

Thermochemistry

Chemical Thermodynamics -- The chemical science dealing with the relationships between heat and other forms of energy known as work.

System: The substance under study

Universe (Surroundings): Everything except the substance under study

Internal Energy: The total of all forms of energy present in a substance

Energy is transferred out of a system when heat is lost from the system or when the system does work on the surroundings

Energy is transferred into the system when heat is gained by the system or when the surroundings do work on the system

Thermochemistry -- A branch of thermodynamics dealing with the determination and study of heat absorbed or evolved during chemical reactions or during phase changes.

Energy: The capacity to supply heat or do work.

Kinetic energy (E_K) (Energy of motion) vs. Potential Energy (E_p)(Stored energy)

Conservation of Energy Law: Energy cannot be created or destroyed; it can only be converted from one form into another.

Heat: A measure of molecular motion which moves from one body to another due to a difference in temperature

Temperature: A measure of transferable heat energy

-degree Fahrenheit

-degree Celsius

-Kelvin

Heat Measurement Units

- Calorie: The energy needed to raise one gram of water by one degree Celsius
- kilocalorie (kcal)
- Joule: The SI unit for all forms of energy including heat energy
- Kilojoule
- $4.184 \text{ J} = 1 \text{ cal}$

First Law of Thermodynamics: The energy of the universe is constant.

First Law: $\Delta E = q + w$

$\Delta E = \text{change in system's internal energy}$

$q = \text{heat}$

$w = \text{work}$

State Function

- Depends only on the present state of the system - not how it arrived there.
- It is independent of pathway.

Standard State Conditions -- 298.15 K (25°C), 1 atmosphere, and unit activities

Work

- work = force x distance
- since pressure = force / area,
- work = pressure x volume
- $w_{system} = -P\Delta V$

Calculating the amount of PV work

Example: Calculate the work in kilojoules done during a reaction in which the volume expands from 12.0 L to 14.5 L against an external pressure of 5.0 atm.

$$w = -P\Delta V = (5.0 \text{ atm})(2.5 \text{ L}) = -12.5 \text{ L} \cdot \text{atm}$$

Then: $w = (-12.5 \text{ L} \cdot \text{atm}) \left(101 \frac{\text{J}}{\text{L} \cdot \text{atm}} \right) = 1.3 \times 10^3 \text{ J} = 1.3 \text{ KJ}$

Conversion factor to convert to kJ

Enthalpy Changes (ΔH) -- The heat lost or gained by a system under constant pressure, with the only work done being due to expansion or contraction of the system under this constant pressure.

Enthalpy (H)

- Also known as heat of reaction
- Enthalpy change (ΔH)
- $\Delta H = E + PV$

Change in Enthalpy

- Can be calculated from enthalpies of formation of reactants and products.

Calculation of Enthalpy Change

$$\Delta H = \sum \Delta H_{\text{product(s)}} - \sum \Delta H_{\text{reactant(s)}}$$

Enthalpy of Fusion (ΔH_{fus}) -- The amount of heat required to change 1 mol of substance from the solid to the liquid state at constant temperature

$$\Delta H_{\text{fus}} \text{ for water is } 6.01 \text{ KJ/mol at } 0^\circ\text{C}$$

Enthalpy of Vaporization (ΔH_{vap}) -- The amount of heat required to evaporate 1 mol of a liquid at a constant temperature

$$\Delta H_{\text{vap}} \text{ of water is } 44.01 \text{ KJ/mol at } 25^\circ\text{C}$$

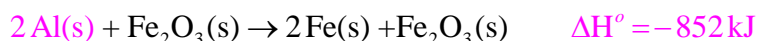
$$\Delta H_{\text{vap}} \text{ of water is } 40.67 \text{ KJ/mol at } 100^\circ\text{C}$$

Enthalpy of Combustion -- The enthalpy change for the combustion of 1 mol of substance under standard state conditions

Standard Molar Enthalpy of Formation (ΔH°) -- The heat absorbed or released during the formation of 1 mol of a pure substance from free elements in their most stable states under standard state conditions.

Calculating the amount of Heat Released during a Chemical Reaction:

How much heat in kilojoules is evolved when 5.00 g of aluminum reacts with a stoichiometric amount of Fe_2O_3 ?



$$5 \text{ g Al} \times \frac{1 \text{ mol Al}}{26.98 \text{ g Al}} \times \frac{-852 \text{ kJ}}{2 \text{ mol Al}} = -78.8 \text{ kJ}$$

Calorimetry: The process of measuring the amount of heat involved in a chemical or physical change

- Calorimeter
 C_{cal} -- calorimeter constant
- $q_{\text{reaction}} + q_{\text{soln}} + q_{\text{calorimeter}} = 0$

The Bomb Calorimeter – A device to conduct calorimetry experiments

Heat Capacity (C) -- The amount of heat required to raise the temperature of an object or substance by a given amount.

$$C = \frac{q}{\Delta T}$$

Specific Heat(C) -- The amount of heat required to raise the temperature of 1 gram of a substance by 1 °C.

$$q = C \times m \times \Delta T$$

Hess's Law -- If a process can be written as the sum of several stepwise processes, the enthalpy change of the total process equals the sum of the enthalpy changes for each step.

Entropy

- Standard entropy: The entropy content of exactly 1.0 mole of substance under standard state conditions.
- The driving force for a spontaneous process is an increase in the entropy of the universe.
- Entropy, S , can be viewed as a measure of randomness, or disorder.

Spontaneous Processes and Entropy

- Thermodynamics lets us predict whether a process will occur but gives no information about the amount of time required for the process.
- A spontaneous process is one that occurs without outside intervention.

During a Spontaneous Chemical Change:

- Systems tend toward a state of lower energy
- Systems tend toward a state of maximum disorder

Entropy of Solids, Liquids and Gases

- Entropy reflects the degree of disorder in a system.
- Therefore,
- $S_{solid} < S_{liquid} \ll S_{gas}$

The Third Law of Thermodynamics

- . . . the entropy of a perfect crystal at 0 K is zero.
- Because S is explicitly known ($= 0$) at 0 K, S values at other temps can be calculated.

Free Energy

- $\Delta G = \Delta H - T\Delta S$ (from the standpoint of the system)
- A process (at constant T, P) is spontaneous in the direction in which free energy decreases:
- $-\Delta G$ means $+\Delta S_{univ}$

Effect of ΔH and ΔS on Spontaneity

<u>ΔH</u>	<u>ΔS</u>	<u>Result</u>
–	+	spontaneous at all temps
+	+	spontaneous at high temps
–	–	spontaneous at low temps
+	–	not spontaneous at <u>any</u> temp

The Second Law of Thermodynamics -- In any spontaneous process there is always an increase in the entropy of the universe. ($\Delta S_{univ} > 0$ for a spontaneous process.)

Fossil Fuels >> Heats of Combustion --- The most useful chemical reaction for the production of heat.

- Requires oxygen
- Produces water and carbon dioxide
- Releases large amounts of energy

Fossil Fuels

- Hydrocarbons
 - Natural gas
 - CH_4
 - C_2H_6
 - C_3H_8
 - C_4H_{10}
 - H_2S (Contaminant & must be removed)

- Petroleum – Used for the production of various oils and gases and has a variable composition

- Coal
 - Variable sulfur content
 - Major source of energy for the production of electricity