

THERMODYNAMICS

IV for chemical Rxn

$$\Delta n_g > 0$$

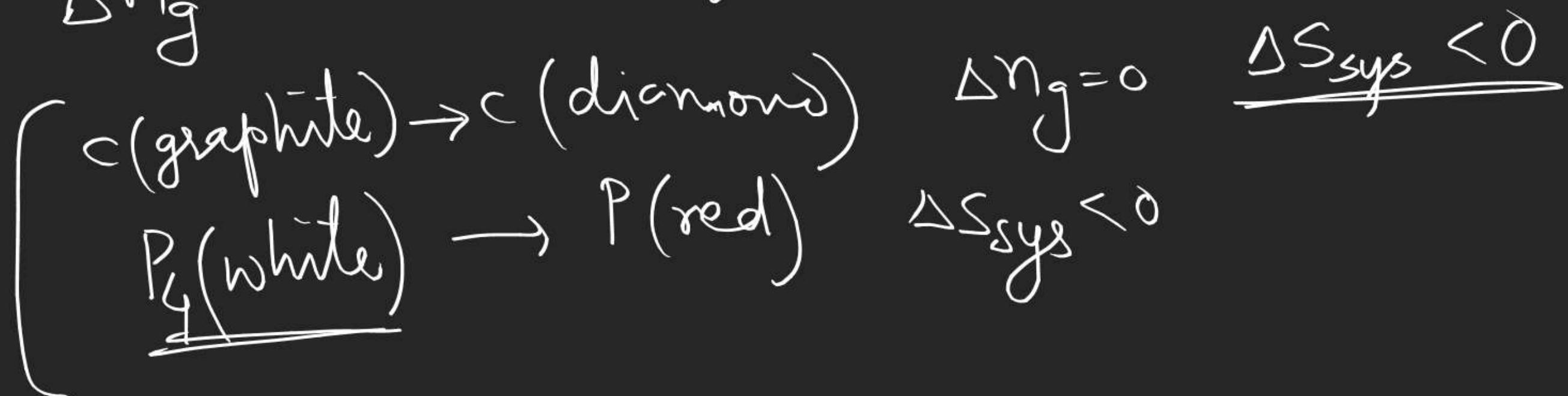
$$\Delta S_{sys} > 0$$

$$\Delta n_g < 0$$

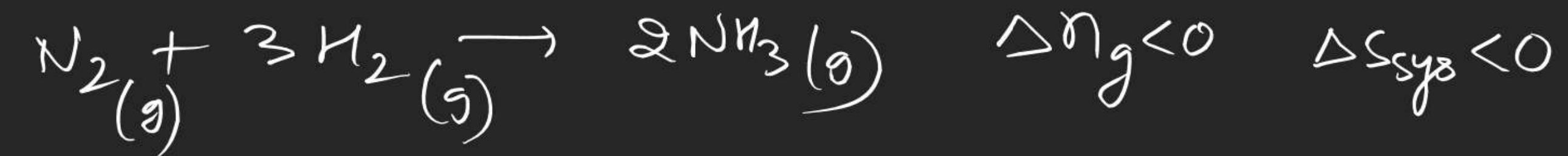
$$\Delta S_{sys} < 0$$

$$\rightarrow \Delta n_g = 0$$

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



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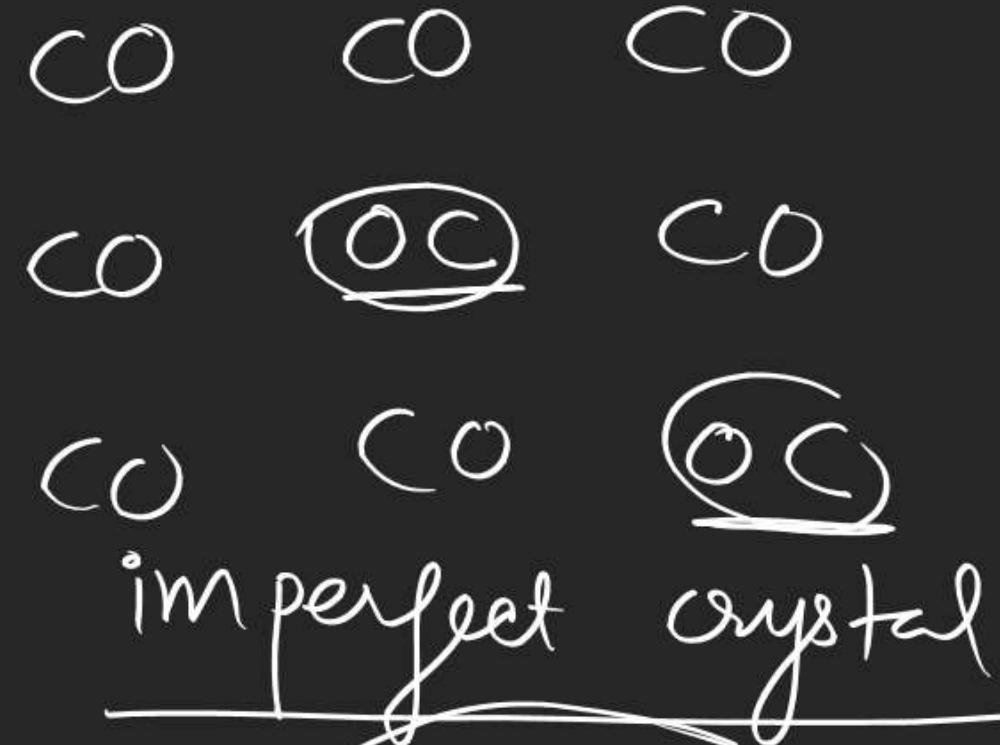


3rd Law of T.D. : At 0 K temperature, entropy of a perfect crystal is zero.



perfect crystal

$$S_{0K} = 0$$



imperfect crystal

$$S_{0K} \neq 0$$

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

Appl' 3rd law of T.D.:

① To determine absolute entropy of a substance at given T & P Sub(0K, P) \rightarrow Sub(T, P)

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

$$S_T = \int_0^T nC_p \frac{dT}{T}$$

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$$\underline{S_T} = \int_0^{T_m.pt} n G_p \frac{dT}{T} + \frac{\Delta H_{\text{fusion}}}{T_m.pt} + \int_{T_m.pt}^{T_b.pt} n G_p(\text{liq}) \frac{dT}{T} + \frac{\Delta H_{\text{vap}}}{T_b.pt}$$

$$+ \int_{T_b.pt}^T n G_p \frac{dT}{T}$$

25°C, 1 bar

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② To determine ΔS_r : \rightarrow



$$\Delta S_r = (cS_c) - (aS_A + bS_B)$$

$$\Delta S_r = \sum S(P_i) - \sum S(R)$$

for chemical Rxn

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

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

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

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

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

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

$$(\Delta S_r)_{T_2} - (\Delta S_r)_{T_1}$$

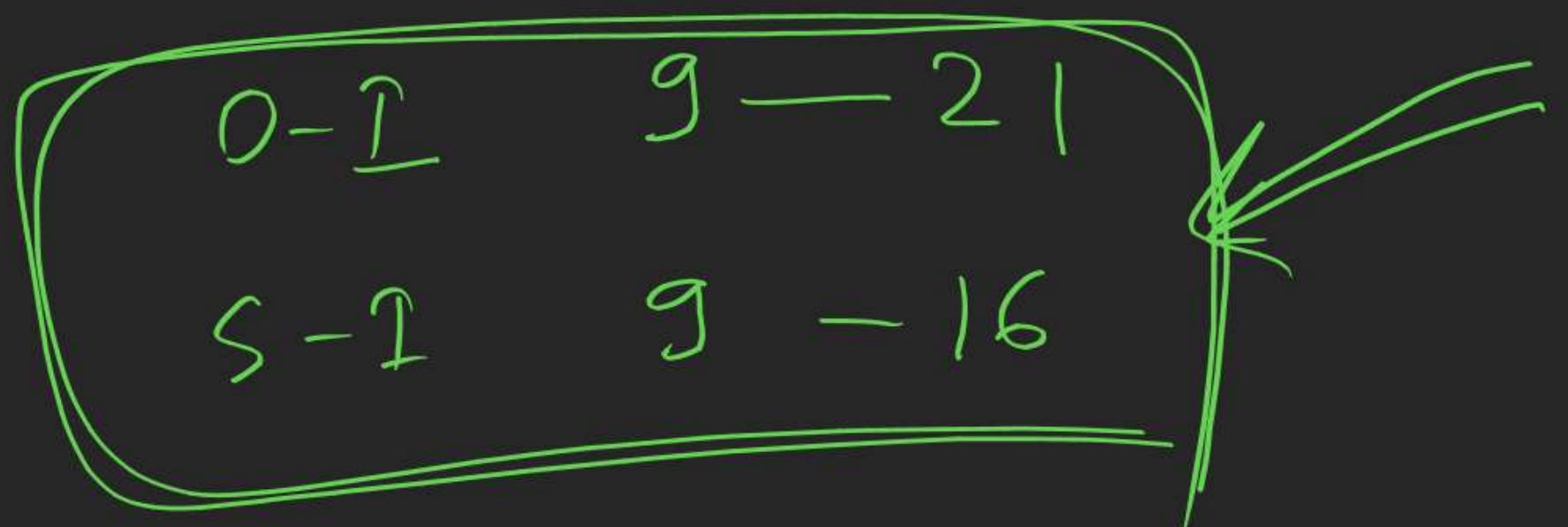
$$= [c(C_p)_c - a(C_p)_A - b(C_p)_B]$$

$$\times \ln \frac{T_2}{T_1}$$

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

$$(\Delta C_p)_r = C_p(\rho r) - C_p(r)$$

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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 -

$$Q_1 = 6000 \text{ J,}$$

$$Q_2 = -5500 \text{ J;}$$

$$W_{\text{Total}} = -Q_{\text{Total}} = -1500$$

$$Q_3 = -3000 \text{ J;}$$

$$Q_4 = 3500 \text{ J}$$

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 %

$$\frac{1500}{9500}$$

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

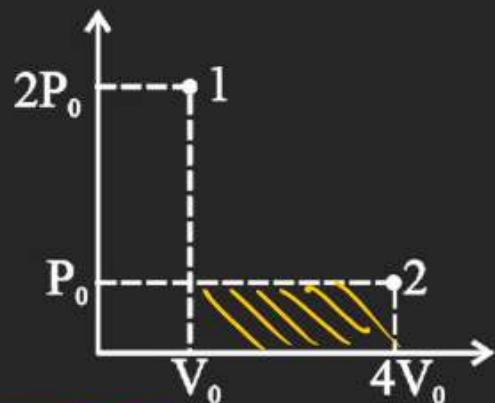
(C) $3R \ln \left(\frac{573}{473} \right)$

(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



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

$$(B) \Delta H = P_0 V_0$$

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

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

$$\begin{aligned} \Delta H &= \Delta U + (4P_0 V_0 - 2P_0 V_0) \\ &= \underline{\underline{-P_0 V_0}} \end{aligned}$$

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

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

$$B-8 \rightarrow 400 \text{ gm} = \frac{1}{128} \times 400 = \frac{10}{3} = 3.33$$

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.

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

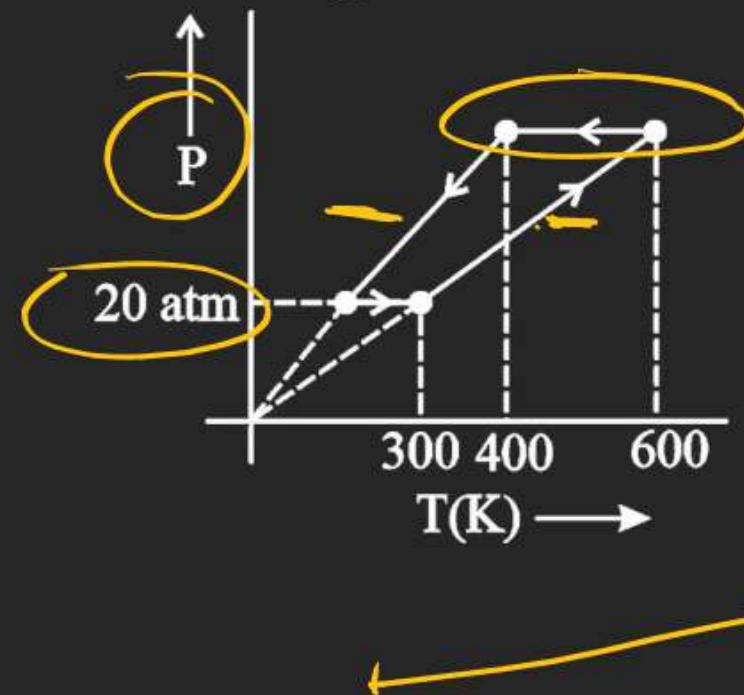
$$PV^{-1} = \text{Const}$$

$$\gamma = -1$$

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

$$300 \rightarrow |2w$$

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'

