

Thermochemistry Notes

Thermochemistry: The study of energy changes related to chemical reactions.

Work and Energy

Energy is defined as the capacity to do work

Potential energy (such as mgh)

Kinetic energy ($\frac{1}{2}mv^2$)

SI unit of energy is the joule (J)

Work is defined as applying a force F through a distance d $W = Fd$

A force of 1N applied through a distance of 1m does 1J of work (Units: $\text{kg m}^2/\text{s}^2$ or Nm)

Note: Work and energy have the same units = joules

Thermochemistry Definitions

System: The portion of the universe under study.

Surroundings: Everything else besides the system.

Interaction: Exchange of energy and or matter between the system and its surroundings.

Systems:

Open system: Exchanges both matter and energy with its surroundings.

Closed system: Exchanges only energy with its surroundings.

Isolated system: Exchanges neither energy nor matter with its surroundings.

Internal Energy (E) = Total energy of the system

Kinetic (thermal) energy:

Translational

Rotational

Vibrational

Potential energy

-Nuclear forces

-Electrostatic attractions (Chemical energy)

-Intramolecular - Bonds between atoms

-Intermolecular - Attractions between molecules

Heat (q) = energy *transfer* (kinetic energy)

Caused by temperature differences

System and surroundings reach thermal equilibrium

A system does not *contain* heat.

Energy (in the form of thermal kinetic energy) is transferred from the hotter region to the colder region until thermal equilibrium is established.

Work (w)

Transfer of energy between a system and its surroundings.

Usually due to some physical change to the system.

A system does not *contain* work.

Focus is on pressure-volume (P-V) work: Work done when gases are expanded or compressed.

$$P = F/A = PA$$

$$\begin{aligned} \text{Work (w)} &= \text{force (F)} \times \text{distance (h)} \\ &= P \times A \times h \end{aligned}$$

$$(A)h = \Delta V \quad \therefore$$

$$\text{Work (w)} = P\Delta V \quad (\Delta V = V_f - V_i)$$

A negative is added as a sign convention to show that when a system loses energy (i.e. is

transferred from the system to the surroundings) the work is negative. Therefore

$$w = -P\Delta V$$

1st Law of Thermodynamics

Internal energy (E) is a **state function**.

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

A **state function** only depends on the current conditions of the system and not upon how that state was reached.

Cannot measure absolute internal energy

Internal energy is a *state function*

Depends on the present state of the system and not on its history

Heat (q) and work (w) are *not* state function (They are not contained in the system and exist as a consequence of a change in the system)

For a given change, different combinations of heat and work can lead to the same ΔE .

Functions of state are reversible.

Law of Conservation of Energy: In a physical or chemical change, energy can be exchanged between a system and its surroundings, but no energy can be created or destroyed.

First Law of Thermodynamics:

$$\Delta E = q + w$$

Heat absorbed by the system	Increases energy of the system	$q > 0$
Work done on the system		$w > 0$
Heat given off by the system	Decreases energy of the system	$q < 0$
Work done by the system		$w < 0$

So “positive” is measured relative to the system.

Heats of Reaction and Enthalpy Change, ΔH

	Isolated System	Open/Closed System
Exothermic Reaction Chemical energy \rightarrow Thermal energy	System Temperature increases	Heat given off to surroundings ($q < 0$ for system)
Endothermic Reaction Thermal energy \rightarrow Chemical energy	System Temperature decreases	Heat absorbed from surroundings ($q > 0$ for system)

Heat of Reaction (q_{rxn}): The quantity of heat exchanged between the reaction system and its surroundings for a reaction *occurring at a fixed temperature*.

(Assume only pressure-volume type of work for the following examples)

For reactions that take place at **constant volume**:

$$w = -P\Delta V = 0 \text{ (no volume change)}$$

$$\Delta E = q + w = q_v$$

$$q_v = \Delta E$$

For reactions that take place at constant pressure:

$$\Delta E = q + w = q_p - P\Delta V$$

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

Enthalpy

Most reactions are carried out at constant pressure in open vessels.

$$\text{Enthalpy (H)} \equiv E + PV$$

$$q_p = \text{enthalpy change for a reaction} = \Delta H$$

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

Properties of Enthalpy

1. Enthalpy is an extensive property (depends upon the amount present)
2. Enthalpy is a state function (E, P and V are state functions)

3. Enthalpy changes have unique values
($\Delta H = q_p$)

An enthalpy diagram can be used to illustrate the enthalpy change of a reaction. The enthalpy, H, is plotted on the Y-axis and the progression of the reaction on the X-axis. ΔH is the value that is determined.

Calorimetry

Measurement of heat energy transfer

Heat Capacity (C) \equiv Quantity of heat required to change the temperature of a system by 1°C (or 1K)

$$C = q/\Delta T$$

Molar Heat Capacity/Specific Heat

Molar heat capacity = C/n , where C is the heat capacity and n is the moles.

Specific heat = $C/m = q/(m\Delta T)$, where m is the mass in grams and $\Delta T = T_f - T_i$

1calorie = 1 cal = amount of energy required to raise the temperature of 1g of water by 1°C (at 1 atm).

$$1\text{cal} = 4.184\text{J}$$

$$1\text{kilocalorie} = 1\text{Cal} = 1,000\text{cal}$$

The specific heat of water is $4.184\text{J/g}^\circ\text{C}$

Enthalpy, Specific heats and Chemical reactions:

Using a Styrofoam cup calorimeter:
All the heat lost by the hot solid is gained by the water in the cup.

The Styrofoam acts as a good insulator and has a low specific heat.

If a reaction takes place inside a insulated calorimeter $q_{\text{rxn}} = -q_{\text{calorimeter}}$ If this reaction takes place under constant pressure $q_{\text{rxn}} = q_p$

Bomb Calorimeter

For combustion reactions and other reactions involving gases.
The chamber of the bomb calorimeter keeps the system at a constant volume.

$$\Delta E = q_v = q_{\text{rxn}} = -q_{\text{calorim}} \quad \text{where } q_{\text{calorim}} = \text{heat capacity of calorimeter} \times \Delta T$$

Note that this is not necessarily the enthalpy ΔH . Enthalpy is measured at constant pressure. (i.e. $q_p = \Delta H = \Delta E + P\Delta V$)

Hess's Law of Heat Summation

The heat of a reaction is constant, whether the reaction is carried out directly in one step or indirectly through a number of steps.

Reversing an equation:

Changes the sign of ΔH

Multiplying coefficients in an equation:

Multiplies the value of ΔH by the same amount.

Multiplying factors may be fractional.

Standard Enthalpy of Formation

Scale of relative enthalpies.

Standard state of solid or liquid:

Pure element or compound at 1atm and the temperature of interest (often 25°C)

Standard state of gas:

Pure gas substance acting ideal at 1atm and the temperature of interest.

Standard enthalpy of reaction (ΔH°) is the enthalpy change for standard state reactants yielding standard state products.

Standard enthalpy of formation (heat of formation) (ΔH_f°) = enthalpy change in creating 1 mole of a substance at standard state conditions from its elements at standard states and in its reference form.

The standard enthalpy of formation of a pure element in its reference form is 0. (ex. Carbon as graphite. Graphite is the reference form of carbon.)

To determine the standard enthalpy of a reaction from standard heats of formation:

$$\Delta H^\circ = \sum v_p \times \Delta H_f^\circ(\text{products}) - \sum v_r \times \Delta H_f^\circ(\text{reactants})$$

and v refers to the stoichiometric coefficients of the reactants and products.

Ionic Reactions in Solutions:

Since cations and anions cannot be formed in isolation, you cannot directly extend enthalpy to the formation of single ions.

$H^+_{(aq)}$ is arbitrarily assigned an enthalpy of formation of zero. The formation of other ions are measured relative to this.