

Thermodynamics

6.1 Endothermic and Exothermic Processes

It takes energy to break bonds and attractive forces and frees energy when forming bonds and attractive forces. In a constant pressure system, the net energy change is called the enthalpy (ΔH°).

System: the part of the universe we are studying

Surroundings: everything external to the system

Temperature changes in a system indicate energy changes. Those changes can be described as endothermic and exothermic processes such as the heating or cooling of a substance, phase changes, or chemical transformations.

When a chemical reaction occurs, the energy of the system either decreases (exothermic reaction), increases (endothermic reaction), or remains the same. For exothermic reactions, the energy lost by the reacting species (system) is gained by the surroundings, as heat transfer from work done by the system. Likewise, for endothermic reactions, the system gains energy from the surroundings by heat transfer to or work done in the system.

If energy needed to break bonds is greater than energy released when bonds are formed, then the process is endothermic ($+\Delta H^\circ$). If energy need to break bonds is less than energy released when bonds are formed, then the process is exothermic ($-\Delta H^\circ$).

The formation of a solution may be an exothermic or endothermic process, depending on the relative strengths of intermolecular/interparticle interactions before and after the dissolution process.

Exothermic Flow

1. Heat (q) flows from the system to the surroundings (increases temperature in surrounding).
2. Work is done by the system ($-$) $work = -P\Delta V$ (expansion).

Endothermic Flow

1. Heat (q) flows into the system from the surroundings (decreases temperature in surroundings).
2. Work is done on the system (+).

6.2 Energy Diagrams

A physical or chemical process can be described with an energy diagram that shows the endothermic or exothermic nature of the process.

Exothermic

- The potential energy of products is lower than the reactants, thus the products are more stable
- The process is energetically favorable
- Since $E_P < E_R$, energy is released from the system into the surroundings
- Enthalpy is negative

$$\Delta H^\circ = E_P - E_R = -kJ/mol$$

Endothermic

- The potential energy of products is higher than the reactants, thus the products are less stable
- The process is energetically unfavorable
- Since $E_P > E_R$, energy is drawn in from the surroundings into the system
- Enthalpy is positive

$$\Delta H^\circ = E_P - E_R = +kJ/mol$$

6.3 Heat Transfer and Thermal Equilibrium

Temperature is a measure of average kinetic energy. The particles in a warmer body have a greater average kinetic energy than those in a cooler body. Collisions between particles in thermal contact can result in the transfer of energy. This process is called “heat transfer,” “heat exchange,” or “transfer of energy as heat.” Eventually, thermal equilibrium is reached as the particles continue to collide. At thermal equilibrium, the average kinetic energy of both bodies is the same, and hence, their temperatures are the same.

6.4 Heat Capacity and Calorimetry

Heat capacity is the amount of heat a substance can absorb before $\Delta T = 1^{\circ}C = 1K$.

Specific vs. Molar Heat Capacity

Specific heat capacity:

$$c_P = \frac{J}{g \cdot ^{\circ}C}$$

Molar heat capacity:

$$C_P = \frac{J}{mole \cdot ^{\circ}C}$$

Heat Transfer Equations

The heating of a cool body by a warmer body is an important form of energy transfer between two systems. The amount of heat transferred between two bodies can be quantified by the heat transfer equation:

$$q = mc\Delta T$$

Calorimetry experiments are used to measure the transfer of heat.

The first law of thermodynamics states that energy is conserved in chemical and physical processes.

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

The transfer of a given amount of thermal energy will not produce the same temperature change in equal masses of matter with differing specific heat capacities. Heating a system increases the energy of the system, while cooling a system decreases the energy of the system. The specific heat capacity of a substance and the molar heat capacity are both used in energy calculations.

Chemical systems change their energy through three main processes: heating/cooling, phase transitions, and chemical reactions.

6.5 Energy of Phase Changes

Energy must be transferred to a system to cause a substance to melt (or boil). It takes energy (heat) to break attractions as a system undergoes a solid-to-liquid (or liquid-to-gas) phase transition. Likewise, energy (heat) is released when as the system undergoes liquid-to-solid (or gas-to-liquid) phase transition. The temperature of a pure substance remains constant through a phase change. The phase change from solid-to-liquid is faster than a phase change from liquid-to-gas.

Gaseous systems are at a relatively high potential energy and solid systems are at a relatively low potential energy.

The energy absorbed during a phase change is equal to the energy released during a complementary phase change in the opposite direction. For example, the molar heat of condensation of a substance is equal to the negative of its molar heat of vaporization.

$$\begin{aligned}-\Delta H_{\text{condensation}}^{\circ} &= \Delta H_{\text{vaporization}}^{\circ} \\ -\Delta H_{\text{freezing}}^{\circ} &= \Delta H_{\text{melting}}^{\circ}\end{aligned}$$

The molar enthalpy of fusion ($\Delta H_{\text{fusion(melting)}}^{\circ}$) is the energy required to melt a substance. The molar enthalpy of vaporization ($\Delta H_{\text{vaporization}}^{\circ}$) is the energy required to vaporize a substance.

6.6 Introduction to Enthalpy of Reaction

The enthalpy change of a reaction gives the amount of heat energy released (for negative values; exothermic) or absorbed (for positive values; endothermic) by a chemical reaction at a constant pressure.

The amount of heat produced or absorbed based on the conditions and specific quantities given in the problem is called “q” instead of ΔH .

6.7 Bond Enthalpies

During a chemical reaction, bonds are broken and/or formed, and these events change the potential energy of the system. The average energy required to break all of the bonds in the reactant molecules can be estimated by adding up the average bond energies of all the bonds in the reactant molecules. Likewise, the average energy released in forming the bonds in the product molecules can be estimated. If the energy released is greater than the energy required, the reaction is exothermic. If the energy required is greater than the energy released, the reaction is endothermic.

$$\Delta H_{rxn} = \sum (\text{bond energy of bonds broken}) + \sum (\text{bond energy of bonds formed})$$

Bond energy of bonds formed is negative because energy is being released as the bonds are formed.

6.8 Enthalpy of Formation

The standard enthalpy of formation (ΔH_f°) is a reference value that exists for compounds or elements. It represents a change in enthalpy when a substance forms. Those values can be used to estimate the overall enthalpy change of a reaction (ΔH_{rxn}°).

$^\circ$ indicates that the value is measured in the standard state.

- For gases: 1 atm of pressure
- For liquids and solids: the substances most common, stable form at 1 atm and 25°C (example: $O_{2(g)}$ not $O_{(g)}$)
- For solutions: a concentration of 1 M

For a pure element in its standard state, $\Delta H_f^\circ = 0 \text{ kJ/mol}$. For a pure element not in its standard state, ΔH_f° will not be 0.

$$\Delta H_{reaction}^\circ = \sum \Delta H_{f \text{ products}}^\circ - \sum \Delta H_{f \text{ reactants}}^\circ$$

6.9 Hess's Law

Although the concept of a “state function” is not required for the course, two principles of Hess's law should be understood. First, when a reaction is reversed, the enthalpy change stays constant in magnitude but becomes reversed in mathematical sign. Second, when two (or more) reactions are added to obtain an overall reaction, the individual enthalpy changes of each reaction are added to obtain the net enthalpy of the overall reaction.

When the products of a reaction are at a different temperature than their surroundings, they exchange heat with the surroundings to reach thermal equilibrium. Thermal energy is transferred to the surroundings from the products of an exothermic reaction. Thermal energy is transferred from the surroundings to the products of an endothermic reaction.