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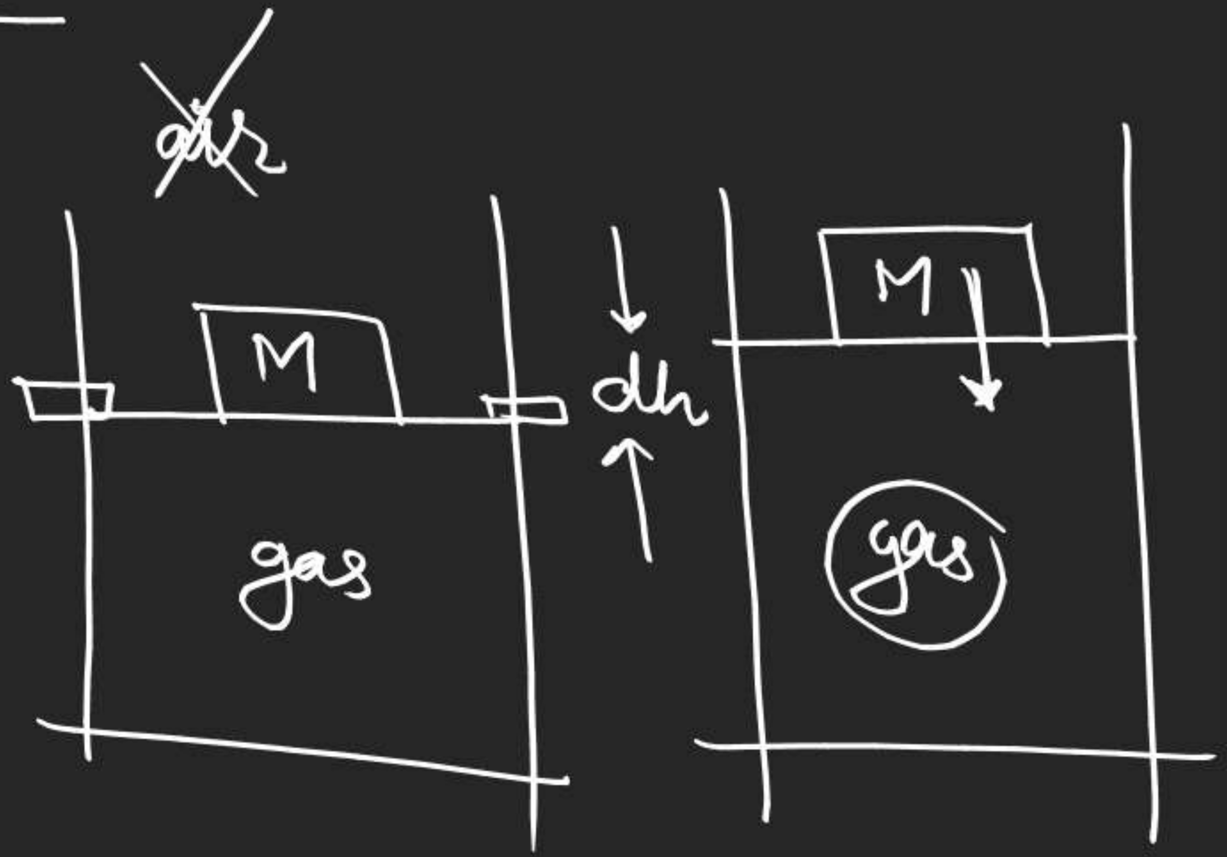
THERMODYNAMICS

Work



$$|W| = \text{change in PE}$$

$$= \frac{Mg}{A}(dh \cdot A)$$

$$|W| = P_{ext}\, dV$$

as per sign convention

$$W = -P_{ext}\, dV$$

Always applicable for PV-work → $$\boxed{W = -\int P_{ext}\, dV}$$

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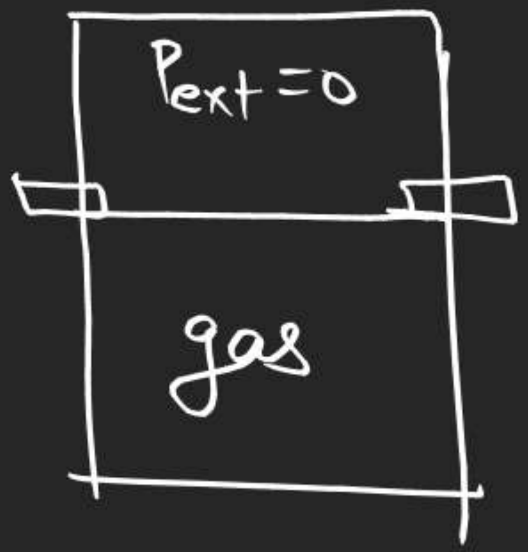
W will be zero if

(i) $V =$ Constant

(ii) $P_{ext} = 0$ (free expansion)



$W = 0$

$$W = -\int P_{ext}\, dV$$

W	P_{ext}	dV
atm.lit	atm	lit
J	Pa	m^3
bar.lit	bar	lit

$$1 \text{ atm.lit} = 1.01325 \times 10^{5}\ \text{Pa} \times 10^{-3}\ \text{m}^3$$

$$= 101.325\ \text{J}$$

$$1 \text{ bar.lit} = 100\ \text{J}$$

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Q. Calculate w for the expansion of a gas from 2 lit to 5 lit against

(i) Constant external pressure 10 bar.

(ii) Variable external " $\left[5 + 2V(\text{lit}^{-1})\right]$ atm

J

atm. lit

Soln (i) $W = -P_{ext}\int dV = -P_{ext}(V_2 - V_1)$

$= -10(5-2) = -30 \text{ bar lit} = -3000 \text{ J}$

(ii) $W = -\int_2^5 (5+2V)\,dV = -\left[5V + \frac{\cancel{2}V^2}{\cancel{2}}\right]_2^5 = -\left[15 + (25-4)\right] = -36 \text{ atm lit}$

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Internal Energy (U or E)

(I) Energy due to system itself

$$U = U_{KE} + U_{PE} + U_{nucleus} + U_{e^-} + U_{mc^2}$$

due to intermolecular or interatomic forces

(II) Energy due to external factors

e.g gravitational P.E

electric forces

Energy due to such factors are not considered.

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for a change

$$\Delta U = \Delta U_{KE} + \Delta U_{PE} + 0 + 0 + 0$$

due to intermolecular forces

for an ideal gas

$$\Delta U = \Delta U_{KE} + 0$$

$$U = f(T)$$

for any substance

$$KE = f(T)$$

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for any substance

$$U = f(Sub, P, V, T) = f(\underline{Sub}, \underline{n}, \underline{V}, \underline{T})$$

for a substance not undergoing any chemical & phase change

$$U = f(V, T) = f(P, T) = f(P, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V \underline{dT} + \left(\frac{\partial U}{\partial V}\right)_T \underline{dV}$$

$$\boxed{dU = C_V\, \underline{dT} + \left(\frac{\partial U}{\partial V}\right)_T \underline{dV}}$$

$$\frac{q_V}{dT} = C_V$$

$$dU = \underline{q_V} + \cancel{w} \rightarrow 0$$

$$\left(\frac{dU}{dT}\right)_V = C_V$$

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Simplified form of above eqn

Case-I for an ideal gas undergoing any process

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

$$= C_v dT + 0$$

$$dU = C_v dT$$

for 'n' moles

$$\boxed{dU = nC_v dT}$$

$U = f(T)$

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

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Case-II for a real gas undergoing constant volume process

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

$U = f(T, V)$

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

$dV = 0$

$$\boxed{dU = nC_v dT}$$ at constant volume

$$f = x^2 \cdot e^{-x}$$

$$df = (2x) \cdot e^{-x} dx + (x^2)(-e^{-x}) dx$$

$$f = x^2 \; y^3$$

$$df = (2x \cdot y^3)\, dx + (x^2 (3y^2))\, dy$$

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$$

$M \times f$