Matter and Energy

Energy at a microscopic scale

1. Internal energy of a substance

Mechanical energy of a body, meaning the sum of its kinetic energy and its potential energy, is its energy at a macroscopic scale.

There is a microscopic equivalent to this mechanical energy. The internal energy of a substance, U is equal to the sum of the microscopic kinetic energy and the microscopic potential energy of all the entities forming the substance:

$$\boldsymbol{U = KE_{\mu} + PE_{\mu}}$$

- The substance's microscopic kinetic energy is associated with the thermal agitation of its constituent entities (atoms, ions, molecules)

Note: The temperature of a substance is a macroscopic evidence of its average microscopic kinetic energy.

- The microscopic potential energy of the substance is associated with the chemical energy of its constituent entities (binding energy through covalent bonds, ionic bonds or Van der Waals interactions)

Note: An absence of interaction/bond corresponds to 0 potential energy. In the meanwhile, energy is needed to break a bond. Thus potential energy is negative: An energy input increases it AND brings it closer to 0

2. A substance exchanging heat with its surroundings

When a substance receives heat energy from its surrounding, 2 things can happen:

- The received heat energy is turned into kinetic energy
  - ⇨ The temperature of the substance increases
    This change in temperature depends on the amount of energy received, the nature of the substance and its nature.

$$Q = mc\Delta T$$

With: Q the heat energy received, in J
m the mass of the substance, in kg
c the heat capacity of the substance, in J.kg-1.K-1 (or J.kg-1.°C-1)
DT the temperature of the substance in K (or °C)

OR

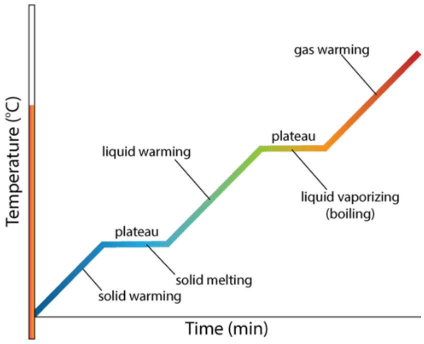
- The received heat energy is turned into potential energy.
  This happens when the substance is at its temperature of change of state.
  - ⇨ The substance changes state, and the temperature remains constant as long as the 2 states are present simultaneously

$$Q = mL$$

With: Q the heat energy received, in J
m the mass of the substance, in kg
L the latent heat of the substance, in J.kg-1

A graph associated with this will show different phases, some during which the temperature changes, and some during which the state changes at constant temperature.

Note: The same reasoning can be done with heat energy being lost by the substance. The temperature will then decrease.



H instead of U in chemistry

1. 1st principle of thermodynamics

The internal energy of a substance can be change through an input/output of energy, either through heat or work.

$$\Delta U = W + Q$$

- Work, W, involves a force acting UPON the substance.
- Heat, Q, is an energy transfer due to a gradient of temperature between the substance and its surroundings.

2. Problem with some chemical reactions

Chemical reactions are susceptible to involve gases. Gases might expand or contract (depending on the pressure), thus acting ON their environment. These actions OF a substance ON their environment not being taken in account, the 1st principle of thermodynamics might not be convenient in chemistry.

3. Concept of enthalpy

Enthalpy is defined as

$$H = U + PV$$

With:

- U: internal energy
- P: pressure
- V: volume

Enthalpy includes both energy changes in bonds/interactions and energy exchanged due to gas expansion/contraction.

4. Enthalpy and interactions

Breaking an interaction involves an energy/enthalpy input, which is absorbed by the entities previously linked. Therefore, the change in enthalpy involved in breaking an interaction is negative. Reasoning backwards, forming this same interaction will involve an energy/enthalpy output, leading to a negative change in enthalpy.

However, the value of this change of enthalpy will be the same in both cases.

Ex: $\Delta H_{fusion}(water) = 6.01\ kJ.mol^{-1}$; $\Delta H_{solidification}(water) = -6.01\ kJ.mol^{-1}$

An energy input is needed to melt an ice cube into water, while energy is lost to the environment when water turns into an ice cube.

The value of a change in enthalpy generally depends on the nature of the interaction between the entities involved: $\Delta H_{covalent\ bond} > \Delta H_{ionic\ bond} > \Delta H_{H-bond} > \Delta H_{other\ Van\ der\ Waals\ bonds}$

Ex: $\Delta H_{vaporisation}(C_{graphite}) = 715\ kJ.mol^{-1}$ *Covalent bonds between the carbon atoms*

$\Delta H_{vaporisation}(NaCl) = 130\ kJ.mol^{-1}$ *Ionic bonds between Na^+ and Cl^-*

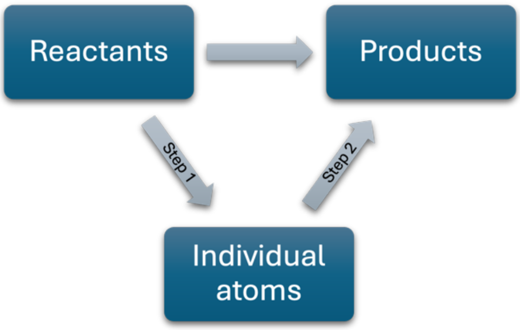
$\Delta H_{vaporisation}(Glycerol) = 92\ kJ.mol^{-1}$ *Hydrogen bonds between glycerol molecules*

$\Delta H_{vaporisation}(I_2) = 42\ kJ.mol^{-1}$ *London dispersion interaction between iodine molecules*

Note: London dispersion interaction is the weakest of the 3 types of Van der Waals interactions, the other 2 being the dipole-dipole interaction and the Hydrogen bonding.

A first energetic approach to chemical reactions

1. "LEGO® approach" of a chemical reaction



From an energetical point of view, a chemical reaction can be described as a 2-steps process:
The first step involves an energy input, to break the bonds between atoms of the reactants, thus forming individual atoms. Enthalpy change involved in step 1 is positive.

The second step consists in the creation of new bonds, thus forming the products. It produces energy, which is lost to the environment as heat. Enthalpy change involved in step 2 is negative.

2. Bonding enthalpy

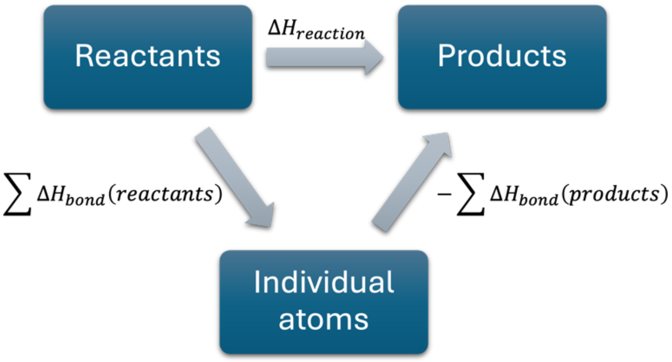
Bond	**Bond Enthalpy ($KJmol^{-1}$)**
C-C	+347
C-H	+413
O=O	+498
O-H	+464
C=O (in CO_2)	+805
C-O	+358
H-H	+436
C=C	+612

Enthalpy change involved in breaking or forming of covalent bonds is usually called "bonding enthalpy".
Usually given in $kJ.mol^{-1}$, it is defined as the enthalpy needed to break 1 mole of bonds.

Note: Bonding enthalpy as it is defined is positive. When a covalent bond is formed, the change in enthalpy involved has the same value, but is negative.

Note for later: The bonding enthalpy of a C=C double bond is not equal to the bonding enthalpy of a C-C single bond. This leads to the idea that 1 double bond has to be different of the addition of 2 single bonds.

3. Hess's law: Enthalpy change during a chemical reaction



Hess's law:

$$\Delta H_{reaction} = \sum \Delta H_{bond}(reactants) - \sum \Delta H_{bond}(products)$$

- If $\Delta H_{reaction}$ is positive, there is an overall energy output. The reaction is said to be exothermic.
- If $\Delta H_{reaction}$ is negative, there is an overall energy input. The reaction is said to be endothermic.
- Sometimes, enthalpy changes in steps 1 and 2 compensate. No overall change in enthalpy occurs. The reaction is then said to be athermic.

Energy in ionic compounds

1. What holds an ionic lattice together?

An ionic compound is a lattice of cations and anions, held together by electrostatic interactions. Using an analogy to the bonding enthalpy, a lattice enthalpy ΔH_{lat} (or LE)can be defined: measured in J.mol^{-1}, it is the energy needed to separate the lattice into individual non-interacting ions.

$$A_nB_{m\,(s)} \xrightarrow{\Delta H_{lat}/LE} nA^{m+}_{(g)} + mB^{n+}_{(g)}$$

2. From atoms to ions

Metal atoms (elements of columns 1 to 13 of the periodic table) are susceptible of losing electrons to form cations.

Ionization energy IE, measured in kJ.mol^{-1}, is the enthalpy change involved in pulling an electron away from these atoms

Note: *Pulling a second electron doesn't involve the same energy than pulling the first electron of an atom. Therefore, we distinguish first ionization energy and second ionization energy.*

Non-metal atoms (elements of columns 14 to 17 of the periodic table) are susceptible of gaining electrons to form anions.

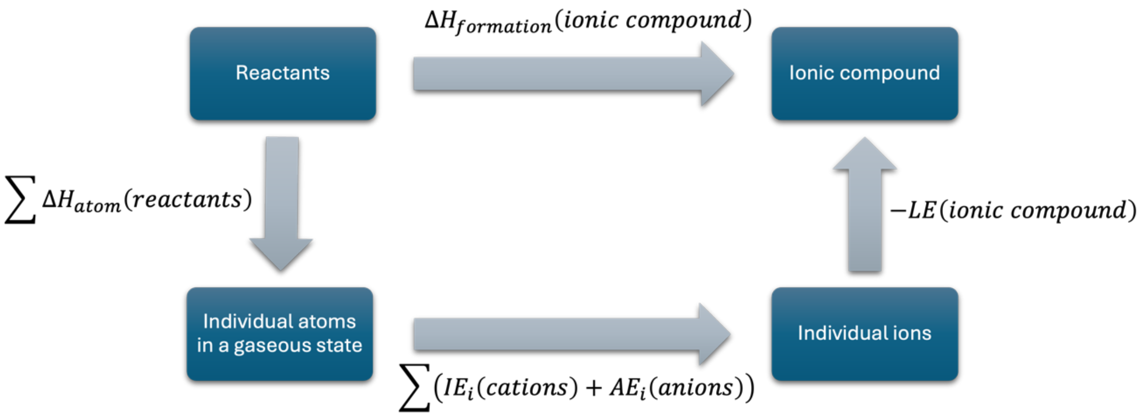
Electron affinity EA, measured in kJ.mol^{-1}, is the enthalpy change involved in adding an electron to these atoms.

Note: *Ionizing a metal atom, turning it into a cation, involves an energy input to go against the natural pull of the nucleus on the electrons* $\Rightarrow IE > 0$.

Ionizing a non-metal atom, turning it into an anion, benefits from the natural pull of the positively charged nucleus on the negatively charged electron. This leads to an energy output $\Rightarrow EA < 0$.

3. Born-Haber cycle

Forming an ionic compound from the initial elements can be modelised by a Born-Haber cycle:



Step 1: Atomization of the elements: They are turned into individual non-interacting atoms (thus in gaseous form). This involves bonding enthalpy and/or change of state enthalpy

Step 2: Ionization of the atoms. This involves Ionization Energy and Electron Affinity.

Step 3: Interaction between the ions to form the lattice. This involves Lattice Enthalpy.

Note: *Lattice enthalpy is a value that cannot be measured experimentally, unlike the other data involved (including the enthalpy of formation of the ionic compound).*

The main purpose of using a Born-Haber cycle is therefore to determine the lattice enthalpy of an ionic compound:

Spontaneous or non-spontaneous processes

1. Entropy, a measure of “disorder”

Entropy S of a substance, measured in J.K^{-1}.mol^{-1}, can be considered as a measure of the disorder in it. The more different configurations are possible for a substance,the higher its entropy.

Note: $S_{solid} < S_{liquid} \ll S_{gas}$

2. Gibbs tells us if it’s possible or not

Enthalpy has been defined as the total energy of a substance. However not all this energy can be used to do useful work (e.g. chemical reaction).
Therefore, another type of energy needs to be introduced, Gibbs Free Energy, G:

$$\boldsymbol{G = H - T \times S}$$

With:

G: Energy available to do useful work
H: Total energy of the substance
TxS: unavailable energy

Comment: As mum and dad always say, disorder never leads to something useful.

Note: Gibbs energy is not an absolute value. It depends on a chosen reference, for which the value is set to 0. Therefore, its value can be positive, but also negative, even if some energy is still available.

As seen previously, a chemical reaction is a process involving an energy input in step 1. If this energy is taken from the system itself, the reaction is considered as spontaneous.

Note: Sometimes, like in combustion reactions, an initial energy input from outside the system is needed, through friction or a spark for example. The temperature increase due to the first individual reactions is then enough to provide the energy needed internally. Therefore, this spark can be neglected, and a combustion reaction is considered as spontaneous.

The energy used by a spontaneous reaction is taken in the stock of available energy, the Gibbs energy, leading to a decrease of its amount.

Criteria of spontaneousity of a chemical reaction: $\boldsymbol{\Delta G < 0}$

Note: A reaction for which $\Delta G \geq 0$ *needs an external input of useful energy to be possible.*