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THERMODYNAMICS

(8) $|W| = +\Delta n_g RT$

$= \dfrac{1 \times 8.3 \times 300}{1000}$

$= \dfrac{24.9}{10}$

$= 2.49\ kJ$

100 mol H_2O_2

$\downarrow$

50 mol O_2

w by 50 mol O_2

2.49×50

$= 124.5\ kJ$

13

$$|W| = nRT\ln\frac{V}{V_i}$$

$$|W| = \underbrace{nRT}_{\text{Slope}}\ln V \underbrace{- nRT\ln V_i}_{\text{Intercept}}$$

$V_i = 1$

$V_i > 1$

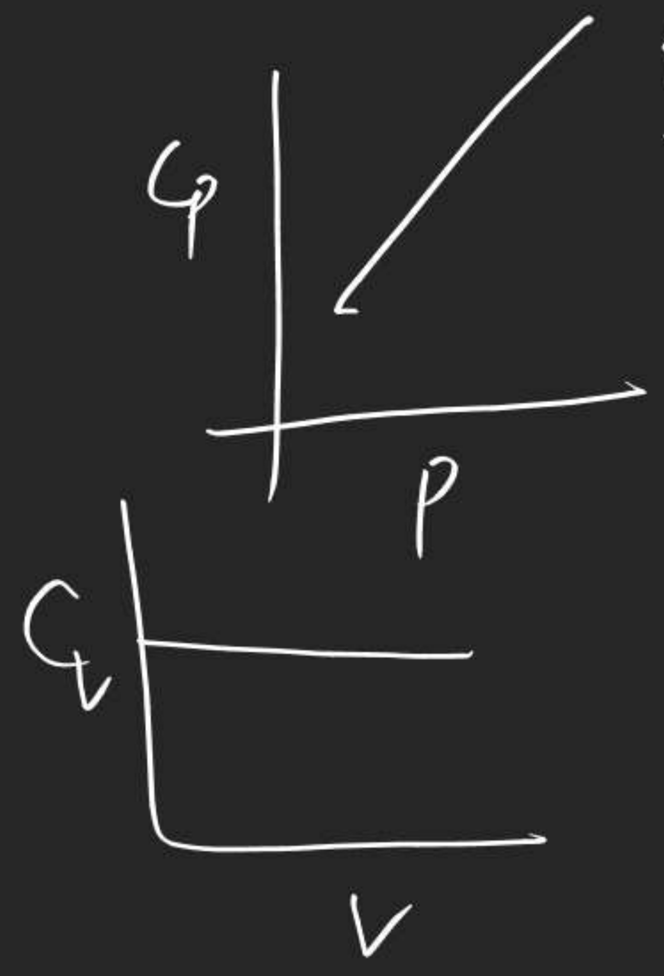
$V_i < 1$

False

$\boxed{C, D}$

C_p

C_v



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17

$$\Delta H = \int n C_p \, dT$$

$$= \int_{300}^{1000} n(23 + 0.01T)\, dT$$

22

$$W = -1\,\text{bar}(10-1)$$

$$= -9\ \text{bar.lit}$$

$$= -900\ \text{J} = -0.9\ \text{kJ}$$

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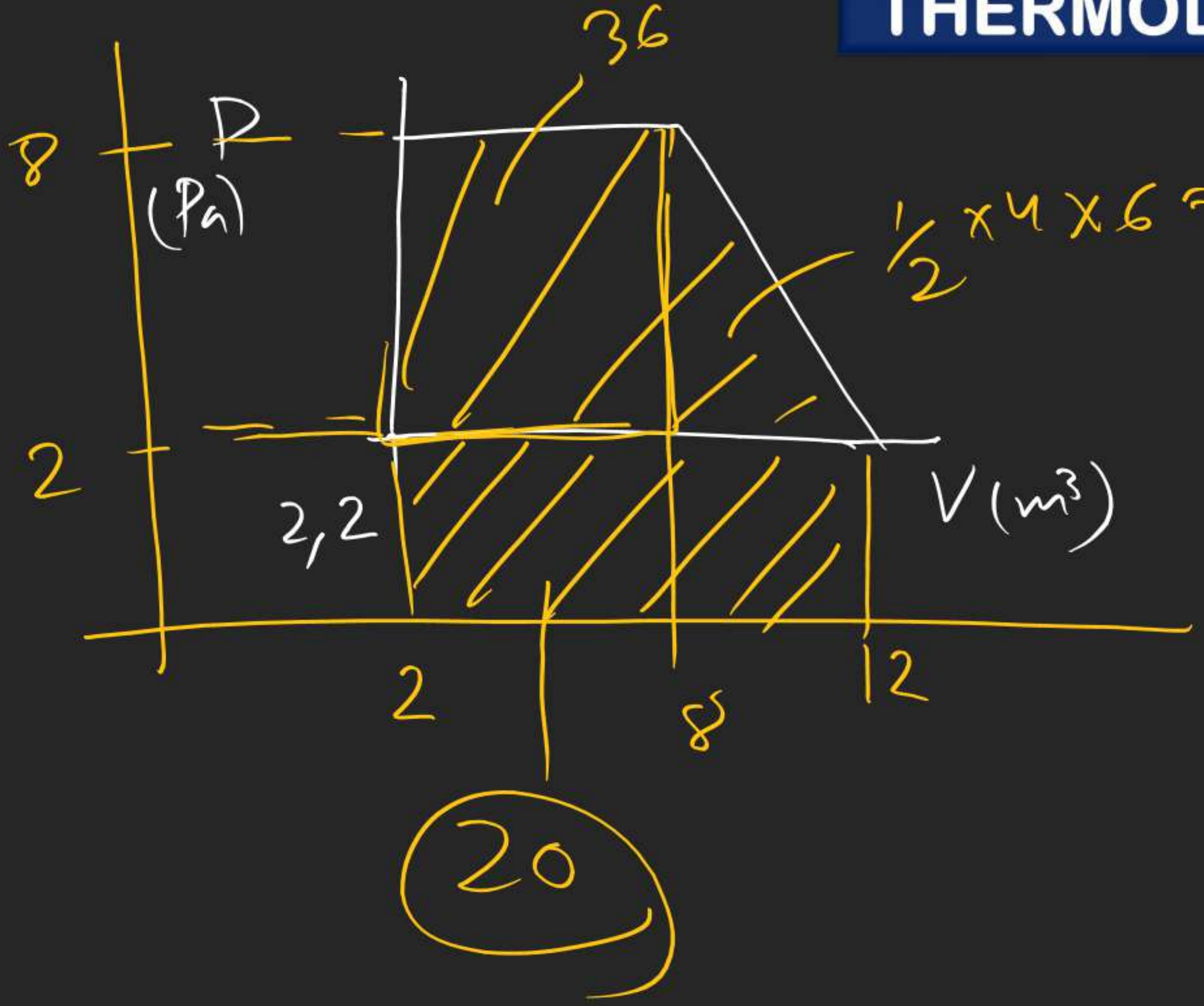

$\frac{1}{2} \times 4 \times 6 = 12$

$\underline{\underline{68}}$

(b) for real gas

$$\Delta S = \int \frac{q_{rev}}{T} = \int \frac{dU - W}{T}$$

$$dU = C_v dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$
$$W = -PdV$$

(i) At constant volume

$$= \int \frac{nC_v dT}{T} = nC_v \ln \frac{T_2}{T_1}$$

(ii) At const Pressure

$$= \int \frac{q_{rev}}{T} = \int \frac{dH}{T} = \int \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

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(c) for solid & liq

$$\Delta S = \int \frac{dU - \cancel{w}^{\,0}}{T} = \int \frac{nC\,dT}{T}$$

$$\boxed{\Delta S = nC \ln \frac{T_2}{T_1}}$$

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$\Delta S_{surroundings}$ (ΔS_{surr})

$$\Delta S_{surr} = \frac{(q_{surr})_{rev}}{T_{surr}} = \frac{q_{surr}}{T_{surr}} = \frac{-q_{sys}}{T_{surr}}$$

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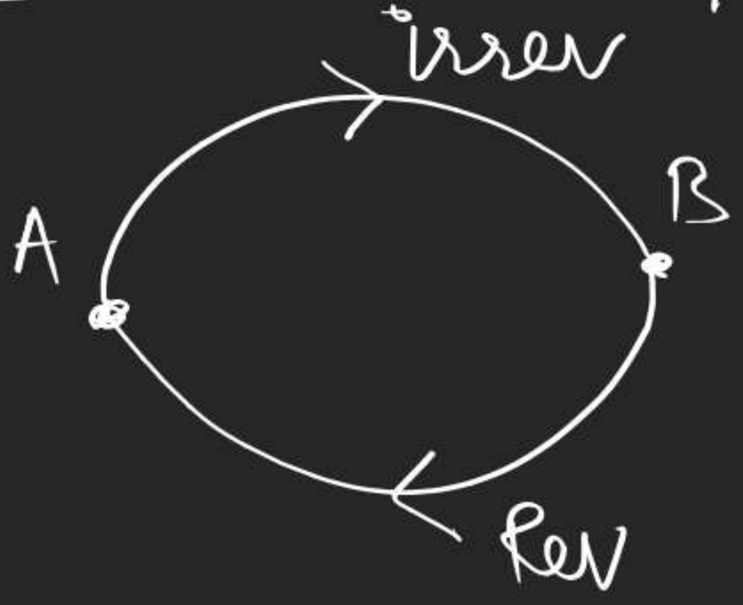
Clausius Inequality



$$\oint \frac{q}{T} \leq 0$$

$$\int_A^B \frac{q_{irr}}{T} + \int_B^A \frac{q_{rev}}{T} < 0$$

$$\int_A^B \frac{q_{irr}}{T} + \Delta S_{BA} < 0$$

$$\int_A^B \frac{q_{irr}}{T} < \Delta S_{AB}$$

$$\frac{q_{irr}}{T} < dS$$

if cycle is rev

$$\frac{q_{rev}}{T} = dS$$

$$\boxed{\frac{q}{T} \leq dS}$$

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$$\frac{q}{T} \lesseqgtr dS$$

irrev

Rev

not feasible

Clausius Inequality

$$\boxed{\frac{q}{T} \le dS}$$

$$\boxed{q \le T\,dS}$$

<u>for an isolated system</u>

$q = 0$

$dS \ge 0$

$dS_{univ} \ge 0$

$dS_{sys} + dS_{surr} = dS_{univ} > 0$ irrev (feasible)

$dS_{sys} +$ " $= dS_{univ} = 0$ rev

" " $dS_{univ} < 0$ not possible

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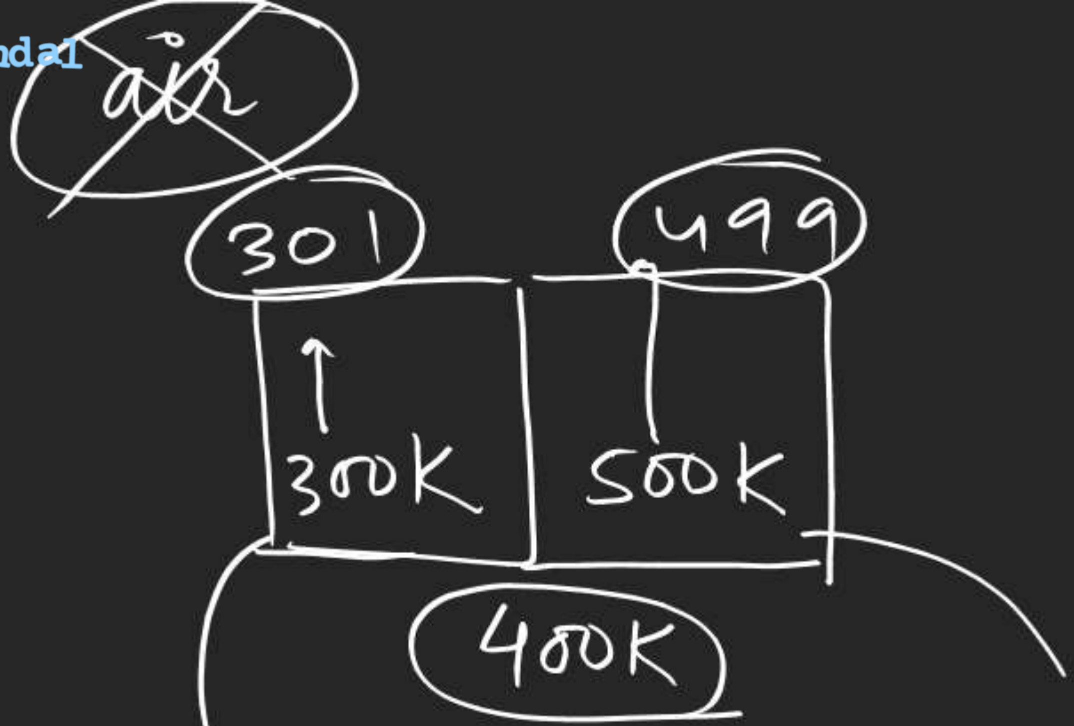
$dS_{sys} + dS_{surr} > 0$ Irrev

$\quad '' \quad\quad '' \quad = 0$ Rev

$\quad '' \quad\quad '' \quad < 0$ not feasible



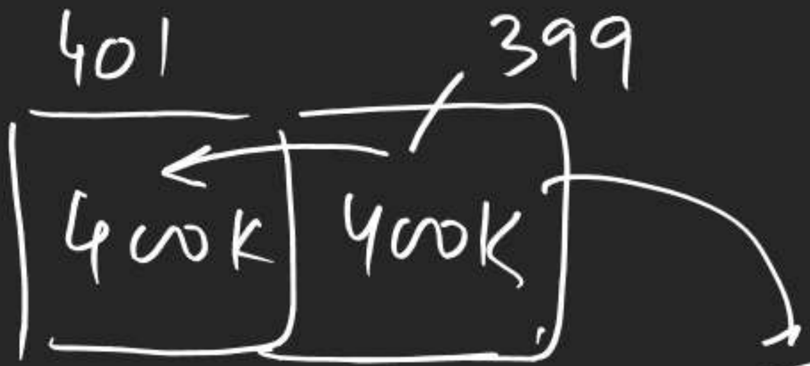
$$\Delta S_{I} = nC \ln \frac{400}{300}$$

$$\Delta S_{II} = -nC \ln \frac{500}{400}$$

$$\Delta S_{univ} = \Delta S_{Total} = \Delta S_{I} + \Delta S_{II} > 0$$

$$\Delta S_{I} = nC \ln \frac{301}{300}$$

$$\Delta S_{II} = -nC \ln \frac{500}{499} > 0$$



$$\Delta S_{I} = nC \ln \frac{401}{400}$$

$$-nC \ln \frac{400}{399}$$

$$< 0$$

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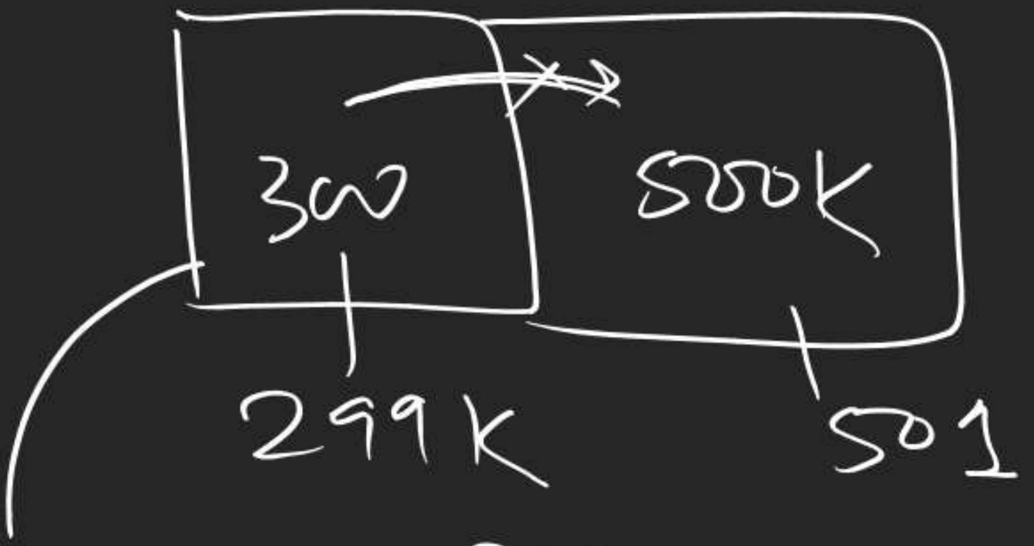

$$\Delta S_{I} = -nC\ln\frac{300}{299}$$

$$\Delta S_{II} = nC\ln\frac{501}{500} < 0$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= 0 + nR \ln \frac{2V}{V}$$

$$\Delta S = nR \ln V$$

$$\Delta S = nC \ln \frac{V}{2V}$$

$$\Delta S = -nC \ln 2$$

not feasible

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Q. find ΔS_{sys}, ΔS_{surr} and ΔS_{univ} for 1mol ideal gas undergoing isothermal expansion from 10 atm to 1atm at 300K

(I) Reversibly

(II) Irreversibly

(III) free expansion

(1) $\Delta S_{sys} = 0 + R\ln 10/1 = R\ln 10$

$\Delta S_{sys} + \Delta S_{surr} = 0$

$\Delta S_{surr} = -R\ln 10$

$$\Delta S_{surr} = -\frac{q_{sys}}{T_{surr}} = \frac{+W}{T} = \frac{-nR\cancel{T}\ln P_1/P_2}{\cancel{T}}$$

$$= -nR\ln P_1/P_2 = -R\ln 10$$

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(II) Irrev

$$\Delta S_{sys} = 0 + R \ln P_1/P_2 = R \ln 10$$

$$\cancel{\Delta S_{surr} = -\Delta S_{sys}}$$

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{w}{T} = \frac{-P_{ext}\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)}{T}$$

$$= -0.9R$$

$$\Delta S_{univ} = R \ln 10 - 0.9R$$

$$= 2.3R - 0.9R$$

$$= 1.4R$$

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TD-2

S-I 1—8

O-I 1—8