THERMOCHEMISTRY
1: THERMOCHEMICAL EQUATIONS

Dr. Sapna Gupta

THERMODYNAMICS

Thermodynamics: Relationship between heat and other forms of energy

Thermochemistry: Study of heat absorbed or evolved by chemical reactions.

Energy: Capacity to do work.

- Law of Conservation of Energy: Energy cannot be created nor destroyed only converted from one to the other. (electrochemical, mechanical, chemical etc.)

- First Law of Thermodynamics: The total energy of the universe is constant. (also, the law of conservation of energy).

ENERGY AND UNITS

Calories are the non-SI units. 1 calorie is the amount of energy required to raise the temperature of 1 g of water by $1^{o}C$.

- SI units of energy are Joules (J).
- 1 cal = 4.184 J (1000 cal = 1 Cal)
- KINETIC ENERGY: Energy of motion ($E = 1/2mv^2$)
  - m=mass and v=velocity
- POTENTIAL ENERGY: Energy of a stationary object (E = mgh)
  - m=mass; g= gravitational force; h=height

INTERNAL ENERGY

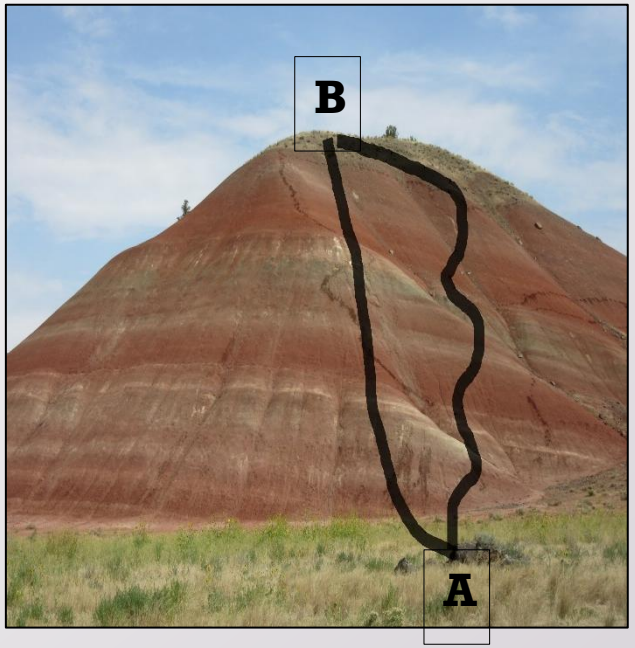
INTERNAL ENERGY (U): Sum of kinetic and potential energies of all particles.

$$E_{total} = E_k + E_p + U$$

- Change in internal energy is generally studied:

  $\Delta U = U$ *(final)* $- U$ *(initial)* where Δ = change

- Internal energy is an extensive property and a state function.
- A state function is a property (solid, liquid, gas) that depends only on its present state, determined by variables such as temperature and pressure.
- E.g. the altitude of the hilltop (B) is a state function – not how one gets there.



$$\Delta E = E_{products(B)} - E_{reactants(A)}$$

This ΔE can be positive or negative

SYSTEM

Thermodynamic system: substance under study in which a change occurs.

Thermodynamic surroundings: everything in the vicinity of the thermodynamic system.

Energy can go from a system to surroundings to the other way.

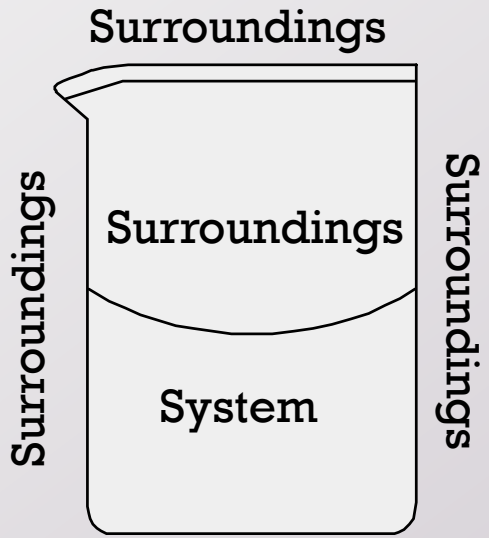
Systems can be open, closed or isolated.

Open System: energy is free flowing everywhere.

Closed System: some energy can go surrounding from system.

Isolated System: all energy stays in system.

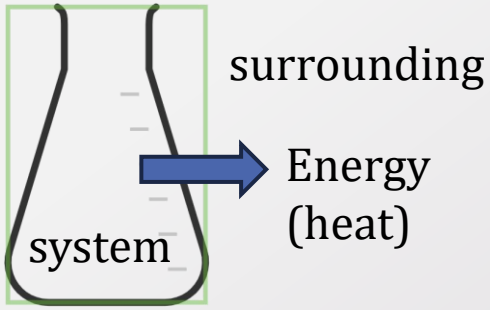
Energy going from system to surrounding causes the system to have lower energy while going from surrounding to system causes surrounding to have lower energy.



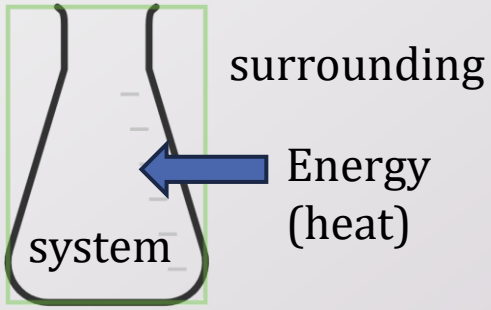
HEAT (q)

Heat, q, is the energy that flows in and out of a system.

- It can be measured by change in temperature.
- When heat is absorbed: q = positive (+q) (heat is added to the system) – ENDOTHERMIC PROCESS. Reaction vessel feels cooler.
- When heat is evolved: q = negative (-q) (heat is removed from the system) EXOTHERMIC PROCESS. Reaction vessel feels warmer.
- Heat of Reaction: Value of q (heat) required to return a system to the given temperature at the end of a reaction.



Exothermic (-q)



Endothermic (+q)

EXOTHERMIC AND ENDOTHERMIC PROCESS

In an **endothermic** reaction:

- The reaction vessel cools.
- Heat is absorbed.
- Energy is added to the system.
- q is positive.

In an **exothermic** reaction:

- The reaction vessel warms.
- Heat is evolved.
- Energy is subtracted from the system.
- q is negative.

ENTHALPY OF REACTION

Enthalpy, H, is internal energy + PV. This enthalpy is the heat change in a chemical reaction.

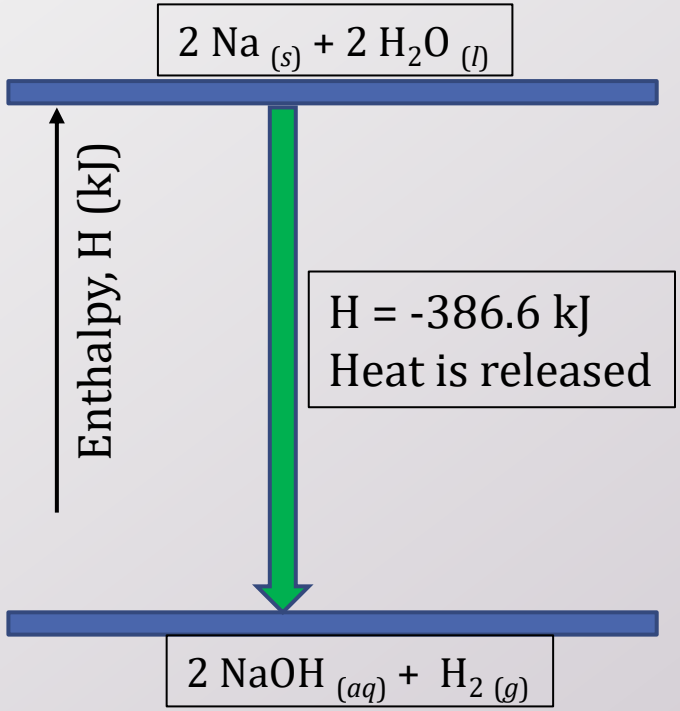
$$H = U + PV$$

The change in enthalpy for a reaction at a given temperature and pressure is given by:

$$\Delta H = H \text{ (products)} - H \text{ (reactants)} \quad \text{where } \Delta = \text{change}$$

E.g., for the following equation of reaction of sodium; the enthalpy change can be shown in the diagram on the right.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}$$



THERMOCHEMICAL EQUATION

Thermochemical equation is one where enthalpy is given along with all the phases of the reaction.

$$2Na_{(s)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)};\ \Delta H = -368.6\ kJ$$

The minus on ΔH value indicates reaction is exothermic (*heat is a product*).

What does this equation mean in terms of stoichiometry? In terms of mols? The amount of energy given per mol can be determined for each chemical in a reaction by the stoichiometric coefficient of a balanced equation.

$$\frac{-368.6\ kJ}{2mol\ Na} \qquad \frac{-368.6\ kJ}{2mol\ H_2O} \qquad \frac{-368.6\ kJ}{2mol\ NaOH} \qquad \frac{-368.6\ kJ}{1\ mol\ H_2}$$

- Since enthalpy is a state function, it can be used to find out the energy given or absorbed if the mols of a substance are changed (doubled or halved etc.) or the equation is reversed.
- Enthalpy can also be used to calculate the energy given or absorbed by gram weight of any substance in a chemical reaction.

EXAMPLE 1: MANIPULATING THERMOCHEMICAL EQUATION

Consider the following equation:

$$S_{8(s)} + 8O_{2(g)} \longrightarrow 8SO_{2(g)};\ \Delta H = -2.39 \times 10^3\ \text{kJ}$$

Write the thermochemical equation for the dissociation of one mol of sulfur dioxide.

Answer:

1) Reverse the equation to have SO_2 a reactant and
2) Divide by 8 to get the per mol value of SO_2.

$$\mathbf{SO_{2(g)} \longrightarrow {}^{1}/_{8}\, S_{8(g)} + O_{2(g)}\ ;\ \Delta H = +299\ kJ}$$

Note:

- When the equation is multiplied by a factor the ΔH must also be multiplied by the same factor.
- If the equation is reversed, then sign of ΔH is also reversed.
- It is okay to have fractions as coefficients in thermochemical equations.

EXAMPLE 2: APPLYING STOICHIOMETRY TO ΔH

How much heat is evolved from burning 15.0 g sulfur in air. The balanced equation for the combustion is given below.

$$S_{8(s)} + 8O_{2\,(g)} \longrightarrow 8SO_{2\,(g)}; \quad \Delta H = -2.39 \times 10^3 \text{ kJ}$$

Answer:

As usual with stoichiometry – convert grams to mol and then use the kJ/mol to find energy as related to energy changes.

Molar mass of S_8 = 256.52g/mol

$$q = 15.0 \text{ g } S_8 \times \frac{\text{I mol } S_8}{256.5 \text{ g } S_8} \times \frac{-2.39 \text{ x } 10^3 \text{ kJ}}{1 \text{ mol } S_8} = \boxed{\mathbf{-1.40 \times 10^3 \text{ kJ}}}$$

EXAMPLE 3: THERMOCHEMICAL EQUATION

Write the thermochemical equation of combustion of S_8 which produces 9.31 kJ per gram of sulfur at constant P.

$$S_{8\,(s)} + 8O_{2\,(g)} \longrightarrow 8SO_{2\,(g)}$$

Answer:

1) Make sure the equation is balanced.
2) Convert heat per gram to heat per mol. (negative (-ve) sign indicates exothermic reaction).

$$\Delta H = \frac{9.31\ kJ}{1\ g\ S_8} \times \frac{256.56\ g\ S_8}{1\ mol\ S_8} = -2.39 \times 103\ kJ/mol$$

Final equation:

$$\mathbf{S_{8(s)} + 8O_{2(g)} \longrightarrow 8SO_{2(g)};\quad \Delta H = -2.39 \times 10^3\ kJ/mol}$$

MANIPULATING THERMOCHEMICAL EQUATION

- When the equation is multiplied by a factor the ΔH must also be multiplied by the same factor.
- If the equation is reversed, then sign of ΔH is also reversed.

EXAMPLE: MANIPULATING THERMOCHEMICAL EQUATION

Consider the following equation:

$CH_{4\,(g)} + H_2O_{\,(g)} \longrightarrow CO_{\,(g)} + 3H_{2\,(g)}$; ΔH = +206 kJ

Which of the following is the most exothermic reaction?

a. $CH_{4\,(g)} + H_2O_{\,(g)} \longrightarrow CO_{\,(g)} + 3H_{2\,(g)}$ **Ans: + 206 kJ**

b. $2CH_{4\,(g)} + 2H_2O_{\,(g)} \longrightarrow 2CO_{\,(g)} + 6H_{2\,(g)}$ **Ans: 2 × (206kJ) = + 412 kJ**

c. $CO_{\,(g)} + 3H_{2\,(g)} \longrightarrow CH_{4\,(g)} + H_2O_{\,(g)}$ **Ans: - 206 kJ**

d. $2CO_{\,(g)} + 6H_{2\,(g)} \longrightarrow 2CH_{4\,(g)} + 2H_2O_{\,(g)}$ **Ans: 2 × (-206 kJ) = - 412 kJ**

EXAMPLE 4: APPLYING STOICHIOMETRY TO ΔH

The daily energy requirement for a 20-year-old man weighing 67 kg is 1.3×10^4 kJ. For a 20-year-old woman weighing 58 kg, the daily requirement is 8.8×10^3 kJ. If all this energy were to be provided by the combustion of glucose, $C_6H_{12}O_6$, how many grams of glucose would have to be consumed by the man and the woman per day?

$$C_6H_{12}O_{6\,(s)} + 6O_{2\,(g)} \longrightarrow 6CO_{2\,(g)} + 6H_2O_{\,(l)};\ \Delta H = -2.82 \times 10^3\ \text{kJ}$$

Answer:

For a 20 yr old woman weighing 58 kg

$$m_{\text{glucose}} = 8.8 \times 10^3\ \text{kJ} \times \frac{1\ \text{mol glucose}}{2.82 \times 10^3\ \text{kJ}} \times \frac{180.2\ \text{g glucose}}{1\ \text{mol glucose}} = \boxed{560\ \text{g}}$$

For a 20 yr old man weighing 67 kg

$$m_{\text{glucose}} = 1.3 \times 10^4\ \text{kJ} \times \frac{1\ \text{mol glucose}}{2.82 \times 10^3\ \text{kJ}} \times \frac{180.2\ \text{g glucose}}{1\ \text{mol glucose}} = \boxed{830\ \text{g}}$$

KEY CONCEPTS

- First law of thermodynamics
- Energy and units
- Heat of reaction
- Enthalpy
- Manipulation of thermochemical equations
- Stoichiometry and heat of reaction