Unit 5: Energetics

1. Introduction to Thermochemistry:

Thermochemistry

Study of energy changes that accompanies physical, chemical and nuclear transformations of matter (energy + energy transfer)

Chemical Systems

Set of reactants and products being studied and are often represented by chemical equations

Surroundings

Matter around the system that is capable of absorbing/releasing energy (everything that is not a part of the chemical system)

Types of Systems

The goal is to achieve an isolated system where all of the matter/energy is kept inside

- Open (Matter + Energy can leave the system)
- Closed (only Energy)
- Isolated (No Matter + Energy can leave the system)

Physical Changes

Change of state that require energy or releases energy. The energy required is used to break intermolecular bonds and the energy released comes from when bonds are formed.

Chemical Changes

Breaking old chemical bonds and building new ones. The atoms within the molecules is also being rearranged.

Nuclear Changes

Rearrangement of the nuclei of an atom and mass is converted into energy ($E = mc^2$) and often produces lots of energy.

Strength of Reactions

Physics ≤ Chemical < Nuclear

Nuclear reactions will always produce more energy than both physical and chemical changes. However, physical and chemical reactions are on the same order of magnitude and some physical reactions have greater energy released than chemical reactions.

Types of Reactions:

- Endothermic
  - Heat is required from the environment
  - Goes from lower physical states to higher (solid - liquid, liquid - gas, solid - gas)
- Exothermic

- Heat is released from the reaction
- Goes from higher physical states to lower (gas - liquid, liquid - solid, gas - solid)

> **a. NaOH (s) = Na^+ (aq) + OH^- (aq)** - Exothermic (generally require more information)
>
> **b. H_2O (s) = H_2O (l)** - Endothermic (solid --> liquid)
>
> **c. $2H_2O$ (l) = $2H_2$ (g) + O_2 (g)** - Endothermic (liquid --> gas)
>
> **d. NaOH (aq) + HCl (aq) = NaCl (aq) + H_2O** - Exothermic (Neutralization is always exothermic)

2. Heat & Heat Transfer

Heat Transfer

The transfer of heat between the system and its surroundings. The quantity of energy is dependent on the mass, change in temperature and the specific heat capacity. The specific heat capacity is defined as the amount of energy required or released to raise the temperature of a substance of a given quantity by one degree Celsius or kelvin.

Higher specific heat capacity means more energy is required to raise its temperature and more energy must be removed to lower its temperature.

It is given by the following:

$$q = mc_{\text{sp}}\Delta T$$

- $q =$ Quantity of energy (Joules)
- $m =$ Mass (Grams, Kilograms)
- $c_{\text{sp}} =$ Specific heat capacity (Joules/gram $^{\circ}$C, Kilojoules/kilogram $^{\circ}$C)
- $\Delta T =$ Change in temperature ($T_{\text{Final}} - T_{\text{Initial}}$)

Latent Heat

Latent heat is the amount of energy required to change the state of a specific mass of a substance but not change its temperature (Ex. melt 10g of ice into water).

It is given by the following equation:

$$q = mL$$

- $q =$ Quantity of Energy (Joules)
- $m =$ Mass (Grams, kilograms)
- $L =$ Latent Heat that is constant for every material (Joules/gram, Kilojoules/Kilogram)

> **1. A sample of ethylene glycol, used in car radiators, has a mass of 34.8g. The sample liberates 783J of heat. If the initial temperature of the sample was 22.1°C, what is its final temp? The specific heat capacity of ethylene glycol is 2.42 J/g°C**
>
> - $q = -783J$
> - $m = 34.8g$
> - $c = 2.42J/g^oC$
> - $\Delta T = T_{\text{Final}} - T_{\text{Initial}}$
> - $T_{\text{Initial}} = 22.1^oC$
>
> $$q = mc\Delta T$$
>
> $$= mc(T_{\text{Final}} - T_{\text{Initial}})$$
>
> $$T_{\text{Final}} = \frac{q}{mc} + T_{\text{Initial}}$$
>
> $$= \frac{-783J}{34.8g \times 2.42J/g^oC} + 22.1^oC$$
>
> $$= 12.8^oC$$

2. A piece of metal with mass 149 g is heated to 98.0°C. When the metal is placed in 75.0g of water at 20.0°C, the temperature of the water rises by 28.5°C. What is the specific heat capacity of the metal?

- $m_1 = 149g$
- $T_{\text{Initial}_1} = 98.0^oC$
- $m_2 = 75.0g$
- $T_{\text{Initial}_2} = 20.0^oC$
- $\Delta T_2 = 28.5^oC$

$$\begin{aligned}
\Delta T_1 &= T_1 - (T_{\text{Initial}_2} + \Delta T_2) \\
&= 98.0^oC - (20.0^oC + 28.5^oC) \\
&= 49.5^oC \\
q &= mc\Delta T \\
m_1c_1\Delta T_1 &= m_2c_2\Delta T_2 \\
&= 75.0g \times 4.18j/g^oC \times 28.5^oC \\
&= 8934.75j \\
8934.75j &= 149g \times 49.5^oC \times c_1 \\
c_1 &= 1.21j/g^oC
\end{aligned}$$

3. How much energy is needed to change 12 g of ice at 0.00 °C to 12 grams of water at 0°C (3.3×10^5 J/kg= heat of fusion of water)

- $m = 12g = 0.012kg$
- $L = 3.3 \times 10^5 j/g$

> $$q = mL$$
>
> $$= 0.012g \times 3.3 \times 10^5 j/g$$
>
> $$= 3960$$
>
> $$= 3.96 \times 10^3 j$$

> **4. How much energy must be lost to change of 110.0 g of water at 0.00°C to 110.0**
>
> **grams of ice at 0.00°C?**
>
> - $m = 110.0g = 0.110kg$
> - $L = 3.3 \times 10^5 j/kg$
>
> $$q = mL$$
>
> $$= 0.110kg \times -3.3 \times 10^5 j/kg$$
>
> $$= -11000$$
>
> $$= -1.1 \times 10^4 j$$

3. Calorimetry

Enthalpy

Unlike heat, which contains only kinetic energy, enthalpy is the sum of both the kinetic and potential energy of a chemical reaction. It is denoted by the ΔH sign.

- If the surrounding temperature increases : the potential energy has been converted into kinetic energy, hence the ΔH is negative .
- If the surrounding temperature decreases : the kinetic energy has been converted into potential energy, hence the ΔH is positive .

The magnitude of ΔH scales with the coefficient of the reactants as more reactants will produce a greater change in enthalpy. The sign of the enthalpy identifies whether a reaction is endothermic or exothermic from the perspective of the chemical system.

> **Calculate the ΔH to produce 1 mole of oxygen gas given:**
>
> $$\mathrm{H_2O\,(l) \longrightarrow H_2\,(g) + \frac{1}{2}\,O_2\,(g)\ \Delta H = 285.8\,kJ}$$
>
> $$\begin{aligned} \mathrm{1\,Mole\ of\ O_2\,(g)} &= 2\ \times \tfrac{1}{2}\,\mathrm{O_2\,(g)} \\ &= 285.8\,\mathrm{kJ}\ \times 2 \\ &= 571.6\,\mathrm{kJ} \end{aligned}$$

Enthalpy can also be included as a term in a balanced chemical equation. However, you cannot have a negative enthalpy value in a chemical equation, instead, it should be moved to the other side of the equation.

- Endothermic: $\mathrm{Reactants + Energy = Product}$
- Exothermic: $\mathrm{Reactants = Product + Energy}$

Possible subscripts to ΔH for different types of reactions include:

- $\Delta\mathrm{H_{combustion}}$
- $\Delta\mathrm{H_{freezing}}$
- $\Delta\mathrm{H_{rxn}}$ or $\Delta\mathrm{H_{reaction}}$
- $\Delta\mathrm{H_{lattice}}$
- $\Delta\mathrm{H_{vaporization}}$
- $\Delta\mathrm{H_{neutralization}}$

Standard Molar Enthalpy

The enthalpy required to carry out one mole of reaction under SATP conditions (not STP).

SATP vs STP Conditions:

The standard ambient temperature and pressure (SATP) indicates that a reaction occurs at $25^{O}C$ or 298K and 100kPa (not 101.3 kPa). However, standard temperature and pressure (STP) conditions are $0^{O}C$ or 273K and 100kPa.

Standard Enthalpy of Reaction

The standard enthalpy of reaction is the enthalpy of a reaction that takes into account the following:

- Energy required to change the reaction from SATP to initiate the reaction
- Energy released during the reaction
- Energy released following the reaction as the products are cooled to SATP conditions

Energy/Reaction Profile

The visual representation of the changes in the chemical and potential energy between reactants and products. The graph should have reaction progress (or time if done experimentally) as the x-axis and the change in Enthalpy (kJ/J) as its y-axis. Ensure that each reaction also has a hump that is required to initiate the reaction and enthalpy is measured from the starting value, not the top of the hump. Arrows are used to indicate the direction of the reaction.

Calorimetry

Inorder to study energy changes, an isolated system is ideally needed. Calorimeter is an instrument used for studying energy changes. It should be insulated, keeps the matter in and reduces heat lost/gained from the surroundings. The variable measured in a calorimeter is usually water (with 4.184 J/g^{o}C) and the temperature change between the start and end of the reaction is determined so that the enthalpy can be measured.

$$q_{H2O} = -\Delta H_{rxn}$$

An calorimetry experiment can be conducted with the following steps:

1. Find the heat transfer of the water (q_{H_2O})
2. Set $\Delta H_{rxn} = -q_{H_2O}$
3. Convert to molar enthalpy or leave as is

Inorder to experimentally determine the enthalpy change through the use of calorimetry, certain assumptions must be made:

- All the energy released/absorbed by the system is transferred to/from the surroundings within the calorimeter (however, the percentage is dependent on the different calorimeters)
- No energy is transferred between the calorimeter and the environment (sufficient insulation)
- Calorimeter does not absorb/release energy
- Dilute aqueous solution is assumed to have a density and specific heat capacity equal to that of water at 4.184 J/g^{o}C.

Coffee Cup Calorimeter

Basic calorimeter that is sufficient for measuring enthalpy change in dissolving, neutralization, heating, cooling among other basic chemical reactions. However, it cannot measure the heat transfer in a combustion reaction. A coffee cup calorimeter has the following components:

- Insulated container with lid (generally a coffee cup)
- Water

- Thermometer
- Stirrer
- Reactant

Bomb Calorimeter

Designed to measure the enthalpy change in a combustion reaction. Has an isolated "bomb chamber" made out a metal with very low specific heat capacity (ex. copper) that allows the heat from the reaction to easily transfer to the water surroundings. A bomb calorimeter h as the following components:

- Insulated container with lid
- Bomb chamber
- Water
- Thermometer
- Stirrer

Data Processing of Experimental Calorimetry

Experimentally, the data collected from a calorimeter will have inaccuracies. The data collected from the experiment can be graphed in a reaction profile with the x-axis being the reaction progress and y-axis being the temperature.

- Reaction start: when the temperature start increasing/decreasing
- Reaction end: highest/lowest point (furthest away from starting)

Inorder to correct for the energy lost/gained, it is assumed that it is constant. Therefore, a straight line can be drawn through the energy lost/gain and extrapolate back to the start of the reaction to get the final temperature if the container had perfect insulation (note: if the reaction did not start at the axis, do not extrapolate back to the axis, only to where the reaction started)

1. In a calorimetry experiment, 7.46g of potassium chloride is dissolved in 100.0ml of water at an initial temperature of 24.1°C. The final temperature of the solution is 20.0°C. What is the molar enthalpy of solution of potassium chloride?

- $\mathrm{m_{water}} = 100.0\,\mathrm{g}$
- $\mathrm{T_{water-initial}} = 24.1^o\mathrm{C}$
- $\mathrm{T_{water-final}} = 20.0^o\mathrm{C}$
- $\mathrm{c_{water}} = 4.18\,\mathrm{J/g^oC}$
- $\mathrm{m_{KCl}} = 7.46\,\mathrm{g}$

$$\begin{aligned}\mathrm{q_{water}} &= \mathrm{mc\Delta T} \\ &= 100.0\,\mathrm{g}\ \times 4.18\,\mathrm{J/g^oC}\ \times (20.0^o\mathrm{C} - 24.1^o\mathrm{C}) \\ &= -1713.8\,\mathrm{J}\end{aligned}$$

$$\begin{aligned}\Delta\mathrm{H_{rxn}} &= -\mathrm{q_{water}} \\ &= 1713.8\,\mathrm{J} \\ \text{Molar Mass KCl} &= 39.10\,\mathrm{g/mol} + 35.45\,\mathrm{g/mol} \\ &= 74.55\,\mathrm{g/mol}\end{aligned}$$

$$\begin{aligned}\frac{7.46\,\mathrm{g}}{74.55\,\mathrm{g/mol}} &= 0.100\,\mathrm{moles} \\ \frac{1713.8\,\mathrm{J}}{0.100\,\mathrm{moles}} &= 17138\,\mathrm{J} \\ &= 17.1\,\mathrm{kJ}\end{aligned}$$

2. In a chemistry experiment to investigate the properties of a fertilizer, 10.0g of urea, NH2CONH2(s) is dissolved in 150ml of water in a simple calorimeter. A temperature change from 20.4°C to 16.7°C is measured. Calculate the molar enthalpy of solution for the fertilizer

urea.

- $m_{water} = 150\,g$
- $T_{water-initial} = 20.4^oC$
- $T_{water-final} = 16.7^oC$
- $c_{water} = 4.18\,J/g^oC$
- $m_{urea} = 10.0\,g$

$$\begin{aligned} q_{water} &= mc\Delta T \\ &= 150\,g \times 4.18\,J/g^oC \times (16.7^oC - 20.4^oC) \\ &= -2319.9\,J \end{aligned}$$

$$\begin{aligned} \Delta H_{rxn} &= -q_{water} \\ &= 2319.9\,J \end{aligned}$$

$$\begin{aligned} \text{Molar Mass } NH_2CONH_2 &= 4 \times 1.01 + 2 \times 14.01 + 12.01 + 16.00 \\ &= 60.07\,g/mol \\ \frac{10.0\,g}{60.07\,g/mol} &= 0.167\,\text{moles} \\ \frac{2319.9\,J}{0.167\,\text{moles}} &= 13935.64\,J \\ &= 13.9\,kJ \end{aligned}$$

4. Hess Law

Hess's Law

The absolute enthalpy change is a state function and it is the same between reactants and products regardless of the steps taken to reach it. Therefore, it also indicates that the enthalpy change is additive seen in the following equation:

$$\Delta H^{\theta}_{\text{reaction}} = \sum \Delta H^{\theta}_{\text{f of Products}} - \sum \Delta H^{\theta}_{\text{f of product}}$$

It also states that the enthalpy change to go from products to reactants is the reverse enthalpy change of the reactants to products.

$$\Delta H^{\theta}_{\text{products}} = -\Delta H^{\theta}_{\text{reactants}}$$

$$\Delta H^{\theta}_{\text{reaactants}} = -\Delta H^{\theta}_{\text{products}}$$

Usually within a Hess's Law question, they will give you

Enthalpy Cycles

Enthalpy cycles are visual representations of Hess's Law. They have arrows that indicate the transformation of between the reactants, intermediate steps until the final product has been reached.

Standard Enthalpy of Formation

The standard enthalpy of formation of quantity of energy associated with the formation of oenomel of a substance from its elements in their standard state. The units of standard enthalpy of formation is kj/mol. The formula for the standard enthalpy of formation is:

$$\Delta H_{\text{rxn}} = \sum \Delta H^{\theta}_{\text{f-product}} - \sum \Delta H^{\theta}_{\text{f-reactant}}$$

If the products of the reaction is identical to reactants then there is no net enthalpy change.

$$H_2\,(g) \longrightarrow H_2\,(g)\ \Delta H^{\theta}_{f} = 0$$

$$Br_2\,(l) \longrightarrow Br_2\,(l)\ \Delta H^{\theta}_{f} = 0$$

It is good to keep in mind the di-atomic molecules which can be memorized using HOFBrINCl (Hydrogen, Oxygen, Fluorine, Bromine, Iodine, Nitrogen, Chlorine) The product of a standard enthalpy of formation always has a coefficient of one. There should also never be a compound on the reactants side and every reactant should be in its standard state. Choose coefficient for the reactant to yield exactly one mole of products.

$$\mathrm{C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)}$$

$$\mathrm{H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)}$$

$$\mathrm{C\,(s) + 2\,H_2\,(g) + \tfrac{1}{2}\,O(2)\,(g) \longrightarrow Ch_3OH\,(g)}$$

All of the reactions of formation are assumed to occur at SATP conditions and the state of the elements can be memorized as follows. The only two elements that are in liquid form at SATP is Mercury and Bromine. The gases are : Hydrogen, Nitrogen, Oxygen, Fluorine, Chlorine and all of the Noble Gases.

Bond Enthalpies

Another application of Hess's Law can be used to determine the enthalpy change of a reaction from the bond enthalpy of the reactants and products. The breaking of chemical bonds requires energy from the surroundings, making it an endothermic process. The reverse is true for the formation of chemical bonds, as it releases energy into the surroundings, making it a exothermic process.

$$\mathrm{Cl_2\,(g) \longrightarrow 2\,Cl\,(g)\ \Delta H^{\theta} = +\,242\,kJ/mol}$$

$$\mathrm{H\,(g) + H\,(g) \longrightarrow H_2\,(g)\ \Delta H^{\theta} = -\,436\,kJ/mol}$$

The bond enthalpy of an element is the amount of energy required to break 1 mole of a given bond when the reactants and products are in a gaseous state. The bond enthalpy values found in the data booklet is always given as average values as the exact bond enthalpy depends on the molecular environment in which the bond exists in.

For example, CH_4 has different exact bond enthalpy than CHF_3 because Fluorine is more electronegative hence changes the $C{-}H$ bond enthalpy.

$$\Delta H = \sum \text{Energy to break reactant bond} - \sum \text{Energy to brak product bond}$$

1. Calculate the heat of reaction for:

$$PbCl_2\,(s) + Cl_2\,(g) \longrightarrow PbCl_4\,(l)$$

Given:

$$Pb\,(s) + Cl_2\,(g) \longrightarrow PbCl_2\,(s)\ \Delta H = -359.4\,kJ \qquad (1)$$

$$Pb\,(s) + 2\,Cl_2\,(g) \longrightarrow PbCl_4\,(l)\ \Delta H = -329.3\,kJ \qquad (2)$$

Solution:

$$PbCl_2\,(s) \longrightarrow Pb\,(s) + Cl_2\,(g)\ \Delta H = 359.4\,kJ$$

$$PbCl_2\,(s) + Pb\,(s) + 2\,Cl_2\,(g) \longrightarrow Pb\,(s) + Cl_2\,(g) + PbCl_4\,(l)\ \Delta H\text{=-}688.7\,kJ$$

$$PbCl_2\,(s) + Cl_2 \longrightarrow PbCl_4\,(l)\ \Delta H = -688.7\,kJ$$

2. Calculate ΔH for the following reaction:

$$4\,NH_3\,(g) + 5\,O_2\,(g) \longrightarrow 4\,NO\,(g) + 6\,H_2O\,(g)$$

Given:

$$N_2\,(g) + O_2\,(g) \longrightarrow 2\,NO\,(g)\ \Delta H = -180.5\,kJ$$

$$N_2\,(g) + 3\,H_2\,(g) \longrightarrow 2\,NH_3\,(g)\ \Delta H = -91.8\,kJ$$

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(g)\ \Delta H = -483.6\,kJ$$

Solution:

$$2\,N_2\,(g) + 2\,O_2\,(g) \longrightarrow 4\,NO\,(g)\ \Delta H = -361\,kJ$$

$$4\,NH_3 \longrightarrow 2\,N_2\,(g) + 6\,H_2\,(g)\ \Delta H = 183.6\,kJ$$

$$6\,H_2\,(g) + 3\,O_2\,(g) \longrightarrow 2\,H_2O\,(l)\ \Delta H = 571.6\,kJ$$

$$4\,NH_3\,(g) + 5\,O_2\,(g) \longrightarrow 4\,NO\,(g) + 6\,H_2O\,(g)\ \Delta H = -1628.2\,kJ$$

3. Calculate ΔH for the following reaction:

$$2\,H_2\,(g) + 2\,C\,(s) + O_2\,(g) \longrightarrow C_2H_5OH\,(l)$$

Given:

$$C_2H_5OH\,(l) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 2\,H_2O\,(l)\ \Delta H = -875\,kJ$$

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g)\ \Delta H = -394.51\,kJ$$

$$H_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \longrightarrow H_2O\,(l)\ \Delta H = -285.8\,kJ$$

Solution:

$$2\,CO_2\,(g) + 2\,H_2O\,(l) \longrightarrow C_2H_5OH\,(l) + 2\,O_2\,(g)\ \Delta H = 875\,kJ$$

$$2\,C\,(s) + 2\,O_2\,(g) \longrightarrow 2\,CO_2\,(g)\ \Delta H = -789.2\,kJ$$

$$2\,H_2\,(g) + O_2\,(g) \longrightarrow 2\,H_2O\,(l)\ \Delta H = -571.6\,kJ$$

$$2\,H_2\,(g) + 2\,C\,(s) + O_2\,(g) \longrightarrow C_2H_5OH\,(l)\ \Delta H = -486\,kJ$$