

(1) 7.90 kJ kg^{-1} K^{-1} (2) 2.64 kJ kg^{-1} K^{-1} (3) 8.49 kJ kg^{-1} K^{-1} (4) 9.26 kJ kg^{-1} K^{-1}

TD0096

15. The process with negative entropy change is : **[JEE-MAINS-(online) 2019]**

(1) Dissolution of iodine in water

(2) Synthesis of ammonia from N_2 and H_2

(3) Dissolution of $CaSO_4(s)$ to $CaO(s)$ and $SO_3(g)$ **TD0097**

(4) Subimation of dry ice

16. For the reaction ; **[JEE-MAINS-(online) 2020]**

$A(l) \rightarrow 2B(g)$

$\Delta U = 2.1$ kcal , $\Delta S = 20$ cal K^{-1} at 300 K **TD0098**

Hence ΔG in kcal is_____ .

17. For a dimerization reaction, **[JEE-MAINS-(online) 2020]**

$2\,A(g) \rightarrow A_2(g)$

at 298 K, $\Delta U^{\ominus}$, = – 20kJ mol^{-1}, $\Delta S^{\ominus} = -30$ J **TD0111**

K^{-1} mol^{-1}, then the $\Delta G^{\ominus}$ will be _____J.

18. The variation of equilibrium constant with temperature is given below : **[JEE-MAINS-(online) 2020]**

Temperature	**Equilibrium constant**
$T_1 = 25^{\circ}C$	$K_1 = 100$
$T_2 = 100^{\circ}C$	$K_2 = 100$

The values of ΔH°, ΔG° at T_1 and ΔG° at T_2 (in kJ mol^{-1}) respectively, are close to

[Use R = 8.314 $JK^{-1}mol^{-1}$]

(1) 0.64, –5.71 and –14.29

(2) 28.4, –7.14 and –5.71

(3) 28.4, –5.71 and –14.29

(4) 0.64, –7.14 and –5.71 **TD0112**

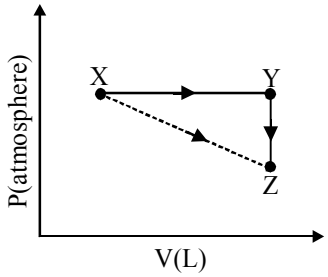
EXERCISE (J-ADVANCE)

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

	Column-I		**Column-II**
(A)	$CO_2(s) \rightarrow CO_2(g)$	(p)	phase transition
(B)	$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	(q)	allotropic change
(C)	$2H\bullet \rightarrow H_2(g)$	(r)	ΔH is positive
(D)	$P_{(white,\ solid)} \rightarrow P_{(red,solid)}$	(s)	ΔS is positive
		(t)	ΔS is negative

TD0099

2. 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 ΔS 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) $\Delta S_{x\rightarrow y\rightarrow z} = \Delta S_{x\rightarrow y}$ **TD0100**

3. For the process **[JEE 2014]**

$$H_2O(l) \rightarrow H_2O(g)$$

at T = 100°C and 1 atmosphere pressure, the correct choice is

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

(C) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} > 0$ (D) $\Delta S_{system} < 0$ and $\Delta S_{surroundings} < 0$ **TD0101**

4. Match the thermodynamic processes given under Column-I with the expressions given under Column-II. **[JEE 2015]**

	Column-I		**Column-II**
(A)	Freezing of water at 273 K and 1 atm	(P)	q = 0
(B)	Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q)	w = 0
(C)	Mixing of equal volumes of two ideal gases at constant temeprature and pressure in an isolated container	(R)	$\Delta S_{sys} < 0$
(D)	Reversible heating of $H_2(g)$ at 1 atm from 300 K to 600 K followed by reversible cooling to 300 K at 1 atm	(S)	$\Delta U = 0$
		(T)	$\Delta G = 0$

TD0102

5. One mole of an ideal gas at 300 K in thermal contact with surroundings expands isothermally from 1.0 L to 2.0 L against a constant pressure of 3.0 atm. In this process, the change in entropy of surroundings (ΔS_{surr}) in J K^{-1} is - **[JEE 2016]**

(1 L atm = 101.3 J)

(A) 5.763 (B) 1.013 (C) –1.013 (D) –5.763 **TD0103**

Paragraph for Q.6 & Q.7

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation : **[JEE 2016]**

$$X_2(g) \rightleftharpoons 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G°$, 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 β . Thus, $\beta_{equilibrium}$ 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 L bar K^{-1} mol^{-1})

6. The equilibrium constant K_P for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is

(A) $\frac{8\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (B) $\frac{8\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$ (C) $\frac{4\beta^2_{equilibrium}}{2-\beta_{equilibrium}}$ (D) $\frac{4\beta^2_{equilibrium}}{4-\beta^2_{equilibrium}}$ **TD0104**

7. 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) $\beta_{equilibrium} = 0.7$

(D) $K_C < 1$ **TD0105**

8. The standard state Gibbs free energies of formation of C(graphite) and C(diamond) at T = 298 K are **[JEE 2017]**

$$\Delta_f G° \text{ [C(graphite)]} = 0 \text{ kJ mol}^{-1}$$

$$\Delta_f G° \text{ [C(diamond)]} = 2.9 \text{ kJ mol}^{-1}$$

The standard state means that the pressure should be 1 bar , and substance should be pure at a given temperature. The conversion of graphite [C(graphite)] to diamond [C(diamond)] reduces its volume by 2×10^{-6} m^3 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 J = 1 kg m^2 s^{-2} ; 1 Pa = 1 kg m^{-1} s^{-2} ; 1 bar = 10^5 Pa]

(A) 14501 bar (B) 29001 bar (C) 58001 bar (D) 1405 bar **TD0106**

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

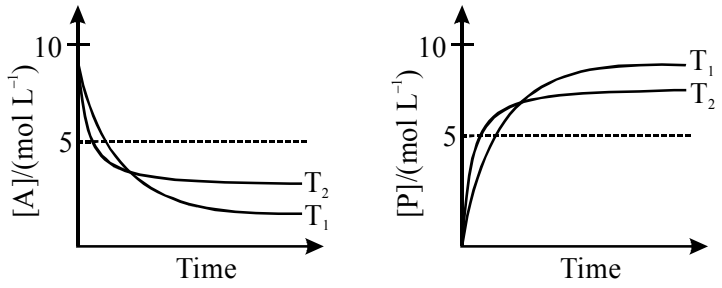
(A) With increase in temperature, the value of K for exothermic reaction decreases because the entropy change of the system is positive

(B) With increase in temperature, the value of K for endothermic reaction increases because unfavourable change in entropy of the surroundings decreases

(C) With increase in temperature, the value of K for exothermic reaction decreases because favourable change in entropy of the surroundings decreases

(D) With increase in temperature, the value of K for endothermic reaction increases because the entropy change of the system negative **TD0107**

10. 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 2018]**



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

(Assume ΔH^θ and ΔS^θ are independent of temperature and ratio of lnK at T_1 to lnK at T_2 is greater than 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) $\Delta G^\theta < 0$, $\Delta S^\theta > 0$ **TD0108**

11. 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

$2Cu(s) + H_2O(g) \rightarrow Cu_2O(s) + H_2(g)$

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 $JK^{-1}mol^{-1}$, ln(10) = 2.3. Cu(s) and $Cu_2O(s)$ are mutually immiscible.

At 1250 K : $2Cu(s) + 1/2O_2(g) \rightarrow Cu_2O(s)$; $\Delta G^\theta = -78{,}000$ J mol^{-1} **TD0109**

$H_2(g) + 1/2O_2(g) \rightarrow H_2O(g)$; $\Delta G^\theta = -1{,}78{,}000$ J mol^{-1}; G is the Gibbs energy) **[JEE 2018]**

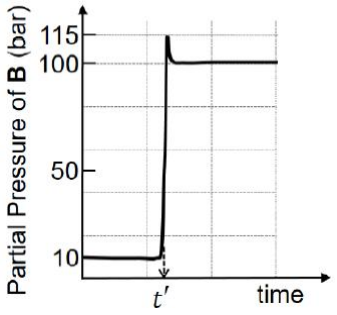
12. Consider the following reversible reaction, **[JEE 2018]**

$$A(g) + B(g) \rightleftharpoons AB(g).$$

The activition energy of the backward reaction exceeds that of the forward reaction by 2RT (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG^{θ} (in J mol^{-1}) for the reaction at 300 K is____.

(Given ; ln (2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy) **TD0110**

13. Consider the reaction A $\rightleftharpoons$ B at 1000 K. At time t', the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment the partial pressure of A was maintained at 1 bar. Given below is the plot of the partial pressure of B with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K? **[JEE 2020]**



TD0113

14. Tin is obtained from cassiterite by reduction with coke. Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place. **[JEE 2020]**

At 298 K : $\Delta_f H°(SnO_2(s))$ = -581.0 kJ mol^{-1}, $\Delta_f H°(CO_2(g))$ = -394.0 kJ mol^{-1}

$S°(SnO_2(s))$ = 56.0 J K^{-1} mol^{-1}, S°(Sn(s)) = 52.0 J K^{-1} mol^{-1} ,

$S°(C\ (s))$ = 6.0 J K^{-1} mol^{-1} , $S°(CO2(g))$ = 210.0 J K^{-1} mol^{-1}.

Assume that the enthalpies and the entropies are temperature independent.

TD0114

ANSWER KEY

EXERCISE (S-I)

1. Ans. 117°C, 52°C
2. Ans. 197°C
3. Ans. (4)
4. Ans. (i) $\Delta S_{syst} = 28.72 J/K$; $\Delta S_{surr} = -28.72$ J/K ; $\Delta S_{total} = 0$
   (ii) $\Delta S_{sys} = 28.72 J/K$; $\Delta S_{surr} = -11.22$ J/K , $\Delta S_{total} = 17.50$ J/K
5. Ans. (a) –250 J/K (b) 333.33 J/K (c) +83.33 J/K. Process is spontaneous.
6. Ans.(5)
7. Ans (200)
8. Ans. 10.325
9. Ans. (i) –90.5 (ii) –374.5 (iii) –3.26 (all in J mol^{-1} K^{-1})
10. Ans. [A] - II ; [B] - II ; [C] - II ; [D] - II
11. Ans. –3.7 kJ
11. Ans 436 kJ
13. Ans. 5.968 kcal
14. Ans.(–7)
15. Ans. (50)
16. Ans.
    (i) $\Delta G = 0$
    (ii) $\Delta S = -5$ J/mole.K
    (iii) $\Delta S_{total} = +1.66$ J/ mole. K ; process in spontaneous
    (iv) $\Delta S_{total} = -$ J/mole. K = $\Delta G = +250$ J/mole. K]
17. Ans. –997.68 J/mol
18. Ans. $\Delta H^\circ = 9.04$ kJ/mol; $\Delta S^\circ = -8.64$ J/mol^{-1} K^{-1}
19. Ans. 26.7

EXERCISE (S-II)

1. Ans. (i) 30 kJ (ii) 60 kJ (iii) 100 J/K
2. Ans. 30 kJ/mole
3. Ans. –1745.94 J/mol; –6983.76 J/mol and 13.97 kJ/mol
4. Ans. (16.66 J/K)
5. Ans.(1195 kJ/mole)
6. Ans. (17.8)
7. Ans.(3360)
8. Ans 10 J/K
9. Ans. 205.08 $JK^{-1}mol^{-1}$

EXERCISE (O-I)

1.	Ans.(C)	2.	Ans.(D)	3.	Ans.(C)	4.	Ans.(D)
5.	Ans.(C)	6.	Ans.(B)	7.	Ans.(A)	8.	Ans.(B)
9.	Ans.(B)	10.	Ans.(B)	11.	Ans.(A)	12.	Ans.(A)
13.	Ans.(C)	14.	Ans.(D)	15.	Ans.(C)	16.	Ans.(B)
17.	Ans.(A)	18.	Ans. (A)	19.	Ans. (C)	20.	Ans.(B)

EXERCISE (O-II)

1.	Ans.(D)	2.	Ans.(D)	3.	Ans.(A)	4.	Ans.(B)
5.	Ans.(A)	6.	Ans.(A)	7.	Ans.(A)	8.	Ans.(C)
9.	Ans.(A)	10.	Ans.(A)	11.	Ans.(B,D)	12.	Ans.(A)
13	Ans (A,C,D)	14.	Ans.(A,C)	15.	Ans.(A,B,D)	16.	Ans.(B,C,D)
17.	Ans.[A,C,D]	18.	Ans.[A,B,C]	19.	Ans.[C]	20.	Ans.[B,C,D]
21.	Ans.(A)	22.	Ans.(C)	23.	Ans.(D)	24.	Ans.(D)

25. Ans.(C)

26. Ans. (A) - S ; (B) - P,R ; (C) - P, S (D) - P, R

27. Ans. (A) - P,S,R ; (B) - P,R ; (C) - P (D) - Q, R, S

EXERCISE (J-MAIN)

1.	Ans.(3)	2.	Ans.(4)	3.	Ans.(4)	4.	Ans.(1)
5	Ans.(1)	6.	Ans.(4)	7.	Ans.(2)	8.	Ans.(3)
9.	Ans.(1)	10.	Ans.(4)	11.	Ans.(4)	12.	Ans.(2)
13.	Ans.(1)	14.	Ans.(4)	15.	Ans.(2)		
16.	Ans.(–2.70 to –2.71)	17.	Ans. by NTA (–13538.00)			18.	Ans.(3)

EXERCISE (J-ADVANCE)

1. Ans.(A)→(p, r, s) ; (B)→(r, s) ; (C)→(t) ; (D)→(p, q, t)

2. Ans.(A,C) 3. Ans. (B)

4. Ans. (A) → R, T ; (B) → P, Q, S ; (C) → P, Q, S ; (D) → P, Q, S, T

5.	Ans. (C)	6.	Ans.(B)	7.	Ans.(C)	8.	Ans.(A)
9.	Ans.(BC)	10.	Ans.(A,C)	11.	Ans.(–14.6)	12.	Ans.(8500)
13.	Ans.(0.25)	14.	Ans.935.00				