

# Basic thermodynamics (1)

**Internal energy (U):** it includes the contribution of the kinetic (thermal energy, radiant energy, movement of electrons) and potential energy (stored in the bonds, concentration gradient, electric properties of all the atoms, ions and molecules of the system)  
It is the total macroscopic energy of the system.

$$U = Q - W$$

where  $Q$  is the heat added to the system and  $W$  is the mechanical work done on a system.

We cannot measure  $U$  but only its variations  $dU = \delta Q - \delta W$

**Enthalpy (H):** is the bond energy

$$H = U + pV$$

In an **exothermic** reaction, the products contain less bond energy than the reactants, the liberated energy is usually converted to heat (the energy of molecular motion), and  $\Delta H$  is negative. In an **endothermic** reaction, the products contain more bond energy than the reactants, heat is absorbed, and  $\Delta H$  is positive. Reactions tend to proceed if they liberate energy (if  $\Delta H < 0$ ).

## Basic thermodynamics (2)

**Entropy (S):** is a measure of the degree of randomness or disorder of a system. Entropy increases as a system becomes more disordered and decreases as it becomes more structured.

$$\Delta S = \Delta Q_{\text{rev}}/T$$

The heat transfer is reversible only if it happens between an environment and a system that have only an infinitesimal T difference.

$$\text{Otherwise, } \Delta S > \Delta Q_{\text{irrev}}/T$$

During a spontaneous process the entropy of a closed system increases.

## Basic thermodynamics (3)

The  $O_2$  and the  $H_2$  strongly and spontaneously react at standard temperature with the formation of  $H_2O$ . But the water passes from a less ordered state to a more ordered one, with a  $\Delta H$  highly negative.

Is this against the second principle of thermodynamics?

We must consider the entropy variation of the overall system. The process adds heat to the environment with an entropy contribution  $\gg$  the loss of enthalpy.

The amount of entropy gained (at constant temperature and pressure):

$$\Delta S_{\text{env}} = \Delta Q_{\text{rev}}/T = -\Delta H/T$$

$$\Delta s_{\text{tot}} = \Delta S_{\text{process}} + \Delta S_{\text{env}} = \Delta s_{\text{process}} - \Delta H/T$$

$$T \Delta s_{\text{tot}} = T \Delta s_{\text{process}} - \Delta H$$

# Gibbs free energy

It is possible to predict the direction of a chemical reaction by using a measure of potential energy, called Gibbs free energy. In general we are interested in free energy changes:

$$\Delta G = G_{\text{products}} - G_{\text{reactants}}$$

sum the first and second principle of thermodynamics and we can differentiate it and get to the classical DeltaG formula

$$G = H - TS$$

Under conditions of constant temperature,  $\Delta G = \Delta H - T \Delta S$   
when also the pressure is constant, as generally found in biological systems:  $\Delta G = - T \Delta S$

A process is spontaneous if  $\Delta G < 0$  (this means  $\Delta S > 0$ )

A reaction is spontaneous if:

- Exothermic reaction:  $\Delta H$  is negative and  $\Delta S$  is positive
- Endothermic reaction:  $\Delta H$  is positive but  $T \Delta S$  is sufficiently positive.

The minimum temperature to make an endothermic reaction spontaneous is:  $\Delta G = \Delta H - T \Delta S = 0$  ;  $T = \Delta H / \Delta S$

$\Delta G^\circ$  is the change in free energy under the conditions of 298 K (25 °C), 1 atm pressure, pH 7.0 (as in pure water), and initial concentrations of 1 M for all reactants and products except protons, which are kept at pH 7.0.