CHEMICAL

THERMODYNAMICS

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Thermodynamics is the study of energy transfer and the effects of energy changes.

Thermochemistry is the study of the heat change of chemical reaction.

System is any totality of bodies separated from the surroundings by a boundary (real or imaginary) inside which matter and/or energy exchange is possible.

Open system: can exchange both matter and energy with the surroundings. A living organism is an open system.

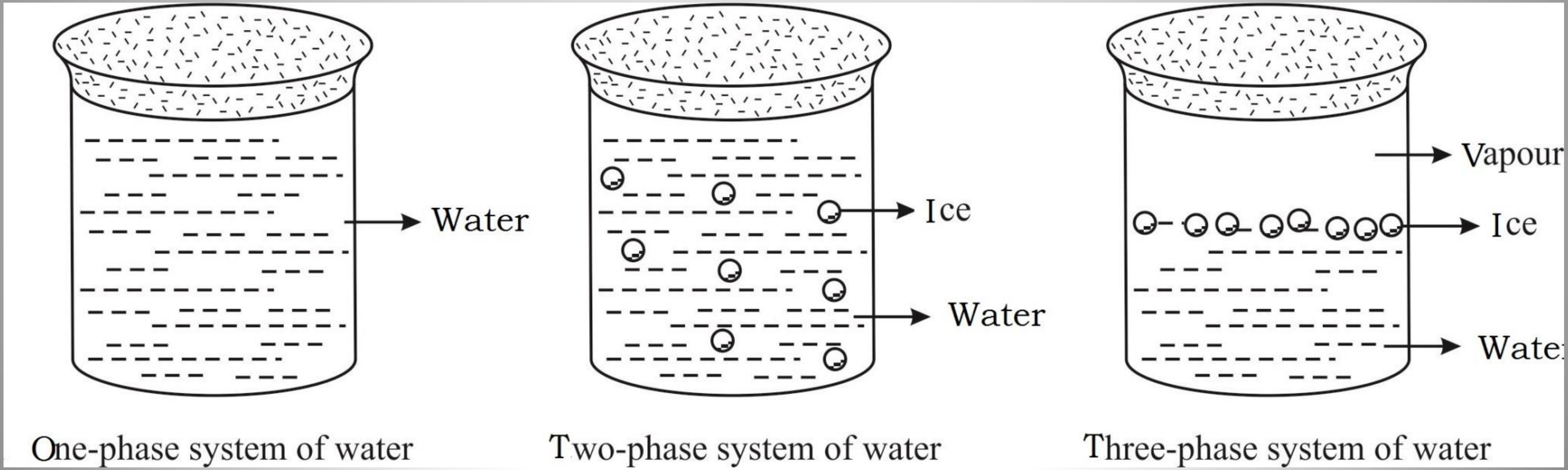
Closed system: can exchange energy but not matter with the surroundings.

Isolated system: exchanges neither matter nor energy with the surroundings.

Homogeneous system is a system consists of one phase only.

Heterogeneous system is a system with more than one phase.

Phase refers to any part of a system which is physically separated from other parts of the system by a distinct boundary. A phase can be a solid, liquid, vapor (gas) or aqueous solution which is uniform in both chemical constitution and physical state (figure 3.1).



One-phase system of water Two-phase system of water Three-phase system of water

Isochoric process is the process that takes place at constant volume (V=const).

Isobaric process is the process that takes place at constant pressure (P=const).

Isothermal process is the process that takes place at constant temperature (T=const).

Exothermic process (reaction) is a process that evolves heat to the surroundings.

Endothermic process (reaction) is a process that absorbs heat from the surroundings.

Thermodynamic parameters are

pressure P, temperature T, volume V

and concentration.

State function is a property that depends only on the state or present condition of a system and not on how this state is attained.

Some common state functions are internal energy (U), enthalpy (H), entropy (S) and free energy (G).

The Laws of Thermodynamics

The first law. Energy is conserved; it can be neither created nor destroyed.

The second law. In an isolated system, natural processes are spontaneous when they lead to the increase in disorder, or entropy.

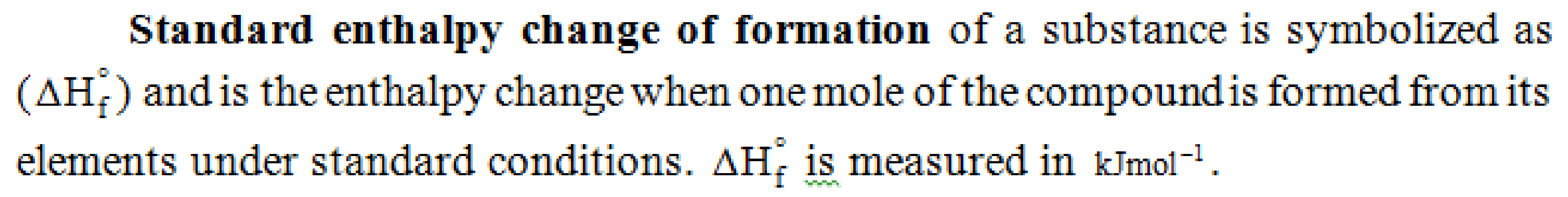
The third law. The entropy of a perfect crystal is zero when the temperature of the crystal is equal to absolute zero (0 K).

Internal Energy and Enthalpy

Internal energy (U) is the sum of the kinetic and potential energies of the particles that form the system.

Enthalpy (H) is a term that describes the heat content of a system.

ΔH = heat absorbed by the system at constant pressure.



Standard enthalpy change of formation of a substance is symbolized as (ΔH_f°) and is the enthalpy change when one mole of the compound is formed from its elements under standard conditions. ΔH_f° is measured in $kJmol^{-1}$.

Standard state conditions are:

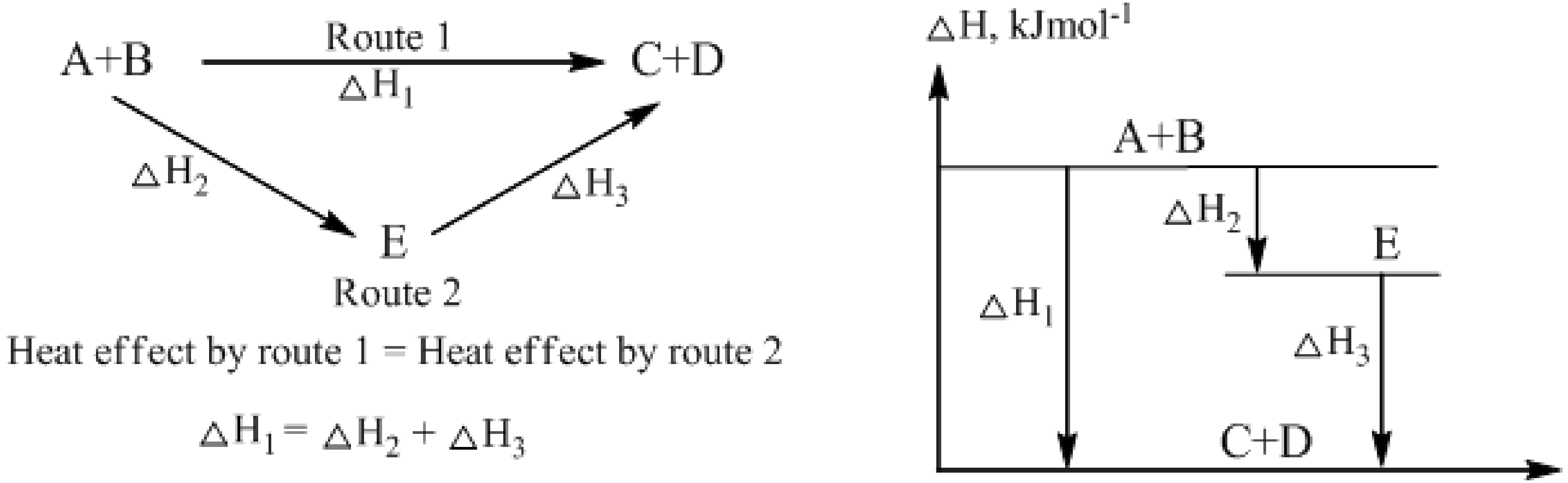
- all substances are in their standard states;
- the pressure is 101.3 kPa (101325 Pa = 1 atm

  = 760 mm Hg);
- the temperature is 298 K (K = ˚C +273).

Thermochemical Equations. Hess’s Law

Thermochemical equations are equations of the reactions in which the physical states of the substances and the values of any thermodynamic function of the state are indicated. The reaction enthalpy in this case is called **heat effect** of the reaction.

Hess's law: Heat effect of chemical reaction is independent of the route of the reaction and depends only by the initial and final state of the system.



Heat effect by route 1 = Heat effect by route 2

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

Figure 3.2 – A diagram showing different routes of chemical reaction

The consequences of Hess’s law are:

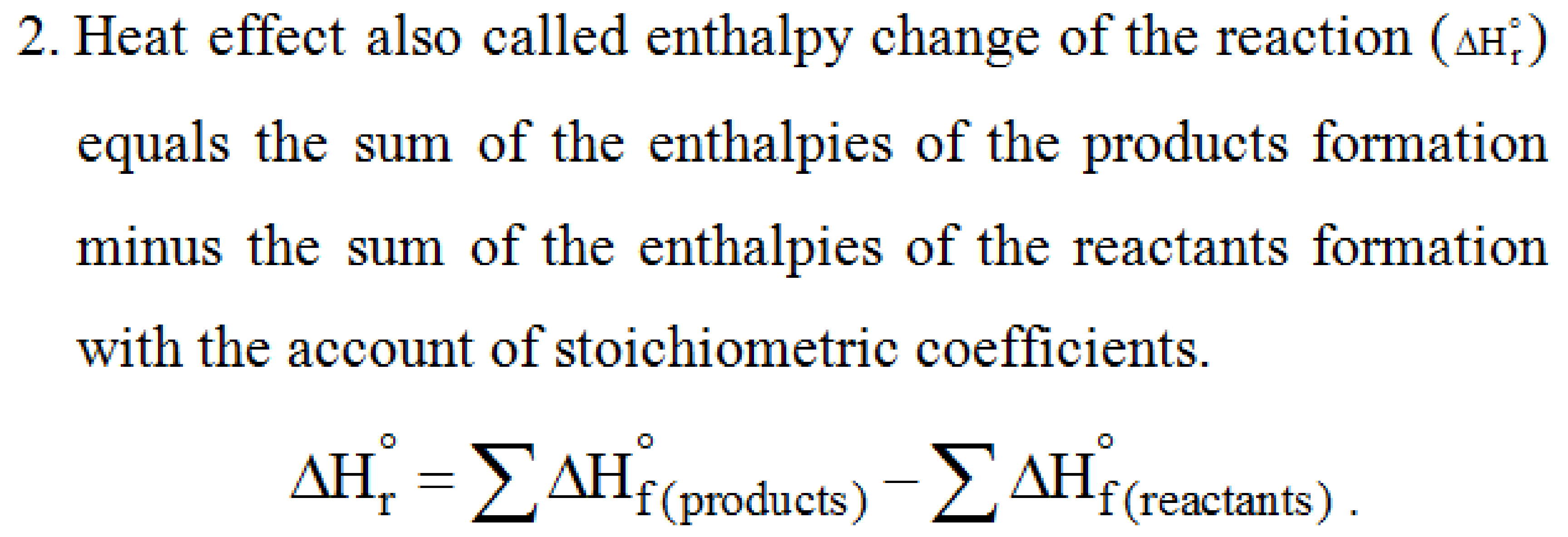
- Heat effect of the forward reaction equals the heat effect of the backward reaction taken with the opposite sine:

$$\Delta H_{\text{forward}} = -\Delta H_{\text{backward}}$$

For example,

$$Ca_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CaO_{(s)};\ \Delta H_r^{\circ} = -635\ \text{kJmol}^{-1}$$

$$CaO_{(s)} \rightarrow Ca_{(s)} + \tfrac{1}{2}O_{2(g)};\ \Delta H_r^{\circ} = +635\ \text{kJmol}^{-1}$$



2. Heat effect also called enthalpy change of the reaction (ΔH_r°) equals the sum of the enthalpies of the products formation minus the sum of the enthalpies of the reactants formation with the account of stoichiometric coefficients.

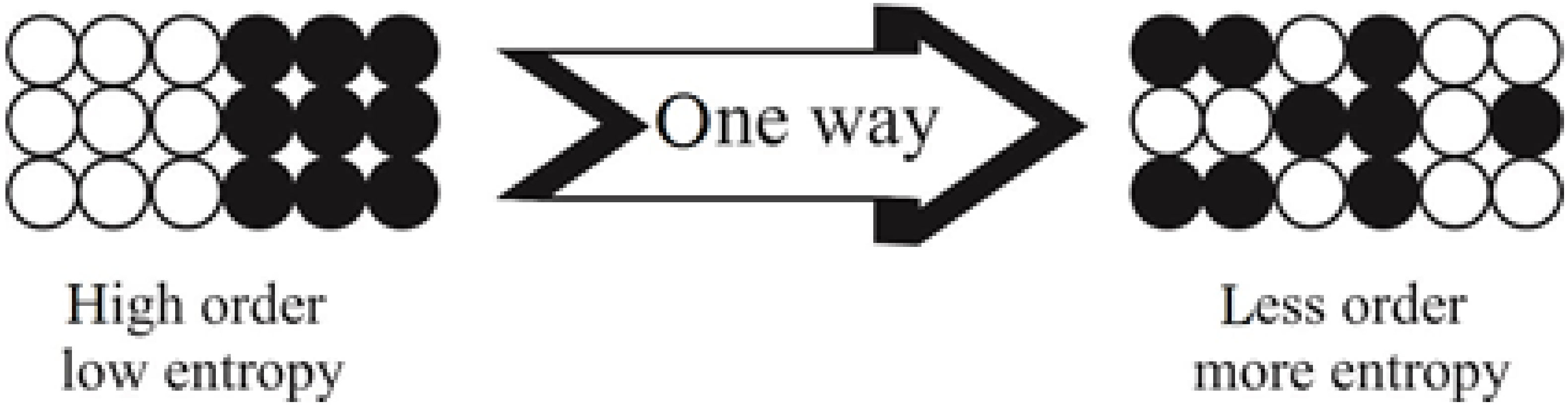
$$\Delta H_r^\circ = \sum \Delta H^\circ_{f\,(products)} - \sum \Delta H^\circ_{f\,(reactants)}\ .$$

Spontaneity and Disorder. Entropy

Spontaneous change is change that has a natural tendency to occur, causes a system to move from a less stable state to a more stable state.


HOT
One way
COLD

Another way to look at the second law is in terms of disorder. The quantitative measure of the disorder of a system is entropy, which is symbolized by S (Fig. 3.5).



The more mixed up a system is the higher its entropy

Entropy (S) is a function of the state, the changes depend only on the initial and final state of the system. S is measured in $Jmol^{-1}K^{-1}$

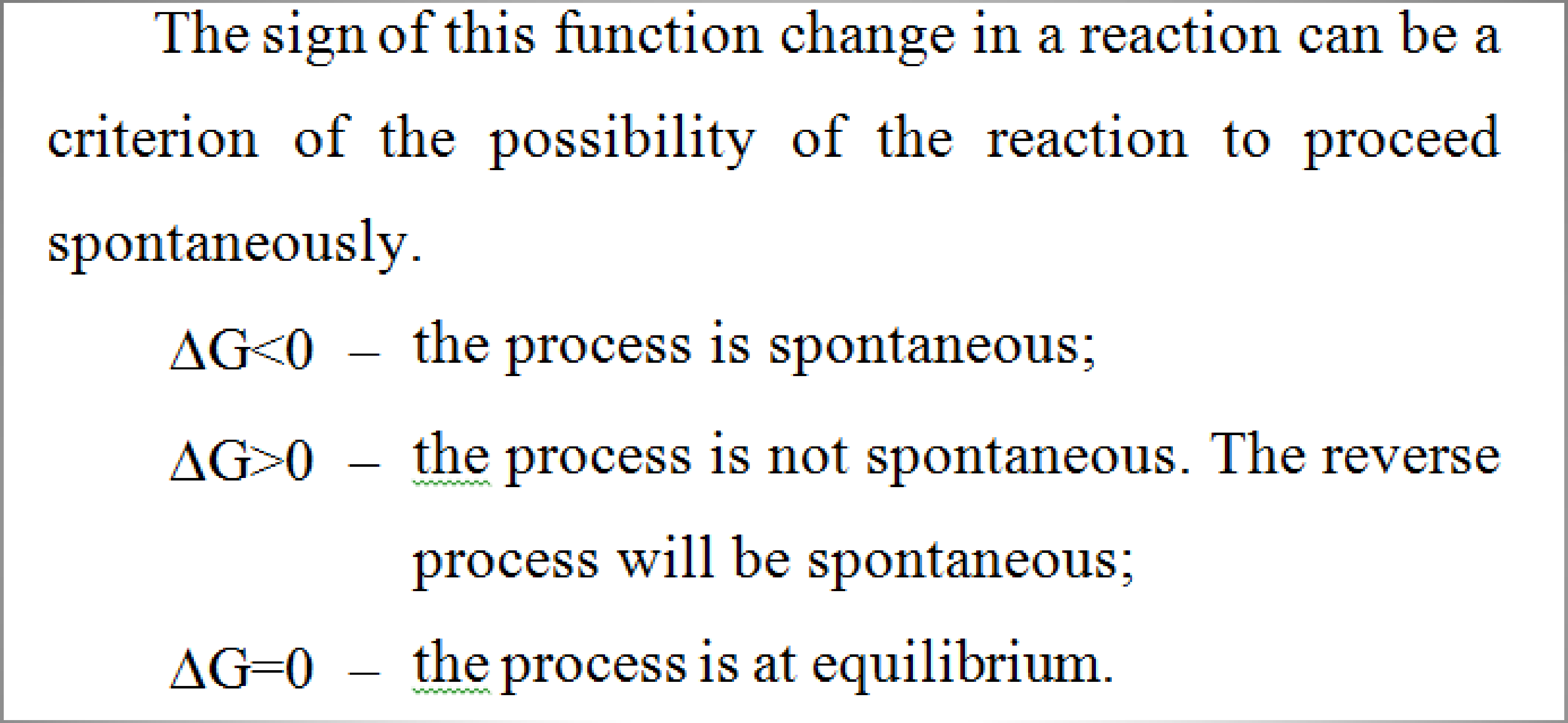
Gibbs Energy. Criteria of Process Direction

The free energy change of a reaction is a **measure** of the **spontaneity** of the reaction. The more negative the free energy change, the more spontaneous the reaction.

The free energy is related to the enthalpy, entropy, and temperature by the equation

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

Gibbs energy is a function of the state, it is measured in kJ.



The sign of this function change in a reaction can be a criterion of the possibility of the reaction to proceed spontaneously.

$\Delta G<0$ – the process is spontaneous;

$\Delta G>0$ – the process is not spontaneous. The reverse process will be spontaneous;

$\Delta G=0$ – the process is at equilibrium.

Sign of			Conclusion	Example
ΔH°	ΔS°	ΔG°		
+	–	+	The process is not spontaneous	photosynthesis
+	+	+	The process is not spontaneous at low temperature	melting (s – L); evaporation (L – g)
–	–	–	The process is spontaneous at low temperature	Condensesion
–	+	–	The process is spontaneous	combustion of organic compounds
–	–	+	The process is not spontaneous at high temperature	$2H \rightarrow H_2$
+	+	–	The process is spontaneous at high temperature	$Br_2 \rightarrow 2Br$

The free energy change in chemical reactions can be calculated either by using standard frees energy of formation (ΔG_f°), or ΔH and ΔS:

$$\Delta G = \sum \Delta G^0_{f(\text{products})} - \sum \Delta G^0_{f(\text{reactants})} ,$$

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

Application of Thermodynamic Law to Living Systems

The reactions that living organisms carry out to obtain the energy they need and to synthesize the compounds they require are commonly known as **metabolism**.

Metabolism can be divided into two parts: **catabolism** and **anabolism**.

Catabolism reactions break down complex nutrient molecules to provide energy and simple precursor molecules for synthesis.

Anabolism reactions require energy and result in the synthesis of complex biomolecules from simple precursor molecules.

Catabolism: complex molecules → simple molecules + *energy*

Anabolism: simple molecules + *energy* → complex molecules