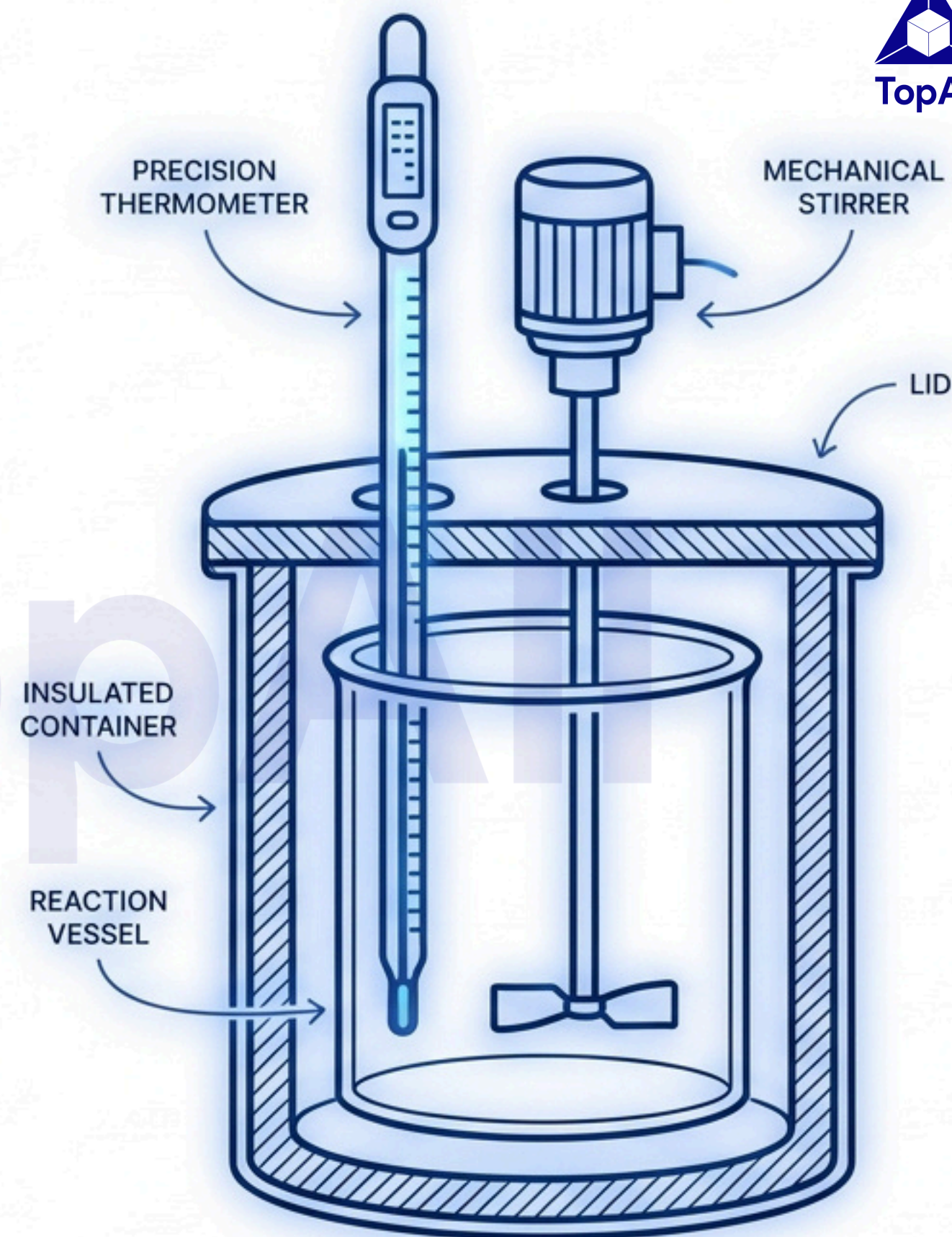


5.3 Calorimetry: Measurement of ΔU and ΔH

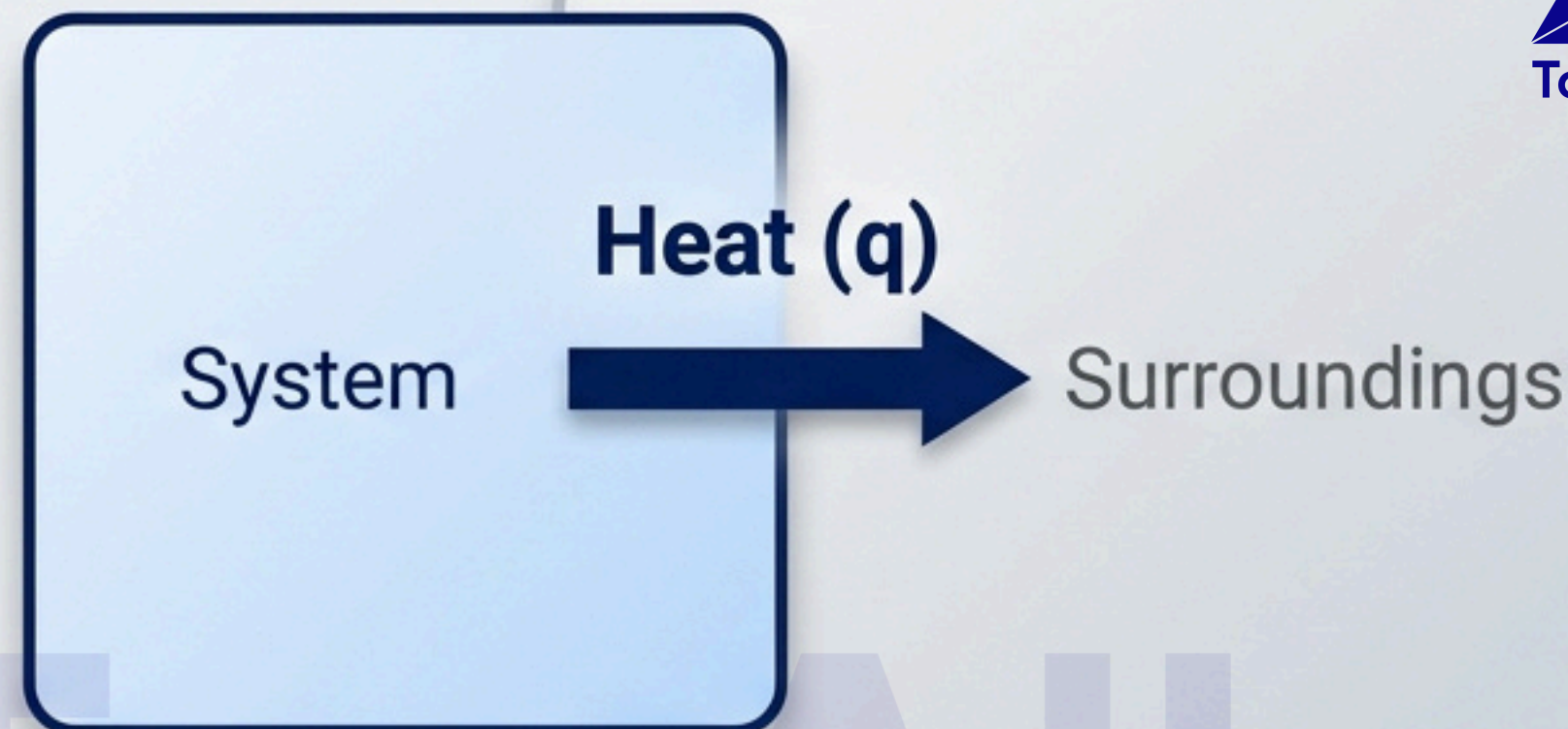
Quantifying energy changes in chemical reactions using constant-volume and constant-pressure techniques.



CORE PRINCIPLE

Measuring Heat Transfer

Calorimetry is the experimental technique used to measure energy changes (heat) associated with chemical or physical processes. We measure the heat supplied or absorbed by monitoring the temperature change of an isolated system.



$$q = C \times \Delta T$$

q = Heat transferred

C = Heat capacity of the system

ΔT = Change in temperature

When Volume is Constrained When Volume is Constrained

If a reaction takes place in a sealed, rigid container, it cannot expand or contract. No mechanical work can be done on or by the system.

Volume is constant $\rightarrow \Delta V = 0$

Since expansion work is $w = -p_{\text{ex}} \times \Delta V \rightarrow w = 0$

The First Law equation $\Delta U = q + w$ becomes $\rightarrow \Delta U = q + 0$

$$q_v = \Delta U$$

At constant volume, the heat absorbed or released is exactly equal to the change in Internal Energy.



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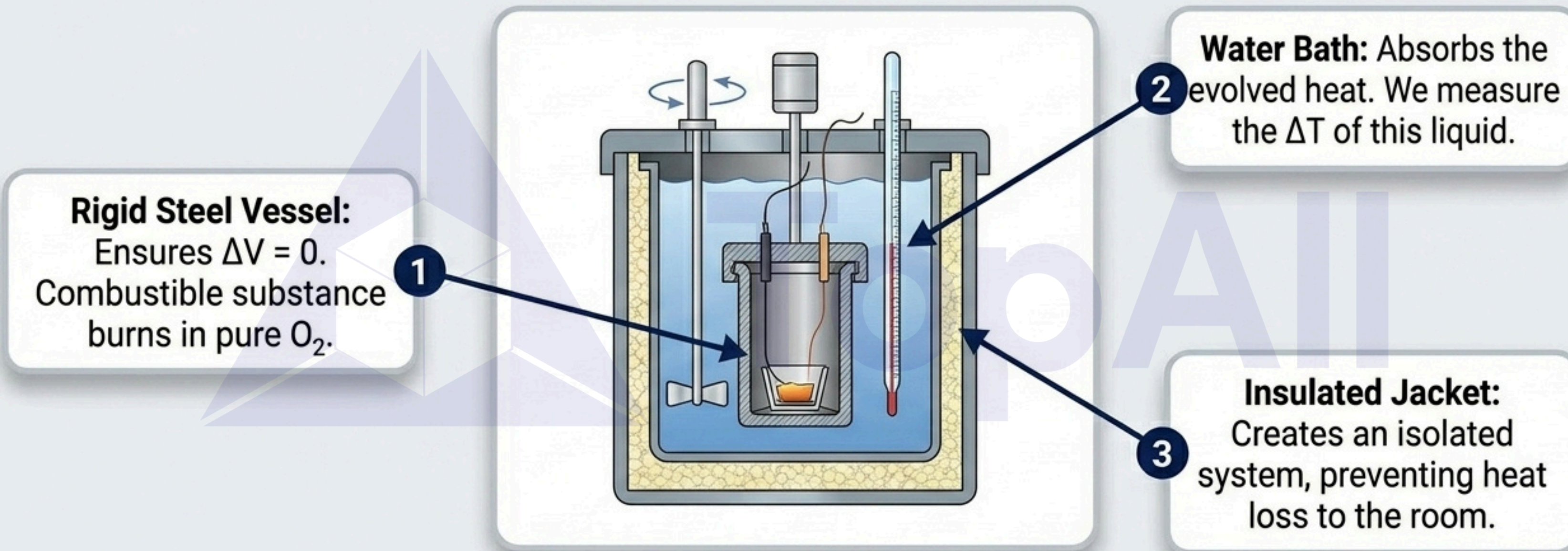
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The Bomb Calorimeter



$$\Delta U = q_v = C_v \times \Delta T$$

(where C_v is the heat capacity of the entire calorimeter)

THERMODYNAMIC CONDITIONS

When Pressure is Constrained

Most chemical reactions in the lab occur in open flasks or test tubes under constant atmospheric pressure. The system can freely expand or contract against the atmosphere, meaning expansion work ($p\Delta V$) can occur.

Enthalpy Definition

Accounts for internal energy plus the energy required to displace the atmosphere.

$$H = U + pV$$

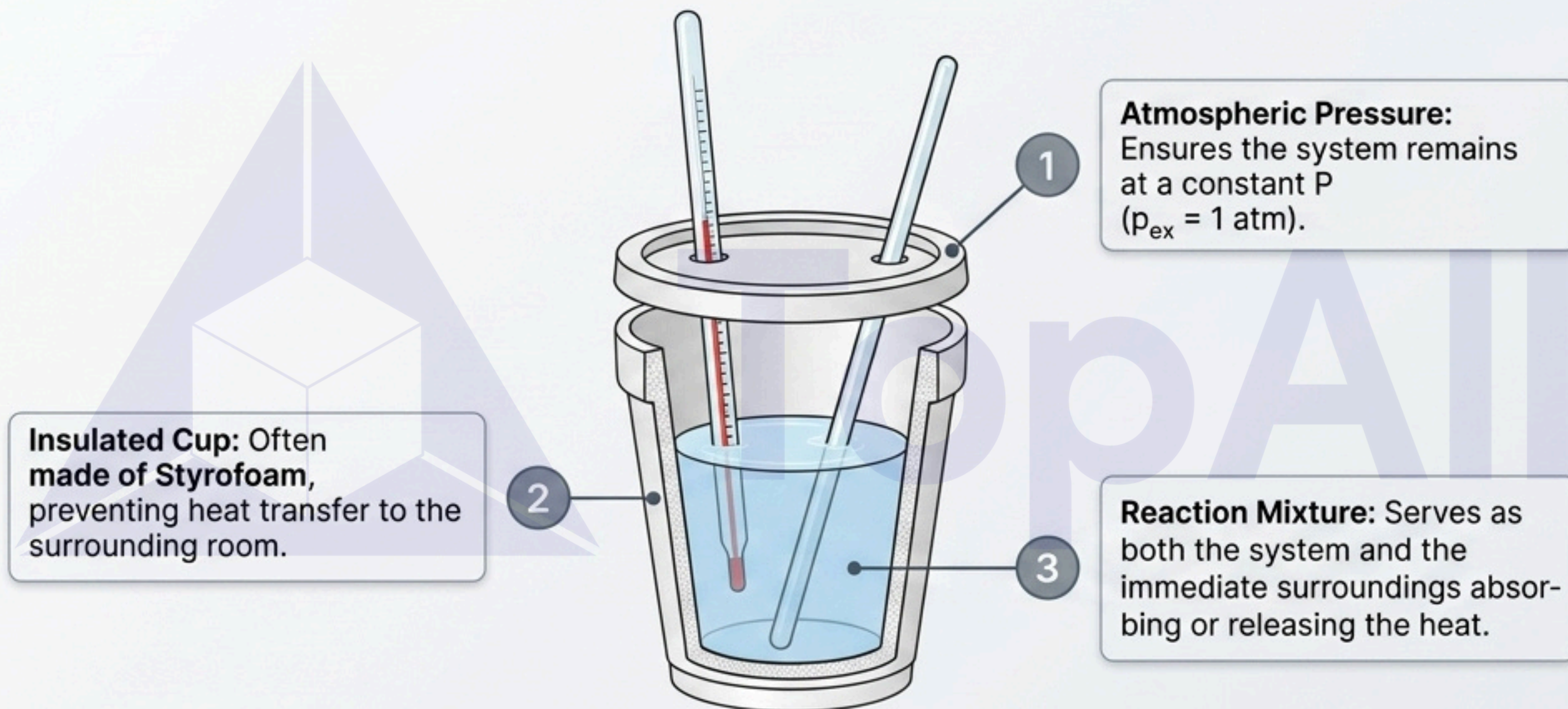
The Math

Because expansion work can be done, the heat flow at constant pressure directly equals the change in Enthalpy rather than Internal Energy.

$$q_p = \Delta H$$

At constant pressure, the heat absorbed or released is exactly equal to the change in Enthalpy.

The Coffee-Cup Calorimeter



Used primarily to measure Enthalpy of Reaction ($\Delta_r H$) for liquid solutions and neutralizations.

The Calorimetry Cheat Sheet

The Master Principle $\rightarrow q = C \times \Delta T$

Constant Volume (Bomb)



Constraint:

$$\Delta V = 0 \text{ (Work} = 0\text{)}$$

Measures:
Internal Energy

$$q_v = \Delta U$$

Best for:
Combustions, Gases

Constant Pressure (Coffee Cup)



Constraint:

$$\Delta P = 0 \text{ (Open to atmosphere)}$$

Measures:
Enthalpy

$$q_p = \Delta H$$

Best for:
Liquid solutions, Neutralizations

Macroscopic properties measured $\rightarrow$ Thermodynamic state functions determined.



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