- Mentored 1 lakh+ Students
- 10 Yrs Teaching experience
- Content Partner in MHRD DIKSHA Project

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Paaras Thakur

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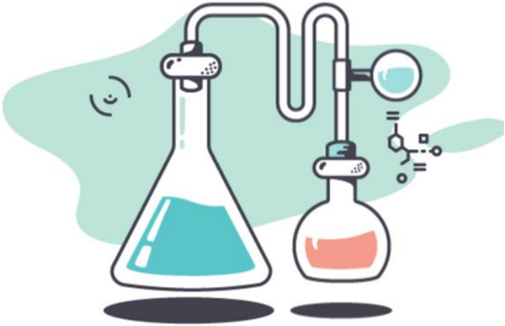
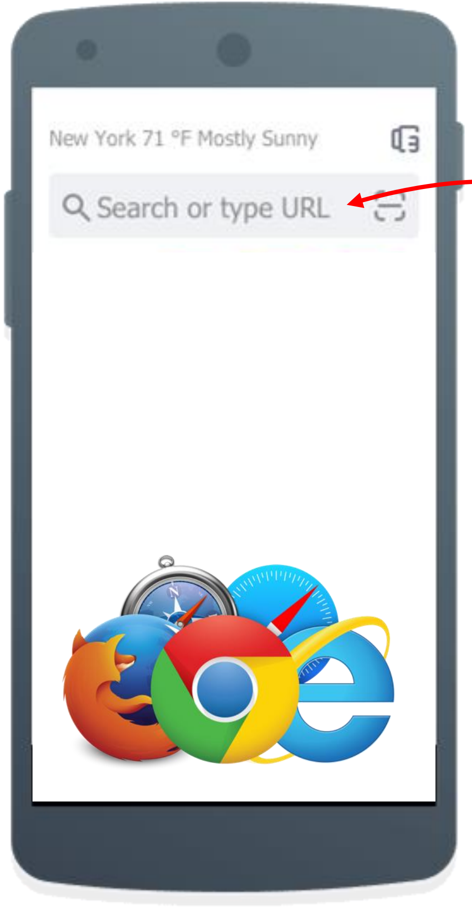
Thermodynamics

Lecture 4





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plus

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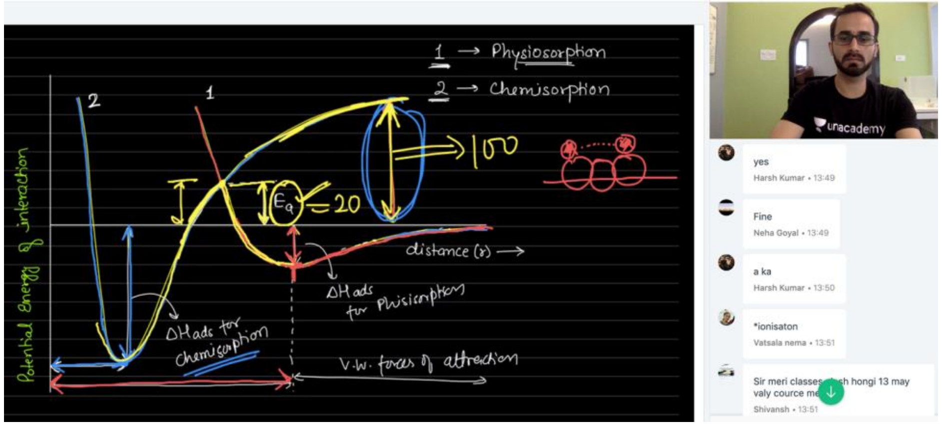
- **Doubt Clearing** Sessions
- Most <u>Personalized</u>



The trouble is,
You think
you have TIME
- Buddha

SAVE

Expense

Time

Energy

LEARN

Why you go to COACHING

Overcome your weakness in subjects

Doubts Clarification

Analyse your performance with Tests, Analysis, Discussion

Online vs Offline

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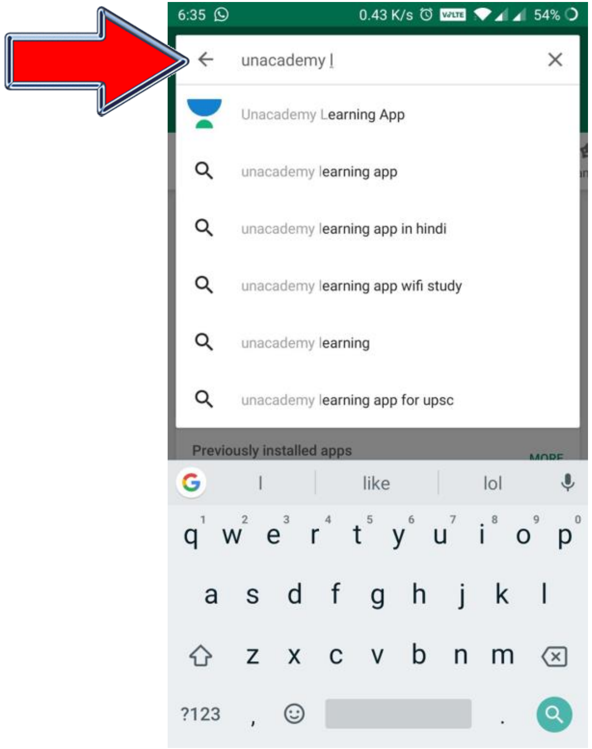
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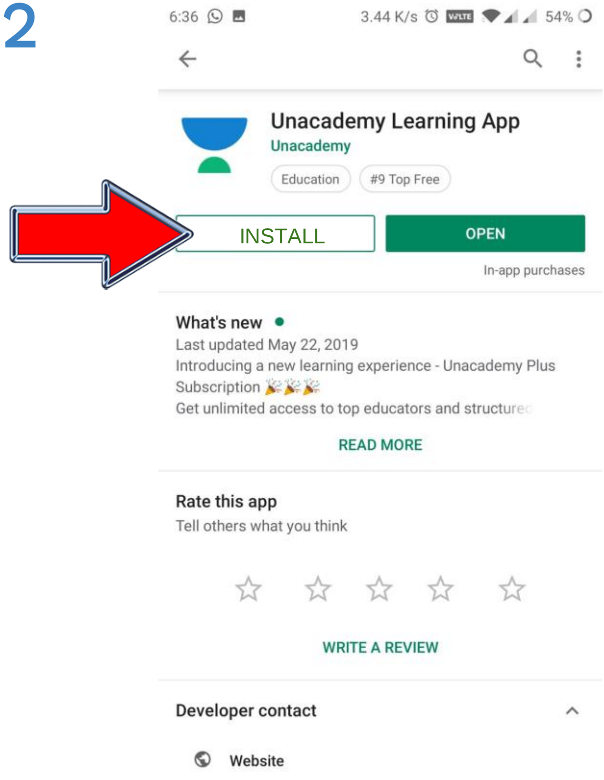
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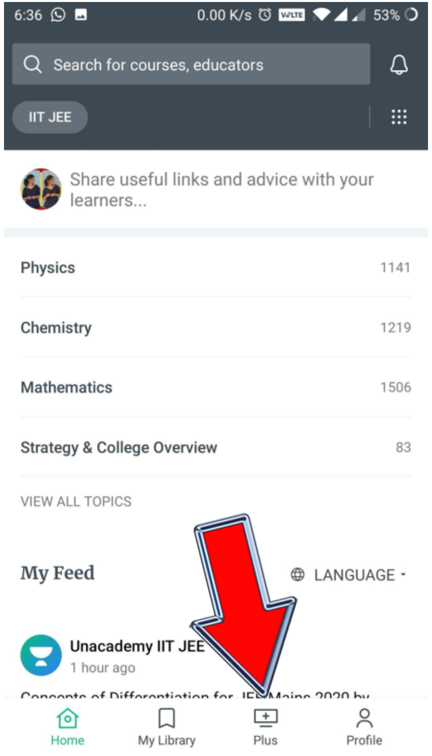
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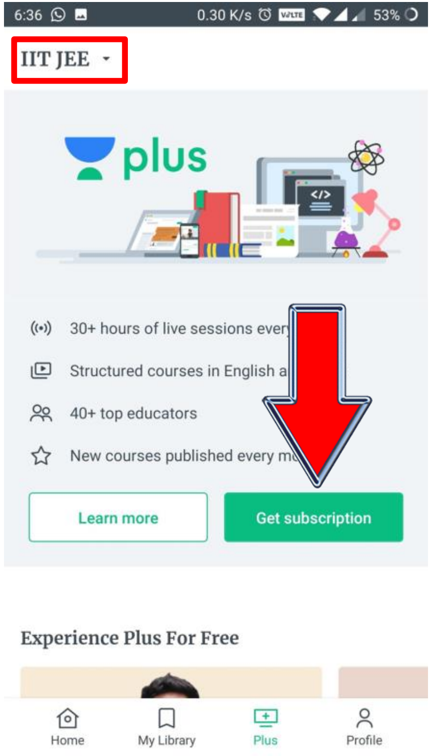
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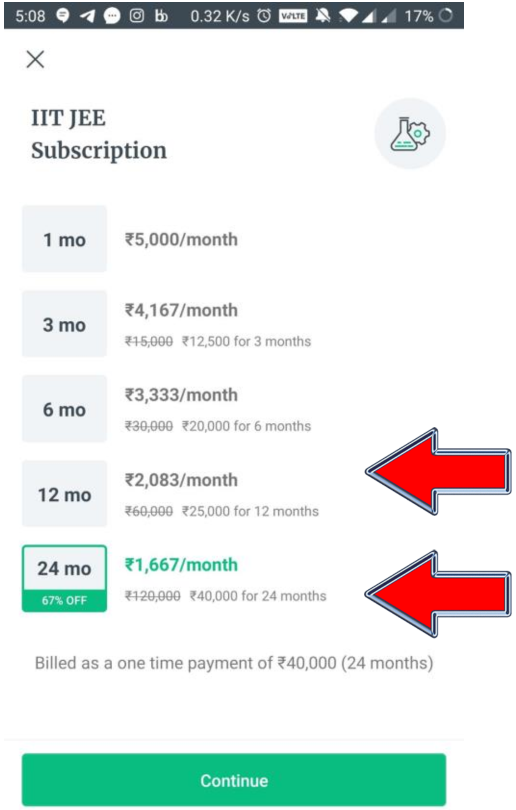
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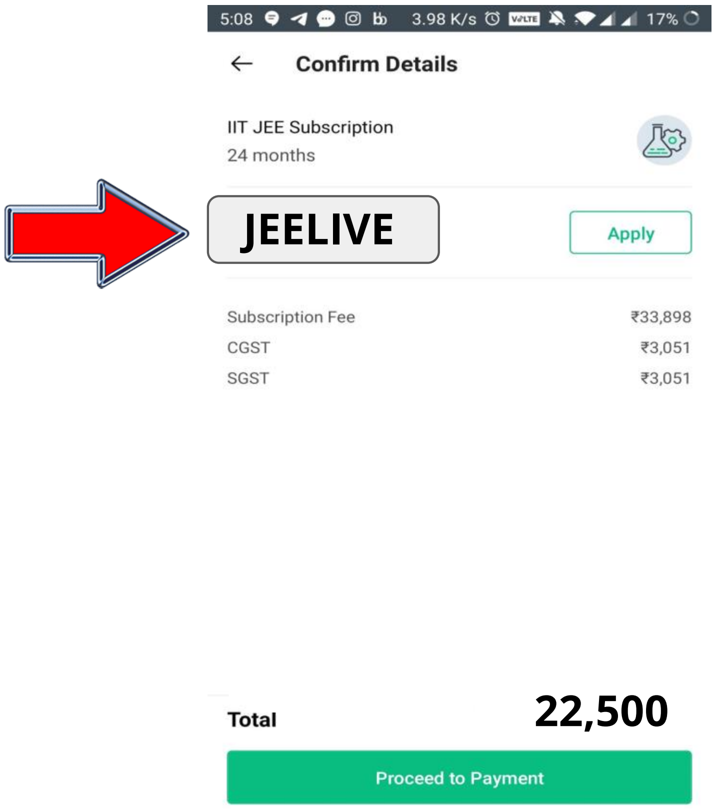
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Example

A gas obeys the equation of state pV = nRT + nbp where b is a constant. If n moles of the gas expand from V_1 to V_2 reversibly at a constant temperature T, the work done is given by

(a) $-$nRT ln[V_2 - nb/V_1 - nb]
(b) nRT ln[V_2 - nb/V_1 - nb]
(c) zero
(d) nRT ln[V_1 - nb/V_2 - nb]

$$W_{Rev} = -nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right)$$

$(PV = nRT)$

$$PV = nRT + nbP$$

$$PV - nbP = nRT$$

$$P(V - nb) = nRT$$

Example

The molar heat capacity of water in equilibrium with ice at constant pressure is

(a) negative

(b) zero

(c) infinity

(d) 40.45 kJ K^{-1} mol^{-1}

$T = const$

$H_2O(s) \rightleftharpoons H_2O(l)$

Melting Point

$C = \frac{q}{\cancel{\Delta T}} \rightarrow 0$

$C \rightarrow \infty$

Example

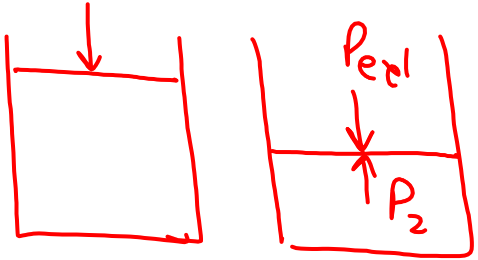
Consider an ideal gas that occupies 2.50 dm^3 at a pressure of 3.00 bar. If the gas is compressed isothermally at a constant pressure p_{ext}, so that the final volume is 0.500 dm^3, calculate the smallest possible value of p_{ext} and the work done using $p_{ext.}$

(a) 20 bar and 100 J
(b) 15 bar and 750 J
(c) 30 bar and 150 J
(d) 10 bar and 375 J

$V_1 \rightarrow 2.5$ lt $\quad P_1 = 3$ bar

$V_2 \rightarrow 0.5$ lt $\quad P_2 = ?$

Isothermal, $PV = \text{const}$



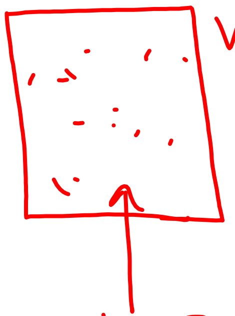
$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{3 \times 2.5}{0.5} = 15 \text{ bar}$$

$$W_{IRR} = -P(V_2 - V_1)$$

Relation between C_p and C_v for an ideal gas

$C_p - C_v = R$



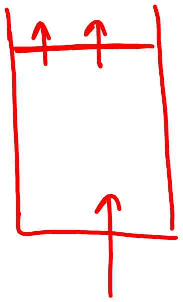
$V = \text{const}$

$T \uparrow$ by 1K

100 J

$C_v = 100\ J$

$\uparrow W_{exp} = 20$



$P = \text{const}$

$\underbrace{100\ J + 20\ J}_{C_p}$

$C_p = C_v + W_{exp}$

$C_p - C_v = R$

For Ideal gas

C_p and C_v are function of T only but taken as constant over a wide range of temp.

$C_p - C_v = R$

Specific heat ratio or heat capacity ratio, $\boxed{\gamma = \frac{C_p}{C_v}}$ gamma

→ Monoatomic gases

e.g. He, Ne, Ar etc.

$C_p = \frac{5}{2}R$

$C_v = \frac{3}{2}R$

$\gamma = 5/3 = 1.66$

For Ideal gas

Diatomic gases

e.g. Air, H_2, O_2 etc.

$C_p = \frac{7}{2}R$

$C_v = \frac{5}{2}R$

$\gamma = \frac{7}{5} = 1.41$

Triatomic gases

e.g. steam, CO_2,

N_2O, SO_2 etc.

$C_p = \frac{9}{2}R$

$C_v = \frac{7}{2}R$

$\gamma = \frac{9}{7} = 1.33$

* $\gamma \downarrow$ as atomicity of gas $\uparrow$
* $\boxed{C_v = \frac{R}{\gamma - 1}}$

Example

When 0.1 mol of a gas absorbs 41.75 J of heat at constant volume, the rise in temperature that occurs is equal to 20 K. The gas must be

a) Triatomic
b) Diatomic
c) polyatomic
d) monoatomic

C_v

0.1 mole ⟶ 41.75 J at V = const

1 mole ⟶ 417.5 J

$C_v = \frac{3}{2}R$ for mono

$C_v = \frac{q}{\Delta T} = \frac{417.5}{20}$ J/mol K

$= \frac{5}{2}R$ for dia

Example

A steam boiler made up of steel weighs 900 kg. The boiler contains 400 kg of water. Assuming 70% of the heat is delivered to boiler and water, how much heat is required to raise the temperature of the whole from 10°C to 100°C? Heat capacity of steel is 0.11 kcal kg^{-1} K^{-1} and heat capacity of water is 1 kcal kg^{-1} K^{-1}.

a) 65321 kcal
b) 64157 kcal
c) 6869 kcal
d) 66549 kcal

Total heat Req $= q_{boiler} + q_{water}$

$= (900 \times 0.11 \times 90 + 400 \times 1 \times 90)$ kcal

$= 44910$

$q = mc\Delta T$

$c = \dfrac{q}{m\Delta T}$

heat supp $\times \dfrac{70}{100} = 44910$

heat supp $= \dfrac{100}{70} \times 44910$

Enthalpy (H)

Most physical and chemical changes occur at nearly constant atmospheric pressure — a reaction in an open flask, the freezing of a lake, a biochemical process in an organism.

Enthalpy, a thermodynamic variable that relates directly to energy changes at constant pressure.

$$dU = q + w$$

at const Pressure

$$(U_2 - U_1) = q_p - P(V_2 - V_1)$$

$$(U_2 + PV_2) - (U_1 + PV_1) = q_p$$

Enthalpy (H)

since $P = \text{const}$

$$P_1 = P_2 = P$$

$$(U_2 + P_2V_2) - (U_1 + P_1V_1) = q_p$$

$$H_2 - H_1 = q_p$$

$$\boxed{\Delta H = q_p}$$

$$H = U + PV$$

$\downarrow$

a state function

$$\Delta U = q + w$$

$$\Delta U = q - P\Delta V$$

at const vol.

$$\Delta U = q_v$$

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Enthalpy (H)

$H = U + PV$

$dH = dU + d(PV)$

$= dU + PdV + VdP + \cancel{dP\,dV}$ neglect

$dH = dU + PdV + VdP$

$= q - \cancel{PdV} + \cancel{PdV} + VdP$

$dH = q + VdP$

if $P = \text{const}$

$\boxed{dH = q_p}$

$\Delta H = \Delta U + P\Delta V + V\Delta P$

$= \Delta U + (P_2V_2 - P_1V_1)$

$= \Delta U + nR\Delta T$

$= \Delta U + \Delta n_g RT$

$C = \frac{q}{dT}$ or $q = CdT$

$C_p = \left(\frac{dH}{dT}\right)_p$, $C_v = \left(\frac{dU}{dT}\right)_v$

Exothermic and Endothermic Processes

Because H is a combination of the three state functions E, P, and V, it is also a state function. Therefore, ΔH equals

$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

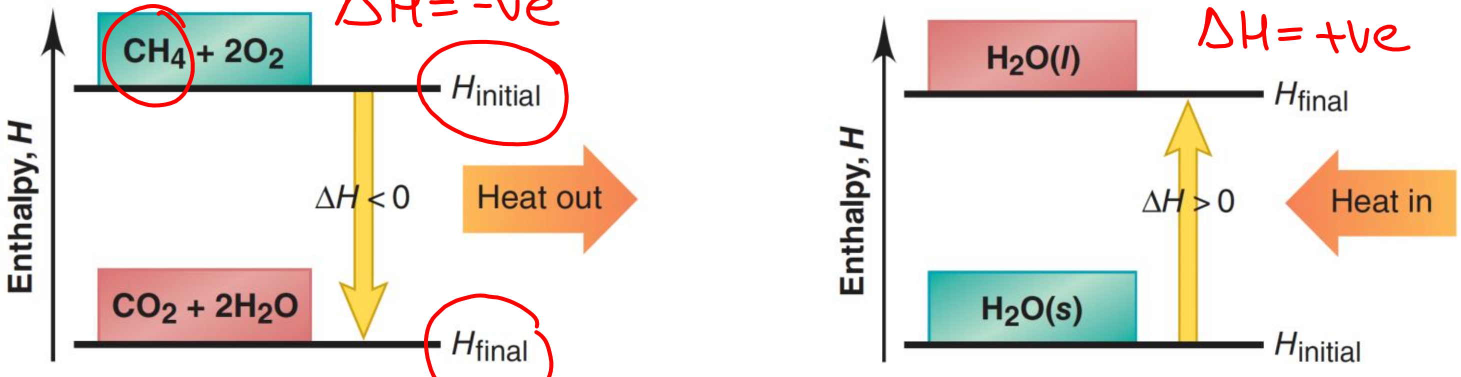
$$\Delta H = q_p = nC_p\Delta T$$

$$\Delta H = nC_p\Delta T$$

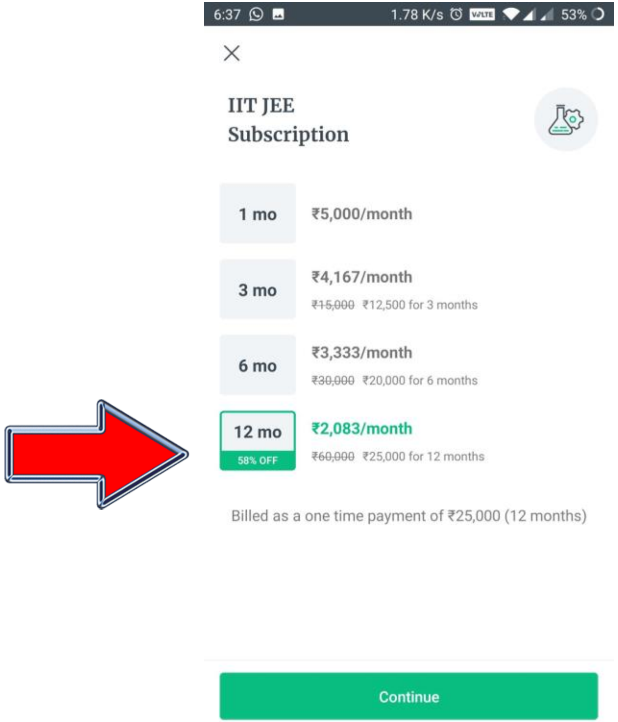
$$\Delta U = nC_v\Delta T$$

Exothermic: $H_2 - H_1 = -ve$ q is released

$\Delta H = -ve$ $\Delta H = +ve$



A Exothermic process   **B Endothermic process**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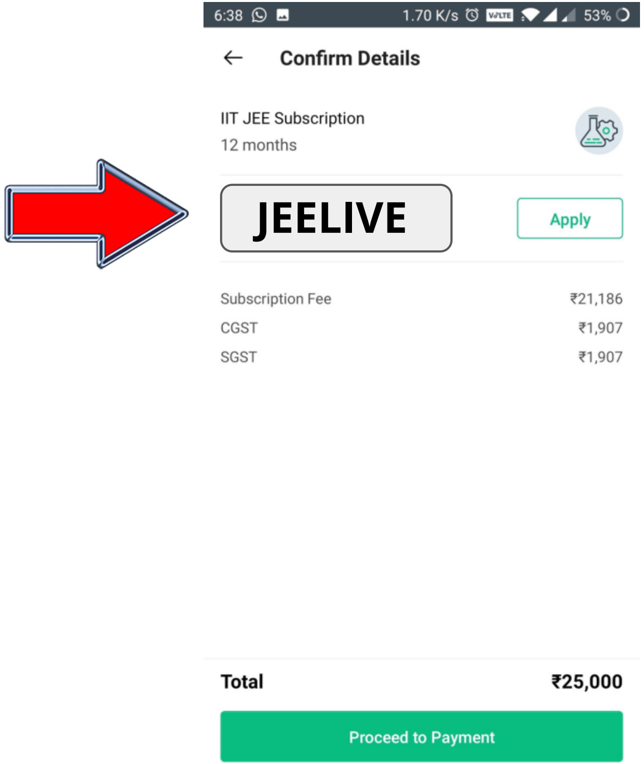
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