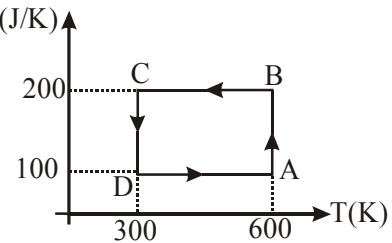


EXERCISE-(S-II)

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

- work delivered by engine in one cycle
- heat taken from the source in each cycle.
- ΔS_{sink} in each cycle.



Ans. (i) 30 kJ

(ii) 60 kJ

(iii) 100 J/K

$$[\text{Sol. (i)}] W_{AB} = -nRT \ln \frac{V_2}{V_1}$$

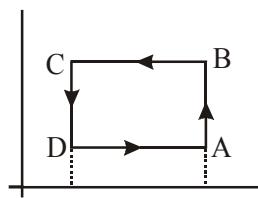
$$\Delta S = \frac{q_{\text{rev}}}{T} = -\frac{W_{AB}}{T}$$

$$\Rightarrow -W_{AB} = T\Delta S = 600 \times 100$$

$$-W_{BC} = -nC_V(T_1 - T_2)$$

$$-W_{CD} = T\Delta S = 300 \times (-100)$$

$$-W_{DA} = -nC_V(T_2 - T_1)$$



$$\text{Net work delivered during one cycle} = -W_{AB} - W_{BC} - W_{CD} - W_{DA} = 300 \times 100 = 30 \text{ kJ}$$

Note : Net work done = area of the rectangle

$$(\text{ii}) \quad \frac{W_{\text{net}}}{q} = \eta \quad \eta = \frac{600 - 300}{600} = \frac{1}{2}$$

$$\Rightarrow q = \text{heat taken from the source} = \frac{-W_{\text{net}}}{1/2} = \frac{30 \text{ kJ}}{1/2} = +60 \text{ kJ}$$

$$(\text{iii}) \quad \Delta S_{\text{sink}} = -\frac{q_{\text{sink}}}{T} \quad \text{also} \quad (q_{\text{source}} + q_{\text{sink}}) = 30$$

$$q_{\text{source}} = 60 \text{ kJ} \Rightarrow q_{\text{sink}} = -30 \text{ kJ}$$

$$\Rightarrow \Delta S_{\text{sink}} = \frac{-q_{\text{sink}}}{T} = \frac{-(30000 \text{ J})}{100} = 100 \text{ J/K} \quad \text{Ans.]}$$

2. At 300 K, $\Delta H^\circ_{\text{combustion}}(\text{sucrose}) = -5000 \text{ KJ/mol}$ & $\Delta G^\circ_{\text{combustion}}(\text{sucrose}) = -6000 \text{ KJ/mol}$. Estimate additional non-PV work that is obtained by raising temperature to 309 K. Assume $\Delta_r C_p = 0$ for this temperature change.

Ans 30 kJ/mole

$$\frac{\Delta H^\circ_{T_2} - \Delta H^\circ_{T_1}}{T_2 - T_1} = \Delta_r C_p$$

Given
 $\Delta H^\circ_{309} = \Delta H^\circ_{300} \text{ K}$
 $\Delta r C_p = 0$

$$\Delta_r S^\circ_{T_2} - \Delta_r S^\circ_{T_1} = \Delta_r C_p \ln \frac{T_2}{T_1}$$

$$\Delta S^\circ_{309} = \Delta S^\circ_{300} \text{ K}$$

$$\Delta G^\circ_{300 \text{ K}} = \Delta H^\circ_{300} - 300 \Delta S^\circ_{300}$$

-6000
-5000

$$\Rightarrow \Delta S^\circ_{309} = 1000/300 \text{ KJ/K} = \Delta S^\circ_{309} \text{ K}$$

$$\Delta G^\circ_{309 \text{ K}} = -5000 - 309 \times \frac{1000}{300} = -6030 \text{ J}$$

$$\Delta G = w_{\text{Non PV}} \Rightarrow \text{Additional Non PV work is } 30 \text{ kJ/mol}$$

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 ($\ln 2 = 0.7$) ?

Ans. **-1745.94 J/mol; -6983.76 J/mol and 13.97 kJ/mol**

$$\Delta G^\circ_{300 \text{ K}} = -RT \ln K_p = -8.314 \times 300 \ln 2 = -1745.94 \text{ J/mol}$$

$$\Delta G^\circ_{400 \text{ K}} = -8.314 \times 400 \ln 8 = -6983.76 \text{ J/mol}$$

$$\ln \frac{K_p_{T_2}}{K_p_{T_1}} = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \Rightarrow \ln \frac{8}{2} = \frac{\Delta H^\circ}{8.314 \times 10^{-3}} \left[\frac{1}{300} - \frac{1}{400} \right]$$

$$\Delta H^\circ = \frac{\Delta H^\circ}{8.314 \times 10^{-3}} \times \frac{100}{300 \times 400}$$

$$\Delta H^\circ = 13.97 \text{ kJ/mol}$$

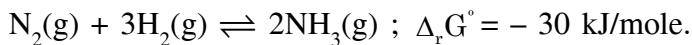
4. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ($\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$) for given process.

Ans. (16.66 J/K)

$$\Delta S = nR \ln \frac{P_1}{P_2} = 10 \times 8.314 \ln \frac{2}{1} = 57.62 \text{ J/K}$$

$$\begin{aligned} Q_r &= -w = -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right) \\ &= -P_{\text{ext}} nRT \left(\frac{1}{P_2} - \frac{1}{P_1} \right) \\ &= -1 \times 10 \times 0.0821 \times 300 \left(\frac{1}{1} - \frac{1}{2} \right) \\ &= -123.15 \text{ J-atm} = -12478.2 \text{ J} \\ \Delta S_{\text{sur}} &= \frac{-Q_r}{T} = \frac{-12478.2}{300} = -41.6 \text{ J/K} \\ \Delta S_{\text{total}} &= +16.03 \text{ J/K} \end{aligned}$$

5. What is $\Delta_r G$ for synthesis of ammonia at 300 K at following sets of partial pressure :



[Take $R = \frac{25}{3}$ J/K mole, $\ln 2 = 0.7$, $\ln 3 = 1.1$, $\ln 5 = 1.6$]

Gas	N_2	H_2	NH_3
Pressure (atm)	1	3	0.02

~~Ans. (-327.75 kJ/mol)~~

$$\Delta_r G = \Delta_r G^\circ + RT \ln Q$$

$$= -30 + \frac{25}{3} \times 10^{-3} \times 300 \ln \frac{(0.02)^2}{1 \times 3^3}$$

$$= -30 + 2.5 \left[\ln(4 \times 10^{-4}) - 3 \ln 3 \right]$$

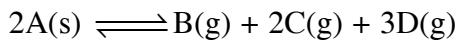
$$= -30 + 2.5 \left[\ln 4 - 4 \ln 10 - 3 \ln 3 \right]$$

$$= -30 + 2.5 \left[1.4 - 4 \times 2.3 - 3 \times 1.1 \right]$$

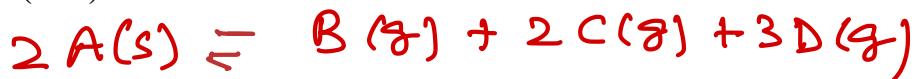
$$= -30 + 2.5 \left[-11.1 \right] = -57.75 \text{ kJ/mol}$$



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



6. Ans. (17.8)



$$\begin{array}{c} AT \\ \text{Gm} \\ \hline \end{array} - \begin{array}{c} P = 2 \\ 2P = 4 \\ 3P = 6 \text{ bar} \end{array}$$

$$6P = 12 \quad | \quad K_p^\circ = 2 \times 4^2 \times 6^3 = 2 \times 3^3$$

$$\Delta G^\circ = -RT \ln K_p^\circ = -\frac{2}{1000} \times (727 + 273) \ln(2 \times 3^3)$$

$$= -2 \times [8 \times 0.7 + 3 \times 1.1]$$

$$= -2 \times 8.9$$

$$= -17.8 \text{ kcal/mol}$$

7. Find $\Delta G(\text{J/mol})$ for the reaction at 300kPa & 27°C when all gases are in stoichiometric ratio of moles.



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

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

$R = 8 \text{ J/mol-K}$

7. Ans.(3360)

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G^\circ = 2\Delta G_f^\circ(NO_2) - \Delta G_f^\circ(N_2O_4) = 0$$

$$\Delta G = 8 \times 300 \ln \left(\frac{2^2}{1} \right) = 3360 \text{ J}$$

8. Oxygen is heated from 300 to 600 K at a constant pressure of 1 bar. What is the increase in molar entropy? The molar heat capacity (in $\text{JK}^{-1} \text{mol}^{-1}$) for the O_2 is (Given : $\ln 2 = 0.7$)

$$C_{\text{P,m}} = 10 + 10^{-2}T$$

8. Ans 10 J/K

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \frac{q_{\text{rev}}}{T} dT = \int_{T_1}^{T_2} \frac{nC_p dT}{T} \\ &= \int_{300}^{600} \frac{1 \times (10 + 10^{-2}T)}{T} dT \\ &\Rightarrow 10 \ln 2 + 10^{-2}(600 - 300) \\ &= 10 \times 0.7 + 3 \\ &= \boxed{10 \text{ J/K}}\end{aligned}$$

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

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

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

(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

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

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

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

9. Ans. $205.08 \text{ JK}^{-1} \text{mol}^{-1}$

$$\begin{aligned}(S_m^{\circ})_{600 \text{ K}} &= (S_m^{\circ})_{0 \text{ K}} + \int_{0}^{200} \frac{(C_p)^{\text{s}} dT}{T} + \frac{\Delta H_{\text{fusion,m}}}{T_m} \\ &+ \int_{200}^{300} \frac{(C_p)^{\text{liq.}} dT}{T} + \frac{\Delta H_{\text{vap,m}}}{T_b} + \int_{300}^{600} \frac{(C_p)^{\text{gas}} dT}{T} \\ &= 205.08 \text{ J/K-mol}\end{aligned}$$

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 its surrounding. The total change in entropy of system is given by ? Suppose heat capacity of each piece is C.

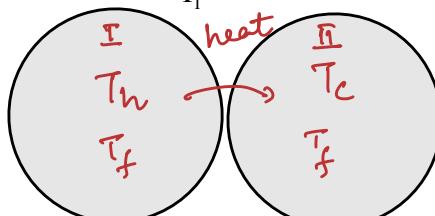
(A) $C \ln \frac{T_c + T_h}{2T_c}$

(B) $C \ln \frac{T_2}{T_1}$

(C) $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$

(D) $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

1. Ans.(D)



$$C(T_h - T_f) = C(T_f - T_c)$$

$$\Rightarrow T_f = (T_h + T_c)/2$$

$$\Delta S_I = C \ln \frac{T_f}{T_h} \quad | \quad \Delta S_{II} = C \ln \frac{T_f}{T_c}$$

$$\Delta S_{\text{Total}} = C \ln \frac{T_f^2}{T_h \cdot T_c} = C \ln \frac{(T_h + T_c)^2}{4T_h \cdot T_c}$$

Q2.

- (A) 1.385 cal/K (B) - 1.2 cal/K (C) 1.2 cal/K (D) 2.77 cal/K

2. Ans.(D)

$$P_2 V_2 = nRT \Rightarrow 1 \times V_2 = 2 \times 0.0821 \times 243.6$$

$$V_2 = 40 \text{ l}$$

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$$= 2 \times 2 \ln \frac{40}{20}$$

$$= 4 \ln 2$$

$$= 4 \times 0.693$$

$$= 2.772 \text{ cal/K}$$

3. For the hypothetical reaction, $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$, $\Delta_r G$ and $\Delta_r S$ are 20 kJ/mole and $-20 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively at 200 K. If $\Delta_r C_p$ is $20 \text{ JK}^{-1} \text{ mol}^{-1}$ then $\Delta_r H$ at 400 K is :-

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

3. Ans.(A)

$$\Delta_r C_{200} = \Delta H_{200} - 200 \Delta S_{200}$$

20 kJ

-20×10^{-3}

$$\Delta H_{200} = 16 \text{ kJ/mol}$$

$$\frac{\Delta H_{400} - \Delta H_{200}}{400 - 200} = \Delta_r C_p$$

$$\frac{\Delta H_{400} - 16}{200} = \frac{20}{1000}$$

$$\Delta H_{400 \text{ K}} = 20 \text{ kJ/mol}$$

4. 1 mole of ice at 0°C is converted in steam at 100°C then calculate 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 $1 \text{ cal gm}^{-1} \text{ degree}$.

(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) $18 \left(\frac{80}{273} + \frac{540}{373} + 100 \right)$

4. Ans.(B)

Sol. $\Delta S_{\text{condensation}} = \frac{-\Delta H_{\text{vap}}}{T} = \frac{-540 \times 18}{373}$

$$\Delta S_{\text{cooling}} = + nC_p \ln \left(\frac{T_2}{T_1} \right) = 18 \ln \left(\frac{273}{373} \right)$$

$$\Delta S_{\text{fusion}} = \frac{-80 \times 18}{273} = - \left[18 \left(\frac{80}{273} + \frac{540}{373} \right) + \left(18 \ln \frac{273}{373} \right) \right]$$

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

5. The value of ΔG_f° of gaseous mercury is 38 kJ/mole. At what total external pressure mercury start boiling at 27°C. ($R \ln 10 = 19 \text{ J/K-mol}$)

(A) $10^{-6.67}$

(B) $10^{-1.67}$

(C) $10^{-13.33}$

(D) $10^{-3.33}$

Ans. (A)



$$\Delta_f G^\circ \quad 0 \quad 38$$

$$\Delta_r G^\circ = 38 - 0 = -2.303 RT \log_{10} K_p^\circ$$

$$\frac{8.3}{1000} \quad 300$$

$$K_p^\circ = 10^{-6.63}$$

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 : $a = 20 \text{ J/mol}$; $b = 10 \text{ J/K-mol}$; $c = 2 \times 10^{-2} \text{ J/K}^2\text{-mol}$] ($\ln 2 = 0.7$)

(A*) 15

(B) 30

(C) 60

(D) 9.78

Ans. (A)

$$[\text{Sol. } \Delta S = n \int \frac{dn dT}{T} = dS = \frac{(b + 2cT)dT}{T}]$$

$$\Delta S = b \ln 2 + 2c (\Delta T)$$

$$= 10 \times 0.7 + 4 \times 10^{-2} \times 200 \Rightarrow 15 \text{ Ans.}]$$

7. Statement -1 : When process $H_2O(s) \rightleftharpoons H_2O(l)$, reaches equilibrium 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.

7. Ans.(A)

$$\text{At } \delta_{\text{m}}, \Delta_r G = 0 = G_{H_2O(l)} - G_{H_2O(s)}$$

i.e. $G_{H_2O(l)} = G_{H_2O(s)}$
 at δ_{m} .

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.

[Sol] Absolute entropies of ions are relative to $H^+(aq)$]

~~Absolute entropy~~
 In case of ions
 there is only
 Relative Entropy.

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.

9. Ans.(A)

$$\cancel{\Delta U = q_r + w} \Rightarrow q_r = -w$$

≈ 0 (cyclic process)

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.

10. Ans.(A)

$$\Delta S = \frac{\cancel{q_r} R w}{T} = n C_v \ln \frac{T_2}{T_1} + n R \ln \frac{V_2}{V_1}$$

11
 0
 - $T_2 < T_1$ + $V_2 > V_1$

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.

11. Ans.(B,D)

A Rev Process $\Delta G = 0$ at const. T & P
for closed System.

C $\Delta S_{\text{univ}} = 0$ for Rev Process
i.e. $\Delta S_{\text{sys}} + \Delta S_{\text{sur}} = 0$ for isolated
system $\Delta S_{\text{sur}} = 0$

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) $\Delta S_{\text{sys}} = 0$ for every adiabatic process in a closed system.
 (D) For every reversible process in a closed system, $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$

12. Ans.(A)

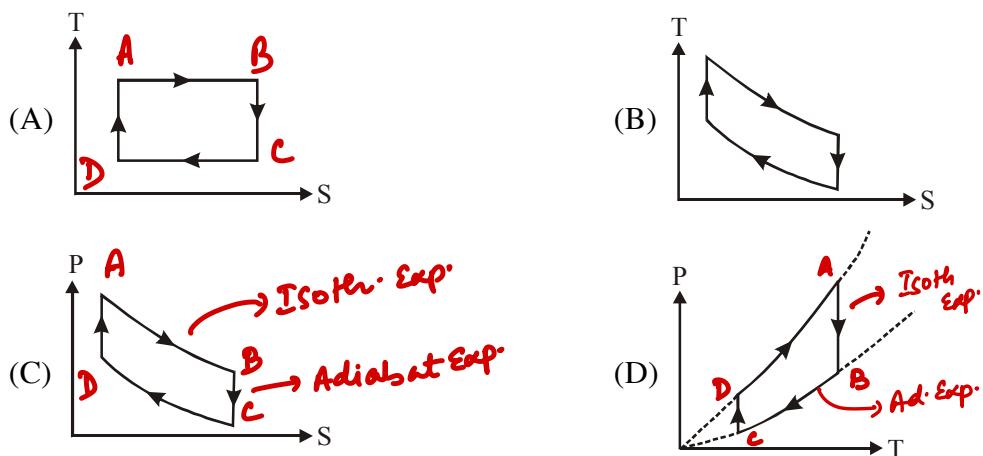
(A) E, H, G \rightarrow Units of Energy
i.e J (J.I.)

(B) $G_{\text{H}_2\text{O}(s)} = G_{\text{H}_2\text{O}(l)}$ at 1 atm
0°C

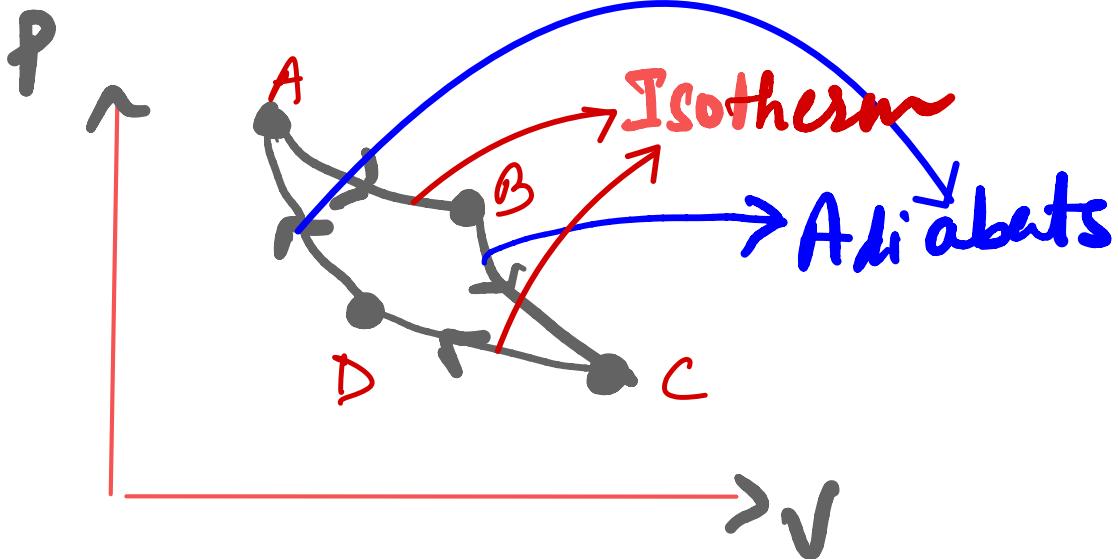
(C) $\Delta S_{\text{sys}} = 0$ for Rev. Ad. process.

(D) $\Delta S_{\text{sys}} = \frac{\Delta H_{\text{sys}}}{T}$ (at const
P & T
for rev.
process)

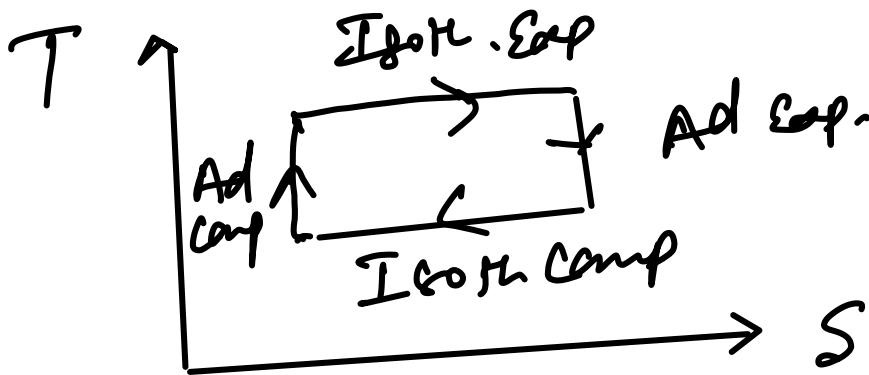
13. Which of the following represents the carnot cycle-



13 Ans (A,C,D)



$$\text{Ad. : } dS = \frac{dq}{T} = 0 \Rightarrow S = \text{const.}$$



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) $\Delta S_{\text{vaporisation}} > 100 \text{ J/K mole}$ at 350 K and 0.5 atm
 (B) $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$ at 350 K and 0.5 atm
 (C) $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$ at 350 K and 2 atm
 (D) $\Delta S_{\text{vaporisation}} = 100 \text{ J/K mole}$ at 350 K and 2 atm

14. Ans.(A,C)

$$\text{At } 350 \text{ K}$$

$$\Delta S = \frac{\Delta H}{T} = \frac{35 \times 10^3}{350} = 100 \frac{\text{J}}{\text{K}}$$

$$\Delta rS_{P_2} - \Delta rS_{P_1} = \Delta n g R \ln \frac{P_1}{P_2} = 100 \times 1 \times 0.5 = 50 \text{ J/K}$$

$$\Delta rS_{0.5 \text{ atm}} - 100 = \ln 2 \Rightarrow \Delta rS_{0.5 \text{ atm}} > 100 \text{ J/K}$$

15. In isothermal ideal gas compression :

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

15. Ans.(A,B,D)

$$(A) w = - \frac{P dV}{+ -} > 0$$

$$(B) dH = n C_p dT = 0$$

$$(C) \Delta S = n R \ln \frac{V_1}{V_2}$$

$$\Delta S > 0 \because (V_2 < V_1)$$

$$(D) dG = V dP - S dT$$

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) ΔG° for an ideal gas is a function of temperature and pressure
- (D) Entropy of a closed system is always maximized at equilibrium

16. Ans.(B,C,D)

(A)

$$\Delta n_g > 0 \Rightarrow \Delta r S > 0$$

(B)

$\Delta G = 0$ for Rev process in closed sys at const T&P

(C)

$\Delta G^\circ = f(T)$ only

(D)

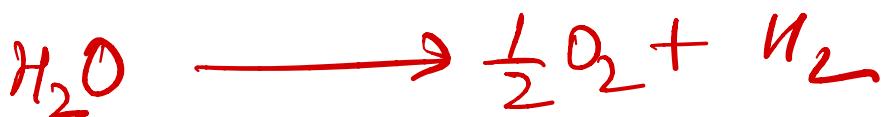
Entropy of closed system and its surroundings is maximised at eqm.

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

17. Ans.[A,C,D]

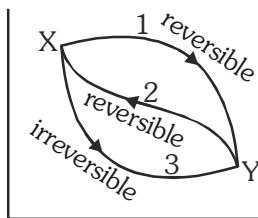
Burning of fossil fuel $\Delta G < 0$



$$\Delta G > 0$$

Non Spont.

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



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

- (A) The state Y is more disordered than state X.
 (B) ΔS_{XY} for path 1 and 3 is same.
 (C) $\Delta S_{YX} = -10 \text{ J/K}$
 (D) The transition X \rightarrow Y must be spontaneous.

- 18.** Ans.[A,B,C]

$$\textcircled{A} \quad S_y - S_x = 10 \Rightarrow S_y > S_x$$

(B) 'S' is a state fn.

$$\textcircled{C} \quad \Delta S_{yx} = -\Delta S_{xy}$$

D ΔS_{sys} alone is not a criteria for spontaneity!

19. Ans.[C]

$$\textcircled{A} \quad \Delta S = nR \ln \frac{V_2}{V_1} > 0 \quad (\because V_2 > V_1)$$

(B) $\Delta S > 0$

$$\textcircled{c} \quad \Delta S = \frac{q_{\text{rev}}}{T} = \frac{0}{T} = 0$$

D Free Exp $\frac{w=0}{q=0}$

$$\Delta T = 0$$

$$T = \text{const}$$

$$\Delta S = n R \ln \frac{V_2}{V_1} > 0$$

20. Ans.[B,C,D]

$$\textcircled{A} \quad \Delta S_{\text{Sur}} = - \frac{\cancel{q'}}{\cancel{T}_{\text{Sur}}} = - \nu e$$

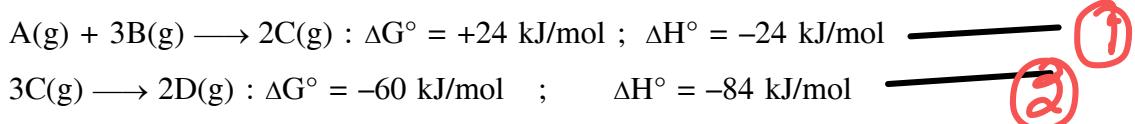
$$\Delta S_{\text{sum}} = - \frac{q_r}{T_{\text{sum}}} \quad \boxed{\begin{array}{l} q_r=0 \\ (B, C, D) \end{array}}$$

B
C
D

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.



All data at 300 K temperature.

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



21. Ans.(A)

$$\textcircled{3} = \textcircled{1} \times 3 + \textcircled{2} \times 2$$

$$\begin{aligned}\Delta H_3^\circ &= 3\Delta H_1^\circ + 2\Delta H_2^\circ \\ &= 3(-24) + 2(-84) = -240 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\Delta G_3^\circ &= 3\Delta G_1^\circ + 2\Delta G_2^\circ \\ &= 3(24) + 2(-60) \\ &= 72 - 120 \\ &= -48 \text{ kJ/mol}\end{aligned}$$

$$\begin{aligned}\cancel{\Delta G_3^\circ} &= \Delta H_3^\circ - T\Delta S_3^\circ \\ -48 &= -240 - 300 \Rightarrow \Delta S_3^\circ = -0.640 \text{ J/K} \\ &= -640 \text{ J}\end{aligned}$$

22. Assuming ΔH° and ΔS° do not vary with temperature. At what minimum temperature reaction $A(g) + 3B(g) \rightarrow 2C(g)$ become spontaneous-
- (A) 6250 K (B) 625 K (C) 150 K (D) 1000 K

22. Ans.(C)

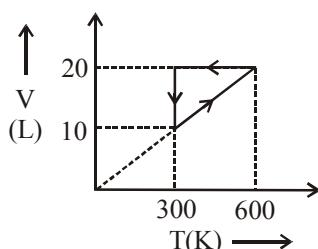
22

$$T_g = \frac{\Delta H}{\Delta S} = \frac{-24}{-48/3} \Rightarrow T_g = 150 \text{ K}$$

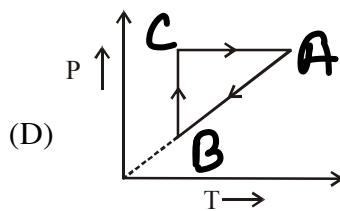
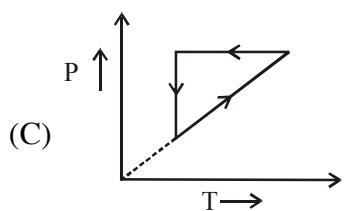
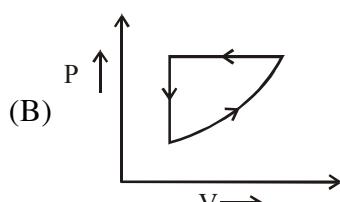
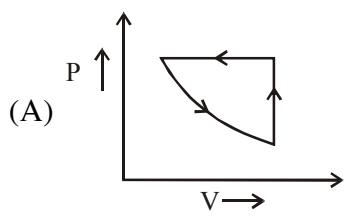
$$\because (+24 = -24 - 3 \text{ J K}^{-1} \text{ mol}^{-1} \Delta S) \quad =$$

Paragraph for Q.23 to Q.24

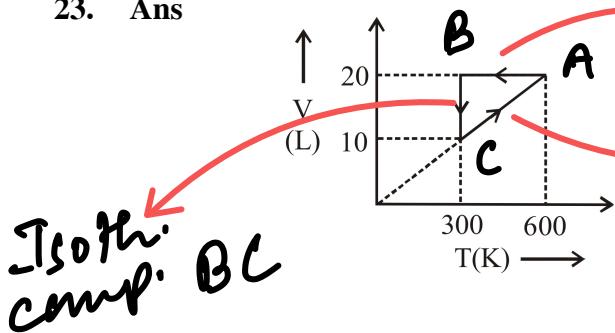
One mol of ideal monoatomic gas undergo the state change as shown in the following graph ($\ln 2 \equiv 0.7$)



- 23.** Correct graph for the process in paragraph is -



23. Ans



Isoch. cooling AB

→ To basic heating

- 24.** Efficiency of the cycle will be -

- 24.** Ans.(D)

$$q_{abs} = nC_p \Delta T = 1 \times \frac{5R}{2} \times 300 = 750 R$$

$$W_{next} = W_I + W_{II} + W_{III} \\ \equiv -1 \times R \times 300 + 0 + 1 \times 300 \times R \ln 2$$

$$\therefore |W| = 300 \text{ R} (1 - 0.7) = 300 \text{ R} \times 0.3 = 90 \text{ R}$$

$$= \frac{|\text{W}|}{q_{\text{abs}}} \times 100 = \frac{90}{750} \times 100 = 12\%$$

MATCH THE LIST :

25

Match the Column :

Column-I

- (P) $\text{H}_2\text{O} (\ell, 1 \text{ atm}, 363 \text{ K})$
 $\rightarrow \text{H}_2\text{O} (\text{g}, 1 \text{ atm}, 363 \text{ K})$
- (Q) $\text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 373 \text{ K})$
 $\rightarrow \text{H}_2\text{O} (\text{g}, 1 \text{ atm}, 373 \text{ K})$
- (R) $\text{H}_2\text{O} (\ell, 1 \text{ atm}, 273 \text{ K})$
 $\rightarrow \text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 273 \text{ K})$
- (S) $\text{H}_2\text{O} (\text{s}, 1 \text{ atm}, 353 \text{ K})$
 $\rightarrow \text{H}_2\text{O} (\ell, 1 \text{ atm}, 353 \text{ K})$

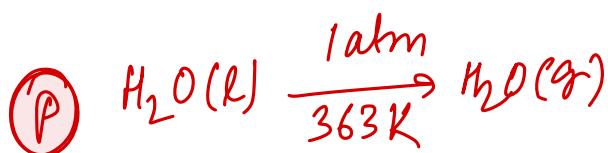
Column-II

- (1) $\Delta_r S > 0$
- (2) $\Delta_r G > 0$
- (3) $\Delta_r H < 0$
- (4) $\Delta_r U > 0$

Code:

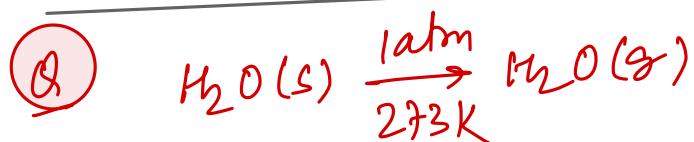
	P	Q	R	S
(A)	2	4	1	3
(B)	4	2	3	1
(C)	2	1	3	4
(D)	4	3	1	2

Ans.(C)



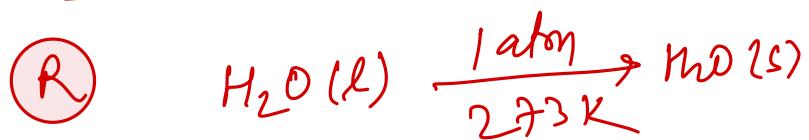
$$\Delta H > 0 \quad \Delta S > 0$$

$$\Delta U > 0 \quad \Delta G > 0$$



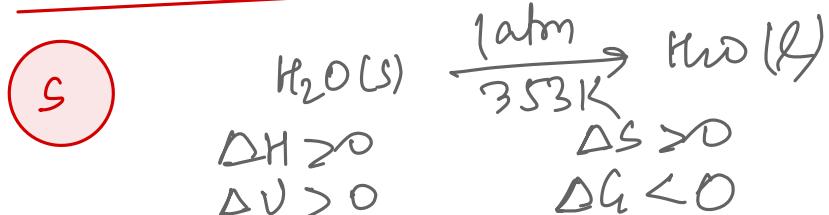
$$\Delta H > 0 \quad \Delta S > 0$$

$$\Delta U > 0 \quad \Delta G > 0$$



$$\Delta H < 0 \quad \Delta S < 0$$

$$\Delta U < 0 \quad \Delta G = 0$$



$$\Delta H > 0 \quad \Delta S > 0$$

$$\Delta U > 0 \quad \Delta G < 0$$

MATCH THE COLUMN :

Column-I

- 26.**
- (A) Reversible adiabatic compression
 - (B) Reversible vaporisation
 - (C) Adiabatic free expansion of ideal gas in vacuum
 - (D) Dissociation of
 $\text{CaCO}_3(\text{s}) \longrightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Column-II

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

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

(A) Rev Ad. $\Delta S_{\text{sys}} = 0, \Delta S_{\text{surrr}} = 0, \Delta S_T = 0$

(B) Rev vapⁿ $\Delta S > 0, \Delta S_{\text{surrr}} < 0, \Delta S_{\text{Total}} = 0$

(C) Ad. free exp. $\Delta S > 0, \Delta S_{\text{surrr}} = 0, \Delta S_T > 0$

(D) $\Delta n_g > 0 \Rightarrow \Delta S_{\text{sys}} > 0 \& \Delta S_{\text{surrr}} < 0$

27**Column-I**

(Related to process)

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

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

Column-II

(Related to system)

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

Ⓐ

$S \rightarrow L$ at T_m^{in} $\Delta G = 0, \Delta S > 0,$
 $\therefore \Delta(PV) \approx 0 \Rightarrow \Delta H \approx \Delta U$

Ⓑ

$L \rightarrow g$ at T_b^{in} $\Delta G = 0, \Delta S > 0$
 $\Delta n_g > 0 \Rightarrow \Delta H > \Delta U$

Ⓒ

$g \rightarrow L$ at T_c^{in} $\Delta G = 0, \Delta S < 0$
 $(\Delta n_g < 0)$

 $\Delta H < \Delta U$

Ⓓ

$S \xrightarrow[\text{B.P.}]{\text{act. N.}} L$ $\Delta G < 0, \Delta S > 0$
 $\Delta H \approx \Delta U$
 $\therefore \Delta(PV) \approx 0$