

Thermodynamics Laws. Main parameters of thermodynamics.

Chemical potential. The van 't Hoff equation

First Law

energy cannot be created or destroyed

$$\Delta U = Q - W, \text{ where}$$

ΔU - change internal energy of a system; Q - heat the system receives from the environment;

W - work done by the system.

The Second Law

In any process, when considering a system with its surroundings, the entropy will either remain constant or increase.

Does a life form violate the second law of thermodynamics?

Life form:

1. take energy from outside and create order
2. propagate the order by having offspring

The Gibbs function principle $\Delta G < 0$ has the second law of Thermodynamics build in.

What drives the process forward?

A system releases energy, $\Delta H < 0$, process enthalpy driven increasing disorder, $\Delta S > 0$, process entropy driven changing temperature, if $\Delta S > 0$, then $\Delta T > 0$ will result in $\Delta G < 0$; if $\Delta S < 0$, then $\Delta T > 0$ will result in $\Delta G < 0$

Example: When a certain protein binds to DNA, the entropy decreases by 2 kcal/K. At the same time, the system releases 700 kcal of enthalpy. What is the Gibbs free energy change for this binding process occurring at $T=310\text{K}$ (37 Celsius)?

Is this process spontaneous?

Classic thermodynamic parameters of a system:

- Enthalpy $H = U + pV$, where

U - internal energy of a system; p - external pressure; V - volume of the system

Changes: $\Delta H = \Delta(U + pV) = \Delta U + \Delta pV + p\Delta V$

or

$\Delta U = \Delta H - \Delta pV - p\Delta V = Q - W$, where $W = p\Delta V$

(W - work done by the system)

so

$$Q = \Delta H - V\Delta p$$

The heat which is provided to the system is associated with:

The change in the enthalpy of a system the energy needed to change the pressure of the system

$$\Delta H = Q + V\Delta p$$

Most biological processes occur at $p = \text{const.}$, thus $\Delta H = Q$.

- Entropy S

S is a measure of disorder in a system and is associated with a number of different ways a system can be in one energy state:

only a few ways to arrange molecules at a given temperature - ordered system with a low S

many possible ways to arrange molecules at a given temperature - disordered system with a high S .

If the change occurs at a constant T :

$$\Delta S = Q/T, \text{ where}$$

S - entropy of a system and T - absolute temperature of a system;

If the heat flows from T_1 to T_2 ($T_1 > T_2$):

$$\Delta S = Q/T_2 - Q/T_1$$

- Gibbs Free Energy **G**:

Gibbs used Clausius's definition of S to define available energy that can be converted into work: free energy (as opposed to the energy lost through dissipation):

$$\mathbf{G = H - TS}$$

G - the energy that remains in the system after the energy losses due to dissipation are accounted for - Gibbs energy change during a process occurring at constant **T**:

$$\Delta\mathbf{G = \Delta H - T \Delta S}$$

For a process that occurs spontaneously, $\Delta\mathbf{G} < \mathbf{0}$, that is the final state has always a lower free energy than the initial state!

This principle is in a way analogous to $F=ma$ (Newons's 2nd law) as it drives all spontaneous processes, including chemical reactions.

The process that takes the system from state **A** to state **B** will occur spontaneously only if

$$\Delta\mathbf{G} < \mathbf{0}$$

- **μ chemical potential**

In thermodynamics, chemical potential, also known as partial molar free energy, is a form of potential energy that can be absorbed or released during a chemical reaction. It may also change during a phase transition. The chemical potential of a species in the mixture can be defined as the slope of the free energy of the system with respect to a change in the number of moles of just that species. Thus, it is the partial derivative of the free energy with respect to the amount of the species, all other species' concentrations in the mixture remaining constant, and at constant temperature. When pressure is constant, chemical potential is the partial molar Gibbs free energy. At chemical equilibrium or in phase equilibrium the total sum of chemical potentials is zero, as the free energy is at a minimum.

$$dG = -SdT + VdP + \sum_i^n \mu_i dN_i$$

The fundamental equation of chemical thermodynamics for a system containing n constituent species, with the i-th species having N_i particles is, in terms of Gibbs energy

$$dG = \sum_i^n \mu_i dN_i = \mu_1 dN_1 + \mu_2 dN_2 + \dots$$

At constant temperature and pressure this simplifies to

$$\mu_i = \left(\frac{\partial G}{\partial N_i} \right)_{T, P, N_{j \neq i}}$$

The definition of chemical potential of the i-th species, μ_i , follows by setting all the numbers N, apart from one, to be constant.

The chemical potential of a species is the slope of the free energy with respect to the number of particles of that species. It reflects the change in free energy when the number of particles of one species changes. Each chemical species, be it an atom, ion or molecule, has its own chemical potential. At equilibrium free energy is at its minimum for the system, that is, $dG=0$. It follows that the sum of chemical potentials is also zero.

$$\mu_1 dN_1 + \mu_2 dN_2 + \dots = 0$$

Use of this equality provides the means to establish the equilibrium constant for a chemical reaction.

$$\mu_i = \left(\frac{\partial H}{\partial N_i} \right)_{S, P, N_{j \neq i}} \quad \text{or} \quad \mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S, V, N_{j \neq i}}$$

• Van 't Hoff equation

The **Van 't Hoff equation** in chemical thermodynamics relates the change in temperature T to the change in the equilibrium constant K , given the standard enthalpy change ΔH° for the process. It was proposed by Dutch chemist J.H. van 't Hoff in 1884. The equation is

$$\frac{d \ln K}{dT} = \frac{\Delta H^\circ}{RT^2},$$

where R is the gas constant.

In practice, the equation is experimentally approximate in that both enthalpy and entropy changes of a process (reaction) vary (each differently) with temperature. Its accuracy is

determined in accounting for the curvature in the standard enthalpy changes over temperature. A major use of the equation is to estimate a new equilibrium constant at a new absolute temperature assuming a constant standard enthalpy change over the temperature range. This can be seen by taking the definite integral of this differential equation between temperatures T_1 and T_2 giving

$$\ln \left(\frac{K_2}{K_1} \right) = -\frac{\Delta H^\ominus}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right).$$

In this equation K_1 is the equilibrium constant at absolute temperature T_1 and K_2 is the equilibrium constant at absolute temperature T_2 .

From the definition of Gibbs free energy

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

where S is the entropy of the system, and the reaction isotherm equation

$$\Delta G^\ominus = -RT \ln K$$

it follows that

$$\ln K = -\frac{\Delta H^\ominus}{RT} + \frac{\Delta S^\ominus}{R}.$$

Therefore, when the range in temperature is small enough so that the standard enthalpy change is essentially constant, a plot of the natural logarithm of the equilibrium constant versus the reciprocal temperature gives a straight line. The slope of the line is equal to minus the standard enthalpy change divided by the gas constant, $-\Delta H^\ominus/R$ and the intercept is equal to the standard entropy change divided by the gas constant, $\Delta S^\ominus/R$. Differentiation of this expression yields the van 't Hoff equation.