

Unit 3 - Thermochemistry

Thermochemistry

Thermochemistry: the study of the energy changes involved in chemical and physical processes.

- kinetic energy is the energy of motion
- potential energy is the stored energy an object has as a result of its condition
- the joule (J) is equivalent to a $\text{kg}\cdot\text{m}^2/\text{s}^2$
- 1 kJ = 1000 J
- the density of water is 1.00 g/mL
- $\Delta T = T_{\text{final}} - T_{\text{initial}}$

Thermal Energy: the sum of all the kinetic energies of all the particles of a sample of matter.

Temperature: a measure of the average kinetic energy of all the particles of a sample of matter.

The ΔT is dependent on:

- amount of heat exchanged
- mass of the substance being measured
- type of substance being measured

Endothermic: describes the process during which heat enters a system.

↔ ΔH is +ve because the enthalpy of the system ↑

Exothermic: describes the process during which heat leaves a system.

↔ ΔH is -ve because the enthalpy of the system ↓

A *system* is the object or substance being studied, and the *surroundings* are everything else in the universe.

Open System: a system that can exchange both matter and energy with the surroundings.

e.g. uncovered pot of potatoes boiling on the stove

Closed System: a system that can exchange only energy with the surroundings.

e.g. pressure cooker with potatoes boiling on the stove

Isolated System: a system that cannot exchange either energy or matter with the surroundings.

e.g. a pot of potatoes inside an insulated container

★ It is difficult to completely isolate a system; there is no truly isolated system except the universe itself.

First Law of Thermodynamics

First Law of Thermodynamics: energy can be converted from one form to another but cannot be created or destroyed.

- $E_{\text{universe}} = \text{constant}$
- $\Delta E_{\text{universe}} = 0$
- universe = system + surroundings
- $E_{\text{universe}} = E_{\text{system}} + E_{\text{surroundings}}$
- $\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0$
- $\Delta E_{\text{system}} = -\Delta E_{\text{surroundings}}$

When a system absorbs energy, the surroundings release it and when a system releases energy, the surroundings absorb it.

Enthalpy

Enthalpy, H : the total energy of the system plus the pressure times the volume, or $H = E + PV$.

e.g. $\text{CO(g)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_3\text{OH(l)} + 128.6\text{ kJ}$ or

$\text{CO(g)} + 2\text{H}_2\text{(g)} \longrightarrow \text{CH}_3\text{OH(l)} \quad \Delta H = -128.6\text{ kJ}$

→ Sometimes called the *heat content* of the system.

→ The enthalpy change of a system depends only on the initial state (condition) and on the final state of the system and is represented as $\Delta H = \Delta E + \Delta(PV)$.

Enthalpy of Solution, $\Delta H_{\text{solution}}$: the enthalpy change associated with a solute dissolving in a solvent.

- bond energy is the energy required to break a chemical bond
- larger bond energies result in stabler bonds
- stable bonds have low potential energy

$\Delta H = \text{Reactant Bond energy} - \text{Product Bond energy}$

→ The difference between the total amount of energy used to break bonds and the total energy released when the bonds reform is equal to the enthalpy change of the reaction.

★ Strong bonds have low potential energy and weak bonds have high potential energy.

Second Law of Thermodynamics

Second Law of Thermodynamics: when two objects are in thermal contact, heat is always transferred from the object at a higher temperature to the object at a lower temperature until the two objects are at the same temperature (related to entropy).

★ When two systems have reached the same temperature, they are in *thermal equilibrium*.

Calorimetry

The following equation enables you to calculate the amount of heat absorbed or released by a substance. e.g. the *law of conservation of energy*

$$Q = m \cdot c \cdot \Delta T$$

- $Q \rightarrow$ heat (J)
- $m \rightarrow$ mass (g)
- $c \rightarrow$ specific heat capacity ($\text{J/g} \cdot ^\circ\text{C}$)
- $\Delta T \rightarrow$ change in temperature ($^\circ\text{C}$)

→ If ΔT is positive, then Q is positive.

+ve value for Q means that heat entered the system.

→ If ΔT is negative, then Q is negative.

-ve value for Q means that heat left the system.

Specific Heat Capacity, c : the amount of energy needed to increase the temperature of one gram of a substance by one degree Celsius.

Q: If the same amount of heat were added to 1 g samples of water, methanol, and aluminum, which substance would undergo the greatest ΔT ?

- $c_{\text{water}} = 4.19\text{ J/g} \cdot ^\circ\text{C}$
- $c_{\text{methanol}} = 2.918\text{ J/g} \cdot ^\circ\text{C}$
- $c_{\text{aluminum}} = 0.900\text{ J/g} \cdot ^\circ\text{C}$

A: Aluminum would undergo the greatest temperature change because it requires the least amount of energy to increase the temperature of one gram of it.
★ The range of enthalpy changes is lowest for physical changes, intermediate for chemical changes, and highest for nuclear changes.

Molar Enthalpy of Combustion

Standard Enthalpy of a Reaction, ΔH_r° : the enthalpy change for the amount in moles of each reactant and product as determined by the coefficient of the term in the chemical equation.

→ The enthalpy change of a reaction is equal to the amount in moles, n , of a specified reactant or product multiplied by the standard molar enthalpy change for the specified reactant or product.

$$\Delta H_r = n\Delta H_r^\circ \quad \text{or} \quad \Delta H_{\text{comb}} = n\Delta H_{\text{comb}}^\circ$$

- ΔH_{comb} represents enthalpy of combustion
- $\Delta H_{\text{comb}}^\circ$ represents the standard molar enthalpy of combustion

→ If you know the enthalpy of a reaction, you can use it to determine the amounts of the reactants or products involved.

★ It is not possible to measure the total enthalpy of a system, but it is possible to measure the *change* in the enthalpy of a system.

Calorimeter

Calorimeter: a device used to measure the heat released or absorbed during a chemical or physical process occurring within it.

Simple Calorimeter: a calorimeter made of two stacked vessels covered by a lid with holes in the top just large enough for a thermometer and a stirrer.

- the process takes place under constant pressure
- the amount of heat that is exchanged between the calorimeter and the system is equal to the change in the enthalpy of the system

Bomb Calorimeter: measures heat released during a combustion reaction at a constant volume.

- the reaction takes place inside an inner metal chamber, called a *bomb*
- the reactants are ignited using an electrical coil
- the units of C are joules per degree Celsius

$$C_{\text{bomb calorimeter}} = C_{\text{water}} + C_{\text{thermometer}} + C_{\text{stirrer}} + C_{\text{container}}$$

Thermochemical Equations

The enthalpy of a reaction is directly proportional to the amounts of the substances that react.

What is the thermochemical equation for this dissolution? Given:

$$m_{\text{NaOH}} = 5.50 \text{ g}, V_{\text{water}} = 175 \text{ mL}, \Delta T_{\text{water}} = 2.1^\circ\text{C}$$

$$q_{\text{water}} = m_{\text{water}} + c_{\text{water}} + \Delta T_{\text{water}} \quad (1)$$

$$= (175 \text{ g})(4.184 \text{ J/g}^\circ\text{C})(2.1^\circ\text{C}) \quad (2)$$

$$= 1537.62 \text{ J or } 1.53762 \text{ kJ} \quad (3)$$

$$n_{\text{NaOH}} = \frac{5.50 \text{ g}}{39.9971 \text{ g/mol}} \approx 0.13751 \text{ mol}$$

$$\Delta H_{\text{rxn}}^\circ = \frac{-1.53762 \text{ kJ}}{0.13751 \text{ mol}} \approx -11 \text{ kJ/mol}$$

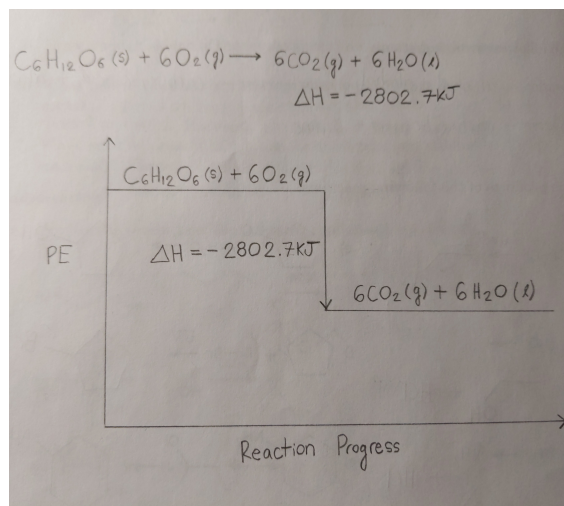


★ Divide the enthalpy of the reaction by the moles of the reactant to solve for the enthalpy term.

Potential Energy Diagram

The slow step (rate-determining) in a chemical process is the step with the highest activation energy.

- breaking a bond is an endothermic process
- forming a bond is an exothermic process

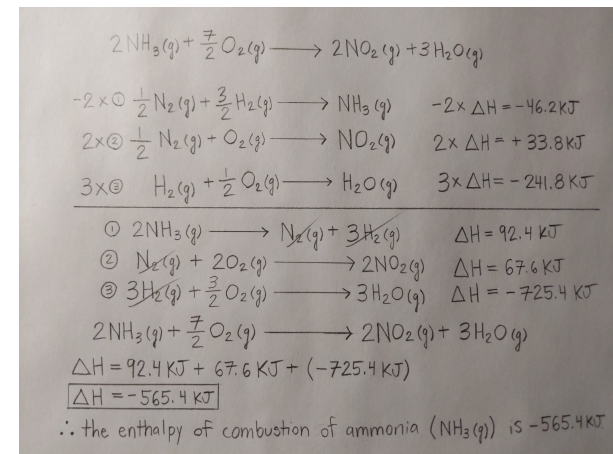


★ There is no difference in enthalpy change for the catalyzed and the uncatalyzed reaction.

Hess's Law

Hess's Law: the enthalpy change of a physical or chemical process depends only on the initial and final conditions of the process. The enthalpy change of a multistep process is the sum of the enthalpy changes of its individual steps.

Manipulating chemical equations:



- if you multiply by a constant, you must multiply the enthalpy change by that same constant
- if you reverse an equation, you must change the sign of the enthalpy change

Standard Molar Enthalpy of Formation, ΔH_f° : the change in enthalpy when 1 mol of a compound is formed directly from its elements in their most stable state at SATP (25°C and 100 kPa).

$$\Delta H_r^\circ = \sum(n\Delta H_f^\circ \text{ products}) - \sum(n\Delta H_f^\circ \text{ reactants})$$

- ΔH_r° represents the enthalpy change of a chemical reaction
- n represents the stoichiometric coefficients for each substance
- \sum means "the sum of"

Note: Oxygen gas, $\text{O}_2(\text{g})$, at SATP is an element in its most stable state. Therefore, its standard enthalpy of formation is zero.

★ The reactants do not actually break down into their elements and then react to form products.

Unit 3 - Chemical Kinetics

Reaction Rates

Reaction Rate: the speed at which a reaction occurs, or the change in the amount of reactants consumed or products formed over a given time interval.

$$\text{reaction rate} = \frac{[A]_{\text{final}} - [A]_{\text{initial}}}{t_{\text{final}} - t_{\text{initial}}} \quad (1)$$

$$= \frac{\Delta[A]}{\Delta t} \quad (2)$$

→ The square brackets represent concentration.

Rate Law: a mathematical relationship that must be experimentally determined for a chemical reaction.

rate = $k[A]^m[B]^n$, where k is the *rate constant*.

→ The order of the overall reaction is $m + n$.

Average Rate of Reaction: the change in the concentration of a reactant or product per unit time over a given time interval as a chemical reaction proceeds.
→ Calculate the slope of a line drawn between the two points that define the time interval.

Instantaneous Rate of Reaction: the rate of a chemical reaction at a particular point in time.

→ Can be found by calculating the slope of a line that is tangent to that particular point in time.

Factors that affect the rate of reaction:

- ↑ temperature = ↑ kinetic energy
- ↑ concentration of reactants = ↑ collisions
- catalysts = lowers the activation energy
- ↑ surface area of a solid reactant = ↑ # of sites
- ↑ pressure of gaseous reactants and products = ↑ collisions due to molecules being closer together

★ A reaction rate is always expressed as a +ve value.

Activation Energy

Activation Energy, E_a : the minimum amount of energy (collision energy) required to initiate a chemical reaction.

For an exothermic reaction: $E_{a(\text{rev})} = E_{a(\text{fwd})} + \Delta H$

For an endothermic reaction: $E_{a(\text{rev})} = E_{a(\text{fwd})} - \Delta H$

★ The activation energy is independent of temperature; it does not change when temperature changes.

Entropy and Spontaneity

Spontaneous: processes that occur on their own in one particular direction.

→ Enthalpy is not the main determining factor in spontaneity (common misconception).

Entropy, S : the degree of molecular randomness or disorder in a system.

→ An increase in entropy is the main contributing factor in determining spontaneity.

↔ Processes tend towards the higher entropy state due to probabilities.

↔ The most probable state is the most likely to be observed.

$$p = \frac{\# \text{ microstates that create an arrangement}}{\text{total } \# \text{ microstates possible}}$$

- the largest # of microstates is the most likely to be observed (even distribution of atoms)
- such an arrangement has the highest entropy

Second Law of Thermodynamics: the universe tends towards increasing entropy, $\Delta S_{\text{universe}} \geq 0$.

→ Systems tend to go toward higher entropy states.

Entropy changes involved with state changes:

- solid < liquid < gas, a substance changes state from a more ordered state to a less ordered state
- there are fewer microstates available in solids due to the restriction of motion
- more microstates are allowed for substances in the liquid or gaseous state

$\Delta S > 0$ if

- there are more moles of the products than reactants
- complex molecules are broken into smaller molecules

Q: Which of the following has a higher entropy? 1 mol of $\text{H}_2\text{O}(\text{s})$ or $\text{H}_2\text{O}(\text{g})$ at a given temp.? 1 mol of $\text{H}_2(\text{g})$ at 1 atm or 0.01 atm at a given temp.?

A: $\text{H}_2\text{O}(\text{g}) > \text{H}_2\text{O}(\text{s})$ and $0.01 \text{ atm} > 1 \text{ atm}$

Gibbs Free Energy

Gibbs Free Energy, G : the amount of energy available to do work in a chemical system.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S^\circ = \sum (n\Delta S^\circ_{\text{products}}) - \sum (n\Delta S^\circ_{\text{reactants}})$$

Exergonic reactions

- release energy → spontaneous
- $\Delta G < 0$

Endergonic reactions

- absorb energy → non-spontaneous
- $\Delta G > 0$

Collision Theory

Collision Theory: the theory that a reaction occurs between two particles (atoms, molecules, or ions) if they collide at the correct orientation and with a certain minimum energy.

For a collision between reactants to be effective:

1. the orientation of the reactants (the collision geometry) must be favourable.
2. the collision must occur with sufficient energy.

The area under a *Maxwell-Boltzmann distribution* curve represents the distribution of the kinetic energy of collisions at a given temperature.

Activated Complex

Activated Complex: a chemical species temporarily formed by the colliding reactant molecules before the final product of the reaction is formed.

→ It is a temporary arrangement of atoms that form as bonds are breaking and new bonds are forming.

Transition State: point when reactant(s) are converted to product(s).

★ Activated complex refers to all possible intermediates whereas the transition state refers to the intermediate with the highest potential energy.