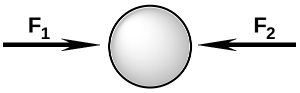
№ 09. CRITERIA FOR PREDICTING THE DIRECTION OF CHEMICAL REACTIONS. EQUILIBRIUM CONSTANT, ENTROPY, AND FREE ENERGY.

I. Chemical equilibrium A given chemical reaction is defined by a *balanced net chemical equation,* conventionally written as: **Reactants** → **Products**. Several questions can be asked for such transformation:

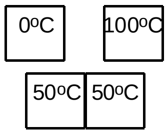
Can it actually take place?
How complete is the reaction?
} Answered with knowledge of thermodynamics

How fast does the reaction occur?
What is the mechanism of the reaction?
} Answered with knowledge of kinetics

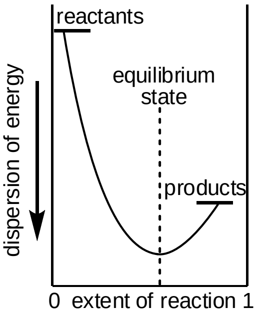
What is equilibrium? The term refers, basically, to what might be called a "balance of forces". Mechanical equilibrium: this is its literal definition. When two equal forces act in opposite direction on a body, it remains static (motionless) or in a state of unchanging motion, *F* = *ma*).



Thermal equilibrium: In contact, heat will flow from the warmer object to the cooler one until their temperatures become identical. Thermal equilibrium arises from the tendency of thermal energy to become as dispersed as possible.



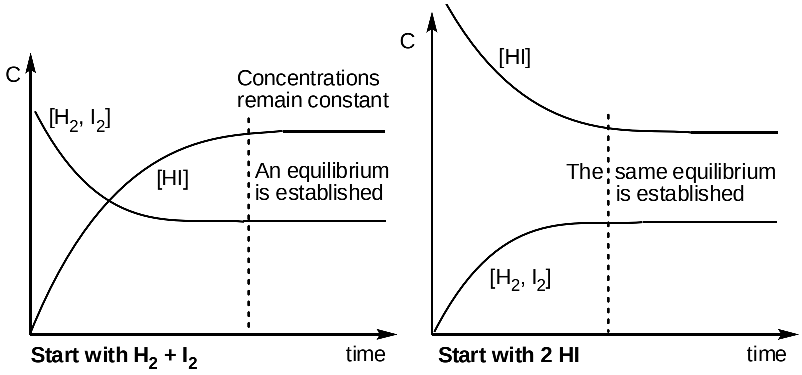
Chemical equilibrium When a chemical reaction takes place in a container which prevents the entry or escape of any of the substances involved in the reaction, the quantities of these components change as some are consumed and others are formed. **Eventually this change will come to an end, after which the composition will remain unchanged as long as the system remains undisturbed. The system is then said to be in its *equilibrium state*, or simply, "at equilibrium“.** What is the nature of the "balance of forces" that drives a reaction toward chemical equilibrium? It is essentially the balance struck between the tendency of energy to reside within the chemical bonds of stable molecules, and its tendency to become dispersed and diluted. Exothermic reactions are particularly effective in this, because the heat released gets dispersed in the infinitely wider world of the surroundings. **Chemical equilibrium is a state characteristic for reversible reactions:** Reactants $\rightleftharpoons$ Products



When the reaction products can interact to give back the initial reactants, the reaction is called reversible. Both the forward and the backward reactions occur simultaneously. Therefore, their chemical equations are denoted using two arrows pointing in opposite direction. **A chemical reaction is at equilibrium when there is no tendency for the quantities of reactants and products to change**. The direction in which we write a chemical reaction (and thus which components are considered reactants and which are products) is arbitrary. Thus the two equations

$H_2 + I_2 \longrightarrow 2\,HI$ **"synthesis of hydrogen iodide"**
$2\,HI \longrightarrow H_2 + I_2$ **"dissociation of hydrogen iodide"**

represent the same chemical reaction system in which the roles of the components are reversed, **and both yield the same mixture of components when the change is completed.** This last point is central to the concept of chemical equilibrium. **It makes no difference whether we start with two moles of HI or one mole each of H_2 and I_2; once the reaction has run to completion, the quantities of these three components will remain constant**. Once this equilibrium composition has been attained, no further change in the quantities of the components will occur with time as long as the system remains undisturbed, as the graphic shows.



(The graphic symbol […] means molar concentration, M in mol.L^{-1} of the compound in square brackets.)
Chemical equilibrium is something humans definitely want to avoid for themselves as long as possible. **The myriad chemical reactions in living organisms are constantly moving *toward* equilibrium, but are prevented from getting there by input of reactants and removal of products.** So rather than being in equilibrium, we try to maintain a "steady-state" condition which physiologists call ***homeostasis* − maintenance of a constant internal environment**. For living Nature equilibrium is death!

The equilibrium composition is independent of the direction from which it is approached. Guldberg and Waage (in the period 1864-1879) showed that an equilibrium can be approached from either direction (as seen in the HI illustration), implying that any reaction $a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$ is really a competition between a "forward" and a "reverse" reaction. **When a reaction is at equilibrium, the rates of these two reactions are identical. No *net* (macroscopic) change is observed, although individual components are actively being transformed at the microscopic level.** Both forward and reverse reactions still occur at molecular level but there is no observable change of all participants' amounts. The characteristics of a chemical equilibrium are: **Rate of forward reaction = Rate of reverse reaction and the concentrations of all substances involved are constant with time at equilibrium (but *not* equal).** Guldberg and Waage showed that for a reaction **$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$, the rate of the reaction in either direction is proportional to the molar concentrations (then called "active masses") of the various components**. In algebraic expressions:
rate of forward reaction = $k_f.[A]^a.[B]^b$ and rate of reverse reaction = $k_r.[C]^c.[D]^d$. At equilibrium:

$$k_f.[A]^a.[B]^b = k_r.[C]^c.[D]^d$$

(In other notation the symbol c_A is used instead of [A] – molar concentrations). It is very important to understand the significance of this relation. The equilibrium state is one in which there is no net change in the quantities of reactants and products. But do not confuse this with a state of "no change"; at equilibrium, the forward and reverse reactions continue, but *at identical rates*, essentially cancelling each other out. **Equilibrium is macroscopically static, but is microscopically dynamic!**

II. Equilibrium constant The composition of the equilibrium state depends on the ratio of the forward- and reverse-rate constants.

$$\frac{k_f}{k_r} = K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

IMPORTANT!

The number **K_C (sometimes K_{eq}) is called equilibrium constant.** According to the definition: **Equilibrium constant K_C is equal to the ratio of the product of equilibrium concentrations of reaction products and the product of equilibrium concentrations of starting compounds, each concentration raised to power value equal to the corresponding number of moles (coefficients) in the balanced chemical equation.** If the rate of the forward reaction is much larger than the rate of the reverse reaction, **$k_f \gg k_r$**, then the equilibrium constant is very large **$K_C \gg 1$** which means**: the equilibrium composition lies strongly on the "right"; the reaction can be said to be "complete" or "quantitative“.** If the rate of the forward reaction is much smaller than the rate of the reverse reaction, **$k_f \ll k_r$**, then the equilibrium constant has very small value, **$K_C \ll 1$**, which means that the concentrations of the products are very small; **the equilibrium lies strongly on the "left"; in extreme cases − "the reaction does not take place“.** When there are measurable reactant and products concentrations, the rates constants are comparable, **$k_f \approx k_r$**, and **$K_C \approx 1$: significant concentrations of products and reactants are present at equilibrium; we say the reaction is "reversible" and "incomplete".**
The equilibrium constant K_C is simply a number, tabulated for many reactions and conditions, known and useful for calculations. It could be very large number, very small number, or about unity. The important features of K_C are:

- **K_C is a constant (just a number) for any given reaction going at constant temperature;**
- **Equilibrium constant depends only on the temperature and on the nature of the substances involved in the equilibrium;**

- **K_C does not depend on the concentration of the compounds or on the presence of catalysts;**
- **K_C indicates the components that are in greater concentration at equilibrium – the products or the reactants;**
- **K_C is *independent of the number of intermediate steps* in the reaction mechanism (that is because K_C is expressed with the equilibrium concentrations);**
- **The concentration of solid substances is not included in the equilibrium constant since they are assumed constant.**

If the reaction $aA + bB \rightleftharpoons cC + dD$ **has not reached equilibrium** (that is, it has begun with more (A+B) or more (C+D) than necessary for an equilibrium) then the expression $Q = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ **is called reaction quotient.**

In the general case in which the concentrations can have any arbitrary values (including zero), this expression is called the *reaction quotient* (the term *equilibrium quotient* is also commonly used). If the concentration ([…]) terms correspond to *equilibrium* concentrations, then the above expression is called *equilibrium constant* and coincides with K_C value, *i.e.* $Q = K_C$. **Reaction quotient is expressed for non equilibrium conditions.** *Kc is thus the special value that Q has when the reaction is at equilibrium.* The value of Q in relation to K_C indicates the direction in which any net reaction must proceed in order to reach equilibrium state. For the general chemical equation: $aA + bB \rightleftharpoons cC + dD$

$$Q = \frac{[\text{products}]}{[\text{reactants}]} \qquad K_C = Q = \frac{[\text{products}]}{[\text{reactants}]} \qquad Q = \frac{[\text{products}]}{[\text{reactants}]}$$

$Q > K_C$ — **net reaction to the left**

$Q = K_C$ — **no net reaction**

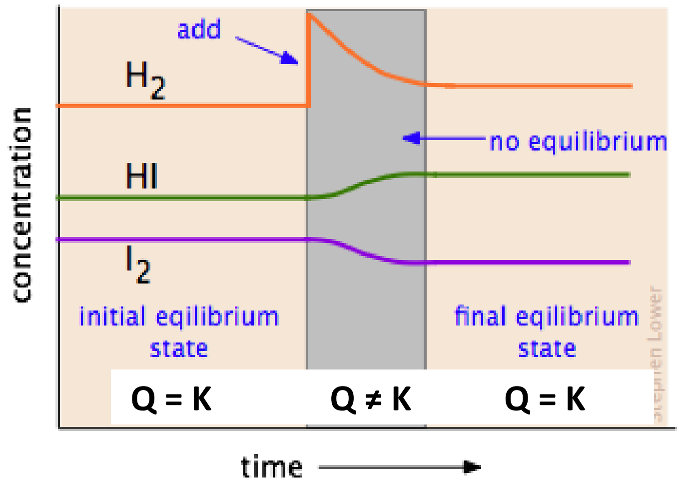
$Q < K_C$ — **net reaction to the right**

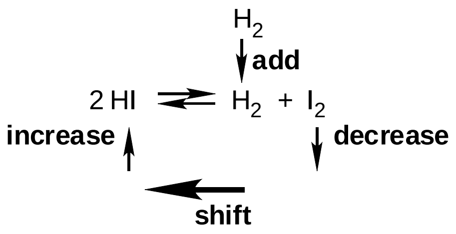
The ratio Q / Kc is used (by simple application of the le Châtelier principle - in the next section) **to predict whether, and in which direction, a net reaction will occur as the system moves toward its equilibrium state.**

Q / K_C	
> 1	**Product concentration is too high for equilibrium; net reaction proceeds to the left.**
= 1	**System is at equilibrium; no net change will occur.**
< 1	**Product concentration is too low for equilibrium; net reaction proceeds to the right.**

The Le Châtelier principle: If a system at equilibrium is subjected to a change of pressure, temperature, or the number of moles of a component, there will be a tendency for a net reaction in the direction that reduces the effect of this change.

In more general words: **if a system at equilibrium is disturbed by an external stress, the system shifts in whichever direction that most directly and effectively minimizes the stress and restores a new equilibrium.**





New equilibrium state; K_C remains the same!

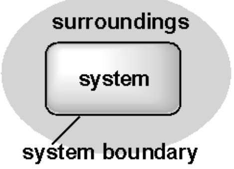
The principle of Le Châtelier for a reaction $\mathbf{A + 2B \rightleftharpoons C + Q\ (\Delta H < 0)}$ that includes thermal effect and number of moles change is summarized in the following Table:

Applied stress	Result (direction of shift)
Increase of concentration of any reactant	**Forward**
Decrease of concentration of any reactant	**Reverse**
Increase of concentration of any product	**Reverse**
Decrease of concentration of any product	**Forward**
Increase of volume (or decrease of pressure)	**Toward the reaction yielding more molecules**
Decrease of volume (or increase of pressure)	**Toward the reaction yielding less molecules**
Increase of temperature	**Toward the endothermic reaction (reverse)**
Decrease of temperature	**Toward the exothermic reaction (forward)**
Addition of catalyst	**No change**

For any concentration, p, and V disturbances: the K_C value remains the same. Only a change in temperature alters K_C value.

III. Thermodynamics

Thermodynamics is the branch of natural science concerned with the interconversion of various kinds of energy (relations between heat and other forms of energy, such as mechanical, electrical, or chemical energy) and the changes in physical properties that are involved. ***«Energy cannot be created or destroyed»*** **— this fundamental law of Nature, more properly known as conservation of energy, is familiar to anyone who has studied science.** Under its more formal name of the **First Law of Thermodynamics**, it governs all aspects of energy in science and engineering applications. (There are several non-scientific discoveries that violate the First law of thermodynamics, most notably generators of power (thermal, electrical, cold fusion) that produce more than they consume!!!) Confining such studies to chemical changes and chemical substances ONLY, we can define **Chemical thermodynamics.** It's special importance in chemistry arises from the fact that virtually all chemical reactions are accompanied by the uptake or release of energy.



III.1. Basic terms and concepts ***Thermodynamic system*** is that part of the world to which we are directing our attention. Everything that is not a part of the system constitutes the ***surroundings***. The system and surroundings are separated by a ***boundary*** (real or imaginary).

A system contains definite amount of one or more substances, and their corresponding energy. Depending on the properties of the boundary the system is:

- **open** – it can exchange both matter and energy with the surroundings (living organisms are open systems);
- **closed** – only energy exchange, but not matter;
- **isolated** – it can not exchange neither matter, nor energy.

Properties and the state of a system The **properties** of a system are those quantities such as the pressure (P), volume (V) , temperature (T), and system's composition, etc., which are in principle measurable and capable of assuming definite values. ***State properties are P, V, T.*** When their values are known then the system is in a definite ***state***. A **thermodynamic process** occurs when the state of the system changes. The first and the last state are called initial state and final state, respectively.

The various physical properties of a system are conveniently divided into two main types: extensive and intensive properties. **Extensive properties depend on the quantity of matter contained in the system.** Common examples are **mass, volume, heat capacity**. The **intensive properties depend on the nature of substances** and are independent of the substance amount. Representative intensive properties are temperature, pressure, density, surface tension, specific heat.

Change of state: the meaning of Δ . A thermodynamic process occurs when the system changes from one state (initial state) into another state (final state). We must be able to unambiguously define the change in the state of a system when it undergoes some process. This is done by **specifying changes in the values of the different state properties using the symbol Δ (*delta*)** as illustrated here for a change in the volume: $\Delta V = V_{final} - V_{initial}$ (or simply $V_2 - V_1$). We can compute similar delta-values for changes in P, V, n_i (the number of moles of component *i*), and the other state properties.

Types of thermodynamic processes:

- **Isothermal process: T = const The system temperature remains constant throughout the process.**

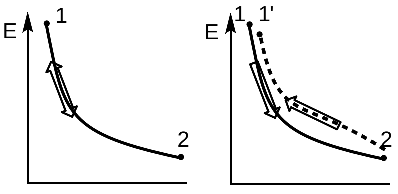
This requires heat to flow freely from the system to the surroundings and *vice versa* in order to keep the temperature of the system constant.

- **Adiabatic process: When the process is carried out without allowing heat exchange between the system and surroundings, the process is adiabatic.** The system is thermally isolated from the surroundings.
- **Isobaric process: P = const The pressure of the system is kept constant** during the change.
- **Isochoric process: V = const The volume of the system is kept constant**.

Reversible and irreversible processes:

- **Reversible process:** The change of state is carried out in such way that **the system can be returned to its initial state along the same path.** Only when the processes are carried out in an ***infinite*** number of steps will the system *and* the surroundings be restored to their initial states – this is the meaning of thermodynamic reversibility. All steps occur within extremely small time intervals and the overall process happens infinitesimally slowly. The system retains almost equilibrium state with surroundings at every stage of the reversible process.
- **Irreversible process:** Such process **does not meet the requirements for reversibility**. An irreversible process is carried our rapidly. Thus the successive steps cannot be retracted in the same path, and at each step the system is away from equilibrium.

A real process that is a good approximation of a reversible one will occur infinitesimally slowly (so that system is always almost at equilibrium). The reversible process is an idealization. **All natural processes are known to be irreversible**, e.g. energy is lost during the return and the initial conditions cannot be reached along the same path.



Reversible **Irreversible**

III.2. Internal energy (U)

The distribution of energy (its release and absorption) is always associated with a definite and intrinsic for every substance or the entire system amount of energy. **The internal energy is simply the sum of all forms of kinetic and potential energy of the system: $U = E_e + E_n + E_c + E_p + E_k$** where: (e) – electronic energy; (n) – nuclear energy, (c) – chemical bonds energy, (p) – potential energy, (k) – kinetic energy (the kinetic energy is a sum of translational + vibrational + rotational energy). Every system (substance) has definite amount of internal energy. Thermodynamics is NOT concerned with the absolute value of **U** because it involves certain quantities which cannot be measured. However, **the change of internal energy** (**ΔU**), when the reactants change into products or when a system changes from initial state to the final state, **is measurable**.

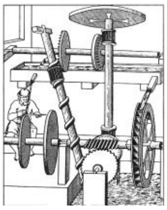
Internal energy is a state function. It depends only upon the state of the system (P, V, T) and is independent of the method (pathway) by which this state has been attained. This means that a given change in internal energy **ΔU can follow an infinite variety of *pathways* corresponding to all the possible combinations of heat (Q) and work (W**, some textbooks use the symbol **A** for work) **that can add up to a given value of ΔU.** The change of internal energy is **$\Delta U = U_2 - U_1$**. Obviously: when **$U_1 > U_2$**, **ΔU** is negative, **$\Delta U < 0$ – total internal energy decreases;** when **$U_1 < U_2$**, ΔU is positive, **$\Delta U > 0$ – total internal energy increases**. The difference **ΔU is negative when the system loses energy, either by giving up heat, or working ON the surroundings; ΔU is positive when the system gains energy by absorbing heat or by work DONE ON THE SYSTEM.**

IV. THE FIRST LAW

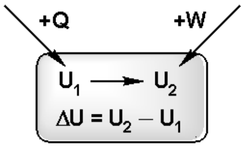
This law is one of the most fundamental principles of the physical world. Also known as the **Law of Conservation of Energy**, it states that **energy cannot be created or destroyed**; it can only be redistributed or changed from one form to another. A way of expressing this law that is generally more useful in Chemistry is that **any change in the internal energy of a system is given by the sum of the heat Q that flows across its boundaries and the work W done on the system by the surroundings, $\Delta U = Q + W$** IMPORTANT!

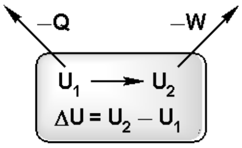
This says that there are two kinds of processes, heat and work, that can lead to a change in the internal energy of a system. Since both heat and work can be measured and quantified, this is the same as saying that **any change in the energy of a system must result in a corresponding change in the energy of the world outside the system – in other words, energy cannot be created or destroyed.** From the First law follows:

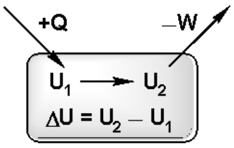
- **It is impossible to construct perpetual motion machine.**
- **When energy is consumed, it must be produced in other part (of Universe).**
- **The total amount of energy in the Universe remains constant (in particular, of a system and its surroundings) although the energy undergoes transformations from one form into others.**



There is an important sign convention for heat and work. **If heat flows into a system or the surroundings do work on it, the internal energy increases and the sign of Q or W is positive.** Conversely, heat flow out of the system or work done by the system will be at the expense of the internal energy, and will therefore be negative.





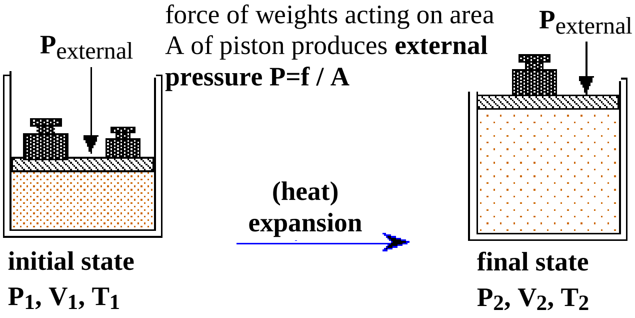


In summary:

Work	**– W**	**The system performs work on the surroundings** (work done by the system).
	+ W	**The surroundings work on the system** (work done on the system).
Heat	**– Q**	**Heat flows out from the system to the surroundings** (heat released out by the system).
	+ Q	**Heat enters the system from surroundings** (heat is absorbed by the system).
Energy	**– ΔU**	**Energy is released out by the system** (the systems' internal energy decreases)
	+ ΔU	**Energy is gained by the system** (the systems' internal energy increases).

IV.1. Pressure–volume work

The kind of work most frequently associated with chemical change occurs when the volume of the system changes owing to the disappearance or formation of gaseous substances. When system state changes with change of pressure and/or volume the associated work is called **expansion work or *PV*-work.**

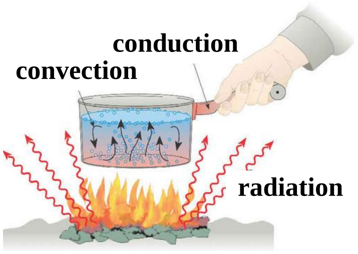


When the system decreases its volume due to external pressure increase, the PV-work is positive and proportional to the volume change: **for *contraction* $W = P.\ \Delta V$**. If the system increases volume, then the system works on the surroundings and PV-work is negative: **for *expansion*, $W = -P.\ \Delta V$.**

It is important to note that although P and V are state functions, the *work* is not. Work and heat are *processes* and cannot be stored.

IV.2. Heat (Q)

What is heat? The term "heat" has a special meaning in thermodynamics: **it is a *process* in which a body** (the contents of a tea kettle, for example) **acquires or loses energy as a direct consequence of its having a *different temperature* than its surroundings** (the rest of the world). Heat is another mode of energy exchanged between the system and the surroundings. The internal energy of a system increases when **heat is absorbed by the system from surroundings**. Then heat has a positive value: **$Q > 0$**.



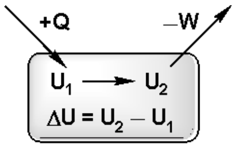
When heat flows out of the system, its internal energy decreases and heat has negative value: **$Q < 0$ when the system releases heat to surroundings. Thermal energy can only flow from a higher temperature to a lower temperature. It is this flow that constitutes "heat".** Heat is transferred by conduction or radiation.

Internal energy is a state function, but **work and heat are not state functions because their values depend upon the path followed.**

If the system under consideration contains an ideal gas, the change of its internal energy is sum of the heat exchanged and performed work: **$\Delta U = Q + W$**

In an adiabatic change, $Q = 0$, so the First Law becomes **$\Delta U = 0 + W$**. Since the temperature of the gas changes with its internal energy, it follows that **adiabatic compression** (**$W > 0$**) of a gas will cause it to **warm up**, whereas **adiabatic expansion** (**$W < 0$**) will result in **cooling**.

In an isothermal process (expansion of gas) **the internal energy remains constant** (**$\Delta U = 0$**) and we can write the First Law as **$0 = Q + W$**, or **$Q = -W$**, illustrating that the heat flow and work done exactly balance each other. **For an isothermal process, pressure-volume work affects the heat Q.** We shall consider only pressure-volume work in this lesson. If the process takes place at constant pressure, then the work done by the system is given by **$P\Delta V$** and the change in internal energy is: **$\Delta U = Q - W$; $\Delta U = Q - P\Delta V$,** then **$Q = \Delta U + P\Delta V$**



Thus, the amount of heat that passes between the system and the surroundings is given by the last equation.

In an isochoric process (constant volume), **$\Delta V = 0$**, and **$\Delta U = Q_v$**. Hence, the internal energy change is the heat absorbed or given out at constant volume (with subscript "v").

IV.3. ENTHALPY (HEAT CONTENT)

The important thermodynamic function of state, **enthalpy is defined for an isobaric process** (at constant pressure). Because most chemical changes we deal with take place at constant pressure, it would be tedious to have to explicitly deal with the pressure-volume work details that were described above. Fortunately, chemists have found a way around this; they have simply defined a new state function that incorporates and thus hides within itself any terms relating to incidental kinds of work (*P-V*, electrical, etc.). From the First law: **$\Delta U = Q + W$**, or **$Q = \Delta U - W$** follows **$Q_p = \Delta U + P\Delta V$** when the change occurs at **P = const** and work is done by the system (expansion, then **$W < 0$**). Let us assume that the system absorbs **Q_p** (calories) amount of heat. Its internal energy increases from **U_1** to **U_2**, and the volume increases from **V_1** to **V_2**. These changes are expressed as **$\Delta U = U_2 - U_1$** and **$\Delta V = V_2 - V_1$**. Substituting these expressions in the relationship of **Q_p**:

$$Q_p = (U_2 - U_1) + P(V_2 - V_1) = U_2 - U_1 + PV_2 - PV_1 \quad \text{or} \quad Q_p = (U_2 + PV_2) - (U_1 + PV_1)$$

The thermodynamic quantity **$U + PV$** is also a state function – it depends only on the initial and final state. **The quantity $U + PV = H$ is called enthalpy of the system. The change of enthalpy, $\Delta H = H_2 - H_1 = Q_p$, is equal to the heat exchanged at P=const.** Replacing **Q_p** with **ΔH** in **$Q_p = \Delta U + P\Delta V$**, we obtain:

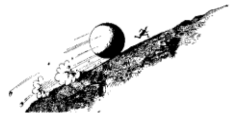
$$\Delta H = \Delta U + P\Delta V$$

IMPORTANT!

The heat that is absorbed or released when a process takes place at constant pressure, **Q_P**, must also be a state function and is known as the **enthalpy change ΔH**. The enthalpy change of a system can be explained also as the sum of internal energy change and P-V work done, e.g. the work of expansion. Remember the sign convention: **a flow of heat or performance of work that supplies energy is positive; if it consumes energy, it is negative**. Thus work performed by the surroundings diminishes the energy of the surroundings (**$W_{surr} < 0$**) and increases the energy of the system (**$W_{sys} > 0$**). In this respect is IMPORTANT! to remember: Sign of enthalpy change for chemical reactions is negative, **– ΔH** when heat is released by the system (its heat content decreases) and the reaction is **exothermic** (**+ Q**); **+ ΔH** means that heat content increases by taking up heat from the surroundings, i.e. **endothermic reaction** (**– Q**).

V. Spontaneous and non-spontaneous processes

The First law of thermodynamics states that energy cannot be created or destroyed; it can only be redistributed or changed from one form to another. The law states that there is **an exact equivalence between the various forms of energies** involved in any process. **This law DOES NOT provide information on *whether the process is possible or not.*** Some processes (including chemical reactions) proceed spontaneously, some do not. The First law cannot predict spontaneity or feasibility of a process. **The Second law of thermodynamics provides answer to the question which is a spontaneous process.**



What is a spontaneous process? Is the cartoon veraciously depicting a stone chasing human uphill?

Consider four experiments: 1) A stack of one hundred coins all aligned "heads up" is thrown into the air. After they have come to rest on the floor, the numbers that land "heads up" and "tails up" are roughly equal. Results – *Net change:* randomized coins; *Energetics:* no relevant net change in energy; ***Does not go in reverse***: almost zero probability for "all heads". 2) Two identical blocks of copper, one at 200°C and the other at 100°C, are brought into contact in a thermally-insulated environment. Eventually the temperatures of both blocks reach 150°C. Results – *Net change:* block 1 (200°) + block 2 (100°) ⟶ combined blocks (150°); *Energetics:* Heat (randomized molecular kinetic energy) flows from the warmer block to the cooler one until their temperatures are identical. **Why it does not go in reverse**: Dispersal of kinetic energy amongst the copper atoms is a random process and it is impossible to "order" the atoms at < 150°C. 3) A book or some other solid object is held above a table top, and is then allowed to fall. Results – *Net change:* book in air ⟶ book on table top; potential energy ⟶ organized kinetic energy ⟶ thermal energy; *Energetics:* The potential energy is completely transformed into kinetic during the fall; at the impact moment the last is transformed into heat (thermal motions of the atoms, both of the object itself and of the area of the table top where the impact occurred); **Why it does not go in reverse**: Once the kinetic energy of the book has been dispersed amongst the molecules of the book and the table top, the probability for the reverse is zero. 4) One mole of gas, initially at 300 K and 2 atm pressure, is allowed to expand to double its volume, keeping the temperature constant. Results – *Net change:* Increase in volume of gas; *Energetics:* No change in energy; **Why it does not go in reverse**: Due to simple statistics, there is no probability that *N* randomly moving objects (atoms, molecules) will at any time all be located in one half of the container. Similar examples could explain the irreversibility of: – dissolution of a chunk of sugar in water; – flow of river downhill, etc. **All of the changes described above take place spontaneously**, meaning that:

- Once they are allowed to commence, they will proceed to the finish without any outside intervention.
- It would be inconceivable that any of these changes could occur in the reverse direction (that is, be undone) without changing the conditions or actively disturbing the system in some way.

Processes that proceed in a definite direction when left to themselves and in the absence of any attempt to drive them in reverse – are known as *natural processes* or *spontaneous* changes.

Some of the spontaneous processes require initiation, e.g.:

- Burning of a wax candle needs initial ignition; $2\ C_{10}H_{22} + 31\ O_2 \longrightarrow 20\ CO_2 + 22\ H_2O$
- Combustion of hydrogen in oxygen also needs ignition. $2\ H_{2\,(g)} + O_{2\,(g)} \longrightarrow 2\ H_2O_{\,(l)}$

Such reactions and processes are feasible. They may proceed by themselves or after initiation in only one direction, regardless of their rate.

Non-spontaneous process is such change that cannot take place by itself, nor after initiation. Examples of everyday non-spontaneous processes are: (i) Flow of water uphill; (ii) Elevation of an object against gravity;(iii) Flow of heat from a cold body to hot body; (iv) Gas particles moving from low pressure to high pressure.

What determines the direction in which spontaneous change will occur? **It is clearly not always a fall in the energy**, since in most cases cited above the energy of the system did not change.

There should be a force that drives in particular direction any process. **The driving force for a spontaneous process is acquired from two tendencies:**

1. **Tendency for minimum energy**
2. **Tendency for maximum randomness.**

1. Tendency for minimum energy

In order to acquire maximum stability, every system tends to have minimum energy. For example:

- A stone lying at a height has a tendency to fall down so as to have minimum potential energy.
- Water flows down a hill to have minimum energy.
- Heat flows from hot body to cold body so that heat content of the hot body becomes minimum.

All chemical reactions that have heat content of products less than heat content of reactants are spontaneous. They have **$\Delta H < 0$ (negative value of enthalpy change, exothermic reactions)**.

- **All exothermic reactions** are accompanied by evolution of heat and **are spontaneous because they are accompanied by decrease of energy.**

$$H_{2\,(g)} + 1/2\ O_{2\,(g)} \longrightarrow H_2O_{(l)} \quad (\Delta H = -286\ \text{kJ/mol})$$
$$N_{2\,(g)} + 3\ H_{2\,(g)} \longrightarrow 2\ NH_{3\,(g)} \quad (\Delta H = -92.4\ \text{kJ/mol})$$
$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \quad (\Delta H = -394\ \text{kJ/mol})$$

All reactions on the left are accompanied by evolution of heat. Their products have less heat content than that of reactants and this excess is liberated as heat. The enthalpy change is negative. However, one should not conclude that spontaneous reactions are always associated with decrease of enthalpy.

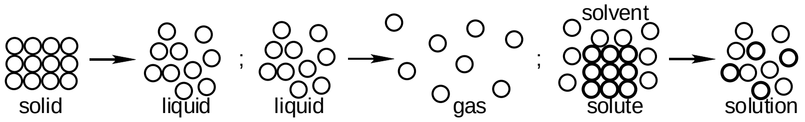
The direction of a spontaneous process is not always governed by the energy change…and thus the First Law of Thermodynamics alone cannot predict the direction of a natural process, such as:

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \quad (\Delta H = +5.9\ \text{kJ/mol})$$
$$H_2O_{(l)} \longrightarrow H_2O_{(g)} \quad (\Delta H = +44.0\ \text{kJ/mol})$$
$$NH_4Cl_{(s)} \xrightarrow[(aq)]{} NH_4{}^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \quad (\Delta H = +15.1\ \text{kJ/mol})$$

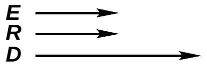
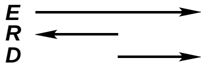
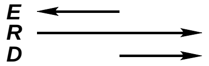
All of these transformations require energy to happen (they are endothermic) but they are spontaneous. Hence, **ΔH is not the only criterion** that predicts feasibility of a process.

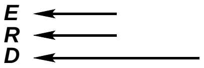
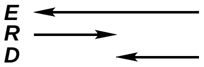
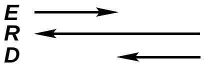
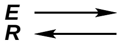
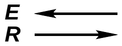
2. Tendency for maximum randomness

The spontaneity of endothermic processes can be explained with acquiring maximum randomness.



Ice melts and water evaporates because H_2O molecules have more randomness (less order) in liquid or gas phase, respectively. Ammonium chloride crystal dissolves spontaneously in water because the ammonium cation and chloride anion are much less ordered when dispersed and surrounded by water molecules than when they are properly arranged in crystal lattice. It should be emphasized that similarly to the energy factor (**ΔH**), the randomness factor cannot be the only criterion for spontaneity of a process. Water freezes spontaneously, too, although molecules in ice are more ordered than in liquid water. Some other spontaneous processes, such as liquefaction of a gas or solidification of a liquid are also accompanied by decrease of randomness. Both factors (1. tendency for minimum energy, and 2. tendency for maximum randomness) should be considered in order to predict the direction of a spontaneous process. The overall tendency as driving force can be represented schematically as sum of the individual tendencies, akin summation of vectors, as shown.

<table>
<tr><td colspan="3">Consider hypothetical process A → B . The tendency for minimum energy is labeled «<i>E</i>», the tendency for maximum randomness – «<i>R</i>», and the total driving force – «<i>D</i>». The combinations of direction and magnitude of «<i>E</i>» and «<i>R</i>» give different possibilities for the direction and size of «<i>D</i>».</td></tr>
<tr><td colspan="3">1. The net driving force is in forward direction, towards product B.</td></tr>
<tr><td>
D = E + R
Both <i>E</i> and <i>R</i> favor forward</td><td>
D = E – R
<i>E</i> favors forward but <i>R</i> opposes.</td><td>
D = R – E
<i>E</i> opposes, <i>R</i> favors forward, and</td></tr>
</table>

process.	Since *E*>*R*, the net driving force is smaller favoring the forward process.	since *R*>*E*, the net driving force is towards products (forward).
2. The net driving force is in reverse direction, toward reactant A.		
 $-D = -E - R$ Both *E* and *R* oppose. The net driving force is toward reverse process.	 $-D = R - E$ *E* opposes, *R* favors, and since *E*>*R*, the net driving force is toward reverse process.	 $-D = E - R$ *E* favors, *R* opposes, and *R*>*E*. The net driving force is toward reverse process, reactants.
3. The net driving force is zero (equilibrium conditions)		
 $D = 0$ *E* favors, *R* opposes and they are with equal magnitudes.	 $D = 0$ *E* opposes, *R* favors and they are with equal magnitude.	

THERMODYNAMIC CRITERIA FOR PREDICTING THE SPONTANEITY OF CHEMICAL REACTIONS

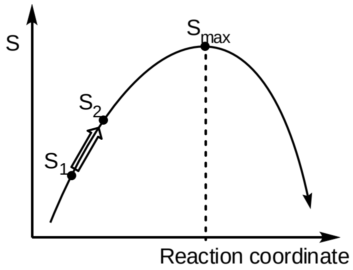
Thermodynamics uses quantitatively both factors**: 1. Minimum energy** and **2. Maximum entropy** in order to predict precisely the direction and extend of a chemical reaction. Before describing the mathematical relationship, the concept of entropy is presented: **VI. ENTROPY**

The second law of thermodynamics is commonly known as the Law of Increasing entropy. The second law of thermodynamics introduces the concept of entropy (**S**) and its relation with spontaneous processes. This law states: **In any spontaneous macroscopic change, the entropy of the world increases.** Keep in mind that our system under consideration and its surroundings ARE "the world": **System + surroundings = the world!** This statement is expressed as: $\Delta S_{system} + \Delta S_{surr} = \Delta S_{total}$ and it is namely ΔS_{total} that is positive. All natural processes that allow the free exchange of thermal energy amongst chemically-significant numbers of particles are accompanied by a spreading or "dilution" of energy that leaves the world forever changed. In other words, **all spontaneous change leads to an increase in the entropy of the world**. At first sight, this might seem to be inconsistent with our observations of very common instances in which there is a clear decrease in entropy, such as the freezing of a liquid, the formation of a precipitate, or the growth of an organism ... but **it's the entropy of the system *plus* surroundings that counts!** It is important to understand that the criterion for spontaneous change is the entropy change of the system and the surroundings – that is, of the "world", which we denote by ΔS_{total}. Thus the **freezing of water** is accompanied by a flow of heat (the heat of fusion) *into* the surroundings, causing ΔS_{surr} to increase. Heat flows from system into surroundings. The randomness in the system decreases, but it is compensated by larger increase of randomness in the surroundings, so ΔS_{world} exceeds zero. At temperatures below the freezing point, this increase more than offsets the decrease in the entropy of the water itself, so ΔS_{total} exceeds zero and the process is spontaneous. **What is entropy**? Entropy is one of the most fundamental concepts of physical science, with far-reaching consequences ranging from cosmology to chemistry. It is also widely misrepresented as a measure of "disorder", convenient but not quite correct. Entropy is still described, particularly in older textbooks, as a measure of disorder. For example, a students' dormitory room is clean and ordered. After some time if all objects taken and used are not returned back to their original places (at expense of energy), the room has high degree of disorder, and we can say "its entropy has increased". This is kind of "spontaneous" process. The reverse, putting everything in order is an organized effort requiring energy input. In a narrow technical sense "entropy – measure of disorder" is correct, since the spreading and sharing of thermal energy does have the effect of randomizing the disposition of thermal energy within a system. But to simply equate entropy with "disorder" without further qualification is extremely misleading because it is far too easy to forget that entropy (and thermodynamics in general) applies only to molecular-level systems capable of exchanging thermal energy with the surroundings.

Carrying these concepts over to macro systems may yield compelling analogies, but it is no longer science. Therefore it is far better to avoid the term "disorder" altogether in discussing entropy.

The physical meaning of entropy is: **Entropy is a measure of the degree of spreading and sharing of thermal energy within a system.**

The entropy change is defined for a process that reversibly and isothermally exchanges a quantity of heat Q_{rev} with the surroundings as: $\Delta S = S_2 - S_1 = \frac{Q_{rev}}{T}$ IMPORTANT!



It is easy to remember: **The greater the randomness, the higher is the entropy.** In principle, when **$\Delta S > 0$, positive value – the process is spontaneous;** when **$\Delta S < 0$, negative value – the process is non-spontaneous** (the reverse may be spontaneous)**;** when **$\Delta S = 0$ ($S = S_{max}$)**, no entropy change **– the process is at equilibrium**, and schematically:

Entropy is an extensive property, directly proportional to the amount of matter in the system, and has units in SI of J / K.mol.

VII. GIBBS FREE ENERGY

In chemical thermodynamics we prefer to focus our attention on the system rather than the surroundings, and would like to avoid having to calculate the entropy change of the surroundings explicitly. Instead of dealing explicitly with surroundings, we focus only on the system changes and introduce a **new thermodynamic function, the free energy. It turns out to be the single most useful criterion for predicting the direction of a chemical reaction and the composition of the system at equilibrium.** The free energy enables calculation of changes that occur **at a constant temperature and pressure (the Gibbs free energy)** or constant temperature and volume (the Helmholtz free energy). (Josiah Willard Gibbs, 1839-1903, is the founder of physical chemistry.) **The Gibbs free energy (G,** also known as the ***Gibbs function***) **is defined as: $G = H - TS$**

where **H** is enthalpy, **T** – absolute temperature, and **S** – entropy of the system. Since **H**, **T** and **S** are all state functions, so is the Gibbs free energy **G**. Thus for any change in state, we can write the extremely important relation for a system change that takes place at constant temperature and pressure:

$G_1 = H_1 - TS_1$ (for the initial state) **$G_2 = H_2 - TS_2$** (for the final state), then the difference of free energies is

$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$ We already know how to express changes:

$\Delta H = H_2 - H_1$ the enthalpy change of the system; **$\Delta S = S_2 - S_1$ the entropy change of the system**

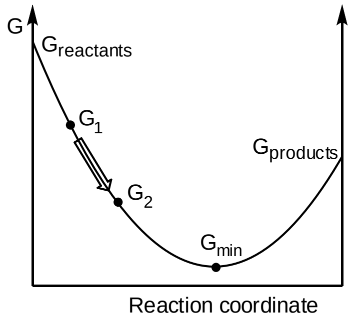
$\Delta G = G_2 - G_1$ change in Gibbs free energy of the system. We derive the Gibbs-Helmholz equation

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

IMPORTANT!

ΔG determines the direction and extent of a chemical change.

In a spontaneous change, Gibbs energy always decreases and never increases.



The importance of the Gibbs free energy can hardly be over-stated: **it serves as the single master variable that determines whether a given chemical change is thermodynamically possible**. Thus if the free energy of the reactants is greater than that of the products, the entropy of the world will increase when the reaction takes place as written, and so the reaction will tend to take place spontaneously. Conversely, if the free energy of the products exceeds that of the reactants, then the reaction will not take place in the direction written, but it will tend to proceed in the reverse direction.

Mathematically this conclusion can be shown:

If the system is isolated (at T=const, P=const): $\Delta G = 0$, because: the enthalpy change is equal to the heat exchanged at P = const, **$\Delta H = Q_p$**, and $\Delta S = \frac{Q_p}{T} = \frac{\Delta H}{T}$ then it follows **$T\Delta S = \Delta H$**, or **$\Delta H - T\Delta S = \Delta G = 0$**.

If the system is not isolated (at T=const, P=const): $\Delta G < 0$, because: $\Delta S > \frac{\Delta H}{T}$; **$T\Delta S > \Delta H$**, or **$\Delta H - T\Delta S < 0$**, therefore **$\Delta G < 0$**, negative value.

Always keep in mind: $G_2 – G_1 = \Delta G < 0$ for a spontaneous reaction!

These relations are nicely summarized as follows:

- **$\Delta G < 0$ reaction can spontaneously proceed to the right: A → B**;
- **$\Delta G > 0$ reaction can spontaneously proceed to the left: A ← B**;
- **$\Delta G = 0$ the reaction is at *equilibrium***; the quantities (concentrations) of **A** and **B** will not change.

The SI units of entropies are J/K.mol, whereas enthalpies and free energies are kJ/mol.

An addition to the definition of Gibbs free energy: **the Gibbs energy is the maximum useful work** (excluding PV-work associated with volume changes of the system) **that a system can do on the surroundings when the process occurs reversibly at constant temperature and pressure.** This work is done at the expense of the internal energy of the system, and whatever part of that is not extracted as work is exchanged with the surroundings as heat, **Q**. This latter quantity of heat will have the value **$Q_p = –T\Delta S$.**

VII.1. The important role of temperature

Recalling the condition for a spontaneous change: **$\Delta G = \Delta H – T\Delta S < 0$**

it is apparent that the temperature dependence of **ΔG** depends almost entirely on the entropy change associated with the process. ("almost" because the values of **ΔH** and **ΔS** are slightly temperature dependent). In particular, notice that in the above equation **the sign of the entropy change determines whether the reaction becomes more or less spontaneous as the temperature is raised**. For any given reaction, the sign of **ΔH** can also be positive or negative. This means that there are four possibilities for the influence that temperature can have on the spontaneity of a process, and the symbolism of treatment in the previous Table becomes obvious:

- **Case 1: $\Delta H < 0$ and $\Delta S > 0$** Under these conditions, **both the ΔH and TΔS terms will be negative, so ΔG will be negative regardless of the temperature**. An exothermic reaction whose entropy increases will be spontaneous at all temperatures.
- **Case 2: $\Delta H < 0$ and $\Delta S < 0$** **If the reaction is sufficiently exothermic it can force ΔG negative only at temperatures below which $|T\Delta S| < |\Delta H|$** (The absolute value (or modulus) **$|x|$** of a real number ***x*** is the non-negative value of ***x*** without regard to its sign.) This means that there is a temperature **$T = \Delta H / \Delta S$** at which the reaction is at equilibrium; **the reaction will only proceed spontaneously *below* this temperature**. The freezing of a liquid or the condensation of a gas are the most common examples of this condition.
- **Case 3: $\Delta H > 0$ and $\Delta S > 0$** The entropy increase must overcome the handicap of an endothermic process so that **$T\Delta S > \Delta H$**. Since the effect of the temperature is to "magnify" the influence of a positive **ΔS**, **the process will be spontaneous at temperatures *above* $T = \Delta H / \Delta S$.**
- **Case 4: $\Delta H > 0$ and $\Delta S < 0$** With both **ΔH** and **ΔS** working against it, **this kind of process will not proceed spontaneously at any temperature.**

Summary of the thermodynamic criteria for spontaneity of a process in all four cases is presented in Table:

Case	Enthalpy change (sign)	Entropy change (sign)	T	$\Delta G = \Delta H – T\Delta S$	Process
1	$\Delta H < 0$ (–)	$\Delta S > 0$ (+)	Any	$\Delta G < 0$ (–)	**spontaneous**
2	$\Delta H < 0$ (–)	$\Delta S < 0$ (–)	Low	$\Delta G < 0$ (–)	**spontaneous**
	$\Delta H < 0$ (–)	$\Delta S < 0$ (–)	High	$\Delta G > 0$ (+)	**non-spontaneous**
3	$\Delta H > 0$ (+)	$\Delta S > 0$ (+)	Low	$\Delta G > 0$ (+)	**non-spontaneous**
	$\Delta H > 0$ (+)	$\Delta S > 0$ (+)	High	$\Delta G < 0$ (–)	**spontaneous**
4	$\Delta H > 0$ (+)	$\Delta S < 0$ (–)	Any	$\Delta G > 0$ (+)	**non-spontaneous**

Conclusion: **Not all exothermic reactions ($\Delta H < 0$) are spontaneous. If ΔS is negative (decreasing entropy), then at high T the term $|T\Delta S| > |\Delta H|$ and $\Delta G > 0$, thus the reaction is non-spontaneous. An endothermic reaction ($\Delta H > 0$) can be spontaneous if the entropy increases ($\Delta S > 0$) and T is high. Then, $T\Delta S > \Delta H$ and $\Delta G < 0$.**

Predicting the effect of temperature

Examples: **1) exothermic reaction with entropy increase**

$$C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \quad (\boldsymbol{\Delta H < 0, \Delta S > 0})$$

This ***combustion reaction***, like most such reactions, **is spontaneous at all temperatures**. The positive entropy change is due mainly to the greater mass of CO_2 molecules compared to those of O_2. Also:

$$2\,O_{3\,(g)} \longrightarrow 3\,O_{2\,(g)} \quad (\boldsymbol{\Delta H < 0, \Delta S > 0})$$

2) exothermic reaction with entropy decrease

$$3\,H_{2\,(g)} + N_{2\,(g)} \longrightarrow 2\,NH_{3\,(g)} \quad (\boldsymbol{\Delta H < 0, \Delta S < 0})$$

The decrease in moles of gas in the Haber ammonia synthesis drives **the entropy change negative, making the reaction spontaneous only at low temperatures**. Thus higher **T**, which speeds up the reaction, also reduces its extent.

3) endothermic reaction with entropy increase

$$N_2O_{4\,(g)} \longrightarrow 2\,NO_{2\,(g)} \quad (\boldsymbol{\Delta H > 0, \Delta S > 0})$$

Dissociation reactions are typically endothermic with positive entropy change, and are therefore **spontaneous at high temperatures**. Ultimately, all molecules decompose to their atoms at sufficiently high temperatures.

4) endothermic reaction with entropy decrease

$$N_2 + 2\,O_{2\,(g)} \longrightarrow 2\,NO_{2\,(g)} \quad (\boldsymbol{\Delta H > 0, \Delta S < 0})$$

Such reaction is not spontaneous at any temperature, meaning that *its reverse is always spontaneous*. Also:

$$3\,O_{2\,(g)} \longrightarrow 2\,O_{3\,(g)} \quad (\boldsymbol{\Delta H > 0, \Delta S < 0})$$

Additional example of reversible reaction:

$$CaCO_{3\,(s)} \longrightarrow CaO_{(s)} + CO_{2\,(g)} \quad (\text{spontaneous at high T } \boldsymbol{\Delta H > 0, \Delta S > 0})$$

$$CaO_{(s)} + CO_{2\,(g)} \longrightarrow CaCO_{3\,(s)} \quad (\text{spontaneous at low T } \boldsymbol{\Delta H < 0, \Delta S < 0})$$

In lieu of abstract: there are three quantitative criteria for predicting the direction of a chemical reaction:

K – equilibrium constant
ΔS – entropy change
ΔG – free energy change

K and **ΔG** are more useful criteria when describing living organisms.

The third law of thermodynamics is sometimes stated as follows: **The entropy of a perfect crystal at absolute zero is exactly equal to zero, S = 0 J/K.mol.**