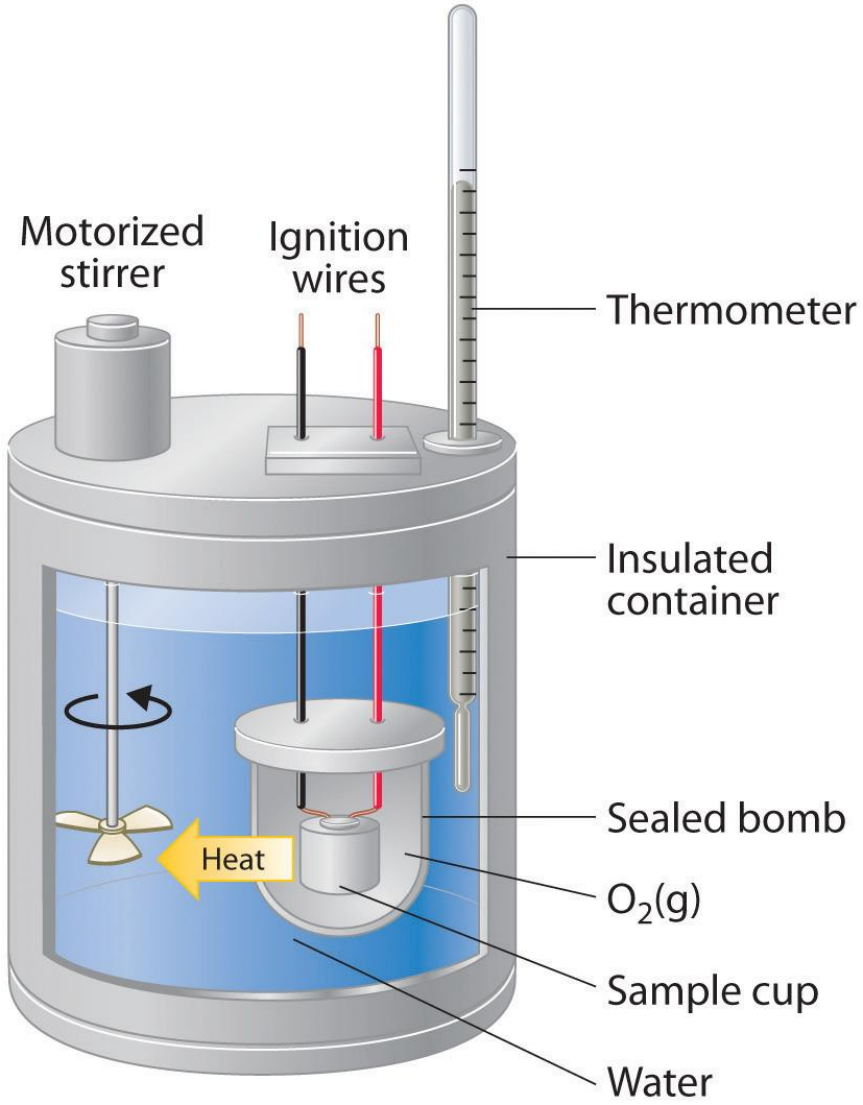
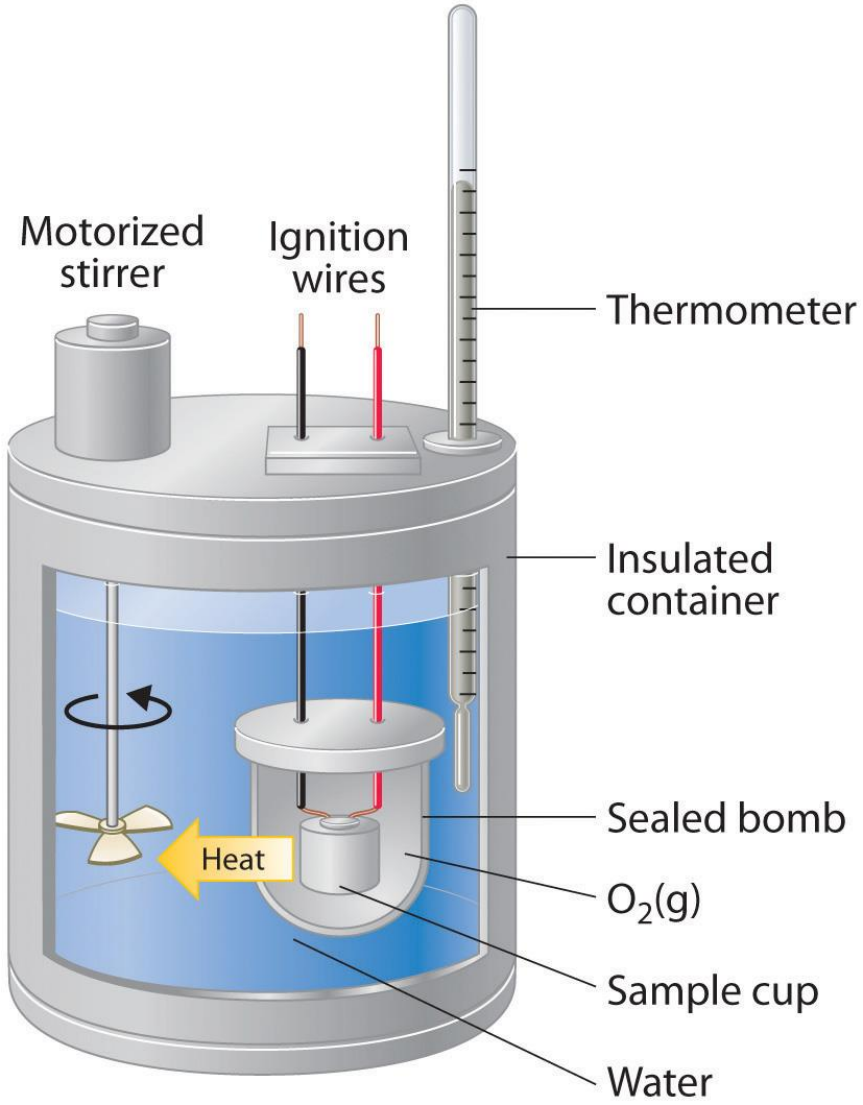
Calorimetry



A constant-volume bomb calorimeter.

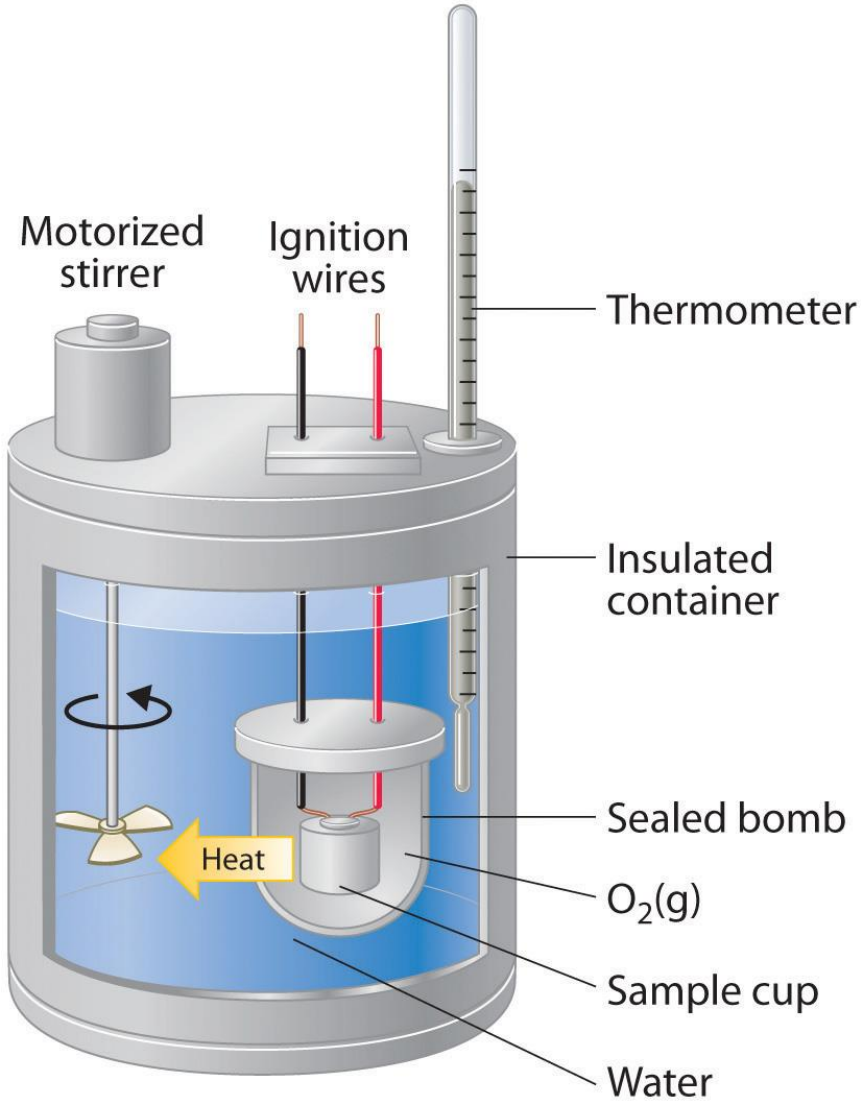
Calorimetry



A constant-volume bomb calorimeter.

$$q = C\Delta T$$

Calorimetry



$$q = C\Delta T$$

calorimeter constant

Calorimeter constant

$$q = C\Delta T$$

If a current of 10.0 A from a 12 V supply is passed for 300 s, then the energy supplied as heat is

Calorimeter constant

$$q = C\Delta T$$

If a current of 10.0 A from a 12 V supply is passed for 300 s, then the energy supplied as heat is

$$q = (10.0\,\text{A}) \times (300\,\text{s}) \times (12\,\text{V}) = 3.6 \times 10^4\,\text{A V s} = 36\,\text{kJ}$$

Calorimeter constant

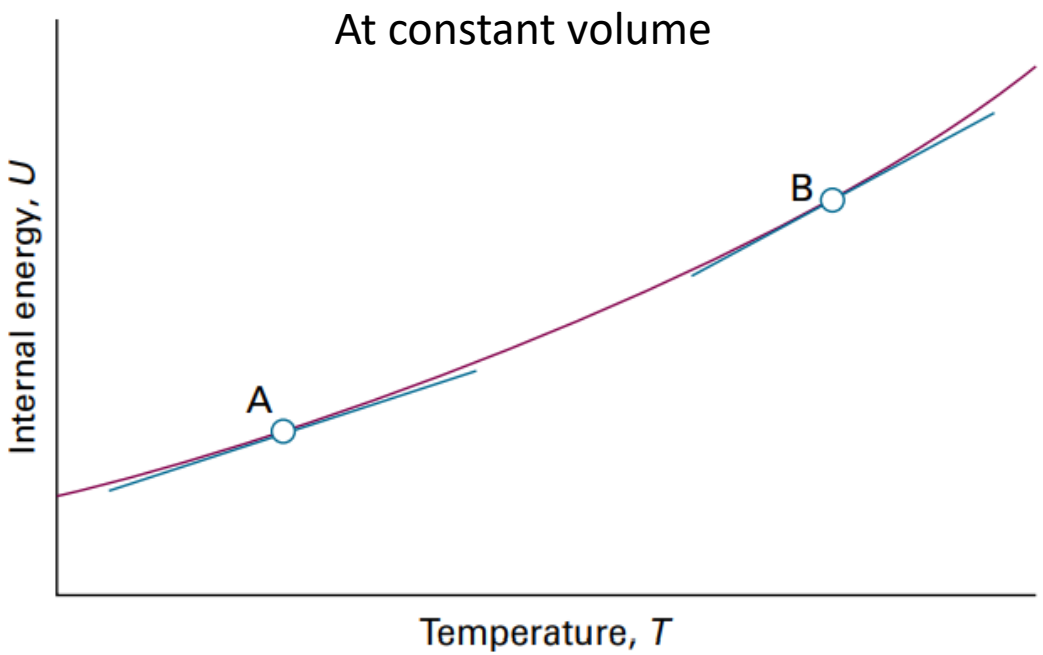
$$q = C\Delta T$$

If a current of 10.0 A from a 12 V supply is passed for 300 s, then the energy supplied as heat is

$$q = (10.0\,\text{A}) \times (300\,\text{s}) \times (12\,\text{V}) = 3.6 \times 10^4\,\text{A V s} = 36\,\text{kJ}$$

If the observed rise in temperature is 5.5 K, then the calorimeter constant is $C = (36\,\text{kJ})/(5.5\,\text{K}) = 6.5\,\text{kJ K}^{-1}$.

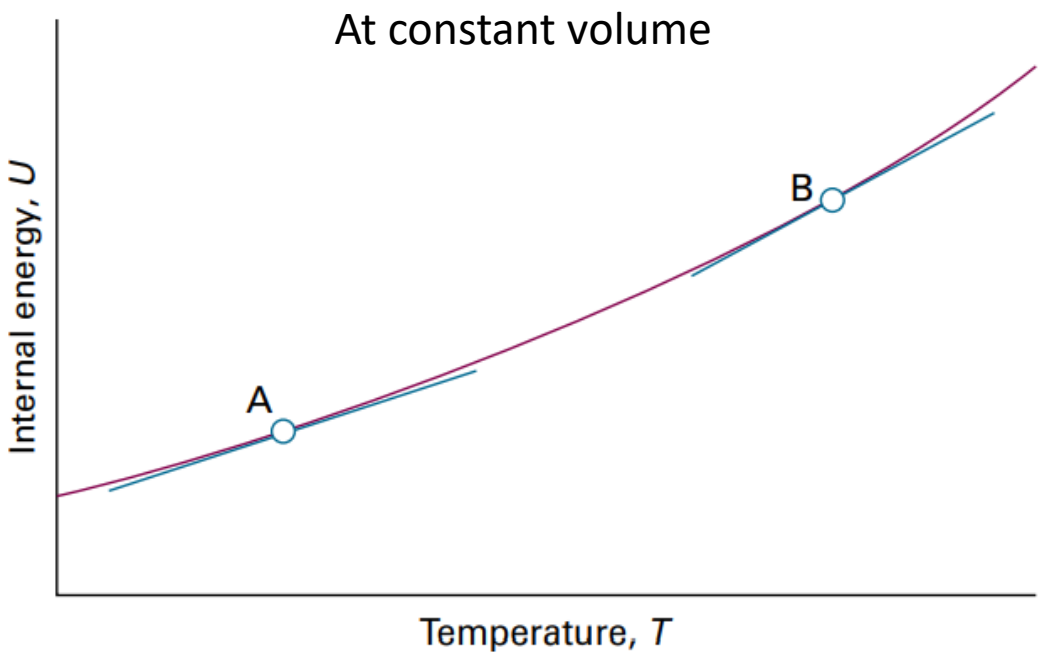
U vs T



The internal energy is only a function of temperature for perfect gases (assuming constant number of moles)

For real gases, U depends on volume

Heat capacity



The internal energy is only a function of temperature for perfect gases (assuming constant number of moles)

For real gases, U depends on volume

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

Molar heat capacity and specific heat capacity

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

extensive

Molar heat capacity and specific heat capacity

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

extensive

$$C_{V,\mathrm{m}} = C_V / n \qquad C_{V,\mathrm{s}} = C_V / m$$

intensive

Internal energy and heat capacity

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

Internal energy change on heating [constant volume]

Internal energy and heat capacity

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

Internal energy change on heating [constant volume]

$$\Delta U = \int_{T_1}^{T_2} C_V \, \mathrm{d}T$$

Internal energy and heat capacity

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

Internal energy change on heating [constant volume]

$$\Delta U = \int_{T_1}^{T_2} C_V \, \mathrm{d}T = C_V \int_{T_1}^{T_2} \mathrm{d}T = C_V \overbrace{(T_2 - T_1)}^{\Delta T}$$

$$\Delta U = C_V \Delta T$$

Focus 2: The First Law

Internal Energy

Enthalpy

Thermochemistry

State functions

Adiabatic changes

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

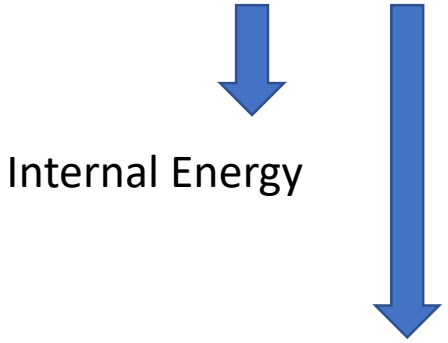
Internal Energy

Energy Required for Expansion

Enthalpy

$$H = U + pV$$

Enthalpy [definition]



Internal Energy

Energy Required for Expansion

- In many practical situations, such as chemical reactions, phase changes, and industrial processes, systems often operate under constant pressure. When a system expands, it performs work on the surroundings, expressed as $W=p\Delta V$.

- Since a portion of the energy input is used for this expansion work, the total energy change must account for both U and pV, leading to the above relationship.

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

The change in enthalpy is equal to the energy supplied as heat at constant pressure

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$H + \mathrm{d}H$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work

$$\mathrm{d}w = -p\mathrm{d}V,$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work

$$\mathrm{d}w = -p\mathrm{d}V,$$

$$\mathrm{d}H = \mathrm{d}q + V\mathrm{d}p$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work

$$\mathrm{d}w = -p\mathrm{d}V,$$

$$\mathrm{d}H = \mathrm{d}q + V\mathrm{d}p$$

At constant pressure, $\mathrm{d}p = 0$,

$$\mathrm{d}H = \mathrm{d}q_p$$

Enthalpy

$$H = U + pV$$

Enthalpy [definition]

$$H + \mathrm{d}H = (U + \mathrm{d}U) + (p + \mathrm{d}p)(V + \mathrm{d}V)$$

$$= U + \mathrm{d}U + pV + p\mathrm{d}V + V\mathrm{d}p + \mathrm{d}p\mathrm{d}V$$

$$= H + \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}H = \mathrm{d}q + \mathrm{d}w + p\mathrm{d}V + V\mathrm{d}p$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work

$$\mathrm{d}w = -p\mathrm{d}V,$$

$$\mathrm{d}H = \mathrm{d}q + V\mathrm{d}p$$

At constant pressure, $\mathrm{d}p = 0$,

$$\mathrm{d}H = \mathrm{d}q_p$$

If no additional work done, the change in enthalpy is equal to the energy supplied as heat at constant pressure

Measurable enthalpy change

$$\mathrm{d}H = \mathrm{d}q_p$$

Measurable enthalpy change

$$\mathrm{d}H = \mathrm{d}q_p$$

$$\overbrace{\int_{\mathrm{i}}^{\mathrm{f}} \mathrm{d}H}^{H_{\mathrm{f}} - H_{\mathrm{i}}} = \overbrace{\int_{\mathrm{i}}^{\mathrm{f}} \mathrm{d}q}^{q_p}$$

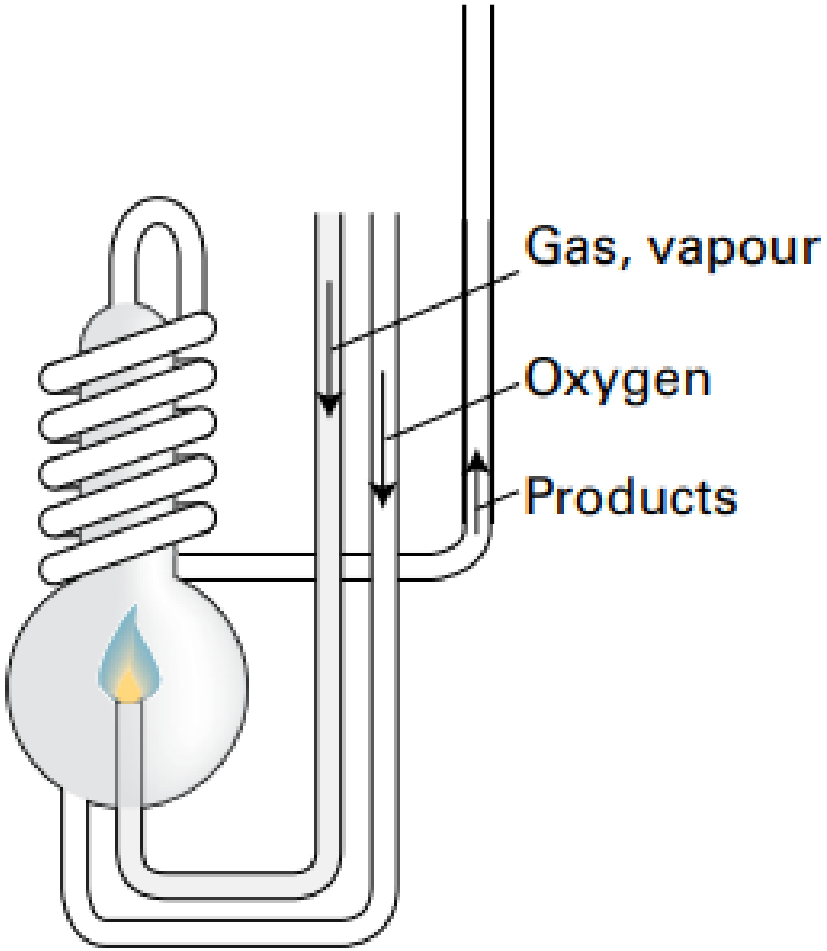
Measurable enthalpy change

$$\mathrm{d}H = \mathrm{d}q_p$$

$$\overbrace{\int_i^f \mathrm{d}H}^{H_f - H_i} = \overbrace{\int_i^f \mathrm{d}q}^{q_p} \longrightarrow \Delta H = q_p$$

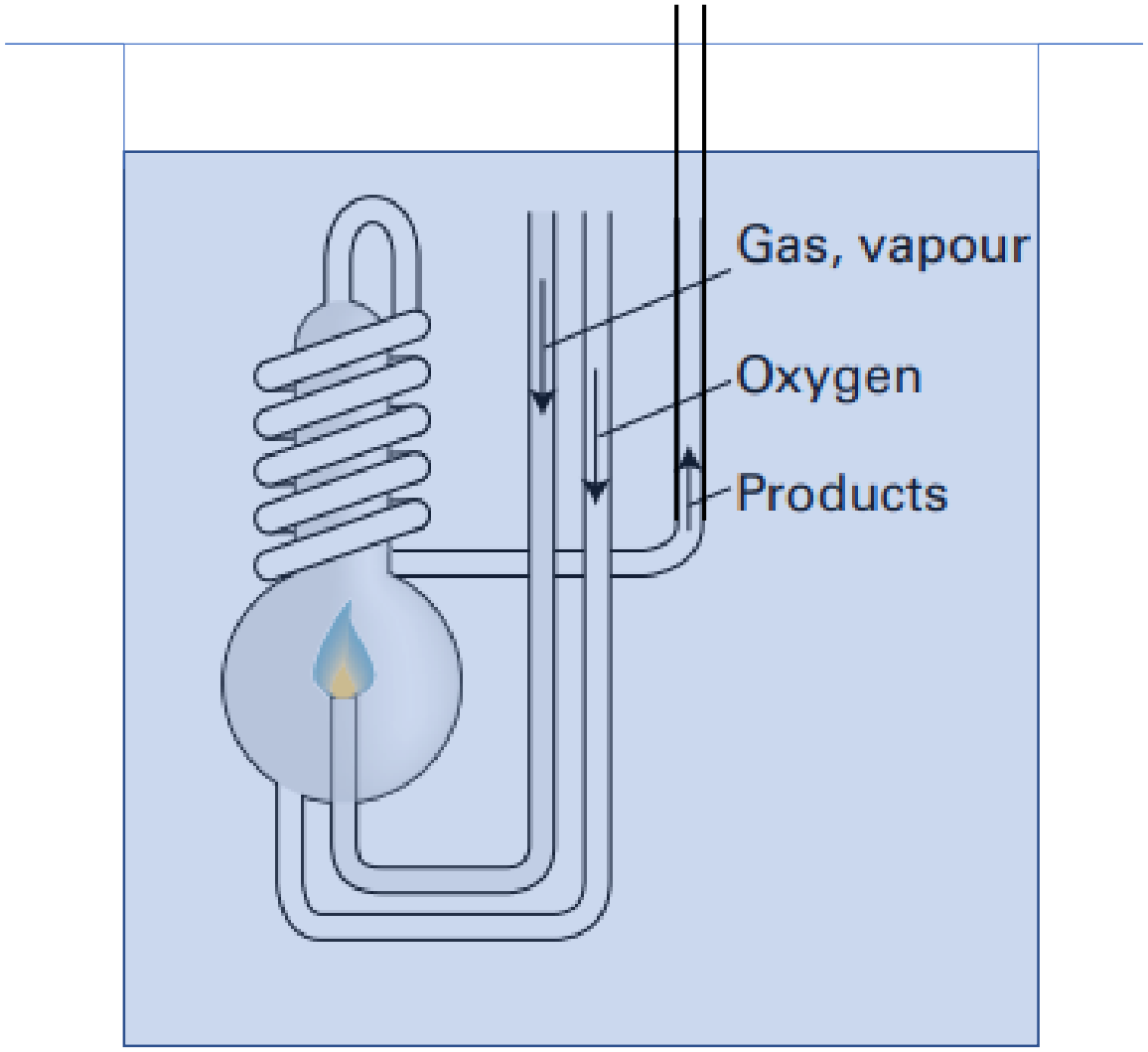
Heat transferred at constant pressure [measurable change]

Isobaric Calorimetry



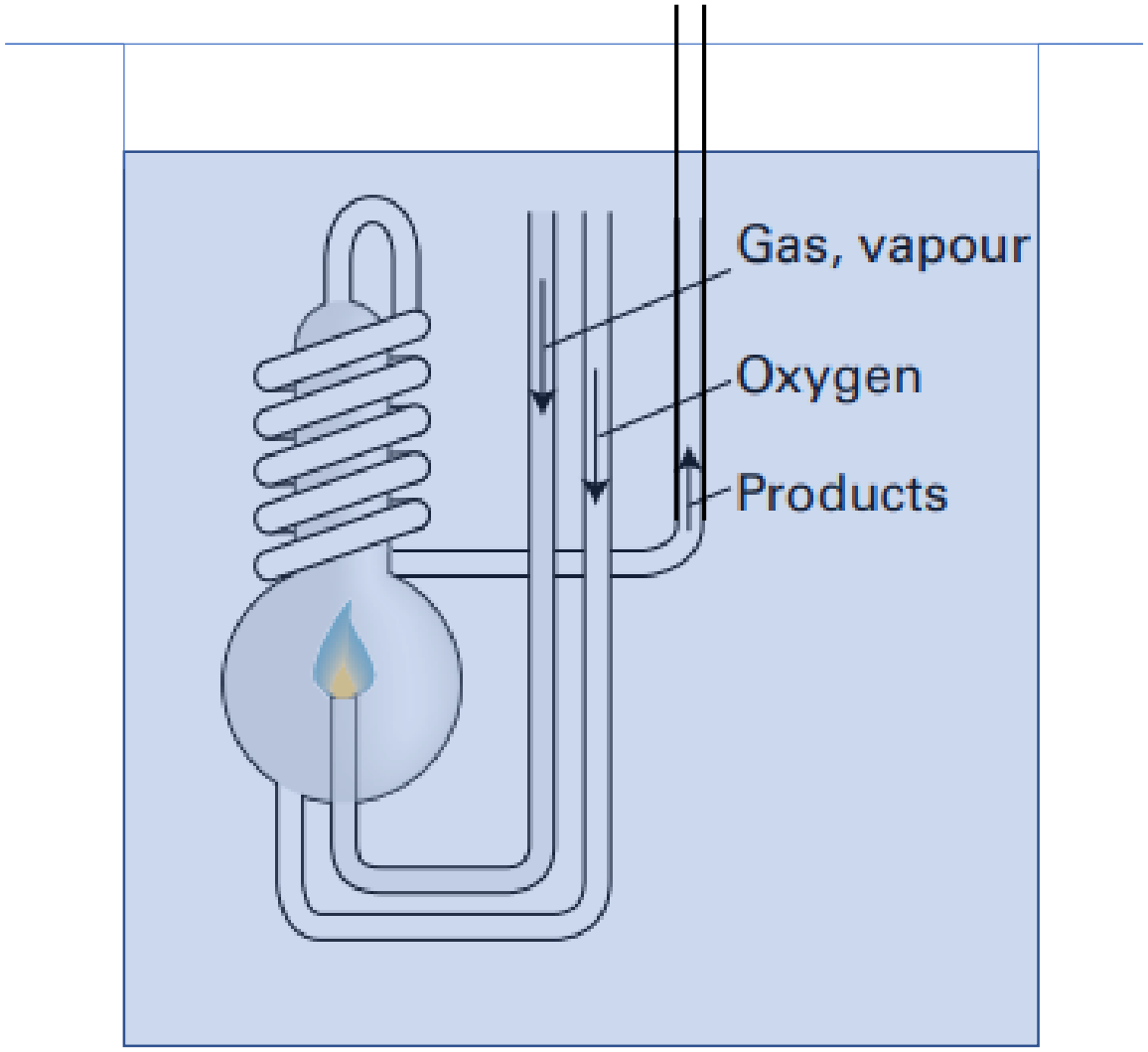
A constant pressure flame calorimeter

Isobaric Calorimetry

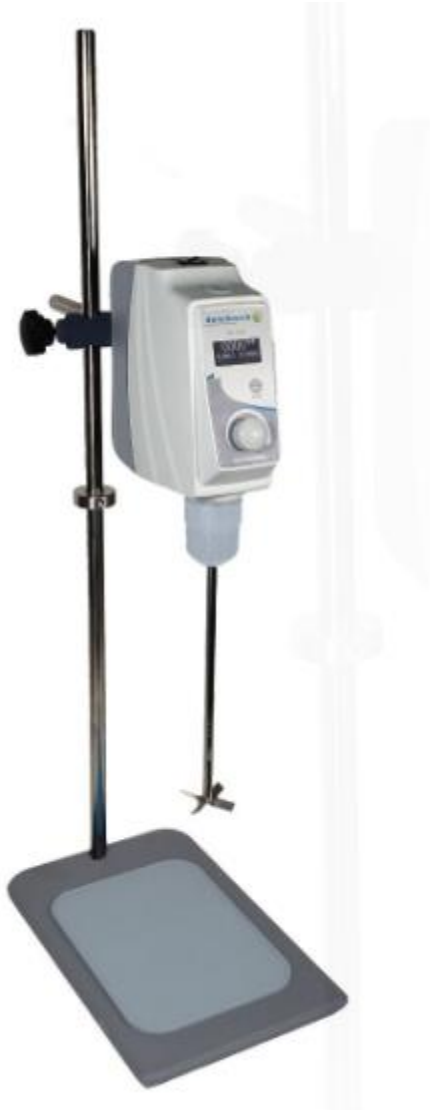


A constant pressure flame calorimeter

Isobaric Calorimetry



A constant pressure flame calorimeter



Enthalpy of a perfect gas

Enthalpy
[definition]

$$H = U + pV$$

Enthalpy of a perfect gas

Enthalpy [definition]

$$H = U + pV$$

For perfect gases

$$H = U + pV = U + nRT$$

Enthalpy

Enthalpy [definition]

$$H = U + pV$$

For perfect gases

$$H = U + pV = U + nRT$$

The change of enthalpy in a reaction that produces or consumes gas under <u>isothermal</u> conditions

$$\Delta H = \Delta U + \Delta n_g RT$$

Enthalpy

Enthalpy [definition]

$$H = U + pV$$

For perfect gases

$$H = U + pV = U + nRT$$

The change of enthalpy in a reaction that produces or consumes gas under <u>isothermal</u> conditions

$$\Delta H = \Delta U + \Delta n_g RT$$

change in the number of moles of gas molecules in the reaction

Enthalpy

Enthalpy [definition]

$$H = U + pV$$

For perfect gases

$$H = U + pV = U + nRT$$

The change of enthalpy in a reaction that produces or consumes gas under <u>isothermal</u> conditions

$$\Delta H = \Delta U + \Delta n_g RT$$

change in the number of moles of gas molecules in the reaction

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l),$$

Enthalpy

Enthalpy [definition]

$$H = U + pV$$

For perfect gases

$$H = U + pV = U + nRT$$

The change of enthalpy in a reaction that produces or consumes gas under <u>isothermal</u> conditions

$$\Delta H = \Delta U + \Delta n_g RT$$

change in the number of moles of gas molecules in the reaction

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l),$$

$$\Delta n_g = -3$$

Enthalpy

Enthalpy [definition]

$$H = U + pV$$

For perfect gases

$$H = U + pV = U + nRT$$

The change of enthalpy in a reaction that produces or consumes gas under <u>isothermal</u> conditions

$$\Delta H = \Delta U + \Delta n_g RT$$

change in the number of moles of gas molecules in the reaction

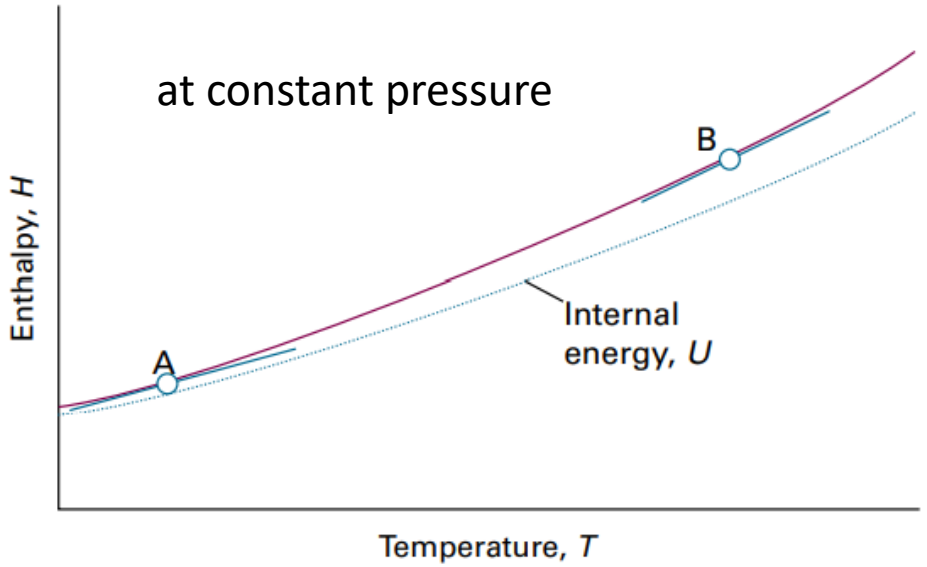
$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l),$$

$$\Delta n_g = -3$$

$$\Delta H - \Delta U = (-3) \times RT \approx -7.5\,\text{kJ mol}^{-1}$$

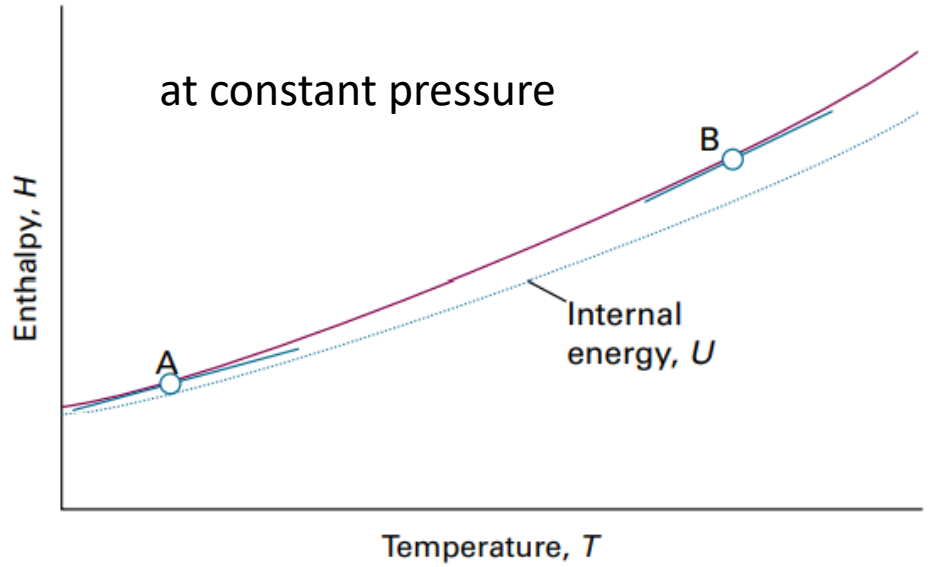
Enthalpy as a function of temperature

The enthalpy of a substance increases as its temperature is raised



Enthalpy as a function of temperature

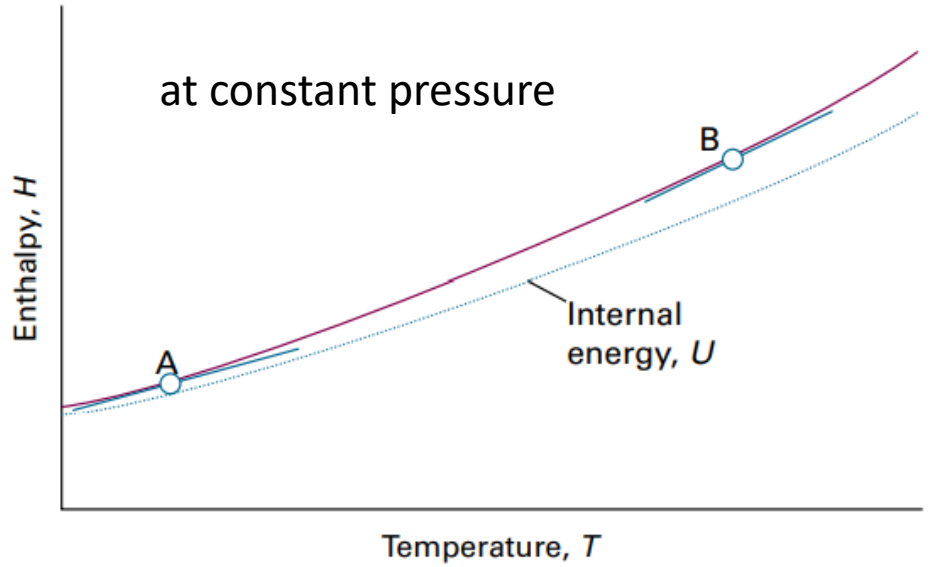
The enthalpy of a substance increases as its temperature is raised



$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

Enthalpy as a function of temperature

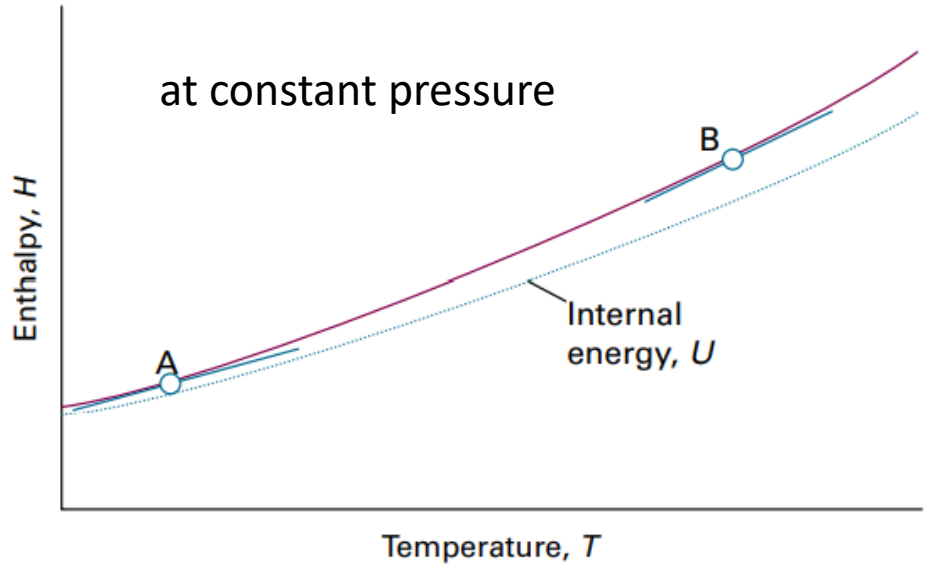
The enthalpy of a substance increases as its temperature is raised



$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \longrightarrow \mathrm{d}H = C_p \mathrm{d}T$$

Enthalpy as a function of temperature

The enthalpy of a substance increases as its temperature is raised



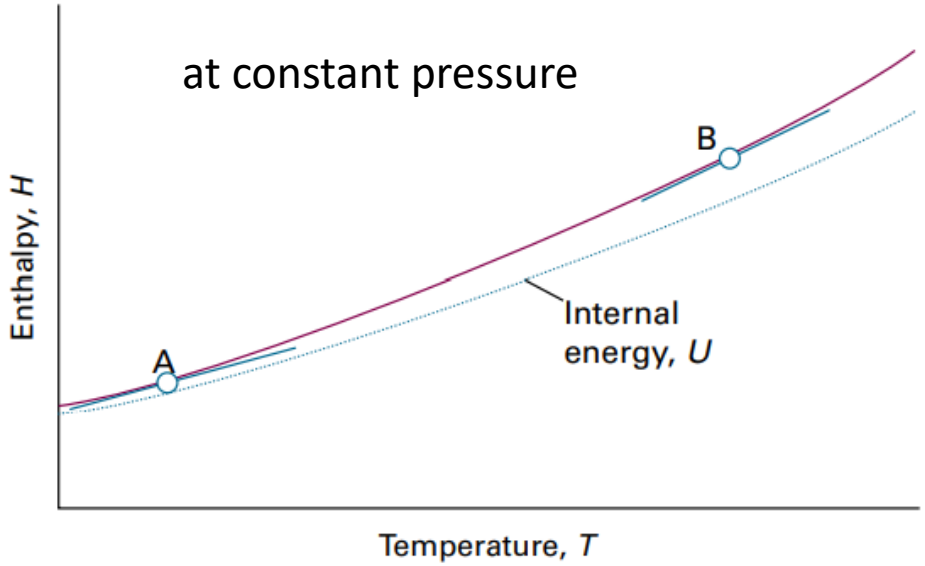
$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \longrightarrow \mathrm{d}H = C_p \mathrm{d}T$$

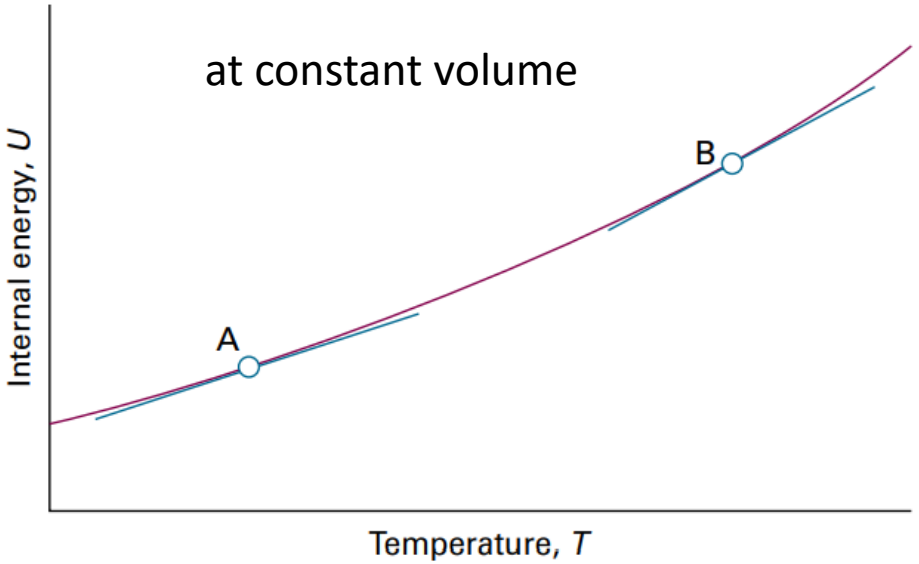
If the heat capacity is constant,

$$\Delta H = \int_{T_1}^{T_2} C_p \mathrm{d}T = C_p \int_{T_1}^{T_2} \mathrm{d}T = C_p \overbrace{(T_2 - T_1)}^{\Delta T}$$

$$= C_p \Delta T$$

C_p and C_v



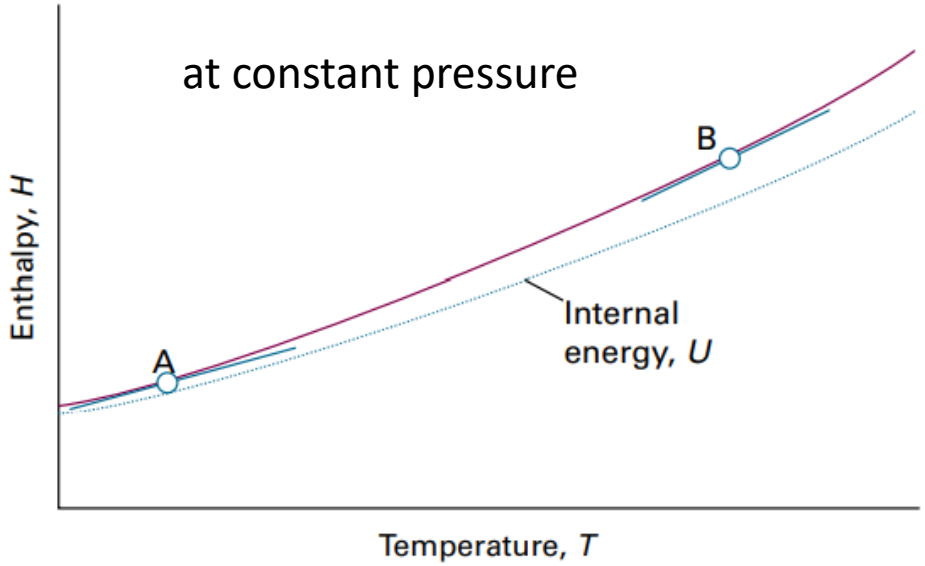


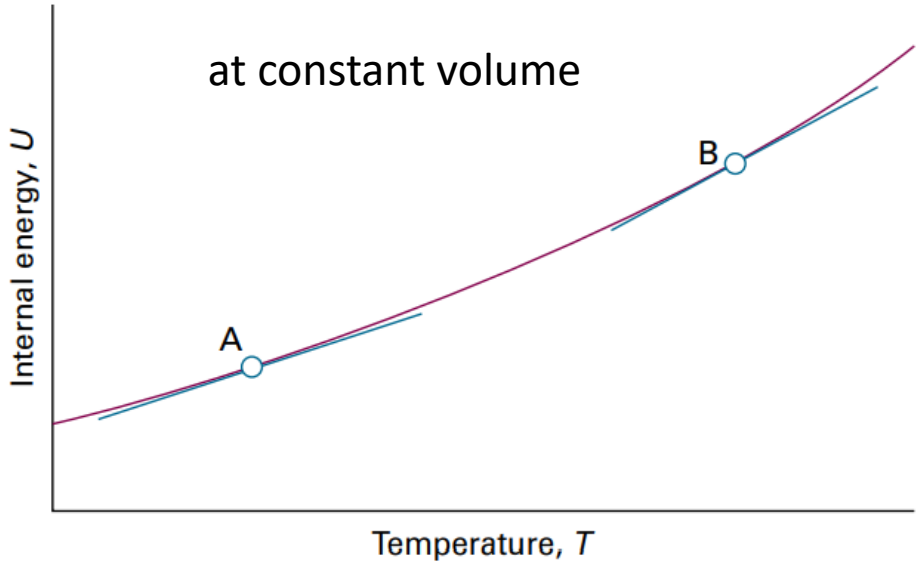
$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

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

At constant pressure, the system expands and does work on the surroundings, requiring more heat to achieve the same temperature change compared to constant volume conditions.

C_p and C_v

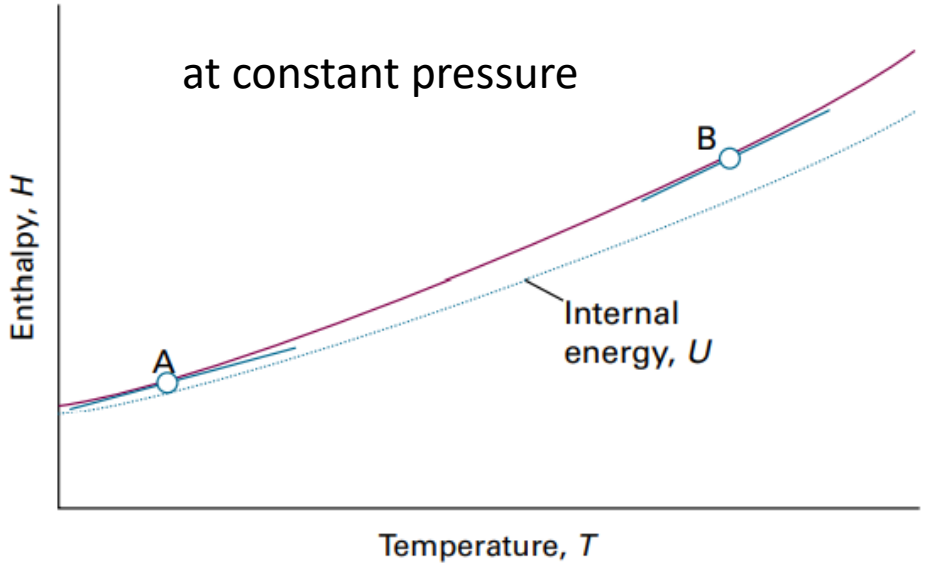


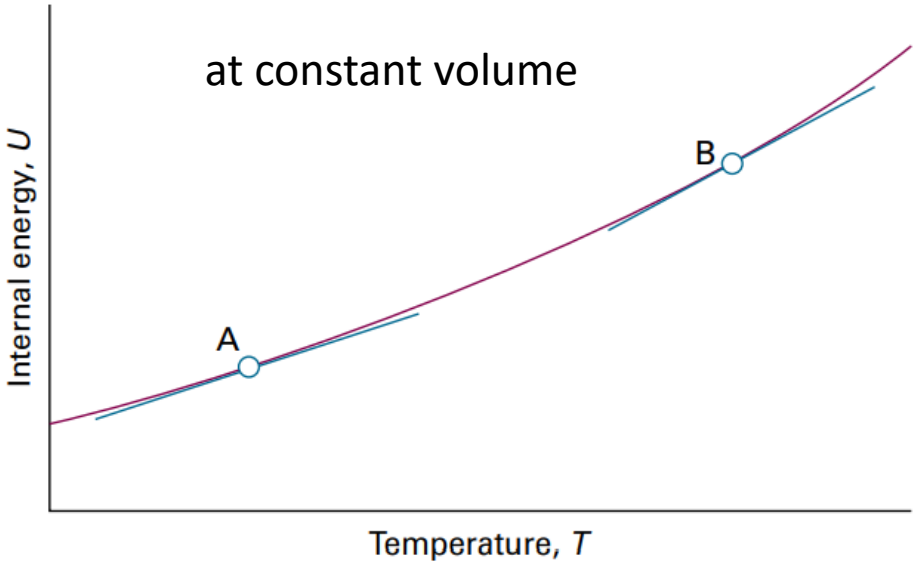


$$C_p = \left(\frac{\partial H}{\partial T}\right)_p > C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

At constant pressure, the system expands and does work on the surroundings, requiring more heat to achieve the same temperature change compared to constant volume conditions.

C_p and C_v





$$C_p = \left(\frac{\partial H}{\partial T}\right)_p > C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

perfect gas: $C_p - C_V = nR$

R = 8.314 J mol^{-1} K^{-1}
= 0.082 05 L atm mol^{-1} K^{-1}