

THERMODYNAMICS

(iv) for chemical Rxn

$$\Delta n_g > 0$$

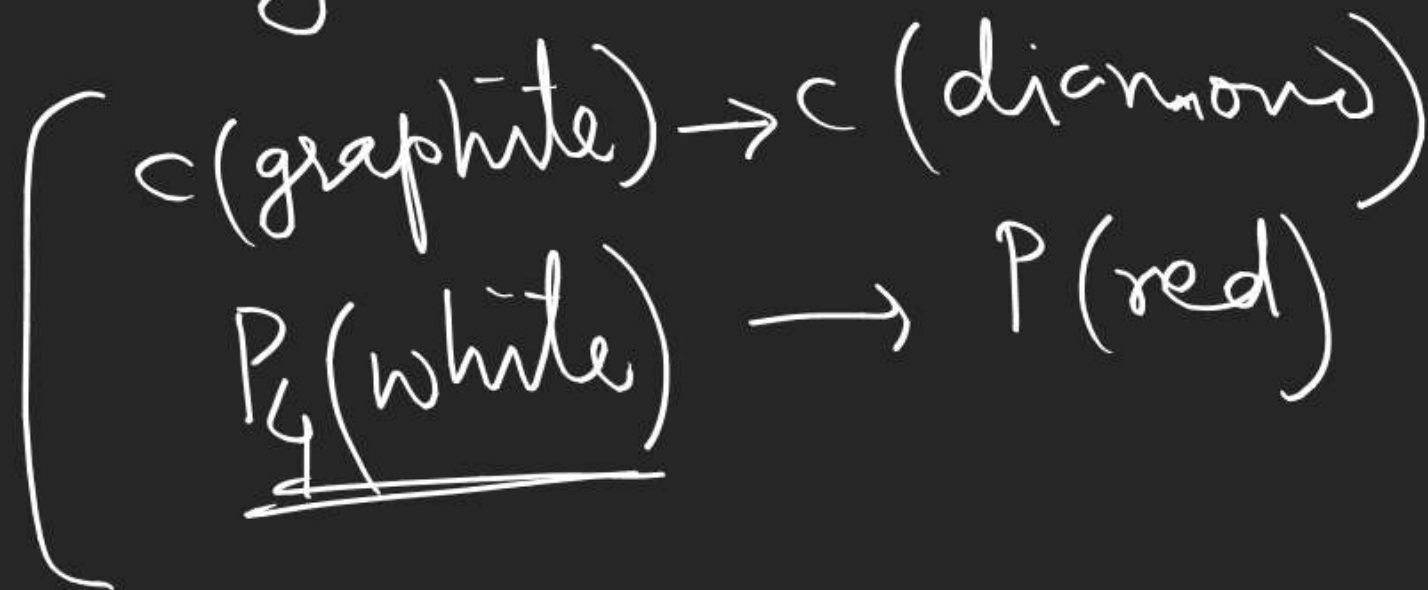
$$\Delta S_{sys} > 0$$

$$\Delta n_g < 0$$

$$\Delta S_{sys} < 0$$

$$\rightarrow \Delta n_g = 0$$

$$\Delta S_{sys} \neq 0$$

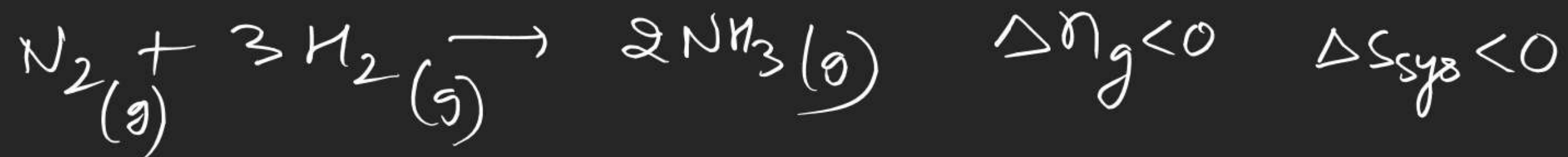


$$\Delta n_g = 0$$

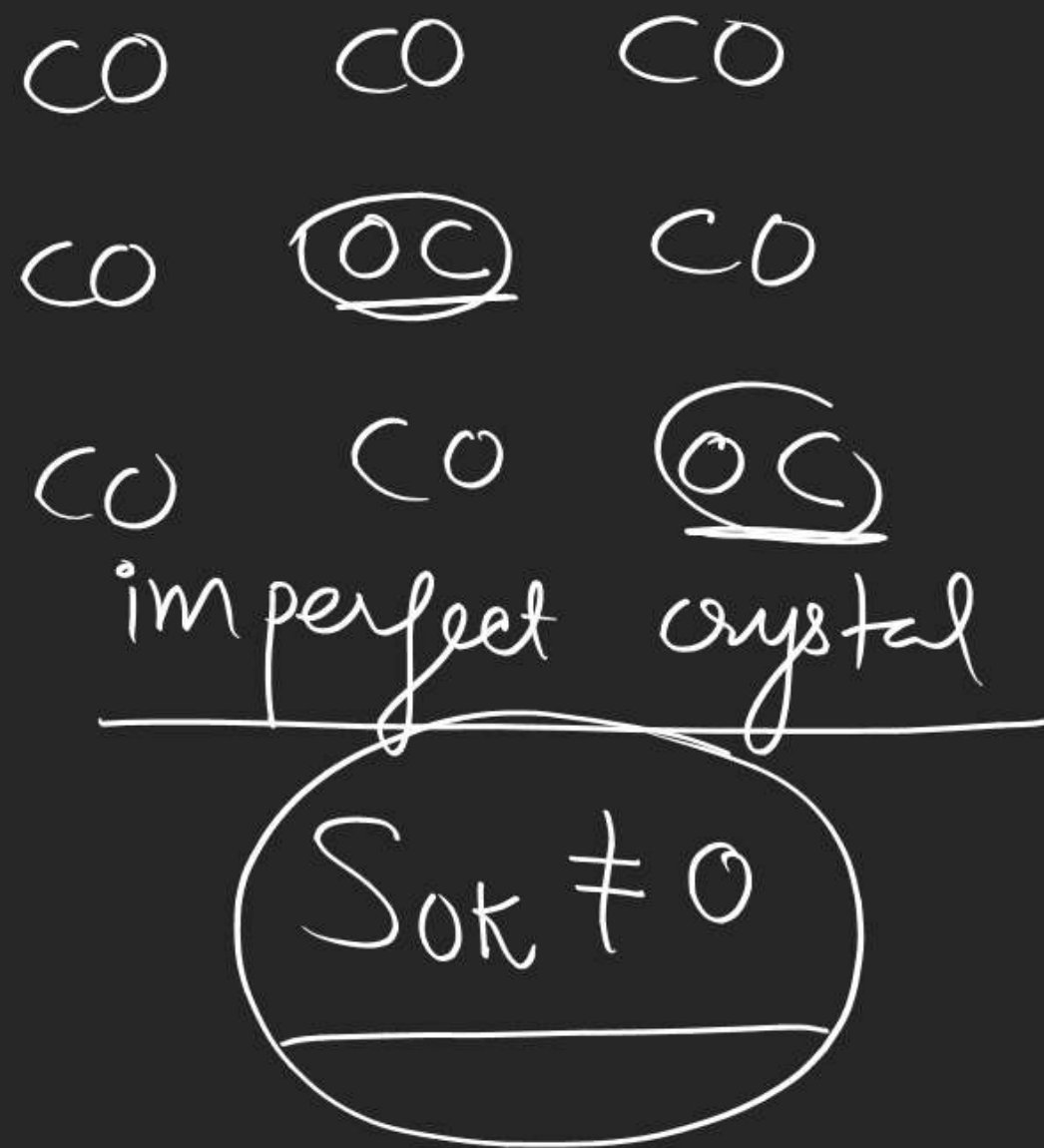
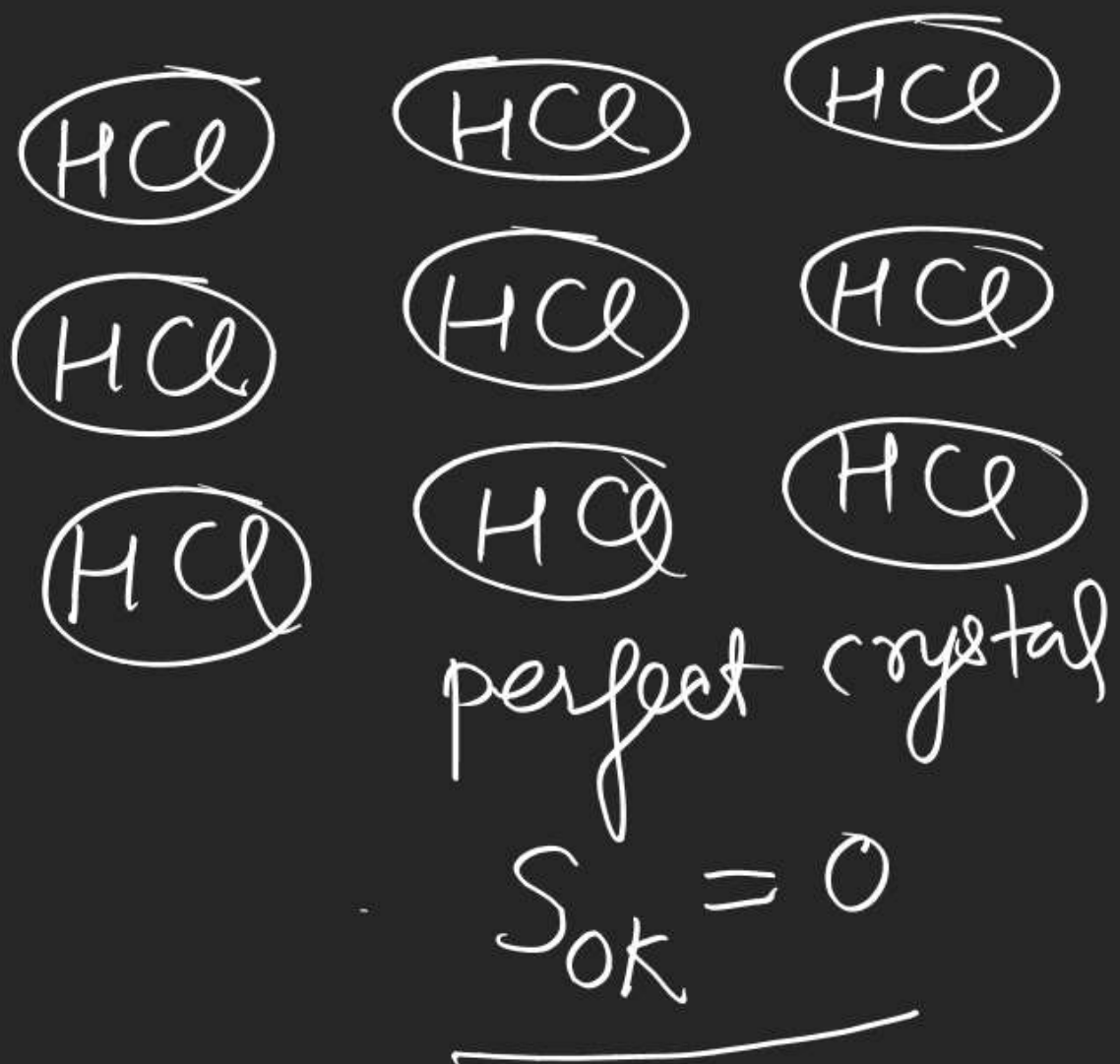
$$\underline{\underline{\Delta S_{sys} < 0}}$$

$$\Delta S_{sys} < 0$$

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3rd Law of T.D: \rightarrow At 0 K temperature, entropy of a perfect crystal is zero.



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for Numerical problem entropy of any sub can be considered to be zero at 0 K.

Applⁿ 3rd law of T.D.: \rightarrow

① To determine absolute entropy of a substance at

given T & P $\text{Sub}(0\text{K}, P) \rightarrow \text{Sub}(T, P)$

$$S_T - \cancel{S_{0\text{K}}} = \Delta S = \int_0^T n C_p \frac{dT}{T}$$

$$S_T = \int_0^T n C_p \frac{dT}{T}$$

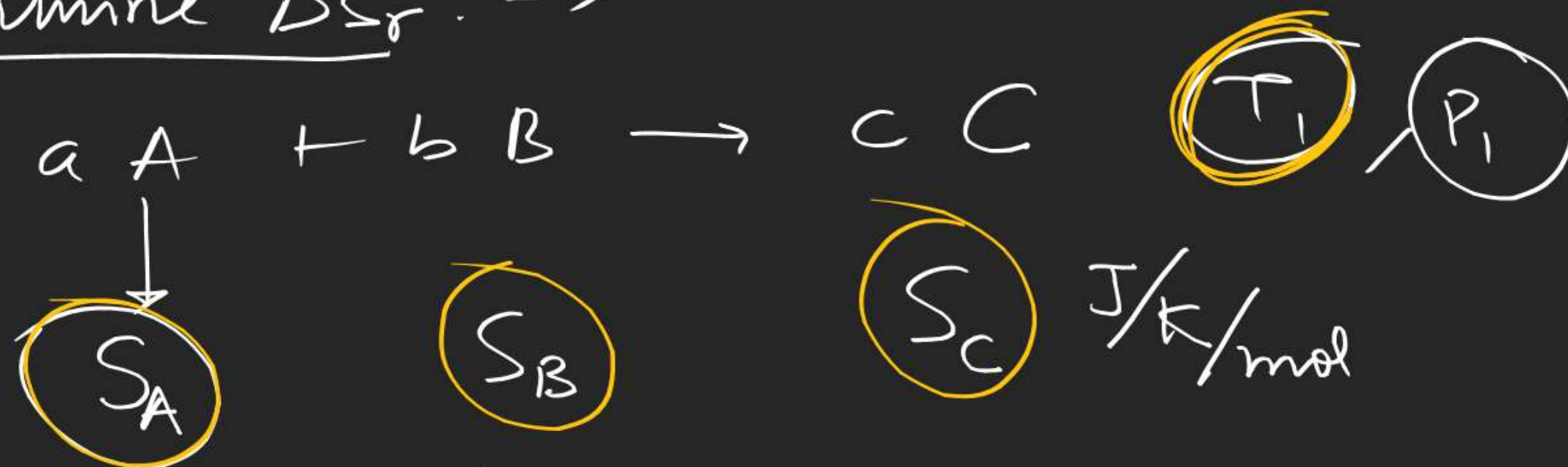
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$$\underline{S_T} = \int_0^{T_{m.pt}} n C_p \frac{dT}{T} + \frac{\Delta H_{fusion}}{T_{m.pt}} + \int_{T_{m.pt}}^{T_{b.pt}} n C_p(lig) \frac{dT}{T} + \frac{\Delta H_{vap}}{T_{b.pt}} + \int_{T_{b.pt}}^T n C_p \frac{dT}{T}$$

25°C, 1 bar

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② To determine ΔS_r : \rightarrow



$$\Delta S_r = (c S_C) - (a S_A + b S_B)$$

$$\rightarrow \Delta S_r = \sum S(P_r) - \sum S(R)$$

for chemical Rxn

$$\Delta S_{\text{sur}} = - \frac{Q_{\text{sys}}}{T}$$

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$$(\Delta S_r)_{T_2} = c(S_c)_{T_2} - a(S_A)_{T_2} - b(S_B)_{T_2}$$

$$\Rightarrow \Delta S = \int_{T_1}^{T_2} n C_p \frac{dT}{T}$$

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} C_p \frac{dT}{T}$$

$$c \times [(S_c)_{T_2} - (S_c)_{T_1}] = \int_{T_1}^{T_2} (C_p)_c \frac{dT}{T} = (C_p)_c \ln \frac{T_2}{T_1}$$

$$a \times [(S_A)_{T_2} - (S_A)_{T_1}] = (C_p)_A \ln \frac{T_2}{T_1}$$

$$b \times [(S_B)_{T_2} - (S_B)_{T_1}] = (C_p)_B \ln \frac{T_2}{T_1}$$

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = [c(C_p)_c - a(C_p)_A - b(C_p)_B] \times \ln \frac{T_2}{T_1}$$

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1} = (\Delta C_p)_r \ln \frac{T_2}{T_1}$$

$$(\Delta C_p)_r = C_p(\text{pr}) - C_p(\text{R})$$

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0-1

g — 21

5-1

g — 16

61. An ideal gas is subjected to cyclic process involving four thermodynamic states, the amounts of heat (Q) involved in each of these processes are -

$$Q_1 = 6000 \text{ J}, \quad Q_2 = -5500 \text{ J}; \quad W_{\text{Total}} = -Q_{\text{Total}} = -1000$$
$$Q_3 = -3000 \text{ J}; \quad Q_4 = 3500 \text{ J}$$

The ratio of the net work done by the gas to the total heat absorbed by the gas is η . The value η is

- (A) 7.5% (B) 10.5% (C) 21% (D) 100 %

$$\frac{1000}{9500}$$

64. The entropy change when two moles of ideal monoatomic gas is heated from 200 °C to 300 °C reversibly and isochorically is

(A) $\frac{3}{2} R \ln \left(\frac{300}{200} \right)$

(B) $\frac{5}{2} R \ln \left(\frac{573}{473} \right)$

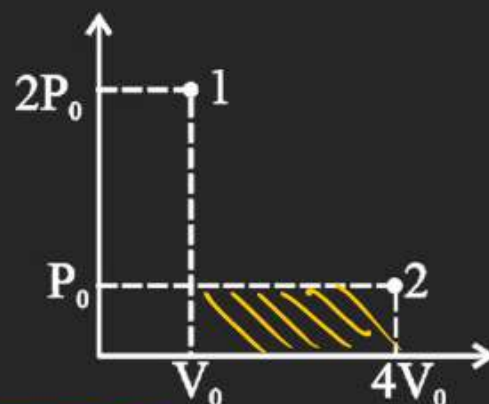
(C) $3R \ln \left(\frac{573}{473} \right)$

(D) $\frac{3}{2} R \ln \left(\frac{573}{473} \right)$

67. Select correct statements -

- F (A) $\int \frac{dq}{T}$ is always independent of path followed between two points
- F (B) Entropy of universe is conserved
- T (C) For a process in isolated system entropy either increases or remain constant
- F (D) Entropy decreases with increase in temperature at constant V

70. A liquid confined inside an adiabatic container is suddenly taken from state 1 to state 2 by single stage process as shown, then ΔH is



(A) $\Delta H = \frac{2\gamma P_0 V_0}{\gamma - 1}$

(B) $\Delta H = P_0 V_0$

(C) $\Delta H = -3P_0 V_0$

(D) $\Delta H = \frac{3\gamma P_0 V_0}{\gamma - 1}$

$$\Delta U = W = -P_0(4V_0 - V_0) = -3P_0 V_0$$

$$\Delta H = \Delta U + (4P_0 V_0 - 2P_0 V_0)$$

$$= \underline{\underline{-P_0 V_0}}$$

79. The density of a pure substance 'A' whose atoms pack in cubic close pack arrangement is 1 gm/cc. If B atoms can occupy tetrahedral void and if all the tetrahedral voids are occupied by 'B' atom. What is the density of resulting solid in gm/cc.

[Atomic mass (A) = 30 gm/mol & Atomic mass (B) = 50 gm/mol]

(A) 3.33

(B) 4.33

(C) 2.33

(D) 5.33

$$A - 4 \rightarrow 120 \text{ gm} \rightarrow \text{1 gm/cc}$$

$$B - 8 \rightarrow 400 \text{ gm} \rightarrow \frac{1}{120} \times 400 = \frac{10}{3} = 3.33$$

81. 1 mol He initially at 300 K are undergoing a process, $T = kV^2$ where its volume is doubled. Calculate $|w|$ (in cal) during the process.

$$\frac{PV}{nR} = T = kV^2$$

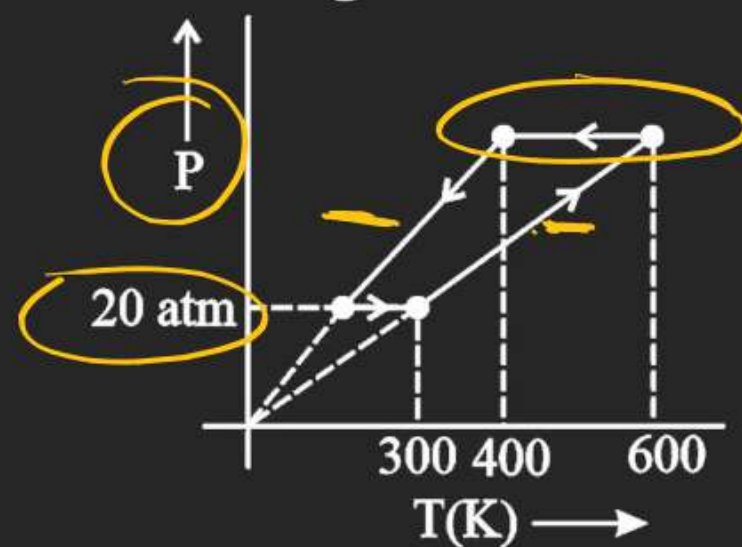
$$PV^{-1} = \text{Const}$$

$$\gamma = -1$$

$$\frac{nR\Delta T}{\gamma - 1}$$

$$300 \rightarrow 1200$$

84. Calculate the magnitude of work done (in atm lit.) for the given cyclic process involving 1 mol of an ideal gas. [Given: $R = 0.08 \text{ atm lit./mol/K}$]



87. In an ionic crystal anion 'B' are present in ccp. If cation 'A' occupy all octahedral voids & also half of tetrahedral voids. If simplest formula of compound is A_xB then what is 'x'

$$\begin{array}{r} 6 \quad \cancel{7} + \underline{3} \\ \hline \begin{array}{c} \text{+4} \quad \text{-1} \\ \downarrow \end{array} \end{array} \quad \begin{array}{c} \text{+4} \quad \text{-1} \end{array}$$