Thermochemistry Intro

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

Energy & Chemistry:
- Energy - capacity to do work or transfer heat
- Heat - form of energy that flows between 2 objects because of their difference in temperature

Directionality of Heat Transfer:
- heat ALWAYS transfers from hotter object to cooler one
- EXOthermic: heat transfers from system to surroundings
- ENDOthermic: heat transfers from surroundings to system

Systems and Surroundings:
- universe = sytem + surroundings
- Open System - can exchange both energy and matter with its surroundings
- Closed System - can exchange energy, but not matter, with its surroundings
- Isolated System - cannot exchange energy or matter

Conservation of Energy:
- the total energy is unchanged in a chemical reaction
- if PE of products is less than reactants, the difference must be released as KE

Units of Energy:
- 1 calorie = heat required to raise temp. of 1.00g of H_2O by 1.0°C
- 1000 cal = 1 kibcalorie = 1 kcal
- 1 KCal = 1 Calorie

* 1 cal = 4.184 Joules

Measurable & Calculated Variables of a System:

- thermal energy: sum of all KE of all the particles of a sample of matter
- temperature: measure of the average KE of all the particles of a sample of matter

Specific Heat Capacity:

- the amount of energy needed to increase the temperature of 1g of substance by 1°C

- the heat (Q) 'lost' or 'gained' is related to
  a) mass (m)
  b) change in T (ΔT)
  c) specific heat capacity (c)

$Q = m\Delta tC \quad c = \frac{Q}{m\Delta t}$

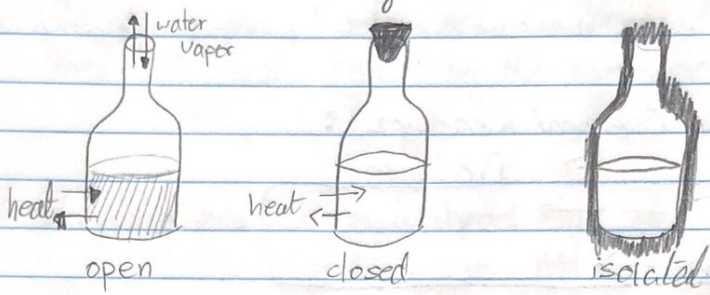
$Q = mL$

Specific Heat Capacity = $\frac{\text{heat lost or gained by substance (J)}}{\text{(mass, g)} \times \text{(t change, °C)}}$

Thermochemistry & Enthalapy

thermochemistry: study of heat exchange in chemical reactions

system: the specific part of the universe that is in the interest of the study



Exothermic Process: any process that gives off heat

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} + \text{energy}$$ (thermochemical equation)

Endothermic Process: any process in which heat has to be supplied to the system from the surroundings

$$\text{energy} + 2HgO_{(s)} \longrightarrow 2Hg_{(l)} + O_{2(g)}$$

First Law of Thermodynamics:

- the total energy of the universe is constant
- $\Delta E_{universe} = \Delta E_{sys} + \Delta E_{sur} = 0$
- energy can be converted from one form to another but cannot be created or destroyed

2nd Law of Thermodynamics:

- when two objects are in thermal contact, heat is always transffered from object at higher temp. to the objeat at a lower temp. until two objects are at same temp.

Enthalapy:

- sometimes called as the Heat content of system, denoted by letter 'H'
- is the total energy of the system plus the pressure times volume, $H = E + PV$
- it is not possible to measure the total enthalapy of a system

Enthalapy Changes in Chemical Reactions:

Reactants ⟶ Products

bonds broken ⟶ bonds made — endothermic
energy absorbed > energy released

bonds broken ⟶ bonds made — exothermic
energy absorbed < energy released

Phase Change:

- as heat is added to a substance, the temperature of the substance increases until it reaches its melting point, or boiling point
- temperature then remains steady as the substance undergoes a phase change

• $\Delta H^\circ_{melt} = -\Delta H^\circ_{freezing}$ • $\Delta H^\circ_{vapor} = -\Delta H^\circ_{condensation}$

• Enthalpy is used to quantify the heat flow into or out of a system in a process that occurs at constant pressure

$$\Delta H = H(products) - H(reactants)$$

Thermochemical Equations:

- the stoichiometric coefficients always refer to the number of moles of a substance

$H_2O_{(s)} \longrightarrow H_2O_{(l)} \quad \Delta H = 6.01 kJ/mol$

- If you multiply both sides of the equation by a factor of n, then ΔH must change by the same factor n

$2H_2O_{(s)} \longrightarrow 2H_2O_{(l)} \quad \Delta H = 2 \cdot 6.01 kJ/mol$

$\Delta H = 12.0 kJ/mol$

- If you reverse a reaction, the sign of ΔH changes

$H_2O_{(s)} \longrightarrow H_2O_{(l)} \quad \Delta H = -6.01 kJ/mol$

Word Probems.

1. $2Al_{(s)} + 3Cl_{2(g)} \longrightarrow 2AlCl_{3(s)} \quad \Delta H_{rxn} = -1408 kJ/mol$

$m_{Al} = 1000g \quad n_{Al} = \frac{m}{M}$

$= \frac{1000g}{26.982 g/mol}$

$= 37.06 mol$

$\Delta H_2 = \frac{(37.06 mol)(-1408 kJ/mol)}{2}$

$= -26091.46389 kJ/mol$

2. $C_2H_2 + \frac{5}{2}O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(l)}$

$m_{H_2O} = 1.50g \quad n_w = \frac{m}{M} = \frac{1.5}{18.02}$

$= 0.0832 mol$

$\Delta H = \frac{(0.0832 mol)(-1300 kJ/mol)}{1}$

$= -108.213 kJ/mol$

3. $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)} \quad \Delta H_{rxn} = 180.6 kJ/mol$

$m_N = 100g \quad n_N = \frac{m}{M}$

$= \frac{100}{28.02}$

$= 3.5688 mol$

$\Delta H = \frac{(3.5688 mol)(180.6 kJ/mol)}{2}$

$= 322.2698 kJ/mol$

Calorimetry

Standard Enthalpy Values:

- standard enthalpy of formation is defined as the change in enthalpy when one mole of a substance in the standard state is formed from its pure elements under the same conditions

Coffee Cup Calorimeter:

- generally used only for dilute aqueous (water) solutions
- not safe to use for reactions that release alot of energy
- not practical for reactions that occur slowly
- the change in temp. caused by a reaction, combined with values of the specific heat and the mass of the reacting system, makes it possible to determine the heat of reaction

Bomb Calorimeter

- some heat from reaction warms water
  - $q_{water} = Q = mc\Delta t$
- some heat from reaction warms 'bomb'
  - $q_{bomb} = C_{cal}\,\Delta t$
- $\therefore Q_{total} = q_{water} + q_{bomb}$

- a bomb calorimeter measures enthalpy changes during combustion reactions at a constant volume

*the heat capacity (c) of a body of matter is the quantity of heat (q) it absorbs or releases when it experiences a temperature change (Δt) of 1°C

Hess's Law of Heat Summation

- this law states that the enthalpy change of a physical or chemical process depends only on the beginning conditions (reactants) and the end conditions (products)
- the enthalpy change is independent of the pathway of the process and the number of intermediate steps in the process
- it is the sum of the enthalpy changes of all individuals steps that make up the process

- Hess's law allows you to determine the energy of a chemical reaction without directly measuring it
- there are 2 ways in which you can use Hess's law to calculate enthalpy change of a chemical reaction
  1. by combining chemical equations algebraically
  2. by using the enthalpy of a special class of reactions called formation reactions

Standard Molar Enthalpies of Formation.

Standard Enthalpy Values:
- most ΔH values are labelled ΔH°
- measured in standard conditions
  - $P = 1$ bar
  - Concentration = 1 mol/L
  - $T = 25^\circ C$

ΔH_f°:
- the standard molar enthalpy (enthalpy of 1 mole) of formation is the quantity of energy that is absorbed or released when one mole of a compound is formed directly from its elements in their standard states

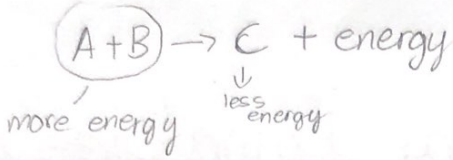
Ex: $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$

↑ Carbon will need to be in its natural state (graphite)

- the enthalpy value also depends on how reaction is written, and phases (states) of reactants and products

Formation Reactions:
- in a formation reaction, a substance is formed from elements in their standard states
- the enthalpy change of a formation reaction is called the standard molar enthalpy of formation (ΔH_f°)

- elements in standard state have enthalpy of ZERO



-the standard enthalpies of formation of most compounds are negative

* $\Delta H^\circ_{reaction} = \sum \Delta H_f^\circ (products) - \sum \Delta H_f^\circ (reactants)$

Writing a Formation Equation:
- always write the elements in their standard state
- a formation equation should also show the formation of exactly one mole of the compound of interest

Ex:

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H_f^\circ = -285.8^\circ C$$