Enthalpy, a measure for chemical change

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)

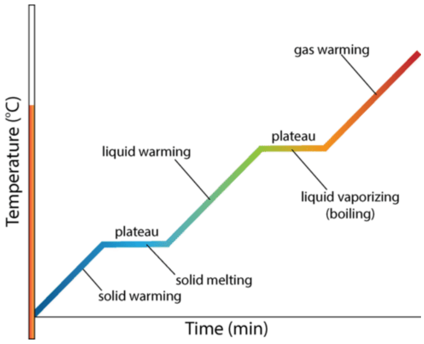
OR

- 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.

$$\Delta \boldsymbol{U} = \boldsymbol{W} + \boldsymbol{Q}$$

- 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

$$\boldsymbol{H} = \boldsymbol{U} + \boldsymbol{PV}$$

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 positive.
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.