Nishant Jindal

THERMODYNAMICS

$$dU = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$ for a substance not undergoing any chemical & phase change

Case-I for an ideal gas undergoing <u>any process</u>

$f = x^2$

$$dU = nC_V dT \qquad \left(\frac{\partial U}{\partial V}\right)_T = 0$$

Case-II for real gas undergoing const 'V' process

$$dU = nC_V dT \qquad \left(\frac{\partial U}{\partial V}\right)_T \neq 0 \qquad dV = 0$$

Case-III for solid/liq undergoing any process

$$dU = nC_V dT \qquad \left(\frac{\partial U}{\partial V}\right)_T \neq 0 \qquad dV \simeq 0$$

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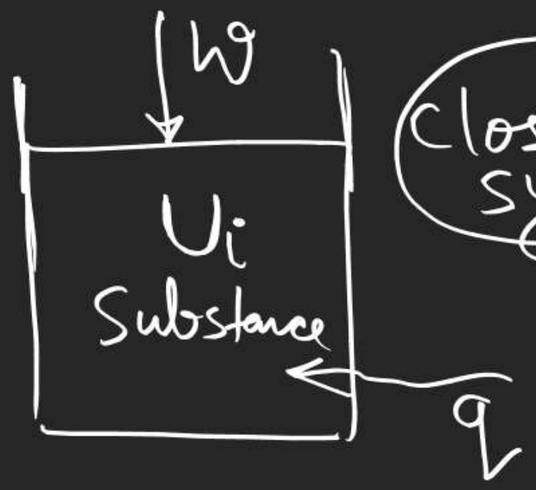
THERMODYNAMICS

1st law of Thermodynamics: — Total energy of universe is constant



Closed system

$$U_f = U_i + q + w$$

$$\boxed{dU = q + w}$$

dq dw

dT q w

$dU = q + w$ is applicable for any system. (False)

1st law of T.D is applicable for any system. True

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Q. Calculate ΔU if a system is given 200 kJ heat and simultaneous 50 kJ work is done by the system.

$Q = 200\ kJ$

$W = -50\ kJ$

$\Delta U = Q + W$

$= 150\ kJ$

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Q. 1 mol ideal gas is subjected to a change from (2 lit, 300 K) to (5 lit, 600 K) against a constant pressure 10 bar. (Gas is monoatomic) find Q, W & ΔU.

$R = 8.314\ J/mol/K$

$$\frac{P_1V_1}{T_2} = \frac{P_2V_2}{T_2}$$

$$\Delta U = nC_v\Delta T$$

$$= 1 \times \frac{3}{2} R \times 300$$

$$= \frac{3}{2} \times \frac{25}{3} \times \cancel{300}^{100}$$

$$= 3750$$

$$Q = nC_v\Delta T$$

$$Q = nC_p\Delta T$$

$$W = -P_{ext}(V_2 - V_1)$$

$$= -10(3)\ bar.lit$$

$$= -30 \times 100\ J$$

$$= -3000\ J$$

$$Q = \Delta U - W$$

$$= 3750 + 3000$$

$$= 6750\ J$$

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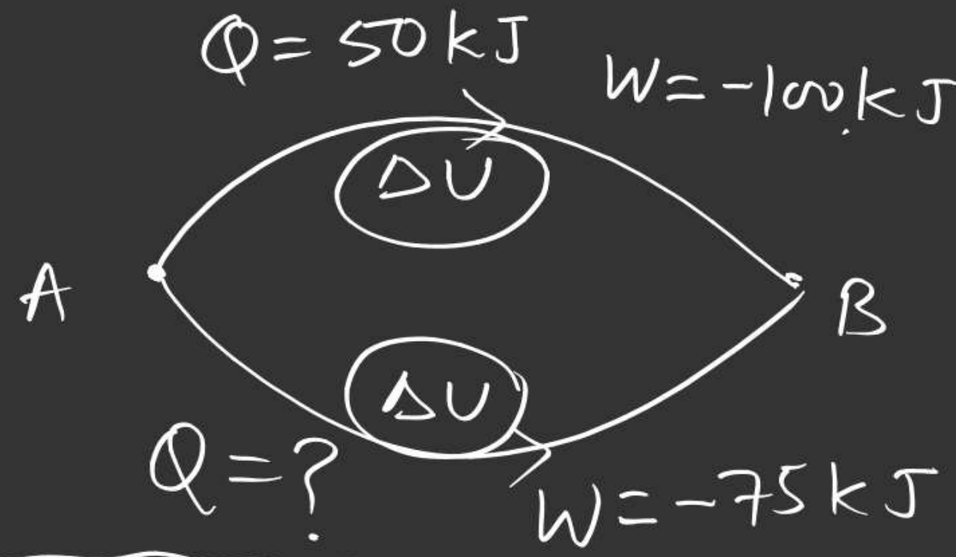
Q.



$\Rightarrow \Delta U = Q + W$
$= -50\ kJ$

$$\Delta U = Q + W = -50$$

$$Q - 75 = -50$$

$$Q = 25\ kJ$$

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Enthalpy (H) :→

$$H = U + PV$$

'H' is a state function

for a change

$$dH = dU + PdV + VdP$$

from 1st law of T.D

$$dH = q + W + PdV + VdP$$

at constant 'P'

$P_{ext} = P$

$W = -P_{ext}dV$

$= -PdV$

$$\boxed{dH = q} - \cancel{PdV} + \cancel{PdV} + 0$$

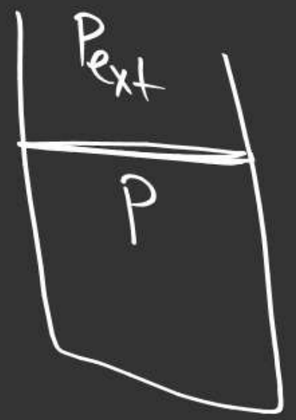
$$dU = q + W$$

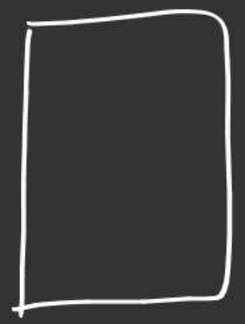
at const volume

$$dU = q_v$$

at const pressure

$$dH = q_p$$





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at const 'p' Q_1 ΔH_1

$Q_1 = \Delta H_1$

if $P \neq$ const Q_2 ΔH_2

$Q_2 \neq \Delta H_2$

$N_2 + 3H_2 \rightarrow 2NH_3$ $\Delta H_f = -100kJ$

heat

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THERMODYNAMICS

for a substance not undergoing any chemical & phase change

$$H = f(P, V) = \underline{f(P, T)} = f(V, T)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

$$\boxed{dH = C_p\, dT + \left(\frac{\partial H}{\partial P}\right)_T dP}$$

Simplified form of above eqn

$$dH = q_p$$

$$\frac{q_p}{dT} = C_p$$

$$\left(\frac{dH}{dT}\right)_P = C_p$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

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Case-I for ideal gas undergoing any process

$$H = f(T)$$

$$\left(\frac{\partial H}{\partial P}\right)_T = 0$$

$$\boxed{dH = nC_p dT}$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$U = f(T)$$

$$H = U + PV$$

for an ideal gas

$$H = U + nRT$$

Case-II for real gas undergoing constant pressure process

$$\boxed{dH = nC_p dT}$$

$$\left(\frac{\partial H}{\partial P}\right)_T \neq 0$$

$$dp = 0$$

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Case-III for solid & liq undergoing process

$$dH = C_p dT + \left(\frac{\partial H}{\partial P}\right)_T dp \qquad dp \neq 0$$

Change in properties of solid/liq is negligible with change in pressure

$$\left(\frac{\partial H}{\partial P}\right)_T \simeq 0$$

$$\boxed{dH = nC_p dT}$$

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THERMODYNAMICS

Rev & irr 7

heat 6

W —— 3

U ⟶ 8

H ⟶ 8

solid state

S – II