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✓ 10 Yrs Teaching experience

✓ Content Partner in MHRD DIKSHA Project



● **LIVE** daily

Paaras Thakur

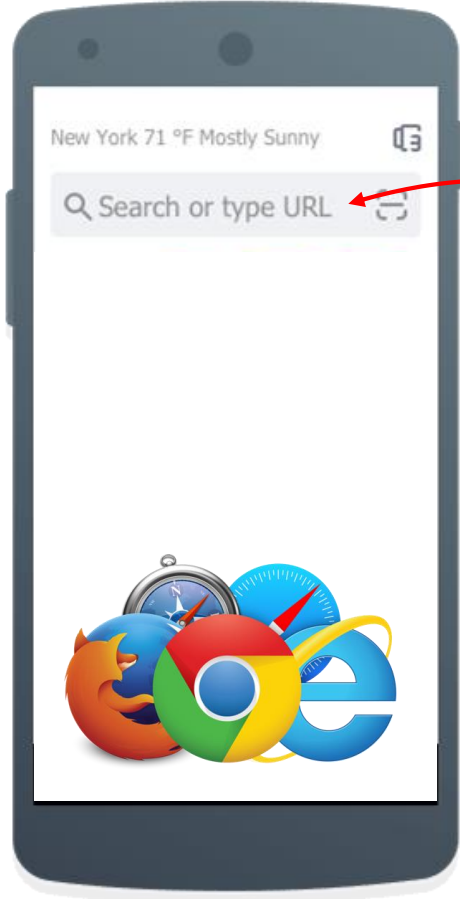


Thermodynamics

Lecture

3





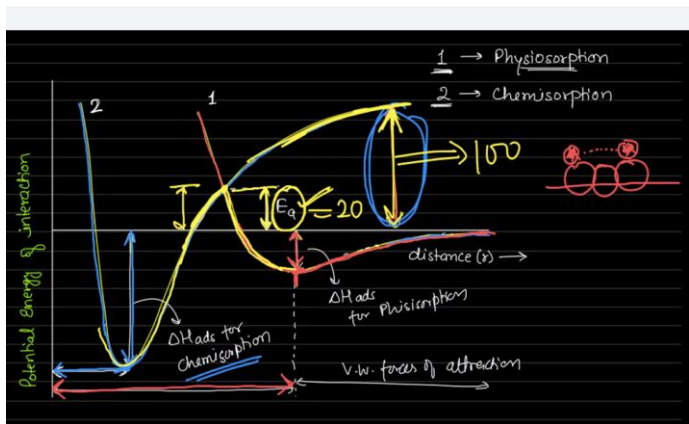
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The *trouble* is,
You think
you have **TIME**
- Buddha



SAVE

Expense

Energy

Time



LEARN



Why you go to **COACHING**

Overcome your weakness in subjects

Doubts Clarification

Analyse your performance with Tests, Analysis, Discussion



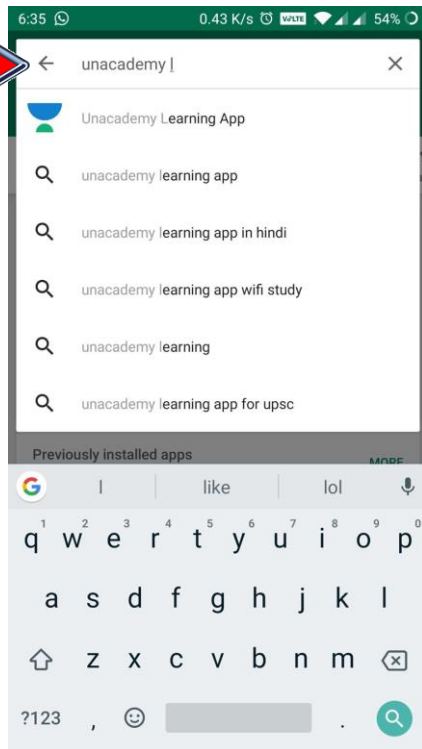
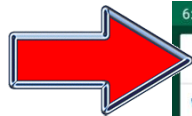
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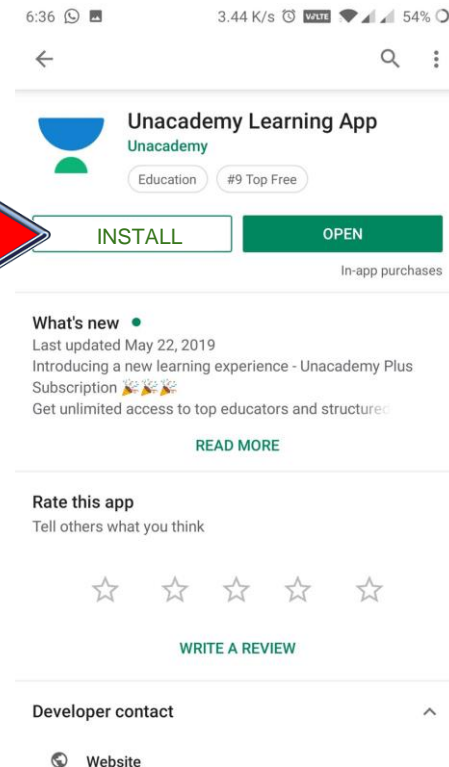
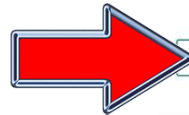
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Step 2



Step 3

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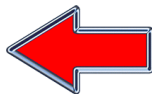
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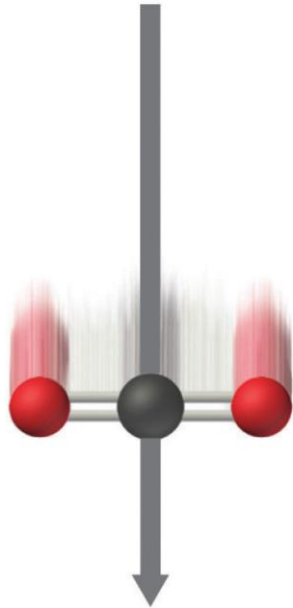


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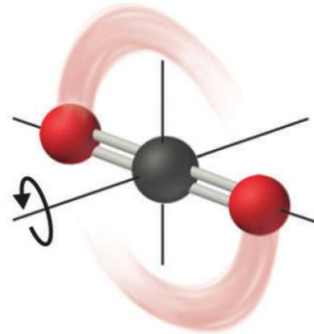
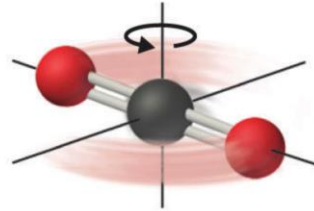


Degree of freedom

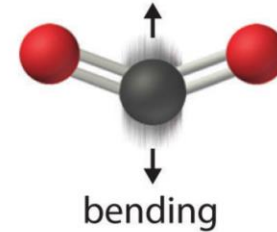
The total no of modes on which a molecule of an ideal gas can exchange energy during collisions is known as its degrees of freedom.



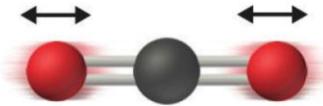
translational motion



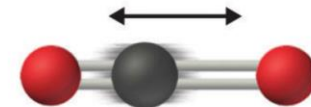
rotational motion



bending



symmetric stretching


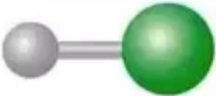




asymmetric stretching

vibrational motion



Degree of freedom

Type of molecule	N	Degrees of freedom	Modes
Monatomic, e.g. Ne 	1	3	3 translational 0 rotational 0 vibrational
Diatomic, e.g. HCl 	2	6	3 translational 2 rotational 1 vibrational
Triatomic linear, e.g. CO ₂ 	3	9	3 translational 2 rotational 4 vibrational
Triatomic non-linear, e.g. H ₂ O 	3	9	3 translational 3 rotational 3 vibrational

Heat Capacity

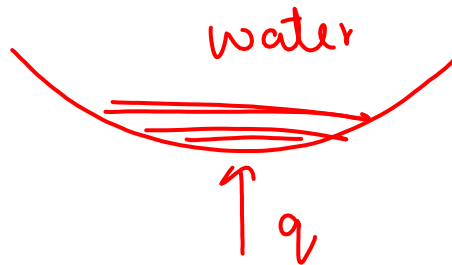
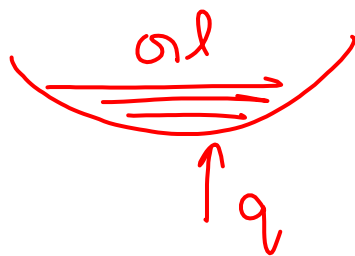
You know from everyday experience that the more you heat an object, the higher its temperature, and the more you cool it, the lower its temperature.

$$\underline{q} \propto \Delta T$$

or

$$q = \text{constant} \times \Delta T$$

$$\Delta T = \frac{q}{K}$$



Every object has its own heat capacity, the quantity of heat required to change its temperature by 1 K.



Heat Capacity

$$q = C \Delta T$$

Heat Capacity

Total Heat Capacity

Heat required to raise the temperature of given mass by unit kelvin

$$C_T = \frac{q}{\Delta T}$$

Molar Heat Capacity

Heat required to raise the temperature of 1 mole by unit kelvin.

$$C_m = \frac{q}{n \Delta T}$$
$$q = n C_m \Delta T$$

Specific Heat Capacity

Heat required to raise the temperature of 1 gram by unit kelvin.

$$C = \frac{q}{m \Delta T}$$



Heat Capacity

eg C for isothermal Process = $\frac{q}{\Delta T} \rightarrow 0 = \infty$

C for adiabatic " = $\frac{q}{\Delta T} \rightarrow 0 = 0$

C for isobaric " = C_p

C for isochoric " = C_v

$$C = \frac{q}{\Delta T}$$



Example

During an expansion of ideal gas the work done by gas is 100 J and the heat capacity of process is found to be $+2 \text{ J/}^\circ\text{C}$. Find ΔU of gas if the final temperature of gas is 25°C higher than its initial temperature.

$$\Rightarrow \begin{array}{l} W = -100 \text{ J} \\ C = 2 \text{ J/}^\circ\text{C} \end{array} \quad \left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\} \begin{array}{l} q \text{ req to raise temp. by } 25^\circ\text{C} \\ q = C \Delta T \\ = 2 \times 25 = 50 \text{ J} \end{array}$$

$$T \longrightarrow T + 25^\circ\text{C}$$

$$\begin{aligned} \Delta U &= q + W \\ &= 50 - 100 \\ &= -50 \end{aligned}$$





Work Done

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved is known as work. It is a **path function**.

Units

✓ Heat & work both are forms of energy . Hence, their units are units of energy.
i.e.S system: Joules (J).

Much data is available in the old units of calories (cal) as well.
 $P \times V$ = (litre. atmosphere) term which has unit of energy . It is useful to remember the conversion
1 litre. atm = 101.3 Joules

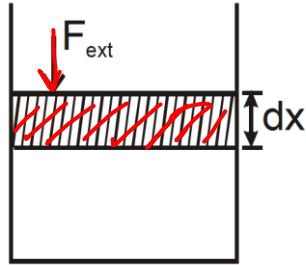
$$\begin{aligned} dW &= F dx \\ &= P \cancel{A} dx \\ &= P dV \end{aligned}$$





P - V Work

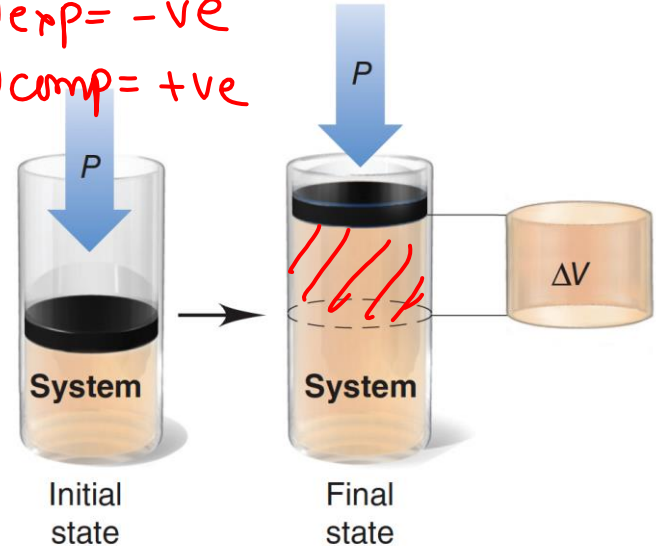
Assuming that under an external force F_x , the piston moves down by a distance 'dx'.



$$\begin{aligned} W &= F dx \\ &= P_{ex} A dx \\ &= P_{ex} dV \end{aligned}$$

$$\begin{aligned} W &= -P_{ext} \Delta V \\ &= -P_{ext} (V_2 - V_1) \end{aligned}$$

$W_{exp} = -ve$
 $W_{comp} = +ve$



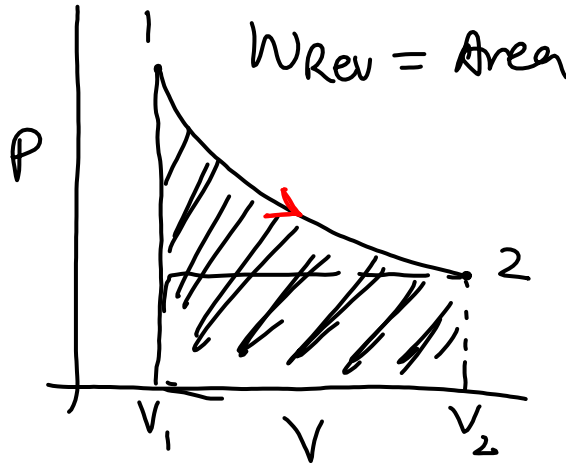


Calculation of work for **Isothermal expansion**

Isothermal reversible expansion:

$$T = \text{const.}$$

$$\left\{ \begin{array}{l} P_{\text{ext}} \approx P_{\text{gas}} \\ P_{\text{gas}} = \frac{nRT}{V} \end{array} \right.$$



$$dW = -P_{\text{ext}} dV$$
$$\int dW = \int_{V_1}^{V_2} -nRT \frac{dV}{V}$$

$$W_{\text{Rev}} = -nRT \int_{V_1}^{V_2} \frac{dV}{V} = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

Work = Area under P-V Curve

$$W_{\text{Rev}} = -2.303 nRT \log_{10}\left(\frac{V_2}{V_1}\right)$$



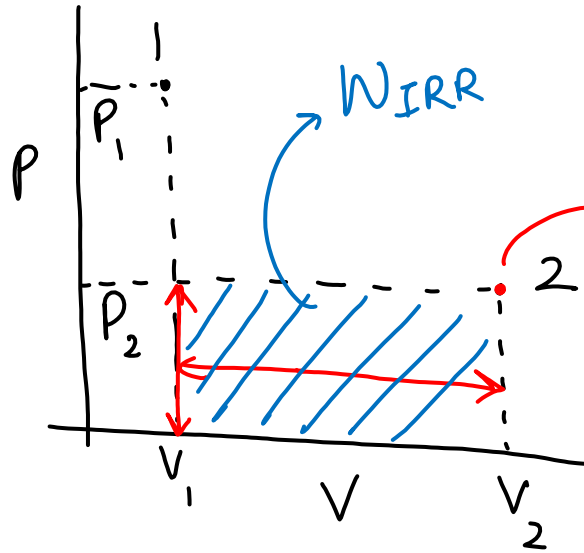
Calculation of work for **Isothermal expansion**

Isothermal reversible expansion :



Calculation of work for **Isothermal expansion**

Isothermal Irreversible expansion :



$$W_{\text{Irr}} = -P_{\text{ext}} (V_2 - V_1)$$

$$P_{\text{gas}} = P_{\text{ext}}$$

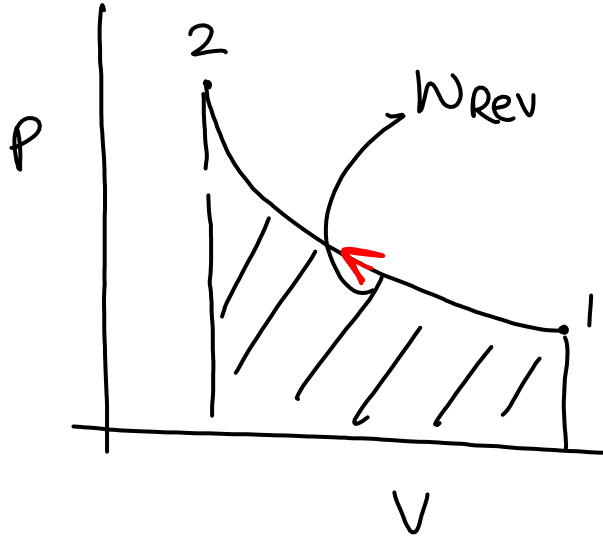
W_{exp} is -ve
For Expansion

$$|W_{\text{Rev}}| > |W_{\text{Irr}}|$$



Calculation of work for **Isothermal expansion**

Isothermal reversible compression :



$$W_{\text{Rev}} = -2.303 nRT \log_{10} \left(\frac{V_2}{V_1} \right)$$

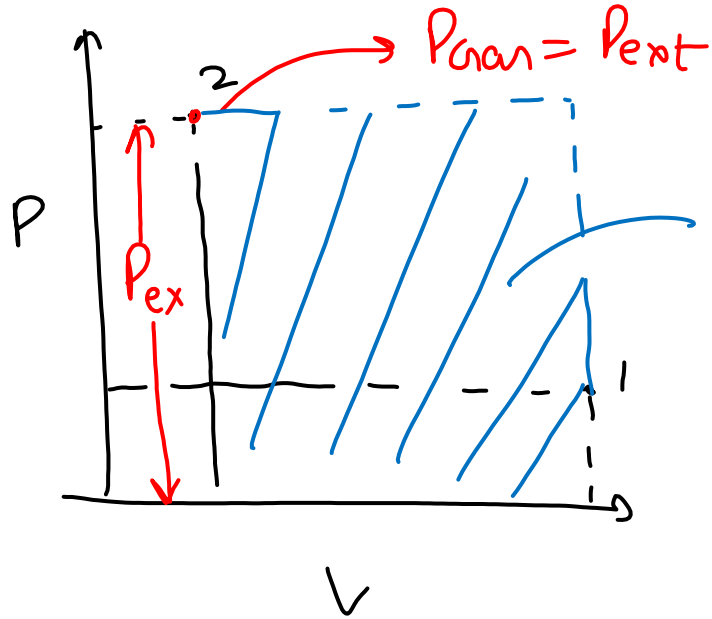
$$PV = \text{const}$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$



Calculation of work for Isothermal expansion

Isothermal Irreversible compression :



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

W_{comp} is +ve

$W_{IRR} > W_{rev}$
for compression



Conclusion :

✓ Whenever work is done on the gas then it will be minimum in case of **reversible process**.

If expansion/compression takes place against constant external pressure then it is **irreversible**.

✓ If there is sudden change then the process is irreversible.



Example

Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°C from 15 to 50 litres.

$$\rightarrow W_{\text{Rev}} = -2.303 \times 2 \times 8314 \times 298 \log \left(\frac{50}{15} \right)$$





Example

If a gas at a pressure of 10 atm at 300 K expands against a constant external pressure of 2 atm from a vol. of 10 litres to 20 litres find work done?

→ IRR. Process

→ Isothermal

$$W_{IRR} = -P_{ext} (V_2 - V_1)$$

$$= -2 \times 10$$

$$= -20 \text{ L atm}$$

$$1 \text{ L atm} = 101.3 \text{ J}$$



Example

A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The value of q and w for the process will be ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) ($\ln 7.5 = 2.01$)

isothermal

(JEE Main 2013)

a) $q = -208 \text{ J}$, $w = -208 \text{ J}$

b) $q = -208 \text{ J}$, $w = +208 \text{ J}$

c) $q = +208 \text{ J}$, $w = +208 \text{ J}$

☒ d) $q = +208 \text{ J}$, $w = -208 \text{ J}$

$$q = +208 \text{ J}$$

$$\cancel{\Delta U} = q + w$$

$$q = -w$$



Example

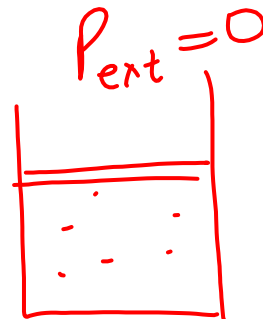
Which of the following is correct option for free expansion of an ideal gas under adiabatic conditions?

- a) $q = 0, \Delta T \neq 0, w = 0$
- b) $q \neq 0, \Delta T = 0, w = 0$
- c) $q = 0, \Delta T = 0, w = 0$
- d) $q = 0, \Delta T < 0, w \neq 0$

$q = 0$

$\Delta U = q + w$

$T = \text{const}$



$w = -P_{\text{ex}} \Delta V$

$w = 0$





Calculation of C_p and C_v

I. Constant volume process (Isochoric)



$$dU = dq + dw$$

$$dU = dq - P dV \rightarrow 0$$

$$dU = dq$$

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

$$C = \frac{q}{\Delta T}$$

$$\boxed{\Delta U = nC_v \Delta T}$$



Calculation of C_p and C_v

II. Constant pressure process (Isobaric)

$$dU = dq - PdV$$

$$(dU + PdV) = dq_p$$

$$dU + PdV = nC_p dT$$

$$C_p - C_v = R$$