FOCUS

• What Thermodynamics?
• What is Enthalpy?
• What is Internal energy?
• How does heat and work affect internal energy?
• How can we measure heat transferred in a reaction (Calorimetry)?

Thermodynamics

Thermodynamics is the study of when heat is transferred into or from a system, either of two scenarios can develop:

Example:

\[ \text{CO}_2(s, -78 \, ^\circ C) \rightarrow \text{CO}_2(g, -78 \, ^\circ C) \]
The First Law of Thermodynamics

The first law of thermodynamics is the same as the law of conservation of energy, i.e.

Energy can neither be created nor destroyed

OR

The total energy of the universe is constant

The First Law of Thermodynamics

When heat (+q) is transferred to a system, some of the heat is used to do work (-w) on the surrounding and the rest is used to increase the internal energy (ΔE) of the system

Conversely, when heat (-q) is transferred from the system to the surrounding work (+w) is done on the system by the surrounding and there is a change in the internal energy of the system (ΔE)

The internal energy in a chemical system is the sum of the KE and PE of all the atoms, ions, or molecules in the system
The First Law of Thermodynamics

How can we mathematically summarize the first law of thermodynamics?

FIRST LAW OF THERMODYNAMICS

Work done by the system is negative (-w)
Work done on the system is positive (+w)

Heat transfer between system (e.g. a chemical reaction) and surrounding can occur under different conditions

It (i.e. heat transfer) can occur under the condition of constant volume in which case:
\[ q = q_v \]

It (i.e. heat transfer) can occur under the condition of constant pressure in which case:
\[ q = q_p = H \text{ (where H is called ENTHALPY)} \]
Heat Energy Transfer in Chemical Processes

When endothermic process

\[ \text{CO}_2(s) \rightarrow \text{CO}_2(g) \]

Occurs in a rigid container (fixed volume), the only energy exchanged is the heat transferred into the system.

By law of conservation of energy,

The heat absorbed at constant volume, \( q_v \), is equal to the energy change in the system \( \Delta E \)

i.e \( q_v = \Delta E \)

FIRST LAW OF THERMODYNAMICS

\[ q = \Delta E + w \]

The kind of work that is represented in the equation above is the type that involves volume change against a resisting pressure (P-V type).

Most chemical reactions occur at constant pressure (e.g. in a beaker under constant atmospheric pressure).

Hence the heat transferred in such reaction is \( q_p \) and can be called Enthalpy (H)

ENTHALPY

Absolute enthalpy of a system cannot be experimentally measured.

Only a change in enthalpy, \( \Delta H \), can be measured (Note: \( H \) can be theoretically calculated from other pieces of information).

Hence we can re-write the first law:

\[ q_p = \Delta H = \Delta E + w \]

\( \Delta H \) = heat transferred at constant P

= change in heat content of the system

= \( H_{\text{final}} - H_{\text{initial}} \)
ENTHALPY

\[ \Delta H = H_{\text{final}} - H_{\text{initial}} \]

If \( H_{\text{final}} > H_{\text{initial}} \) then \( \Delta H \) is positive
Process is ENDOTHERMIC

If \( H_{\text{final}} < H_{\text{initial}} \) then \( \Delta H \) is negative
Process is EXOTHERMIC

EFFECT OF HEAT AND WORK ON INTERNAL ENERGY

\[ q_p = \Delta H = \Delta E + w \]

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<tr>
<th>Change</th>
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<td>Heat transferred from system to surrounding</td>
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Measuring Heats of Reaction
CALORIMETRY

\[ q_{\text{rxn}} + q_{\text{bomb}} + q_{\text{water}} = 0 \]
Octane, C₈H₁₈, a primary constituent of gasoline burns in oxygen according to the equation below:

\[ C₈H₁₈ + \frac{25}{2} O₂ → 8 CO₂ + 9 H₂O \]

A 1g sample of the octane is burnt in a fixed volume calorimeter. The calorimeter contains 1.20kg of water. The temperature of the water and the bomb rises from 25°C (298.15K) to 33°C (306.35K). The specific heat capacity of the bomb is 837J/K and that of water is 4.184J/K.

(a) What is the heat of combustion per gram of octane?
(b) What is the heat of combustion per mole of octane?