

THERMOCHEMISTRY

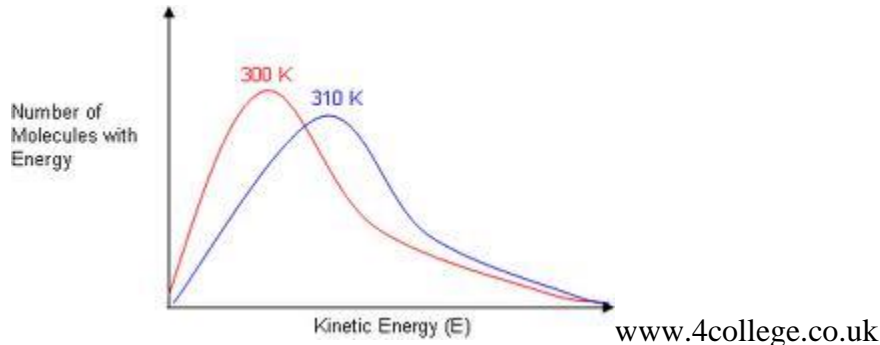
- The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter (Big Idea 5).

Definitions and Conventions:

- **Energy** – the ability to do work
- **Potential energy** – energy due to position or composition. In Chemistry this is associated with a particular geometric arrangement of atoms or ions and the electrostatic interactions between them. In chemical systems, the stored energy is called chemical energy.
- **Kinetic energy** – energy due to the motion of an object. In chemical systems this is thermal energy.
- **System** - the part of the universe being studied
- **Surroundings** – the rest of the universe
- **Open system** – exchanges matter and energy with the surroundings
- **Closed system** – exchanges energy but not matter with the surroundings
- **Isolated system** – exchanges neither energy nor matter with the surroundings.
- **Internal energy (U)** – the total energy contained within the system.
- **Work (w) = force x distance** ($\text{N} \times \text{m} = 1 \text{ kg m}^2 \text{ s}^{-2} = \text{J}$)
Pressure volume work $w = -P\Delta V$ (pressure x change in volume)

Temperature (T):

- A measure of the average kinetic energy of atoms and molecules.
- All of the molecules in a sample are in motion.
- The Kelvin temperature of a sample of matter is proportional to the average kinetic energy of the particles (EK 5.A.1). If the average kinetic energy of particles in a sample doubles, the Kelvin temperature doubles.
- **The Maxwell-Boltzmann Distribution** shows that the distribution of kinetic energies becomes greater (more disperse) as temperature increases.



Heat (q):

- The quantity of thermal energy transferred from one system to another.
- Heat transfer takes place from a hotter object to a colder object.
- Molecules in the warmer object have more kinetic energy than those in the cooler object.
- Energy is transferred as molecules collide.

- Thermal equilibrium is eventually reached. At this point the average kinetic energy of both substances is the same.
- Heat is not a substance. Use the terms “heat exchange” or “transfer of heat energy” rather than saying an object contains a certain amount of heat.
- If thermal energy is transferred between equal masses of materials with differing specific heats, the temperature change will not be the same for each material.

In Chemistry, the signs for work, energy, heat etc are usually from the system’s point of view:

- **Energy** entering a system (endothermic) has a positive sign
- **Energy** leaving a system (exothermic) has a negative sign
- **Heat** absorbed by the system has a positive sign
- **Heat** lost by the system has a negative sign
- **Work** done on a system has a positive sign
- **Work** done by the system has a negative sign

Note: These conventions are not the same for all fields; an engineer may define work from the surroundings point of view.

Law of Conservation Of Energy:

Energy is neither created nor destroyed, but only transformed from one form to another.

- Any change in the energy of a system must be balanced by a transfer of energy either into or out of the system. The energy transfer may be in the form of heat transfer or work. Ex: the expansion of a gas against a piston in an engine. As the gaseous molecules collide with the piston, the gas is doing work on the piston and energy is transferred from the gas to the piston.
- Calculations involving work are limited to those associated with changes in volume of a gas for this course.

Chemical systems undergo 3 main processes that change their energy:

1. **Heating and cooling.**

- Heating a system increases the energy while cooling it decreases the energy.
- **Specific heat capacity (c)** is the amount of energy needed to heat one gram of a substance by 1°C.

2. **Phase transitions:**

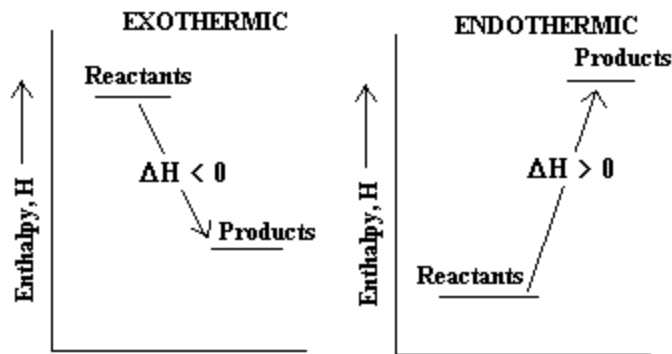
- Energy has to be transferred to a system in order for it to melt (or boil), increasing the energy of the system. Likewise, the energy of a system has to decrease in order for freezing or condensation to take place.
- The **molar enthalpy of vaporization** is the amount of energy needed to vaporize one mole of a pure substance. It will be equal in magnitude to the energy released when the same substance condenses.

- Likewise, the **molar enthalpy of fusion** is the amount of energy absorbed when one mole of a pure substance melts and will be equal in magnitude to the energy released when the liquid freezes.

3. Chemical reactions:

- When a chemical reaction occurs, the energy of the system can decrease (exothermic), increase (endothermic) or stay the same.
- **Enthalpy change (ΔH)** of a reaction gives the amount of energy released (ΔH negative) or absorbed (ΔH positive) by a chemical reaction at constant pressure.
- Note that when a reaction is reversed for a reaction, the enthalpy change has the same magnitude but opposite sign)

Energy (or enthalpy) diagrams show enthalpy changes through a chemical reaction.



Calorimetry:

- An experimental technique that is used to determine the heat exchange in a chemical system.
- Can be used to determine heat capacities, enthalpies of fusion and vaporization, and enthalpies of reactions.

Heat capacity (C) - the quantity of heat required to change the temperature of the system by 1 °C.

$$C = q / \Delta T \quad (\text{units are joules/}^\circ\text{C})$$

Molar heat capacity - the heat capacity of one mole of a substance

Specific heat capacity (c)

- Sp. heat = C / m (heat capacity/mass)
- Water has a relatively high specific heat.
- 1 **calorie** = the quantity of heat required to raise the temperature of 1 gram of water from 14.5 °C to 15.5 °C. (1 cal = 4.184 J)
- Specific heat varies with temperature

$$q = m c \Delta T \quad (\Delta T = T_{\text{final}} - T_{\text{initial}})$$

Measuring specific heat

- Simple calorimeters can be used to determine the specific heat of an insoluble solid.

1. A measured mass of water is placed in the calorimeter and the temperature taken.
2. A measured mass of the solid is heated to a measured temperature then dropped into the water.
3. Heat transfers from the solid to the water - the water temperature rises and the solid temperature falls until they are equal.
4. The final temperature of the water is taken.
5. All the heat lost by the solid is gained by the water in the calorimeter.
6. The quantity of heat transferred can be determined from the mass and temperature change of the water.

For constant pressure calorimetry, $\Delta H = -q_{\text{calorim}}$

Calculating Enthalpy for a Chemical reaction:

Bond dissociation energy:

- The net energy change of a reaction is the sum of the energy required to break the bonds of the reactants and the energy released in forming the bonds of the products.
- Review how to calculate enthalpy using bond dissociation energies.

Hess's Law of Constant Heat Summation:

- Enthalpy is a state function (it depends only on the present state, not on the pathway it took to get there). The heat (or enthalpy) of reaction is constant whether the reaction was carried out directly in one step or indirectly through a number of steps.
- When a reaction is reversed, the sign of the enthalpy of reaction changes.
- When two or more reactions are summed to give an overall reaction, their enthalpies are summed to give the net enthalpy of reaction.

Standard Enthalpies of Formation:

- Can be used to calculate the standard enthalpy of reactions.
- **Standard state for solids and liquids** - the pure element or compound at 1 atm and the temperature of interest.
- **Standard state for a gas** - the gas behaving as an ideal gas at 1 atm and the temperature of interest.
- **Standard enthalpy of reaction (ΔH°)**- the enthalpy change for a reaction where the reactants in their standard states yield products in their standard states.
- **Standard enthalpy of formation (ΔH°_f)** - the enthalpy change that occurs in the formation of 1 mole of the substance from its elements when all substances are in their standard states. (Also called the heat of formation).
 - The elements must be in their reference forms (in their most stable form at 1 atm and the given temp).
 - The standard enthalpy of formation of a pure element in its reference form is 0.

Calculations:

$$\Delta H^\circ_{\text{reaction}} = \Sigma \Delta H^\circ_f(\text{products}) - \Sigma \Delta H^\circ_f(\text{reactants})$$