THERMOCHEMISTRY -1

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

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

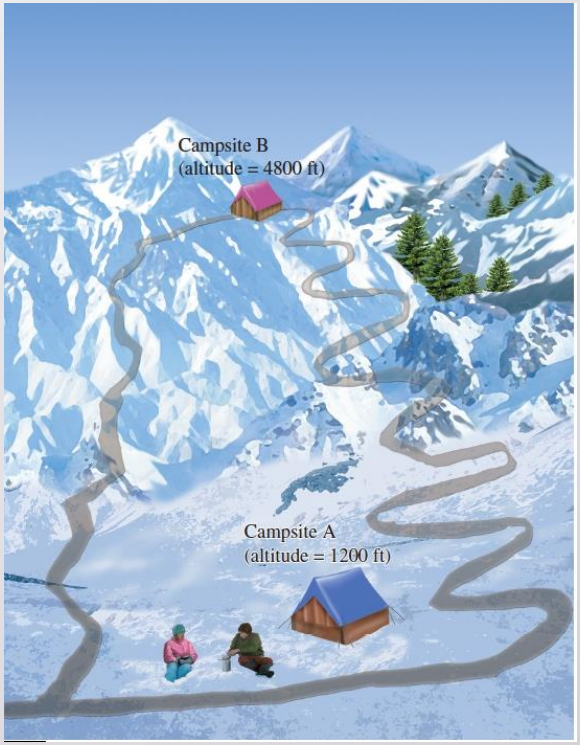
- INTERNAL ENERGY (U): Sum of kinetic and potential energies of all particles.

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

- Energy cannot be created nor destroyed; it can only be converted from one form to another.
- Change in internal energy is generally studied:

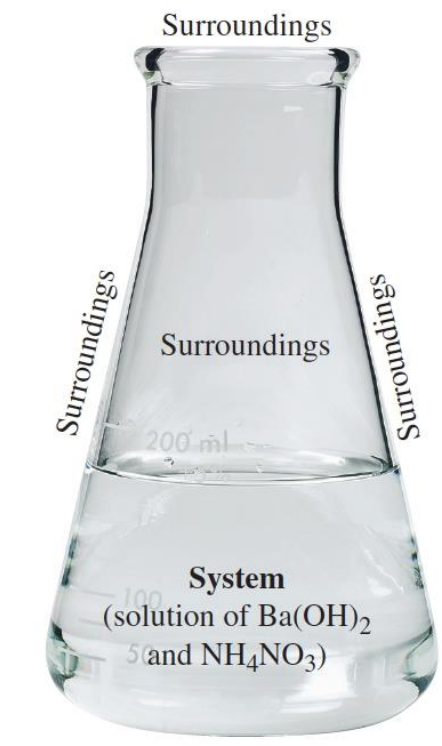
$$\Delta U = U\ (final) - U\ (initial)$$ where Δ = change

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



SYSTEM

- Thermodynamic system: substance under study in which a change occurs.
- Thermodynamic surroundings: everything in the vicinity of the thermodynamic system.



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 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 AND INTERNAL ENERGY

- Enthalpy, H, is internal energy + PV

  $H = U + PV$

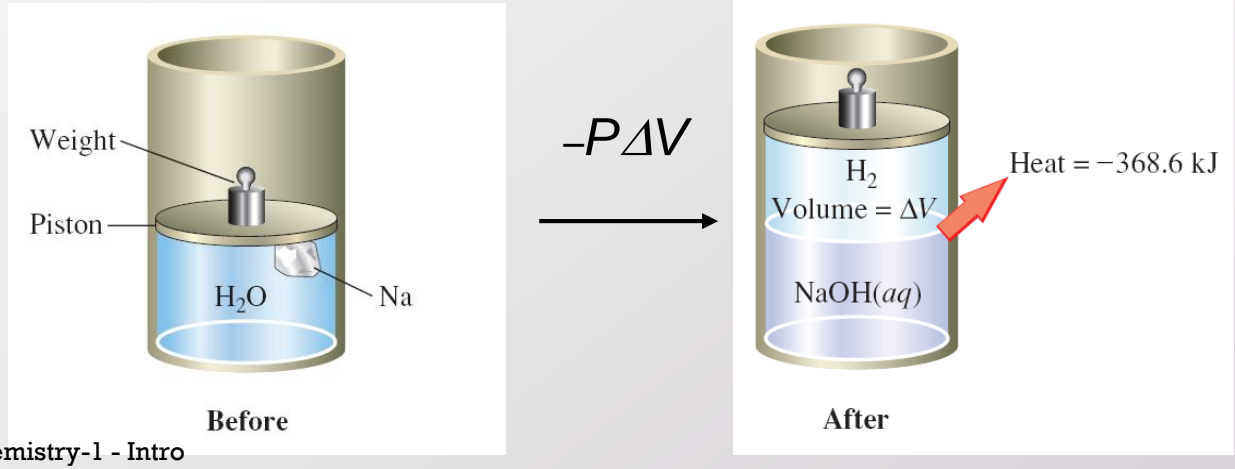
- Many reactions take place at constant P, so change in enthalpy is given by change in the other conditions.

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

  $-P\Delta V$ is the energy needed to change volume against the atm. P.

For example: $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

- The H_2 gas had to do work to raise the piston; at 1 atm, $-P\Delta V = -2.5$ kJ; and 368.6 kJ of heat are evolved.



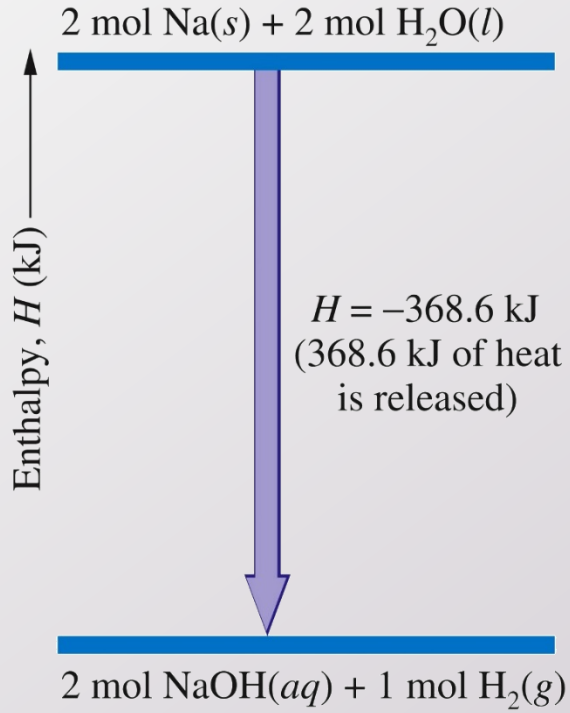
ENTHALPY OF REACTION

- 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.

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$



THERMOCHEMICAL EQUATION

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

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g);\ \Delta H = -368.6\ kJ$$

Example:

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

Answer:

1) Write balanced equation first:

$$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$$

2) Convert heat per gram to heat per mol. (-ve sign indicates exothermic reaction.

$$\Delta H = -\frac{9.31\text{kJ}}{1\text{g}\,S_8} \bullet \frac{256.56\text{g}\,S_8}{1\text{mol}\,S_8}$$

$$\Delta H = -2.3910^3\ \text{kJ}$$

Final equation: $\mathbf{S_8(s) + 8O_2(g) \rightarrow 8SO_2(g);\quad \Delta H = -2.39 \times 10^3\ kJ}$

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:

Consider the following equation:

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$; $\Delta H = 206$ kJ

Which of the following is the most exothermic reaction?

a. $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ **Ans: 206kJ**

b. $2CH_4(g) + 2H_2O(g) \rightarrow 2CO(g) + 6H_2(g)$ **Ans: 2 x (206kJ) = 412kJ**

c. $CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g)$ **Ans: -206kJ**

d. $2CO(g) + 6H_2(g) \rightarrow 2CH_4(g) + 2H_2O(g)$ **Ans: 2 x (-206kJ) = -412kJ**

MANIPULATING THERMOCHEMICAL EQUATION

Another Example:

Consider the following equation:

$$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g); \quad \Delta H = -2.39 \times 10^3 \text{ kJ}$$

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

Answer:

Inverse the equation and 2) divide by 8

$$\mathbf{SO_2(g) \rightarrow {}^{1}/_{8}S_8(g) + O_2(g)\ ;\ \Delta H = +299\ kJ}$$

APPLYING STOICHIOMETRY TO ΔH

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

Example:

You burn 15.0 g sulfur in air. How much heat evolves from this amount of sulfur using the equation below.

$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g)$; $\Delta H = -2.39 \times 10^3$ kJ

Answer:

Molar mass of S = 256.52g/mol

$$q = 15.0\ \text{g}\ S_8 \bullet \frac{1\ \text{mol}\ S_8}{256.5\ \text{g}\ S_8} \bullet \frac{-2.39 \times 10^3\ \text{kJ}}{1\ \text{mol}\ S_8}$$

$q = -1.40 \times 10^2$ kJ

APPLYING STOICHIOMETRY TO ΔH

Another Example:

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?

$$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l);\ \Delta H = -2.82 \times 10^3 \text{ kJ}$$

Answer:

For a 20 yr old woman weighing 58 kg

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

For a 20 yr old man weighing 67 kg

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

KEY CONCEPTS

- Energy and units
- Heat of reaction
- Enthalpy
- Stoichiometry and heat of reaction