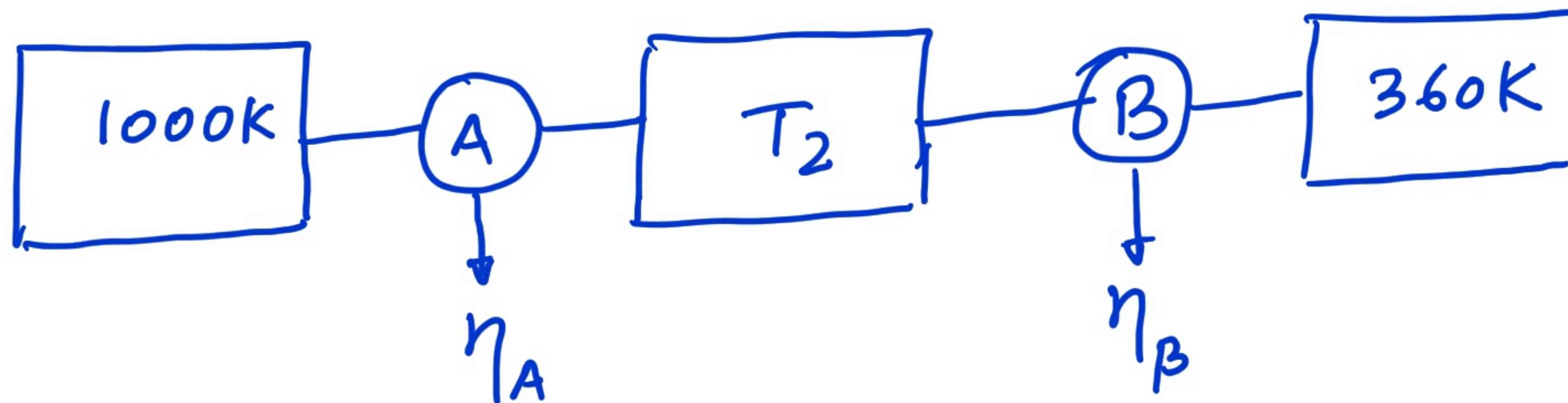


1. A reversible heat engine A (based on carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at T_2 . A second reversible engine B (based on carnot cycle) absorbs the same amount of heat as rejected by the engine A, from the reservoir at T_2 and rejects energy to a reservoir 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



$$\eta_A = \eta_B$$

$$\text{or, } \frac{1000 - T_2}{1000} = \frac{T_2 - 360}{T_2}$$

$$\text{or, } 1 - \frac{T_2}{1000} = 1 - \frac{360}{T_2}$$

$$\text{or, } \frac{T_2}{1000} = \frac{360}{T_2}$$

$$\text{or, } T_2^2 = 36 \times 10^4$$

$$\text{or, } T_2 = \boxed{600\text{K}}$$

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

(A) $Q_{\text{sys}} + Q_{\text{surr}} = 0 \rightarrow \text{correct}$

(C) $\Delta U_{\text{sys}} + \Delta U_{\text{surr}} = 0 \rightarrow \text{correct}$

(B) $W_{\text{sys}} + W_{\text{surr}} = 0 \rightarrow \text{correct}$

(D) $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \rightarrow \text{incorrect}$

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \boxed{\Delta S_{\text{total}} \geq 0}$$

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

- (A) Zero
 (C) Negative

- (B) Positive
(D) Can not be predicted

Entropy of $C(\text{graphite}) > C(\text{diamond})$

$\therefore \boxed{\Delta S < 0}$

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

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

(B) $\Delta S_{\text{system}} > 0$ only

(C) $\Delta S_{\text{surroundings}} > 0$ only

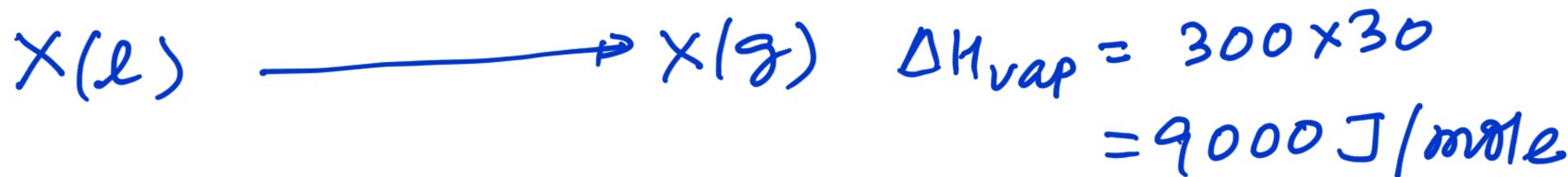
(D) $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

for a process to be spontaneous

$$\Delta S_{\text{total}} > 0$$

$$\text{or, } \boxed{\Delta S_{sys} + \Delta S_{sur} > 0}$$

5. If $\Delta H_{\text{vaporisation}}$ of substance X(l) (molar mass = 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is :-
- (A) 30 J/mol.K (B) -300 J/mol.K (C) -30 J/mol.K (D) -10 J/mol.K



$$T_{\text{bp}} = 300 \text{ K.}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{bp}}} = \frac{9000}{300} = 30 \text{ JK}^{-1}\text{mol}^{-1}.$$

$$\underline{\Delta S_{\text{condensation}}} = -\Delta S_{\text{vap}} = \boxed{-30 \text{ JK}^{-1}\text{mol}^{-1}.}$$

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
 $(R = 2 \text{ Cal/mol-K})$

- (A) $R \ln 2$ ~~(B) $2R \ln 2$~~ (C) $3R \ln 2$ (D) $\frac{R}{2} \ln 2$

$$\frac{T_2}{T_1} = 2, \quad \frac{P_2}{P_1} = \sqrt{2}$$

$$\Delta S = nC_{P_m} \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2}$$

$$= 1 \times \frac{5}{2} R \ln 2 + 1 \times R \ln \frac{1}{\sqrt{2}}$$

$$= \frac{5}{2} R \ln 2 - \frac{1}{2} R \ln 2$$

$$= R \ln 2 \left[\frac{5}{2} - \frac{1}{2} \right] = \boxed{2R \ln 2} \text{ Ans.}$$

7. If S° for H_2 , Cl_2 and HCl are 0.13, 0.22 and $0.19 \text{ kJ K}^{-1} \text{ mol}^{-1}$ respectively. The total change in standard entropy for the reaction, $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$ is :
- (A) $30 \text{ JK}^{-1} \text{ mol}^{-1}$ (B) $40 \text{ JK}^{-1} \text{ mol}^{-1}$ (C) $60 \text{ JK}^{-1} \text{ mol}^{-1}$ (D) $20 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\begin{aligned}\Delta S^\circ &= \{S^\circ\}_P - \{S^\circ\}_R \\ &= (2 \times 0.19) - (0.13 + 0.22) \\ &= 0.38 - 0.35 = 0.03 \text{ KJ K}^{-1} \text{ mol}^{-1} \\ &= \boxed{30 \text{ JK}^{-1} \text{ mol}^{-1}}.\end{aligned}$$

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

$$C_{p,m} = aT^3$$

$$\text{or, } 0.42 = a \times (10)^3 \Rightarrow a = 0.42 \times 10^{-3}.$$

$$S_{m,\text{at } 10K} = \int_0^{10} \frac{C_{p,m} dT}{T} = \int_0^{10} \frac{aT^3}{T} dT = \int_0^{10} aT^2 dT$$

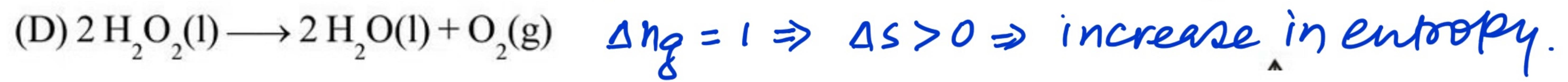
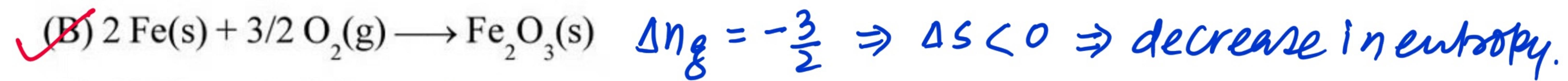
$$= \left[\frac{aT^3}{3} \right]_0^{10} = \frac{0.42 \times 10^{-3}}{3} [1000]$$

$$= \boxed{0.14 \text{ J K}^{-1} \text{ mol}^{-1}}$$

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.

It is 3rd law of thermodynamics.

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



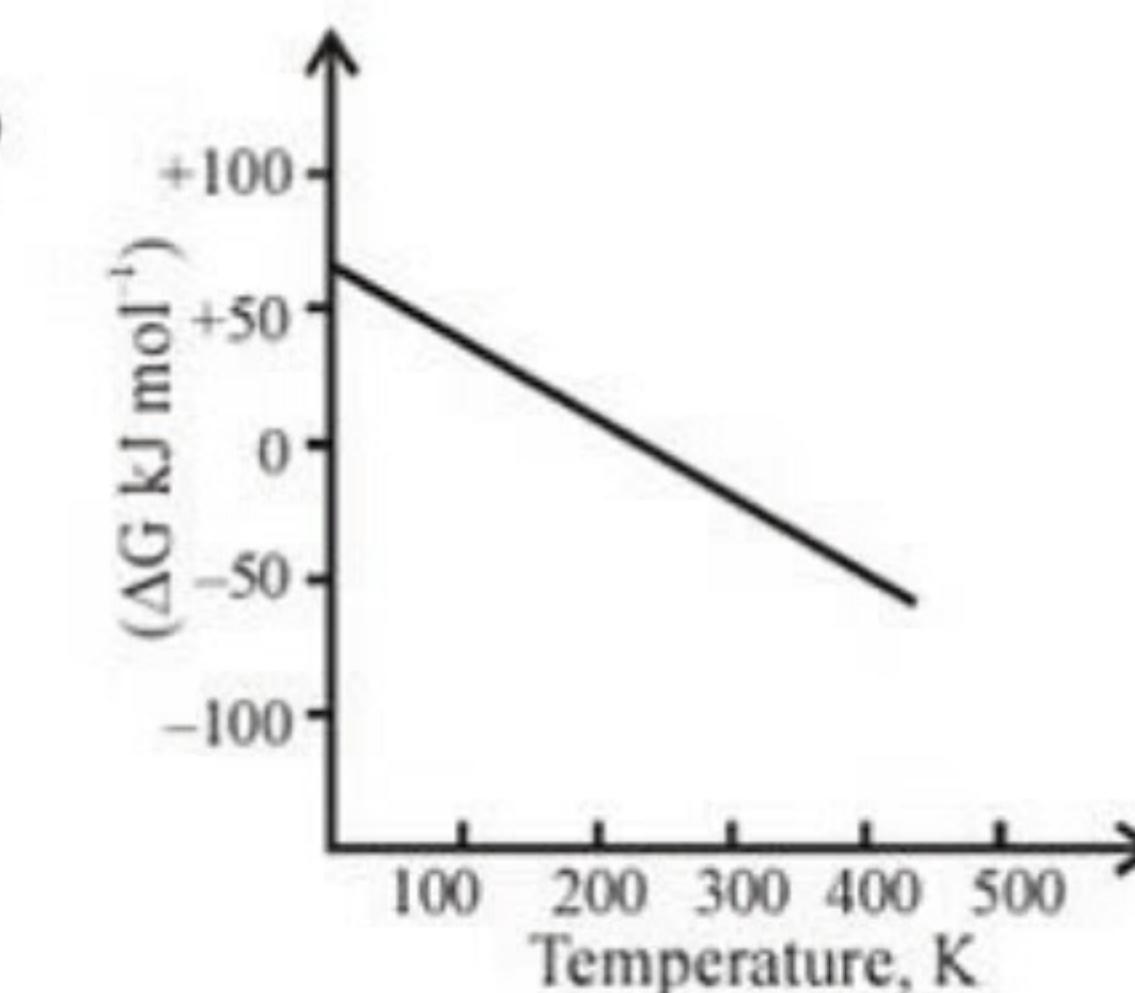
11. What can be concluded about the values of ΔH and ΔS from this graph?

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

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

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

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



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

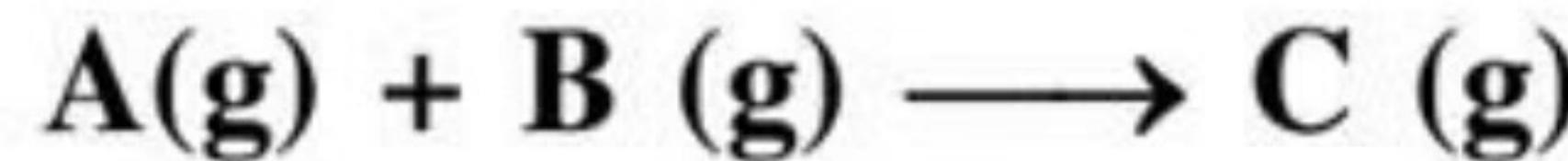
From graph it is clear that when $T=0$ Kelvin, $\Delta G > 0$

$$\Rightarrow \boxed{\Delta H > 0}$$

Also, from graph it is clear that as T increases

ΔG_f decreases $\Rightarrow \boxed{\Delta S > 0}$

12. For the reaction at 300 K



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

value of ΔG is ?

(A) -600 cal

(B) -6600 cal

(C) -6000 cal

(D) none

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

$$\text{so, } \Delta H = -3 + \frac{(-1) \times 2 \times 300}{1000}$$

$$= -3 - 0.6 = -3.6 \text{ KCal.}$$

$$\Delta G_1 = \Delta H - T \Delta S = -3.6 - \frac{300 \times (-10)}{1000}$$

$$= -3.6 + 3 = -0.6 \text{ KCal} = \boxed{-600 \text{ Cal.}}$$

13. For the reaction that taking place at certain temperature $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$, if equilibrium pressure is X bar, then $\Delta_r G^\circ$ would be :-

(A) $-2 \text{ RT} \ln X$ (B) $-\text{RT} (\ln X - \ln 2)$
~~(C) $-2 \text{ RT} (\ln X - \ln 2)$~~ (D) $-0.5 \text{ RT} (\ln X - \ln 2)$



Ateg.

$$\frac{x}{2} \text{ bar}$$

$$K_P = P_{NH_3} \times P_{H_2S} = \frac{x}{2} \times \frac{x}{2} = \frac{x^2}{4}$$

$$\Delta G^\circ = -RT \ln K_p = -RT \ln \frac{x^2}{4} = -RT [\ln x^2 - \ln 4]$$

$$\text{or, } \Delta G^\circ = -RT [2\ln x - 2\ln 2]$$

or, $\Delta G^\circ = -2RT(\ln x - \ln 2)$

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

100°C at 1atm = Normal boiling point, which is equilibrium condition.

∴

$$\boxed{\Delta G_f = 0}$$

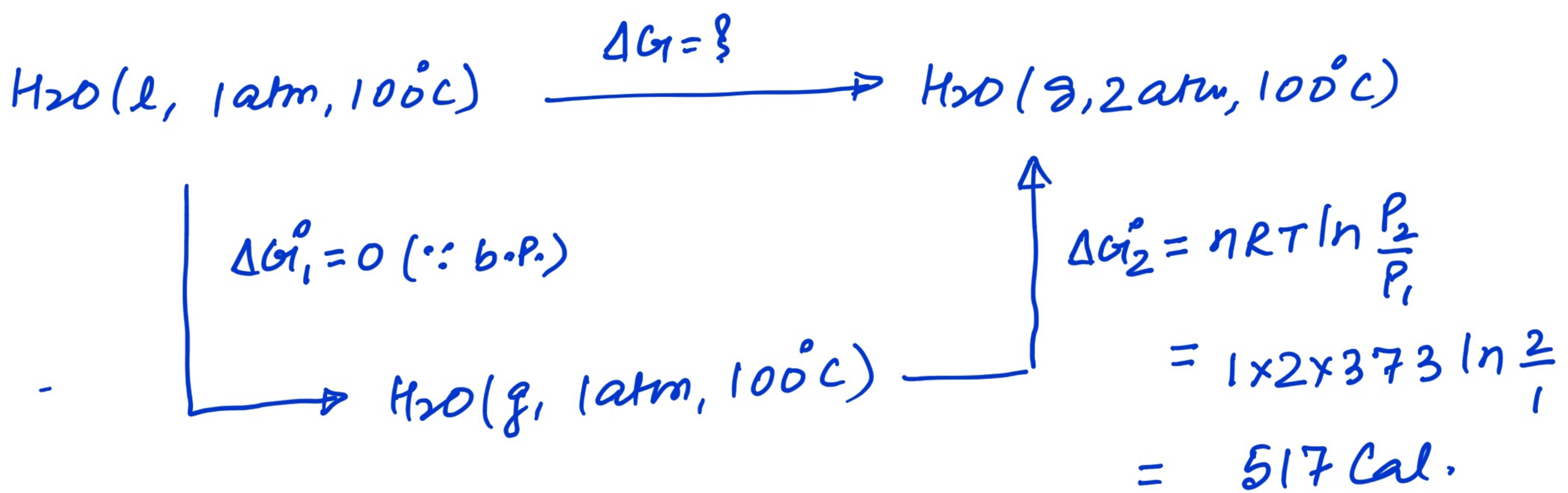
15. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure ?

(A) Zero

(B) 540 cal

~~(C) 517.13 cal~~

(D) 510 cal



$$\begin{aligned}\Delta G_1 &= \Delta G_1^{\circ} + \Delta G_2^{\circ} \\ &= 0 + 517 = \boxed{517 \text{ Cal}}\end{aligned}$$

16. If $\Delta G^\circ > 0$ 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

$$\begin{aligned}\Delta G^\circ &> 0 \\ \Rightarrow -RT \ln K_p &> 0 \\ \Rightarrow \ln K_p &< 0 \\ \Rightarrow \boxed{K_p < 1}\end{aligned}$$

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

rev. isothermal process, $q = -1200 \text{ cal}$, $T = 300 \text{ K}$. $\Delta G_1 = ?$

$$dG_1 = VdP - SdT^0 \quad (\because T = \text{const})$$

$$\text{or, } dG_1 = \frac{nRT}{P} dP$$

$$\text{or, } \int_{G_1}^{G_2} dG_1 = nRT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Rightarrow \Delta G_1 = nRT \ln \frac{P_2}{P_1} = W = -q \quad (\because \Delta V = 0 \\ \therefore W = -q)$$

$$\text{or, } \Delta G_1 = -(-1200)$$

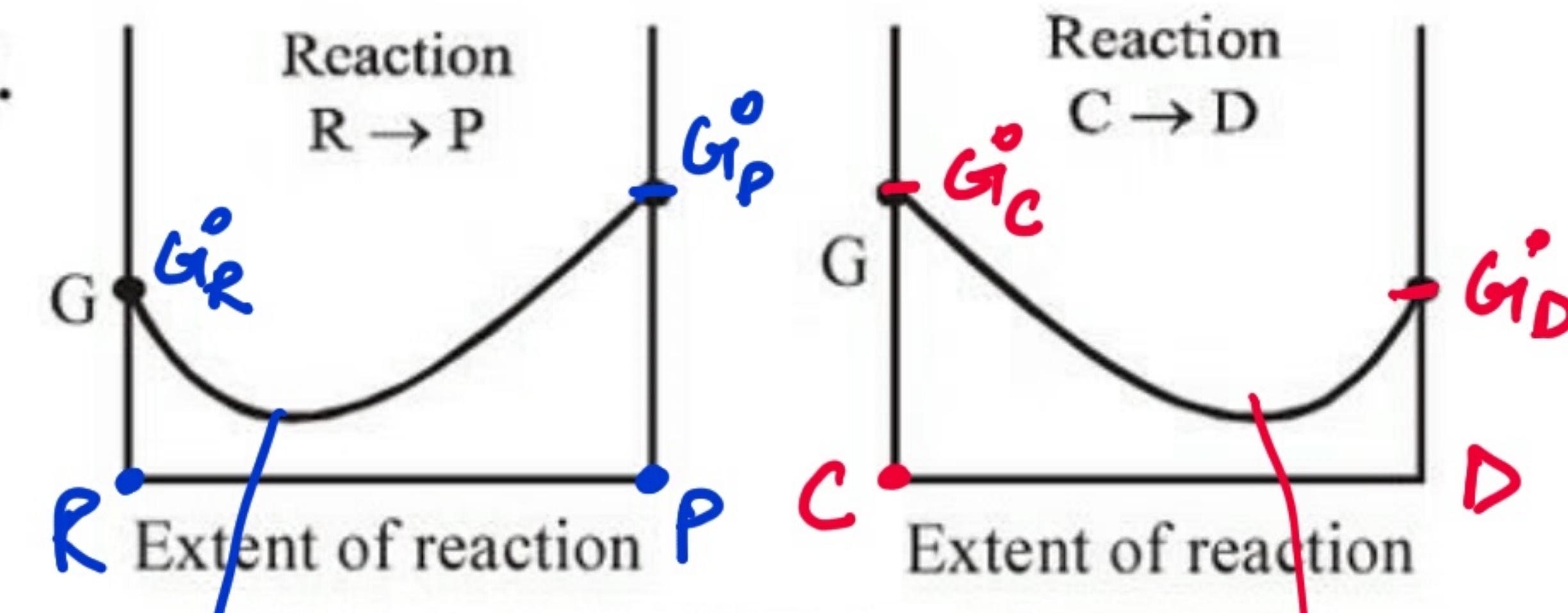
$$= 1200 \text{ cal}_-$$

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.

R will also be partially converted into P.

and neither C nor R will be completely converted.



[At constant temperature & pressure]

$$\Delta G^\circ = G_P^\circ - G_R^\circ > 0$$

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

$$\text{or, } \ln K = \frac{\Delta G^\circ}{-RT} < 0$$

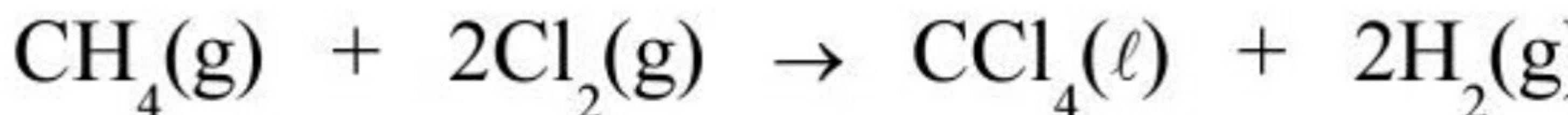
$$\Rightarrow \boxed{K < 1}$$

$$\Delta G^\circ = G_D^\circ - G_C^\circ < 0$$

$$\Rightarrow -RT \ln K < 0$$

$$\Rightarrow \boxed{K > 1}$$

19. Evaluate ΔS° for the reaction below at 25°C.



Given :

	$\text{CH}_4(\text{g})$	$\text{Cl}_2(\text{g})$	$\text{CCl}_4(\text{l})$	$\text{H}_2(\text{g})$
ΔH_f° (kJ/mol)	-74.81	0	-135.4	0
ΔG_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	

$$\begin{aligned}\Delta H^\circ &= \sum (\Delta H_f^\circ)_P - \sum (\Delta H_f^\circ)_R = (-135.4 + 0) - (-74.81 + 0) \\ &= -60.59 \text{ kJ mol}^{-1}.\end{aligned}$$

$$\Delta G^\circ = \sum (\Delta G_f^\circ)_P - \sum (\Delta G_f^\circ)_R = -65.27 - (-50.75) = -14.52 \text{ kJ mol}^{-1}.$$

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

$$\text{or, } -14.52 = -60.59 - \frac{298 \times \Delta S^\circ}{1000} \Rightarrow \boxed{\Delta S^\circ = -154.59 \text{ J K}^{-1}}$$

20. All of the following have $\Delta G_f^\circ = 0$, except -

- (A) O₂(g) ~~(B) Br₂(g)~~ (C) H₂(g) (D) Ca(s)

$$\Delta G_f^\circ \text{ Br}_2 \text{ (liquid)} = 0$$

