

THERMODYNAMICS

(11)

Diagram showing two heat reservoirs at temperatures T_c and T_h . A curved line connects them, representing a process. Below the reservoirs, the formula for the final temperature T_f is given as $T_f = \frac{T_c + T_h}{2}$. To the left, the entropy change of the system is given as $\Delta S_I = C \ln \left(\frac{T_c + T_h}{T_c} \right)$. To the right, the entropy change of the surroundings is given as ΔS_{II} .

(12)

(13)



$$\Delta H = 60 \text{ kJ/mol}$$

$$\Delta S_{\text{sys}} = \frac{60 \times 10^3}{300}$$

$$\Delta S_{\text{univ}} = 0$$

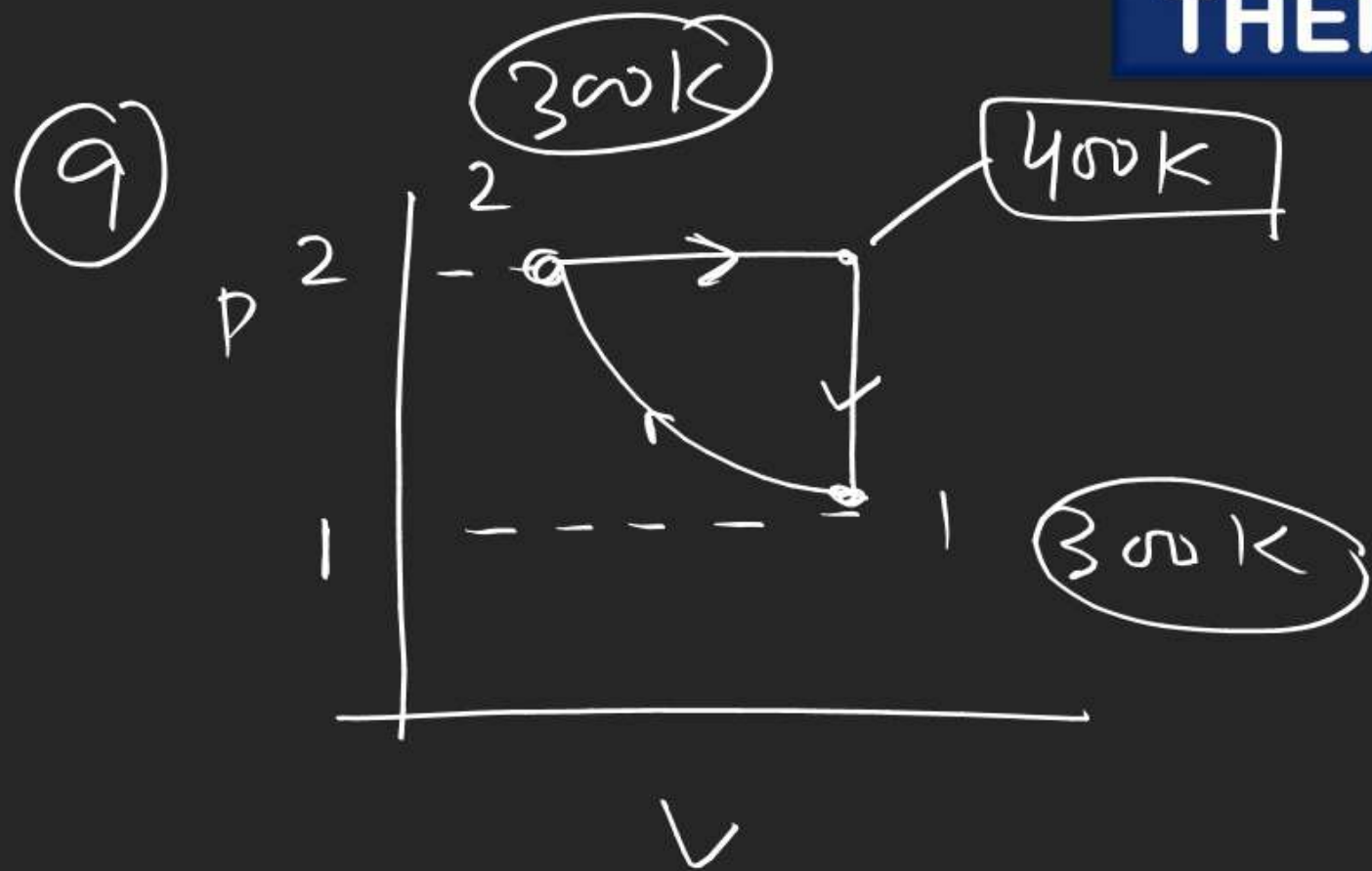
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(21)

$$\Delta S_r = S(p_r) - S(R)$$

$$-266 = 87 \times 6 - 4x - 205$$

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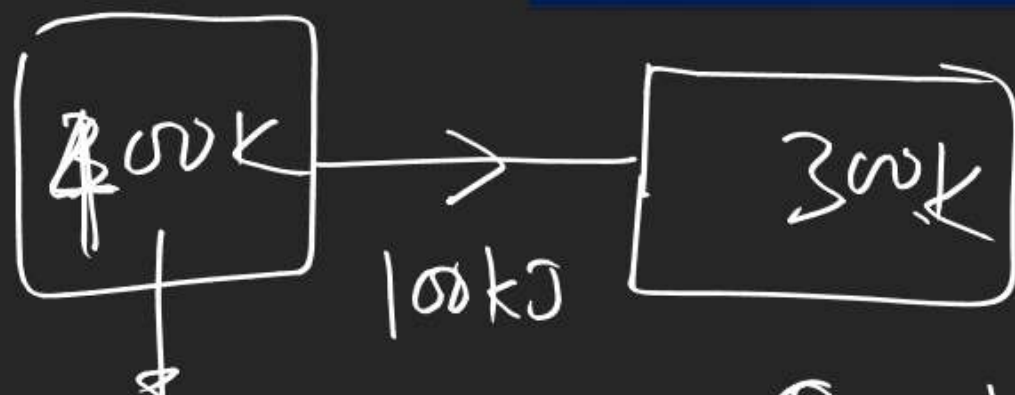
(10)

$$\Delta S = \int_{300}^{600} \left(10 + 10^{-2} T \right) \frac{dT}{T}$$

$$= 10 \ln \frac{T_2}{T_1} + 10^{-2} (T_2 - T_1)$$

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$$Q = -100 \text{ kJ}$$

$$\Delta S = \frac{-100 \times 10^3}{400}$$

$$Q = +100 \text{ kJ}$$

$$\Delta S = \frac{100 \times 10^3}{300}$$

(16)

$$\Delta H = 75 \text{ kJ}$$

$$= Q_{\text{sys}}$$

$$Q_{\text{sur}} = -75 \text{ kJ}$$

$$\Delta S_{\text{sur}} = \frac{Q_{\text{sur}}}{300}$$

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

⇒ Variation of (ΔS_r) with pressure at const 'T'

$$\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$S_{P_2} - S_{P_1} = R \ln \frac{P_1}{P_2}$$

$$\rightarrow Cx \rightarrow (S_c)_{P_2} - (S_c)_{P_1} = R \ln \frac{P_1}{P_2}$$

$$ax \rightarrow (S_A)_{P_2}$$

$$bx \rightarrow (S_B)_{P_2}$$

$$(\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = (c-a-b) R \ln \frac{P_1}{P_2}$$

$$(\Delta S_r)_{P_2} - (\Delta S_r)_{P_1} = \Delta \eta_g R \ln \frac{P_1}{P_2}$$

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$$H_{T_2} - H_{T_1} = C_p dT + \left(\frac{\partial H}{\partial p} \right)_T dp$$

$$(\Delta H_r)_{P_2} = (\Delta H_r)_{P_1}$$

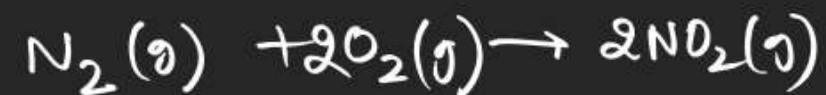
$$(\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1)$$

Kirchoff eqⁿ

$$(\Delta U_r)_{T_2} - (\Delta U_r)_{T_1} = (\Delta C_v)_r (T_2 - T_1)$$

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Q. for the rxn



$$\Delta H_r = 50 \text{ kJ/mol}$$

at 1 atm 300 K

$$\Delta C_{p,r} = 2 \times 25 - 20 - 2 \times 20$$

$$= 50 - 60 = -10$$

$$\left. \begin{array}{l} S_{\text{N}_2(\text{g})} = 100 \text{ J/mol/K} \\ S_{\text{O}_2(\text{g})} = 125 \text{ " } \\ S_{\text{NO}_2(\text{g})} = 150 \text{ " } \end{array} \right\} \begin{array}{l} \text{at 1 atm} \\ 300 \text{ K} \end{array}$$

$$C_p(\text{N}_2) = C_p(\text{O}_2) = 20 \text{ J/K/mol}$$

$$C_p(\text{NO}_2) = 25 \text{ J/mol/K}$$

- find
- (i) ΔS_r at 1 atm 300 K -50
 - (ii) " " 1 atm 600 K
 - (iii) " " 10 atm 300 K
 - (iv) " " 10 atm 600 K

- (v) ΔH_r at 1 atm 600 K
- (vi) " " 10 atm 300 K
- (vii) " " 10 atm 600 K

- (viii) $\Delta S_{\text{surrounding}}$ at 1 atm 300 K
- (ix) " " 1 atm, 600 K
- (x) " " 10 atm, 300 K
- (xi) " " 10 atm 600 K

(ii)

$$(\Delta S_r)_{600} = (\Delta S_r)_{300} + (\Delta C_p)_r \ln T_2/T_1$$

$$= -50 - 10 \ln 600/300$$

$$= -50 - 10 \ln 2$$

$$(\Delta S_r)_{10 \text{ atm}} = -50 + (-1)R \ln 1/10$$

$$= -50 + R \ln 10$$

$$= \frac{-50 \times 10^3}{300}$$

$$= \frac{-47 \times 10^3}{600}$$

$$= \frac{-50 \times 10^3}{300}$$

$$= \frac{-47 \times 10^3}{600}$$

$$(\Delta S_r)_{T_2, P_2} - (\Delta S_r)_{T_1, P_1} = (\Delta C_p)_r \ln \frac{T_2}{T_1} + \Delta n_g R \ln \frac{P_1}{P_2}$$

⑤

$$(\Delta H_r)_{600} = 50 \text{ kJ} + \frac{(-10)(600-300)}{1000}$$

$$= 0 \quad = 50 \text{ kJ} - 3 \text{ kJ}$$

$$= 47 \text{ kJ}$$

⑥

$$(\Delta H_r)_{10 \text{ atm}} = (\Delta H_r)_{1 \text{ atm}} = 50 \text{ kJ}$$

⑦

$$\Delta H_r = 47 \text{ kJ}$$

⑦

$$-50 - 10 \ln 2 + R \ln 10$$

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Gibb's energy (G)

$$G = H - TS$$

$$G = U + PV - TS$$

It is a state function

for a change

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

$$dG = q + \cancel{w_{PV}} + \cancel{W_{non-PV}} + \cancel{PdV} + \cancel{VdP} - Tds - SdT$$

at const T, P and in the absence of non-PV work

$$W = -\underline{P_{ext}}dV = -\underline{PdV}$$

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$$dG_{\text{sys}} = \underbrace{q_{\text{sys}}}_{\text{circled}} - T_{\text{sys}} dS_{\text{sys}}$$

$$dG_{\text{sys}} = -T_{\text{sys}} (dS_{\text{sur}} + dS_{\text{sys}})$$

$$dG_{\text{sys}} = -T_{\text{sys}} dS_{\text{univ}}$$

$$dS_{\text{sur}} = -\frac{q_{\text{sys}}}{T_{\text{sys}}}$$

$$q_{\text{sys}} = -T_{\text{sys}} dS_{\text{sur}}$$

$$(dG_{\text{sys}})_{T,P} < 0$$

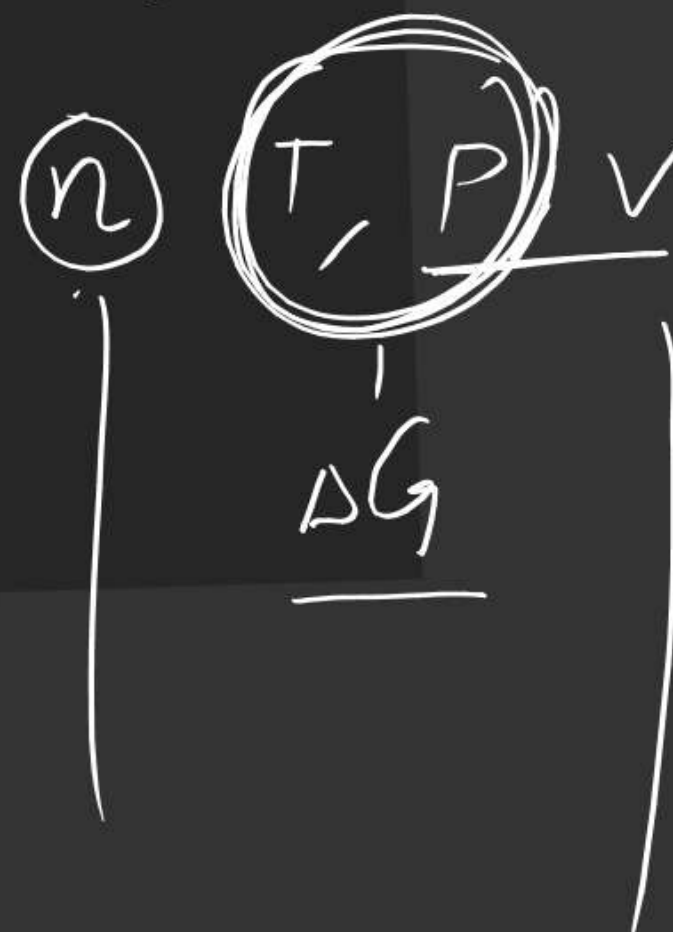
feasible

$$(dG_{\text{sys}})_{T,P} > 0$$

not feasible

$$(dG_{\text{sys}})_{T,P} = 0$$

Reversible



0-1

22-24

5-1

17-18