

Thermochemistry

Chapter 6

ENERGY

- Energy is the capacity to do work.
- Kinetic Energy – thermal, mechanical, electrical, sound
- Potential Energy – chemical, gravitational, electrostatic

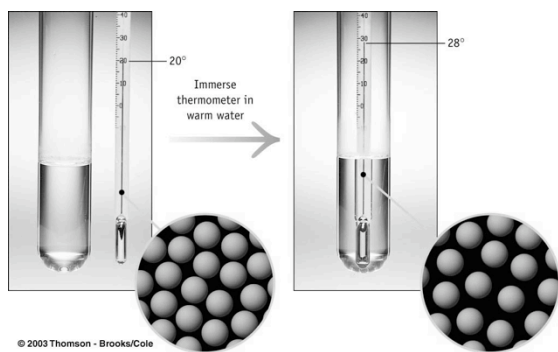
Heat

- *Heat*, or *thermal energy*, is generally measured in one of two units in Chemistry.
- The **calorie** is the amount of heat required to raise the temperature of one gram of water by one Celsius degree.
- When talking about food, one **Calorie** (with a capital C) is equal to one kilocalorie (kcal) or 1000 calories (with a lowercase c).
- However, in recent years, energy is most commonly measured in **joules (J)**. This is an SI derived unit:
 $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2} = \text{N} \cdot \text{m}$
- Joules and calories are easily converted:
 $4.184 \text{ J} = 1 \text{ cal}$ (this is an EXACT conversion - the calorie is now defined in this way.)

Temperature & Heat

- **Misconception:** Temperature is a measure of the heat within an object (this is *incorrect!*).
- **Definitions:**
 - **Temperature** is a measure of the average kinetic energy of particles in a sample. Temperature is DIRECTLY proportional to the average kinetic energy of the particles. $T \propto KE$
 - **Kinetic Energy** is the energy of motion, and is related to the mass of a particle and its velocity (or speed).
 $KE = \frac{1}{2} mv^2$
 - **Heat** (represented by the variable **q**) is a transfer of energy between two objects at different temperatures.

Thermometers & Temperature



Temperature & Heat

HOT object (at high Temp)	Molecules have a high average kinetic energy. They are moving very fast.
Comes into contact with:	
COLD object (at low Temp)	Molecules have a low average kinetic energy. They are moving more slowly.

- Particles in the HOT object collide with particles in the COLD object.
- The kinetic energy of the particles of the HOT object will be transferred to the particles of the cold object.
- The particles in the HOT object move more slowly, and the particles in the COLD object move more quickly.
- This transfer of energy continues until the particles of both objects have the same average kinetic energy, and therefore, the same temperature.
- This process of energy transfer in the form of heat is called **conduction**.

Heat Transfer

Thermal Equilibrium:
When the system and the surroundings reach the same temperature, they are in a state of thermal equilibrium.

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Heat Calculations and Heat Capacity

- Specific Heat Capacity** is the heat required to raise the temperature of **one gram of a substance** by 1 C°.

$$\text{specific heat capacity} = \frac{\text{heat}}{\text{mass} \times \text{change in temperature}} = C_p = \frac{q}{m \times \Delta T}$$

rearranging: $q = mC_p\Delta T$
where: $\Delta T = T_{\text{final}} - T_{\text{initial}}$

- Heat Capacity** is the amount of energy required to raise the temperature of an **object** by one Celsius degree (C°).

$$\text{heat capacity} = \frac{q}{\Delta T} \quad \text{rearranging: } q = (\text{heat capacity}) \Delta T$$

Heat Examples

- How much heat (in Joules) is required to heat 30.0 g of iron from 45.0 °C to 95.0 °C?
 $(C_{p,\text{iron}} = 0.449 \text{ J/g}\cdot\text{C}^\circ)$
- What will be the final temperature if 15.5 kJ of heat is added to 238 g of water at 22.0 °C?
 $(C_{p,\text{H}_2\text{O}} = 4.184 \text{ J/g}\cdot\text{C}^\circ)$

Work

- The work that we will focus on in this course is the work done by an expanding (or compressing) gas, sometimes called PV work.
- It is called PV work because it is measured by looking at the expansion of a gas (ΔV) against some pressure (P).
- Work: $w = -P\Delta V$
- Example:** Calculate the amount of work done by a system when it causes the volume in a piston to expand from 2.0 m³ to 5.5 m³.

The First Law of Thermodynamics

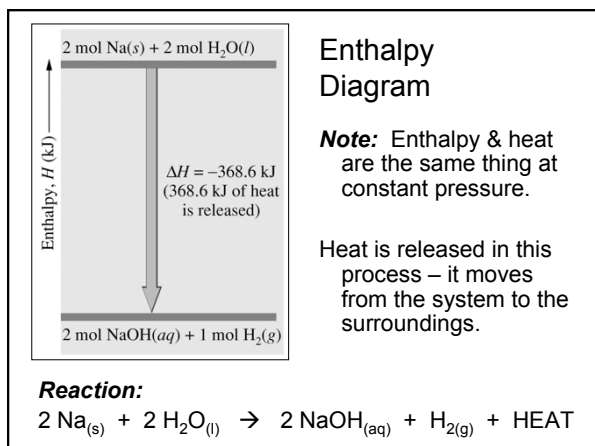
- The first law of thermodynamics is the law of conservation of energy – **the energy in the universe is constant.**
- Mathematical Expression of the 1st Law:

$$\Delta E = q + w$$

The First Law of Thermodynamics

Exothermic:
Heat flows from the system to the surroundings (q is negative). The temperature of the surroundings increases.
Example: Burning Wood.

Endothermic:
Heat flows to the system from the surroundings (q is positive). The temperature of the surroundings decreases.
Example: Water evaporating off of skin.



The 1st Law and Heat Problems

- **Calorimetry** – An application of the first law.

$$-q_{\text{system}} = q_{\text{surroundings}}$$

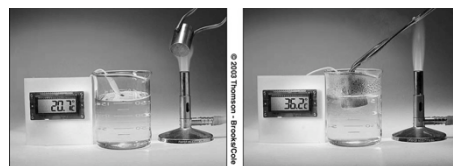
$$-q_{\text{lost}} = q_{\text{gained}}$$

- **Calorimetry** is the measure of heat transferred in a chemical or physical process. A calorimeter is an apparatus that allows us to measure heat transferred in chemical or physical processes.

Example Problems: Calorimetry

3. What is the specific heat of an unknown metal if a 47.55-g block of the metal at 75.2°C is placed in 100.0 g of water at 22.4°C and thermal equilibrium is reached at 28.2°C ?
(Assume no heat is transferred to the calorimeter.)

Bunsen Burner Flame



4. In order to measure the temperature of a Bunsen burner flame, a block of iron with a mass of 70.0 g is heated in the flame of a Bunsen burner. (The temperature of the iron is assumed to reach the same temperature as the flame.)

The iron is then dropped in a calorimeter that contains 400.0 g of H₂O at 20.7°C. The final temperature of the system is 36.2 °C. What was the initial temperature of the iron?
(Assume no heat is transferred to the calorimeter.)

Heat Capacity & the Calorimeter

In the above reactions, we assumed no heat was absorbed by the calorimeter. In reality, heat is absorbed by a calorimeter in a calorimetry experiment. The amount of heat that the calorimeter absorbs can be accounted for if the heat capacity of the calorimeter is known.

$$q_{\text{object}} = (\text{heat capacity})\Delta T$$

Calorimetry Example

5. What is the heat capacity of a calorimeter if adding a 55.0-g block of iron at 50.0 °C to 75.0 g of water at 25.0 °C results in a final temperature of 26.5 °C?

Enthalpy and Internal Energy

- H or ΔH is used to symbolize *enthalpy*.
- The mathematical expression of the First Law of Thermodynamics is: $\Delta E = q + w$, where ΔE is the change in internal **energy**, q is heat and w is work.
- Work can be defined in terms of an expanding gas and has the formula: $w = -P\Delta V$, where P is pressure in pascals (N/m²) and V is volume in m³.

Enthalpy and Internal Energy

- **Enthalpy (H)** is related to energy.

$$H = E + PV$$

- However, absolute energies and enthalpies are rarely measured. Instead, we measure CHANGES in these quantities. Reconsider the above equations (at constant pressure):

$$\Delta H = \Delta E + P\Delta V$$

recall: $w = -P\Delta V$

therefore: $\Delta H = \Delta E - w$

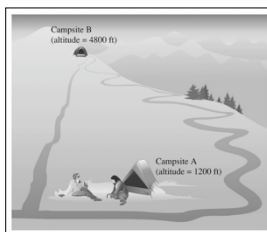
substituting: $\Delta H = q + w - w$

$$\Delta H = q \quad (\text{at constant pressure})$$

- Therefore, at constant pressure, enthalpy is heat. We will use these words interchangeably.

State Functions

- Enthalpy and internal energy are both STATE functions.
- A **state function** is **path independent**.
- Heat and work are both non-state functions.
- A **non-state function** is path **dependent**.



Consider:

Location (position)

Distance traveled

Change in position

Molar Enthalpy of Reactions (ΔH_{rxn})

- Heat (q) is usually used to represent the heat produced (-) or consumed (+) in the reaction of a specific quantity of a material.
- For example, q would represent the heat released when 5.95 g of propane is burned.
- The “enthalpy (or heat) of reaction” is represented by $\Delta H_{reaction}$ (ΔH_{rxn}) and relates to the amount of heat evolved per one mole or a whole # multiple – as in a balanced chemical equation.

$$\text{molar } \Delta H_{rxn} = \frac{q_{rxn}}{\text{moles reacting}} \quad (\text{in units of kJ/mol})$$

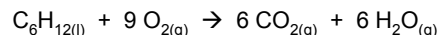
Enthalpy of Reaction

- Sometimes, however, knowing the heat evolved or consumed per gram is useful to know:

$$\text{gram } \Delta H_{rxn} = \frac{q_{rxn}}{\text{grams reacting}} \quad (\text{in units of J/g})$$

Enthalpy of Reaction

7. Consider the combustion of hexene:



The combustion of 12.1 g of hexene in a calorimeter releases (exothermic, negative value) 44,700 J of heat.

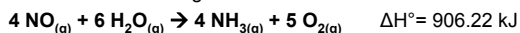
- A) What is the molar heat of combustion of hexene?
- B) What is the gram heat of combustion of hexene?

Enthalpy Change in Chemical Reactions: Thermochemistry and Stoichiometry

- Heat may be considered as a **reactant** for **endothermic** reactions and as a **product** for **exothermic** reactions.
- In stoichiometry problems that involve heat, heat always keep the sign on ΔH to indicate whether heat is produced or consumed.

Example:

8. Consider the following endothermic reaction:



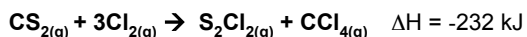
What quantity of heat will be consumed when 58.0 g of NH_3 is produced?

Thermochemistry & Limiting Reagents

- When carrying out stoichiometry problems that involve heat, all the same principles of stoichiometry apply, including **Limiting Reagents**.

Example:

9. How much heat is released when a mixture containing 10.0 g CS_2 and 10.0 g Cl_2 react by the equation:



Enthalpy of Reactions – Summary

Heats of reaction (ΔH) can be calculated in one of three ways, all experimentally derived:

- **Calorimetry** (direct experiment)
- **Hess's Law of Heat Summation**
(using ΔH values of other reactions that were previously determined by experiment)
- **Heats of Formation**
(an application of Hess's Law)

Determining the Enthalpy of Reactions by Calorimetry

- All enthalpies of reaction must be determined **experimentally**, or calculated from the enthalpies of other reactions (which were experimentally determined and compiled in tables – see *appendix L*).
- We can use calorimetry to **directly** determine the enthalpy of a reaction, by measuring the heat transferred between a reaction (**the system**) to some defined **surroundings** (usually a calorimeter and water).

Example: Determining the Enthalpy of Reactions by Calorimetry

10. The 0.548-g of arabinose, $\text{C}_5\text{H}_{10}\text{O}_5$ is completely burned in oxygen in a calorimeter with a heat capacity of 825 J/C° and containing 3.58 kg of water. The temperature rises from $21.203 \text{ }^\circ\text{C}$ to $21.743 \text{ }^\circ\text{C}$.

What is the molar heat of combustion (ΔH) of arabinose?

Example: Determining the Enthalpy of Reactions by Calorimetry

11) Consider the reaction of 10.08-g of aluminum hydroxide with 200.0 mL of sulfuric acid solution with a concentration high enough to react all of the base.

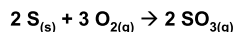
If the reaction takes place in a coffee-cup calorimeter with a heat capacity of 63.5 J/C° , and the temperature of all of the materials rise from $22.31 \text{ }^\circ\text{C}$ to $28.52 \text{ }^\circ\text{C}$, what is the heat of reaction (ΔH) for this neutralization reaction?

(Assume the density and the heat capacity of the solution are the same as water.)

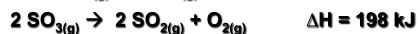
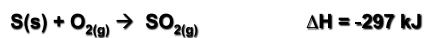
Hess's Law of Heat Summation

If a reaction is the sum of 2 or more reactions, then its overall ΔH is equal to the sum of the ΔH values of the other reactions.

12. Example: Consider the reaction for which ΔH is unknown:



However, the heats of reaction of the following two reactions are known:



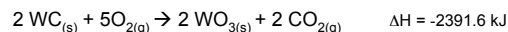
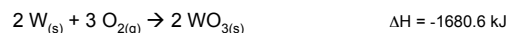
We can calculate the heat of reaction for the reaction for the unknown by combining these two reactions.

Hess's Law Example

13. Consider the reaction:



for which the heat of reaction is not known. Calculate ΔH_{rxn} using the following information:



Enthalpy Diagram

(13 continued) Draw an energy diagram that illustrates the relationships of the ΔH values for each of above reaction steps and the overall reaction.

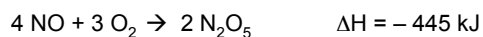


Hess's Law Example

Consider the gas-phase reaction:



A) Based on the gas-phase reactions below with the enthalpies given, determine the ΔH value for the above reaction.



Enthalpy Diagram

B. (continued from previous slide) Draw an energy diagram that illustrates the relationships of the ΔH values for each of above reaction steps and the overall reaction.



Example continued

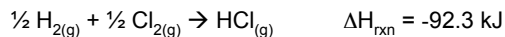
- What quantity of heat is produced or consumed by the decomposition of 25.0 g of dinitrogen pentoxide?

Heats of Formation

- The **standard molar enthalpy of formation** for a compound is the amount of energy required to make one mole of a compound from its elements in their standard states.
- Thermodynamic standard conditions are defined:
 - 1 atmosphere (760 mmHg) pressure
 - 25.00 °C (298.15K)
 - Solutions at 1.00 *M*

Heats of Formation

- Consider HCl. The reaction that defines its standard enthalpy of formation is:



- Therefore, $\Delta H_f^\circ = -92.3 \text{ kJ/mol}$. *Note the units!*
- The standard heat of formation of an element in its standard state is always defined as zero.

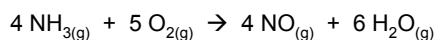
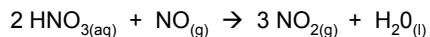
Calculating Heats of Reaction from ΔH_f

- The heat of a reaction can be calculated by the following formula:

$$\Delta H_{\text{rxn}}^\circ = \sum n_p \Delta H_{f,\text{products}}^\circ - \sum n_r \Delta H_{f,\text{reactants}}^\circ$$

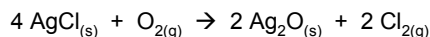
where n_x is the stoichiometric coefficient.

14. Calculate the heat of reaction for the following reactions. (A chart of standard heats of formation can be found in appendix L.)



Heats of Formation – Applied

Calculate what quantity of heat that will be absorbed or released when 15.0 g of silver chloride (AgCl) is converted to silver oxide (Ag₂O) in the following reaction:



Thermochemistry – Applied Example

A 2.21-g sample of C₂H₂ is burned in excess oxygen in a bomb calorimeter with a heat capacity of 453 J/C° that contains 250.0 g of water. What increase in temperature should be observed?

(Assume that ALL reactants and products are in the gaseous state.)

Thermochemistry – Applied Example

Consider the reaction of:

- 100.0 mL of **0.500 M** Ba(NO₃)₂ with 100.0 mL of 1.00 M Na₂SO₄ solution to form solid BaSO₄.

Both solutions start at 25.05°C and are mixed in a calorimeter that absorbs a negligible quantity of heat. The final temperature of the mixture is 28.15°C.

- **What is the enthalpy (ΔH) of the reaction?**

(Assume the density and specific heat of the solution are the same as water.)