

Thermodynamics

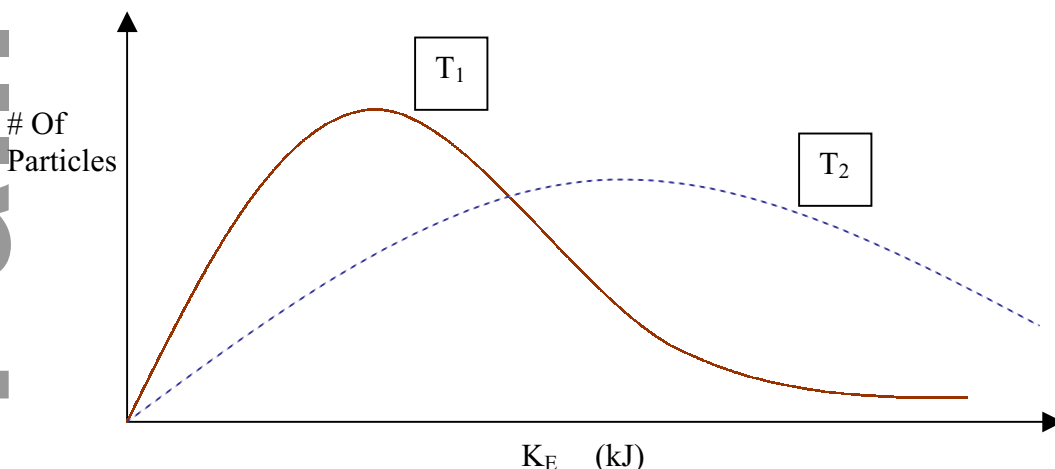
(The study of energy changes during chemical reactions)

****Enthalpy change for a reaction is affected by Temperature, Pressure, the quantities of reactants and the physical state of the reactants and products. Hence molar enthalpy changes are often used. ****

Energy: Is the ability to do work, (Joules). In a chemical system energy is the sum of the K_E and E_p of the particles in the system.

K_E : - Due to rotational, vibrational, and translational movements

- The particles in a system have a wide range of energies, $K_E = \frac{1}{2} mv^2$
- Depends on temperature of the system $K_E \propto T$
- Represented by the Maxwell-Boltzmann distribution graph below, $T_1 < T_2$:



E_p : -due to the position of the particles

- The closer the particles the stronger the attraction and the lower the E_p

Heat and Enthalpy

Heat content of a system is the total amount of energy ($E_k + E_p$) in a system.

Heat content = Enthalpy (of a system) = H

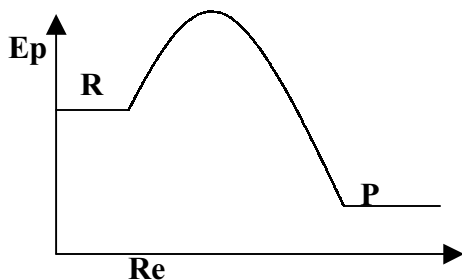
Since there is no way of measuring all the energies of all the particles of a system.

Therefore by convention, arbitrarily: **elements** in their standard state at standard temperature (298K), standard pressure (101.3 kPa) have **ZERO** enthalpy.

Changes in enthalpy are determined by the equation: $\Delta H = H_{\text{Products}} - H_{\text{Reactants}}$ (measured in kJmol^{-1}).

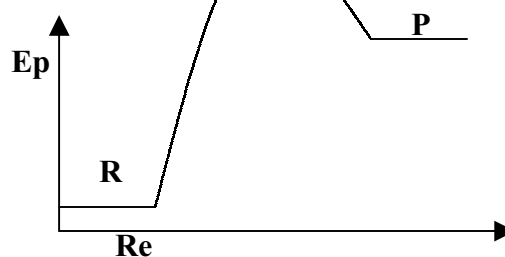
Exothermic and Endothermic reactions

Exothermic:



- 1) $\Delta H = -$ (negative)
- 2) $A \rightarrow B + \text{energy}$
- 3) Temperature increases
- 4) E_p (prod) lower than E_p (reactants)
- 5) Stability of products is greater than that of reactants
- 6) Self-sustaining
- 7) Bonds in product more stable than those in reactants, strong bonds made weak bonds broken.

Endothermic:



- 1) $\Delta H = +$ (positive)
- 2) $A + \text{energy} \rightarrow B$
- 3) Temperature decreases
- 4) E_p (prod) higher than E_p (reactants)
- 5) Stability of reactants is greater than that of products
- 6) Reaction stops when energy input stops.
- 7) Weaker bonds are made: stronger bonds are broken.

Standard Enthalpy Changes, ΔH

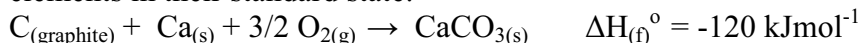
Enthalpy change is measured in kJ/mol. The enthalpy change for a reaction is affected by temperature, pressure, the quantities of the reactants and by the physical state of the reactants and products.

Molar enthalpy change values are used.

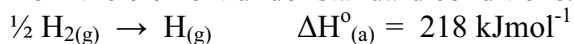
ΔH° Refers to a mole of substance reacting under the standard conditions of 298K (25°C) and 101.3kPa. The chemicals should be in their standard state, and the most stable state at 298 K, example $H_2O(l)$, $CO_2(g)$, $C_{(graphite)}$

ΔH° Refers to enthalpy change measure under standard conditions.

$\Delta H^\circ_{\text{formation}}$ The enthalpy change when one mole of a compound is formed from elements in their standard state:



$\Delta H^\circ_{\text{atomisation}}$ Standard enthalpy of atomization, when one mole of atoms are formed from the element under standard conditions. (gaseous state)

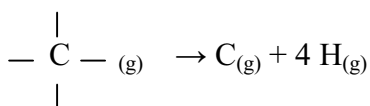


$\Delta H^\circ_{\text{combustion}}$ (in excess O_2 , complete combustion)

$\Delta H^\circ_{\text{neutralisation}}$ Strong Acid + Strong Base: $H^+ + OH^- \rightarrow H_2O$ $\Delta H^\circ_n = -56.7 \text{ kJmol}^{-1}$
Weak Acid + Weak Base: \neq (not -56.7 kJmol^{-1} Why?)

$\Delta H^\circ_{\text{hydration}}$ Or solution enthalpy. When 1mole of an ionic compound is dissolved in an excess of $H_2O(l)$ (relate to lattice energy)

Bond Enthalpy or Bond Dissociation Enthalpy: $X-Y_{(g)} \rightarrow X_{(g)} + Y_{(g)} \quad \Delta H^\circ =$



Mean/Average Bond Enthalpy Value calculation for the C—H bond:

$$\begin{aligned} & 425 \text{ kJmol}^{-1} + 70 \text{ kJmol}^{-1} + 416 \text{ kJmol}^{-1} + 335 \text{ kJmol}^{-1} \\ & = 1646 \text{ kJmol}^{-1} / 4 \\ & = 413 \text{ kJmol}^{-1} \end{aligned}$$

Therefore the average amount of energy needed to break a C-H bond in all types of molecules is 413 kJmol^{-1} .

Bond enthalpies can be used to estimate $\Delta H^\circ_{(rxn)}$

Note: the value of enthalpy of a reaction, $\Delta H^\circ_{(rxn)}$, obtained from bond dissociation calculation is not as accurate as the enthalpy value calculated using Hess's Law.

First Law of Thermodynamics:

**Energy can not be created or destroyed, enthalpy only transformed from one form to another. **

Calorimetry: when a reaction is carried out in a calorimeter, (a container used to detect and monitor changes in temperature during reaction), heat changes are measured during the reaction.

$$Q_{\text{gained/lost by reacting system}} = Q_{\text{lost/gained by the calorimeter and its contents}}$$

Changes in heat contents are calculated using:

1. $Q = \Delta H = mc\Delta T$ $c = \text{specific heat capacity, (J/g } ^\circ\text{C)}$
2. $\Delta H = \frac{Q}{n}$ $n = \text{number of mols used in reaction}$

Heat capacity: $C = Q/\Delta T$ (J/°C) Molar Heat capacity: $C = Q/\Delta T(n)$ (J / °C mol)

The most accurate measurements of heat changes are measured by **Bomb Calorimeter:** where known masses are burnt in an excess of oxygen.

Hess's Law:

Def: Enthalpy change in a chemical reaction depends only on the initial and final states and is independent of the reaction pathway. (Enthalpy is a "state function")

Manipulation of equations:

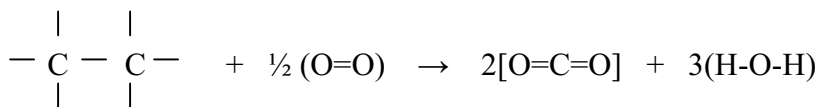
- 1) reverse an equation: ΔH sign reversed
- 2) Multiply by **n**, divide by **n**. Therefore multiply or divide ΔH by the same factor.

$$\Delta H^\circ_{rxn} = \sum \Delta H^\circ_{f(\text{prod})} - \sum \Delta H^\circ_{f(\text{react})}$$

If ΔH_{rxn} (negative), then the reaction is spontaneous, products predominate.

Bond Energies: can be used to estimate $\Delta H^{\circ}_{\text{rxn}}$ kJ/mol

$$\Delta H^{\circ}_{\text{rxn}} = \sum D(\text{reactants, bonds broken}) - \sum D(\text{products, bonds formed})$$



Bonds broken: C-C, 6(C-H), $\frac{1}{2}$ O=O Bonds formed: 4 C=O, 6 O-H $\Delta H^{\circ}_{\text{rxn}}=?$

Discrepancy from ΔH° (Hess's Law) and Bond Energy calculation is due to the mean/average bond enthalpies relating to gaseous state of $\text{H}_2\text{O}_{(\text{g})}$ while ΔH° relate to the standard state (298 K /101.3kPa), i.e. $\text{H}_2\text{O}_{(\text{l})}$. Further due to the fact that values of bond dissociation are MEAN, (average), and are not obtained by direct measurements

Entropy and Gibbs free energy:

Entropy: a measure of the disorder of molecules,

-A measure of number of ways energy in a system can be distributed.

Entropy:

Exothermic reactions are product orientated since E_p of a system decreases.

So why then do endothermic reactions occur? (Entropy of the system is increasing)

Facts about Entropy:

-entropy of elements is not zero.

-A crystal lattice at OK has perfect order, and zero entropy.

-Entropy increases with Temperature

-Entropy increases with molar mass

-Entropy increases with the complexity of molecules

-increases as $L_E \downarrow$ eg: NaI > NaF

-increases with state $s < l < g$

-units of entropy: J/ °C

To calculate the entropy change of a reaction:

$$\Delta S_{\text{rxn}} = \sum S^{\circ}(\text{products}) - \sum S^{\circ}(\text{reactants})$$

If the ΔS° is positive, then the reaction will be spontaneous, product orientated.

Factors that favour reaction are:

COOL (exothermic reaction) **CHAOS** (increase in disorder).

Gibbs Free Energy: energy available to do work.

When a system transfers energy to the surroundings some of this energy is available to do work. This energy is called "free Energy" → Gibb's free energy.

$$\Delta G = \Delta H - T\Delta S$$

ΔG → free energy available to do work

ΔH → total energy transformed between system and surroundings (negative in exothermic reactions)

ΔS → energy used in rearranging the system the one likely to increase especially at high temperatures.

Therefore for **spontaneous reactions: $\Delta G = \text{negative}$**

[Limitations of ΔG : There are many reactions for which ΔG is negative and which should therefore go spontaneously at room temperature, example combustion of fuels, however these reactions are observed not to happen spontaneously. This is because they have a high activation energy. Hence, ΔG values provide information only about the thermodynamic or energetic feasibility of a reaction and not about kinetic stability, the reaction rate is too slow. Activation energy, (this is independent of ΔG), provides information about kinetic stability of a reaction.]

Changes of state: $\Delta G = 0 \quad \therefore \Delta H - T\Delta S = 0$

Hence, the temperature at which the reaction is likely to occur may be determined.

To calculate the Gibb's Free energy for a reaction:

1. We can manipulate given equations in the same way as for enthalpy calculations.
2. We may also use: $\Delta G^{\circ} = \sum \Delta G^{\circ}_f(\text{products}) - \sum \Delta G^{\circ}_f(\text{reactants})$

Conditions for predicting spontaneity of a reaction

| ΔH° | ΔS° | ΔG° | Reaction |
|--------------------|--------------------|--------------------|-------------------|
| exo (-) | increases (+) | - | product-favoured |
| endo(+) | decreases (-) | + | reactant-favoured |
| exo (-) | decreases (-) | ? | T dependent |
| endo (+) | increases (+) | ? | T dependent |

Free Energy and the Equilibrium Constant

The extent of a reaction can be determined by looking at its equilibrium constant. There is a simple relationship between the equilibrium constant, K, and ΔG° : $\Delta G^{\circ} = -RT \ln K$

A **large -ive** ΔG° means that K for the reaction is a **large +ive** value, indicating that the reaction goes left to right. A **large +ive** ΔG° means that K for the reaction is a **very small** value, indicating that the reverse reaction is predominant. If ΔG° is neither small nor large, more of an "equilibrium" situation exists.

Free Energy and Electrode Potential

The potential of a cell is related to the change in free energy that accompanies the cell reaction:

$$\Delta G^{\circ} = -n F E^{\circ}$$

n is the number of moles of electrons transferred during the cell reaction;

F is the value of the Faraday constant (96 487 C),

E° is the emf in volts

Recall that for a spontaneous reaction the free energy decreases or ΔG is negative. Therefore E° must be positive.