EVROPSKÁ UNIE
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Geochemistry on the Earth’s surface for analytical geochemists

1a.

Mineral stability and structure

Tento učební materiál vznikl v rámci projektu Rozvoj doktorského studia chemie
č. CZ.02.2.69/0.0/0.0/16_018/0002593

EQUILIBRIUM

Dissolving limestone

$$\mathrm{CaCO_3}(s) \rightarrow \mathrm{Ca}^{2+}(aq) + \mathrm{CO}_3^{2-}(aq)$$

- What will happen if 1 kg of limestone (calcite) is put into a container with 10 L of clean water?
- When does the reaction stop?

Precipitation of limestone

$$\mathrm{CaCO_3}(s) \leftarrow \mathrm{Ca}^{2+}(aq) + \mathrm{CO}_3^{2-}(aq)$$

- What will happen if tap water is boiled in a kettle and let to cool again?
- When does the reaction stop?

- What determines the direction of the reaction?

Chemical equilibrium

- A chemical reaction does not proceed until the reactants are completely consumed.
- The product molecules react with each other and change back into reactants.
- At some point, the rates of the reverse and forward reactions become equal, and the established steady state is called chemical equilibrium.
- **Chemical equilibrium is a state in which the rates of opposite chemical reactions are equal.**

Equilibrium constant

- It indicates the extent of the reaction before equilibrium is reached.
- It is given by the ratio of products and reactants of a reaction at equilibrium:

$$a\mathrm{A}(g) + b\mathrm{B}(g) \leftrightarrow c\mathrm{C}(g) + d\mathrm{D}(g)$$

$$K_{eq} = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

Equilibrium constant

- From the definition:
  - Concentrations for expressing the equilibrium constant are always in mol.L^{-1}
  - The products are always in the numenator.
  - The reactants are always in the denominator.
  - Exponents are always coefficients in an equation.

Equilibrium constant

- Determines the ratio between reactants and products:

- $K > 10^3$ products significantly dominating
- $K < 10^{-3}$ reactants significantly dominating
- $10^3 > K > 10^{-3}$ the resulting concentrations are similar

Note

- Conventionally, only the concentrations of gases and liquids (solutions) are included in the equation, because solids have a constant concentration that is already included in K.

$$\mathrm{CaCO_3}(s) \leftrightarrow \mathrm{Ca^{2+}}(aq) + \mathrm{CO_3^{2-}}(aq)$$

$$K_{eq} = [\mathrm{Ca^{2+}}][\mathrm{CO_3^{2-}}]$$

$$K_{eq} = 10^{-8.4}$$

- The equilibrium constant is dependent on temperature (and to a much lesser extent on pressure).

Example 3.1

$$3\mathrm{H}_2(g) + \mathrm{N}_2(g) \leftrightarrow 2\mathrm{NH}_3\ (g)$$

$$K_{eq} = ?$$

Combining hydrogen and nitrogen to ammonia
At a temperature of 350 °C, the equilibrium molar concentrations are:
N_2 = 0.885
H_2 = 0.665
NH_3 = 1.230

What is the value of the equilibrium constant?
Will reactants or products predominate?

Example 3.2

- Calculate the value of the equilibrium constant , K_c , for the system shown if a 2-liter experimental vessel contains 0.1908 mol CO_2 , 0.0908 mol H_2 , 0.0092 mol CO, and 0.0092 mol water vapor at equilibrium.

$$CO_2(g) + H_2(g) \leftrightarrows CO(g) + H_2O(g)$$

STABILITY

Assessment

- Which processes will run on their own?

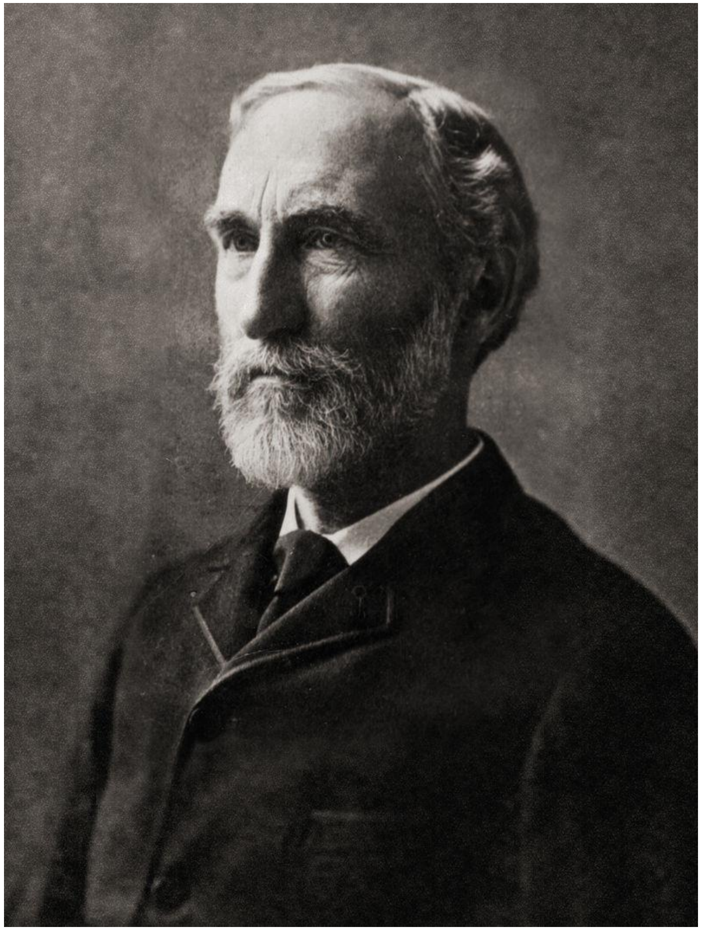
Assessment

- Which processes will occur spontaneously?
  - Total entropy increases ($\Delta S > 0$)
  - Energy is released ($\Delta H < 0$)

- We can therefore base our assessment on ΔH, ΔS and T (particle energy).

$G = H - TS$

GIBBS FUNCTION



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Josiah Willard Gibbs
(1839–1903)

Gibbs function

$$\mathrm{d}q_{p,\text{systém}} = \mathrm{d}H_{\text{systém}}$$

$$\mathrm{d}q_{p,\text{okolí}} = -\mathrm{d}q_{p,\text{systém}} = -\mathrm{d}H_{\text{systém}}$$

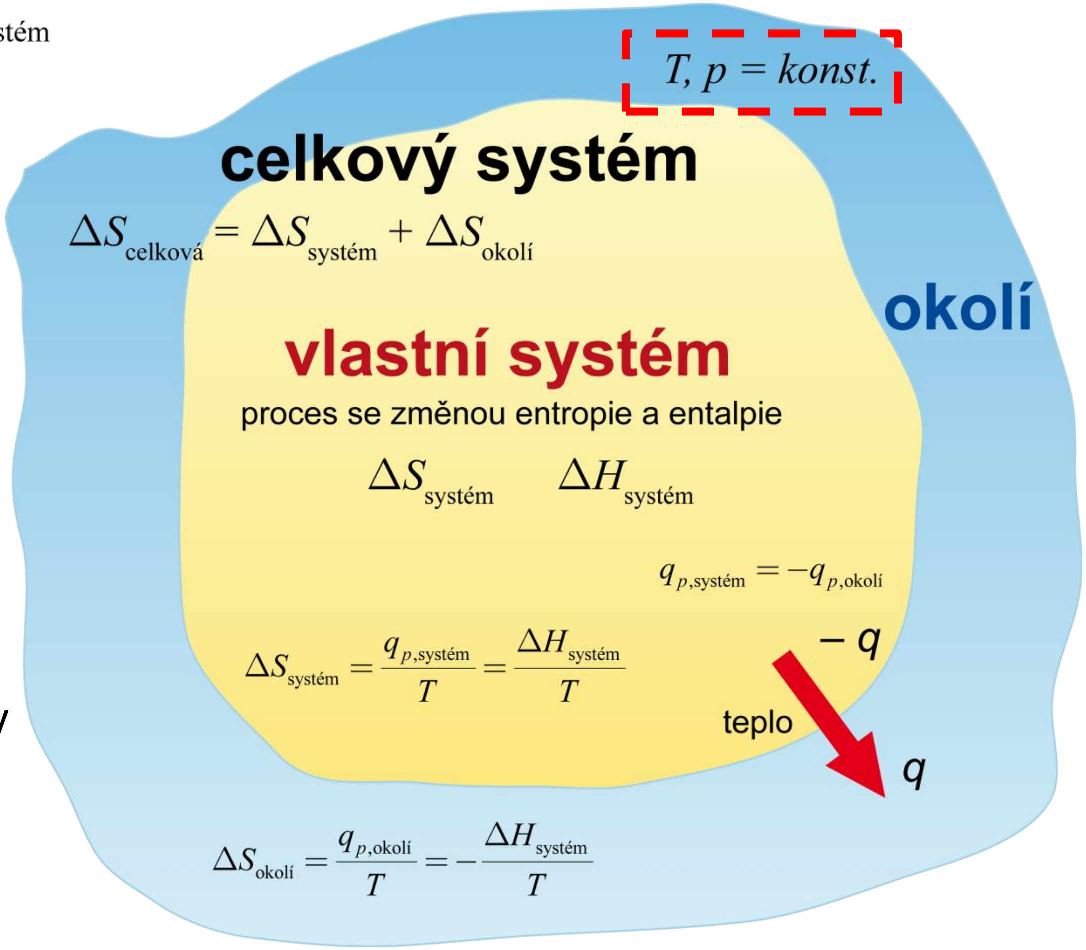
$$\mathrm{d}S_{\text{celková}} = \mathrm{d}S_{\text{systém}} + \mathrm{d}S_{\text{okolí}}$$

$$\mathrm{d}S_{\text{okolí}} = \frac{\mathrm{d}q_{p,\text{okolí}}}{T}$$

$$\mathrm{d}S_{\text{celková}} = \mathrm{d}S_{\text{systém}} + \frac{\mathrm{d}q_{p,\text{okolí}}}{T}$$

$$\mathrm{d}S_{\text{celková}} = \mathrm{d}S_{\text{systém}} - \frac{\mathrm{d}H_{\text{systém}}}{T}$$

entropy change of the system and surroundings expressed by thermodynamic quantities, relating to the system



$T, p = konst.$

celkový systém

$$\Delta S_{\text{celková}} = \Delta S_{\text{systém}} + \Delta S_{\text{okolí}}$$

okolí

vlastní systém

proces se změnou entropie a entalpie

$\Delta S_{\text{systém}}$ $\Delta H_{\text{systém}}$

$$q_{p,\text{systém}} = -q_{p,\text{okolí}}$$

$$\Delta S_{\text{systém}} = \frac{q_{p,\text{systém}}}{T} = \frac{\Delta H_{\text{systém}}}{T}$$

$-q$

teplo

q

$$\Delta S_{\text{okolí}} = \frac{q_{p,\text{okolí}}}{T} = -\frac{\Delta H_{\text{systém}}}{T}$$

Gibbs function

$$\mathrm{d}S_{\text{celková}} = \mathrm{d}S_{\text{systém}} - \frac{\mathrm{d}H_{\text{systém}}}{T}$$

$$T\mathrm{d}S_{\text{celková}} = T\mathrm{d}S_{\text{systém}} - \mathrm{d}H_{\text{systém}}$$

$$-T\mathrm{d}S_{\text{celková}} = \mathrm{d}H_{\text{systém}} - T\mathrm{d}S_{\text{systém}}$$

$$\mathrm{d}G_{\text{systém}} = -T\mathrm{d}S_{\text{celková}}$$

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S$$

$$\mathrm{d}S_{\text{celková}} = -\frac{\mathrm{d}G_{\text{systém}}}{T}$$

A natural process

$$\mathrm{d}S_{\text{celková}} > 0$$

$$\mathrm{d}G < 0$$

Thermodynamic equilibrium

$$\mathrm{d}G = 0$$

Gibbs function

$$G = H - TS$$

$$\mathrm{d}G = \mathrm{d}H - d\left(TS\right) = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T \quad \left(p = konst.\right)$$

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S \quad \left(T = konst.\right)$$

Evaluation of the Gibbs function

- From the value of ΔG, we can assess whether the reaction will take place under the considered conditions.
- **ΔG < 0** means that the products are more stable (they have a smaller G value) and the reaction will proceed **forward**.
- **ΔG > 0** means that the reactants are more stable and the reaction will proceed **in the reverse direction**.
- In any case, the reaction will eventually reach equilibrium and ΔG = 0!

Example 3.3

- Determine ΔG_r^o for calcite dissolution.

$$CaCO_3 => Ca^{2+} + CO_3^{2-}$$

  - $G_f^o(Ca^{2+}) = -553.54$ kJ /mol
  - $G_f^o(CO_3^{2-}) = -527.89$ kJ /mol
  - G_f^o(calcite) = −1129.26 kJ /mol

- What does this say about the nature of the reaction? And about the nature of equilibrium (if we know that the activity of ions in a solution under standard conditions is equal to 1)?

Example 3.4

- What will be the heat of reaction of calcite dissolution?

$$\Delta H^0_{f\,\mathrm{CaCO_3}} = -1206.9 \text{ kJ/mol}$$
$$\Delta H^0_{f\,\mathrm{Ca^{2+}}} = -542.8 \text{ kJ/mol}$$
$$\Delta H^0_{f\,\mathrm{CO_3^{2-}}} = -677.1 \text{ kJ/mol}$$

Example 3.5

- What will be the entropy change when calcite dissolves under standard conditions?
  - $S_f^o(Ca^{2+}) = -53.2$ J/K
  - $S_f^o(CO_3^{2-}) = -56.9$ J/K
  - S_f^o(calcite) = 92.9 J/K

Example 3.6 (final)

- What value will ΔG_r^{o} have for the dissolution of calcite if we calculate it from the value of H and S for the standard state (i.e. the previous two calculations).

Example 3.7

- Find (a) **the change in Gibbs function** and (b) **the total entropy change** during the polymorphic transformation of 1 mole of calcite to aragonite at 25 °C and 1 bar pressure.
- Gibbs function of calcite is –1128.84 kJ /mol and of aragonite is –1127.79 kJ /mol.

Gibbs function

$$G = H - TS$$

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w$$

$$\mathrm{d}U = \mathrm{d}q - p\mathrm{d}V$$

$$\mathrm{d}q = T\mathrm{d}S$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

Gibbs function

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = T\mathrm{d}S - p\mathrm{d}V + p\mathrm{d}V + V\mathrm{d}p$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}p$$

$$\mathrm{d}G = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T$$

$$\mathrm{d}G = T\mathrm{d}S + V\mathrm{d}\mathrm{p} - T\mathrm{d}S - S\mathrm{d}T$$

$$\mathrm{d}G = V\mathrm{d}\mathrm{p} - S\mathrm{d}T$$

$$\mathrm{d}G = \left(\frac{\partial G}{\partial p}\right)_T \mathrm{d}p - \left(\frac{\partial G}{\partial T}\right)_p \mathrm{d}T$$

Dependence of Gibbs function on composition

general dendence of *G* on terms

$$\mathrm{d}G = \left(\frac{\partial G}{\partial T}\right)_{p,n} \mathrm{d}T + \left(\frac{\partial G}{\partial p}\right)_{T,n} \mathrm{d}p + \left(\frac{\partial G}{\partial n}\right)_{T,p} \mathrm{d}n$$

chemical potential

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p}$$

Dependence of *G* on *p*, *T* and composition for substance A

$$\boxed{\mathrm{d}G_{\mathrm{A}} = V_{\mathrm{A}}\mathrm{d}p - S_{\mathrm{A}}\mathrm{d}T + \mu_{\mathrm{A}}\mathrm{d}n_{\mathrm{A}}}$$

Dependence of chemical potential on composition

Gas solutions

$$\boxed{\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{o}} + RT \ln X_{\mathrm{A}}}$$

$$G_{\text{čisté}} = n_{\mathrm{A}}\mu_{\mathrm{A}}^{\mathrm{o}} + n_{\mathrm{B}}\mu_{\mathrm{B}}^{\mathrm{o}}$$

$$G_{\text{smíš}} = n_{\mathrm{A}}\mu_{\mathrm{A}} + n_{\mathrm{B}}\mu_{\mathrm{B}} = n_{\mathrm{A}}\left(\mu_{\mathrm{A}}^{\mathrm{o}} + RT \ln X_{\mathrm{A}}\right) + n_{\mathrm{B}}\left(\mu_{\mathrm{B}}^{\mathrm{o}} + RT \ln X_{\mathrm{B}}\right)$$

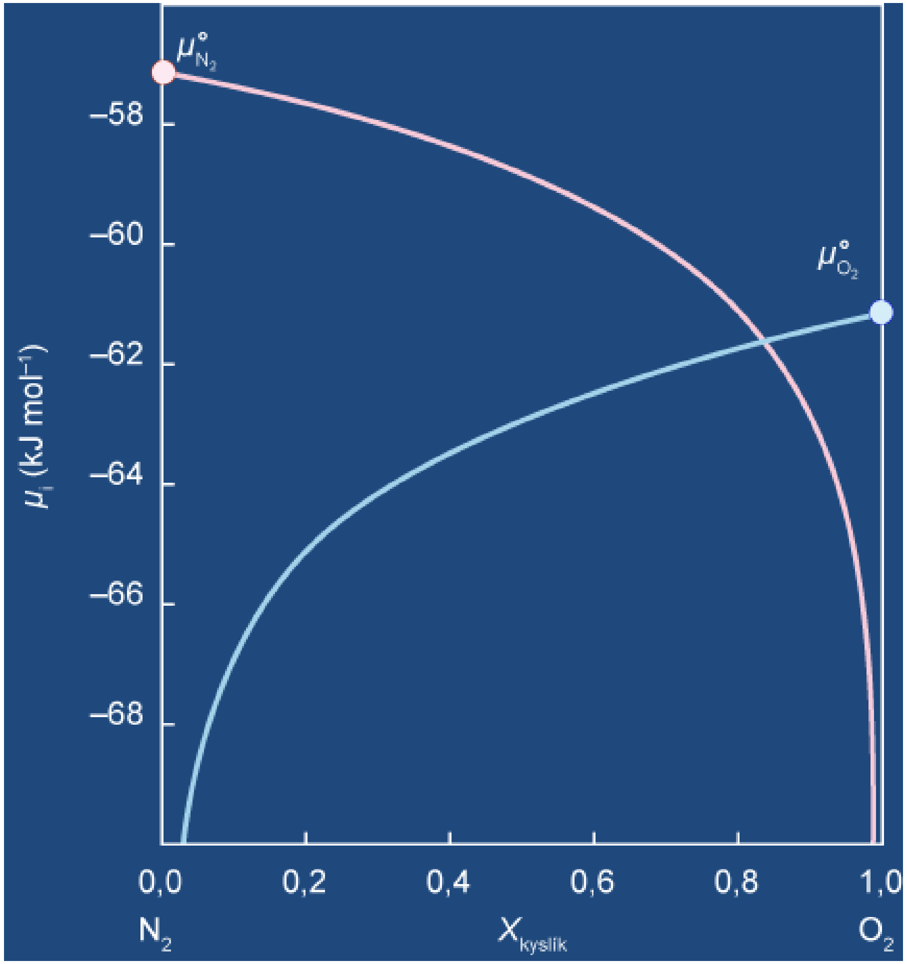
$$\Delta G_{\text{mís}} = G_{\text{smíš}} - G_{\text{čisté}} = n_{\mathrm{A}} RT \ln X_{\mathrm{A}} + n_{\mathrm{B}} RT \ln X_{\mathrm{B}}$$

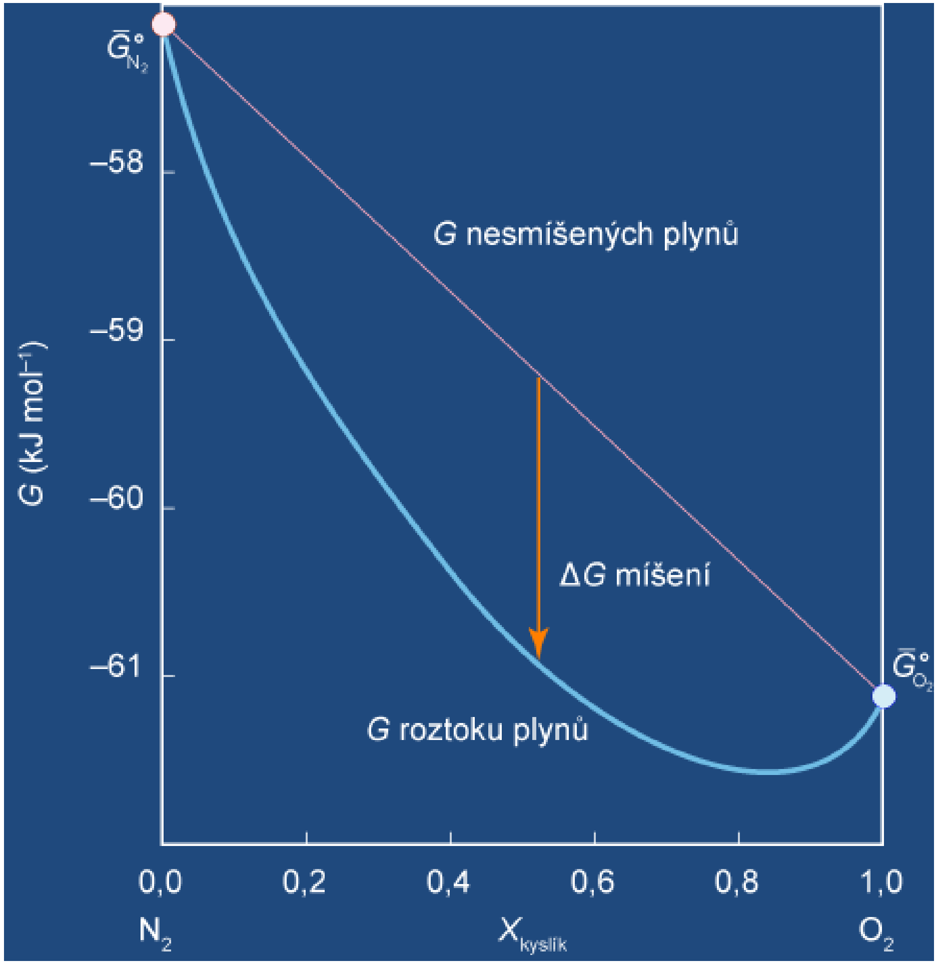
$$\Delta G_{\text{mís}} = nRT\left(X_{\mathrm{A}} \ln X_{\mathrm{A}} + X_{\mathrm{B}} \ln X_{\mathrm{B}}\right)$$

$0 < X_{\mathrm{A}}, X_{\mathrm{B}} < 1$; $\ln X_{\mathrm{A}}, \ln X_{\mathrm{B}} < 0$

expression $X_{\mathrm{A}} \ln X_{\mathrm{A}} + X_{\mathrm{B}} \ln X_{\mathrm{B}}$ is always negative, mixing gases always increases the total entropy

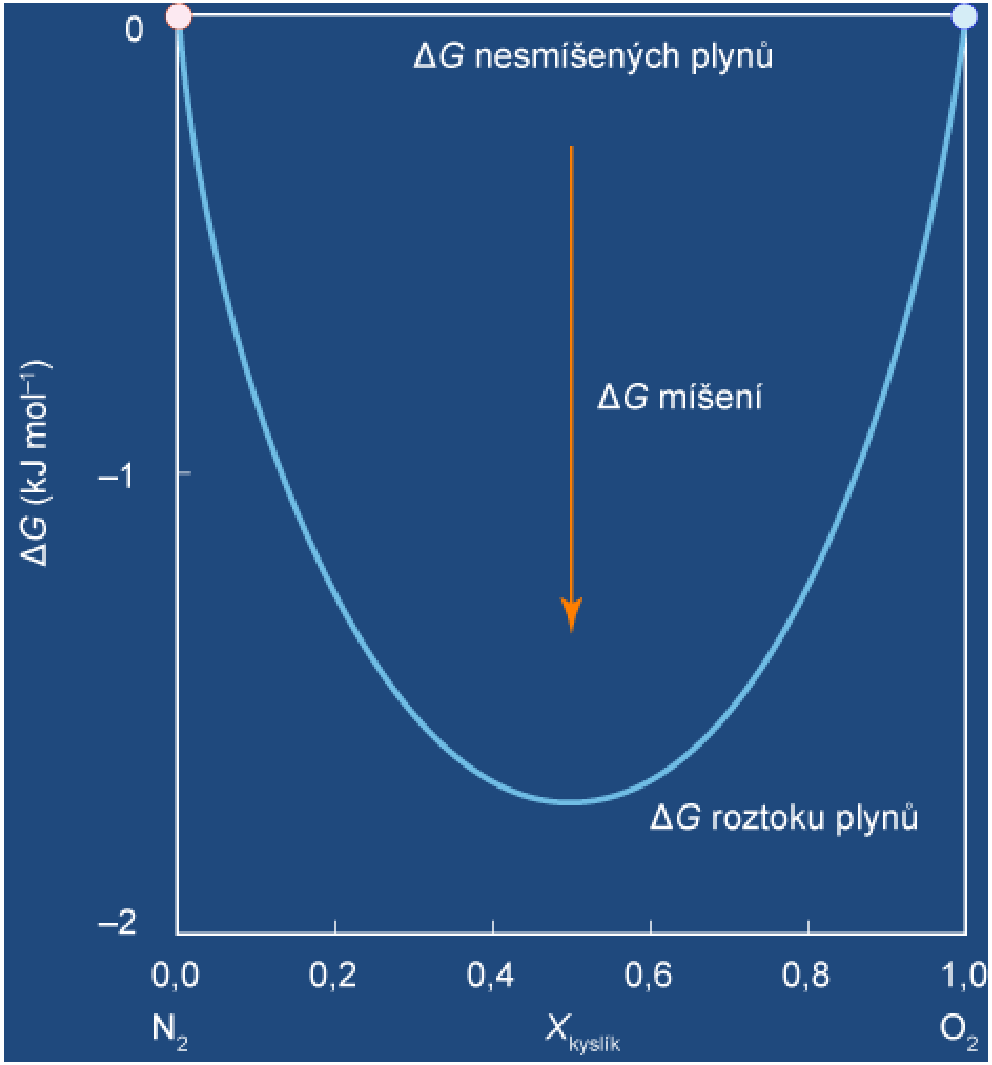
Gas solutions





The formation of a solution will always result in a reduction of chemical potential of individual gases and thus also to a decrease in the value of the Gibbs function of the mixture of gases (there will be an increase in total entropy).

Gas solutions



The formation of a solution will always result in a reduction of chemical potential of individual gases and thus also to a decrease in the value of the Gibbs function of the mixture of gases (there will be an increase in total entropy).

Summary

- The first law tells what processes take place in nature:
  Processes that conserve energy.

- The second law specifies the direction of the processes :
  Processes take place in the direction in which the total entropy increases.

Entropy is defined by the relation

$$S = \frac{q}{T}$$

The measure of total entropy change is the Gibbs function

$$G = H - TS$$

The relationship between the change in the Gibbs function and the total entropy:

$$dS_{\mathrm{celk}} = -\frac{\mathrm{d}G}{T}$$

Summary

The value of the Gibbs function depends on temperature, pressure and composition

$$\boxed{dG = -S\mathrm{d}T + V\mathrm{d}p + \mu\mathrm{d}n}$$

whereas the chemical potential μ of substance A depends on the composition

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{o}} + RT\ln X_{\mathrm{A}}$$

where μ° is equal to the value of the Gibbs function of one mole of pure substance.

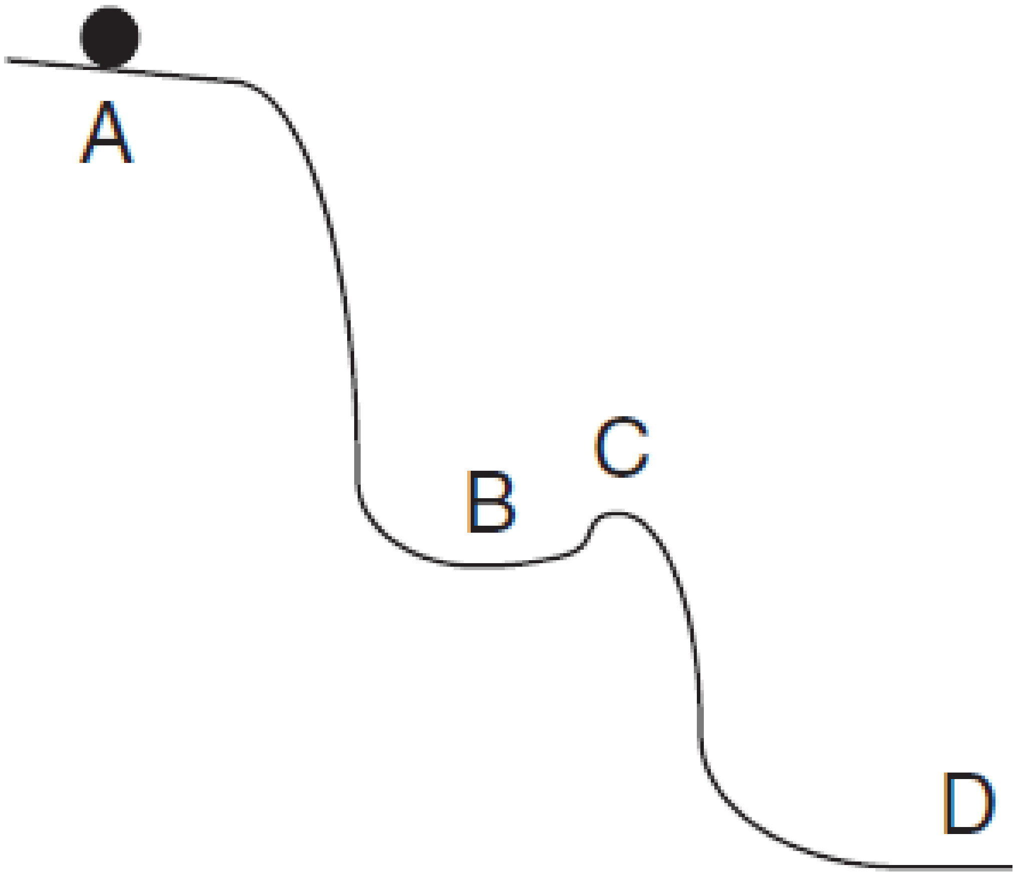
In real systems whose behavior differs from the ideal, concentration is replaced by activity, and deviations from ideality are concentrated into the activity coefficient:

$$\mu_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{o}} + RT\ln a_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{o}} + RT\ln \gamma_{\mathrm{A}} X_{\mathrm{A}} = \mu_{\mathrm{A}}^{\mathrm{o}} + RT\ln X_{\mathrm{A}} + RT\ln \gamma_{\mathrm{A}}$$

Another view

- We can also express the relationship as:
- $H = G + TS$
- The enthalpy of the substance then contains two components:
  - G – the energy component that can be released by the reaction and therefore indicates the instability of the substance (similar to potential energy).
  - TS – energy component that is inseparably bound in the internal disorder of the substance and is unavailable through chemical reactions.

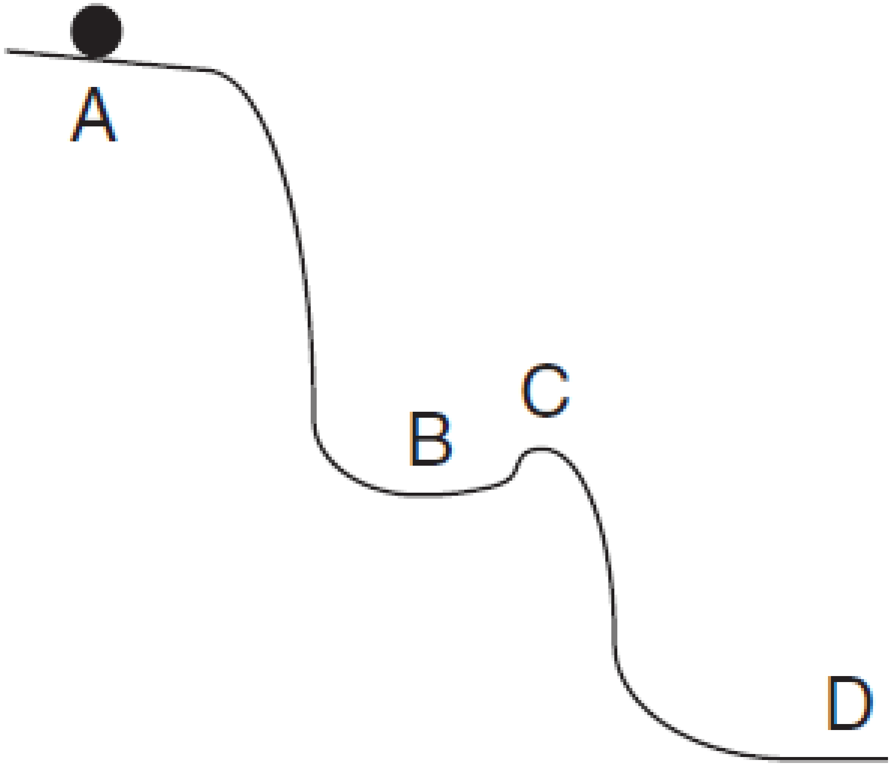
STABILITY



Adapted from Ryan (201

Stability

- The system tries to achieve the minimum value of the Gibbs function for the given conditions

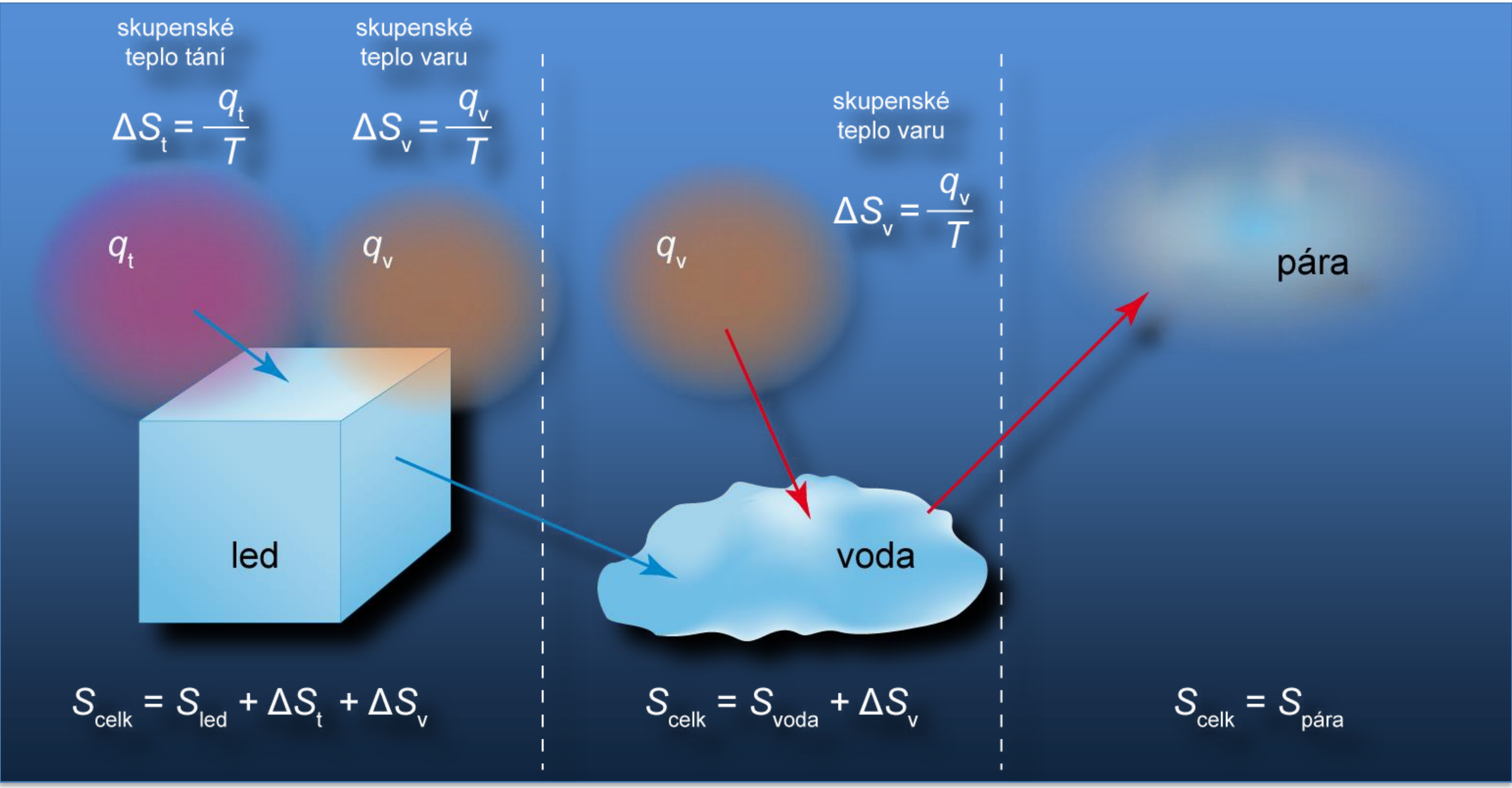


Adapted from Ryan (201

Stability

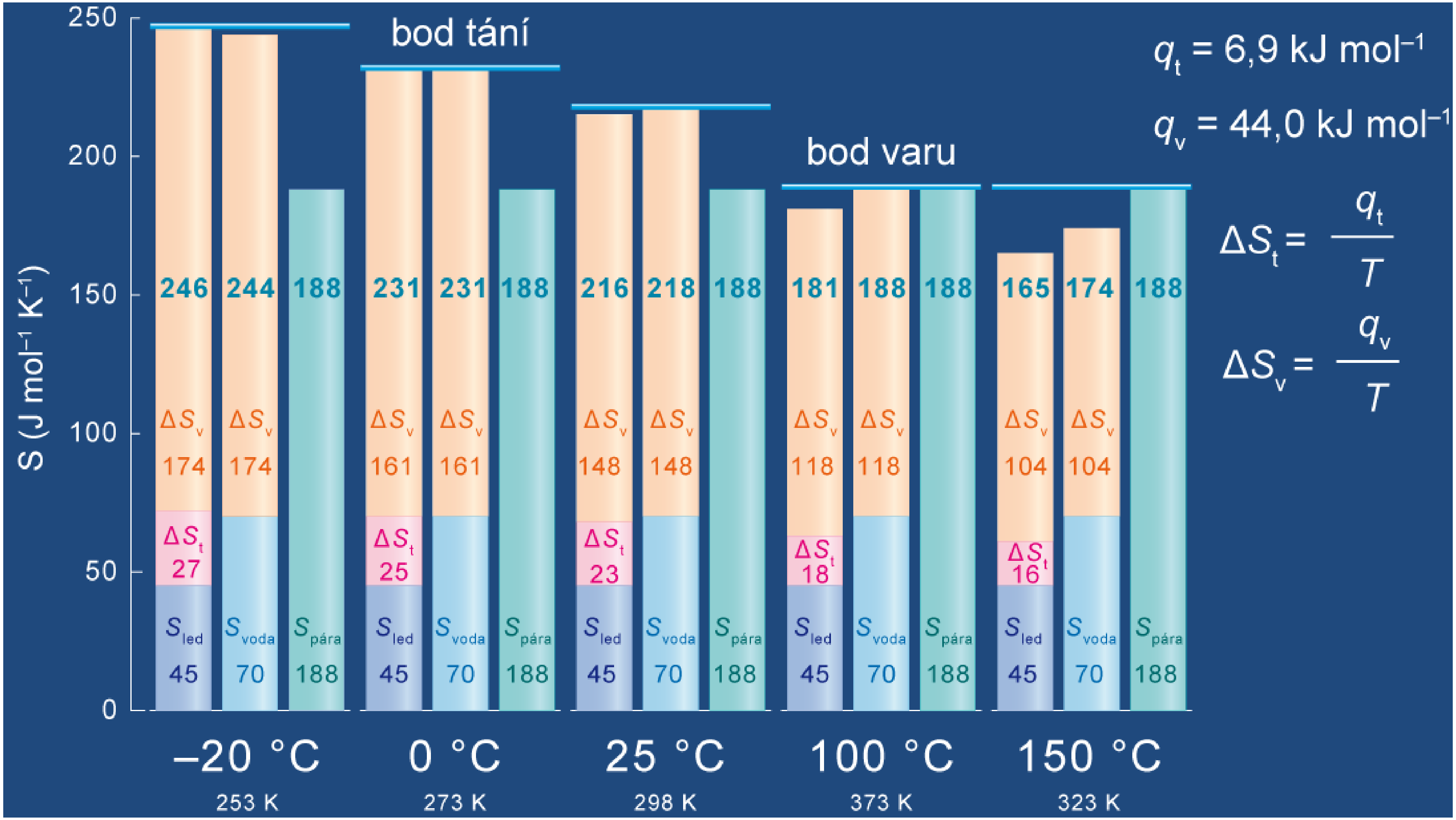
- If under the given conditions (*T* , *p* and composition) there is a state with a lower value of the Gibbs function, Nature tries to convert the system to this state, because this will increase the total entropy. **The system will be unstable under the given conditions** .
- If the system reached the state with the lowest value of the Gibbs function (the highest total entropy) under the given conditions, a change in the state of the system would lead to an increase in the value of the Gibbs function and thus to a decrease in the total entropy. **The system will be stable under the given conditions.**

Comparison of total entropies



Entropy components of the system with H_2O in different states.

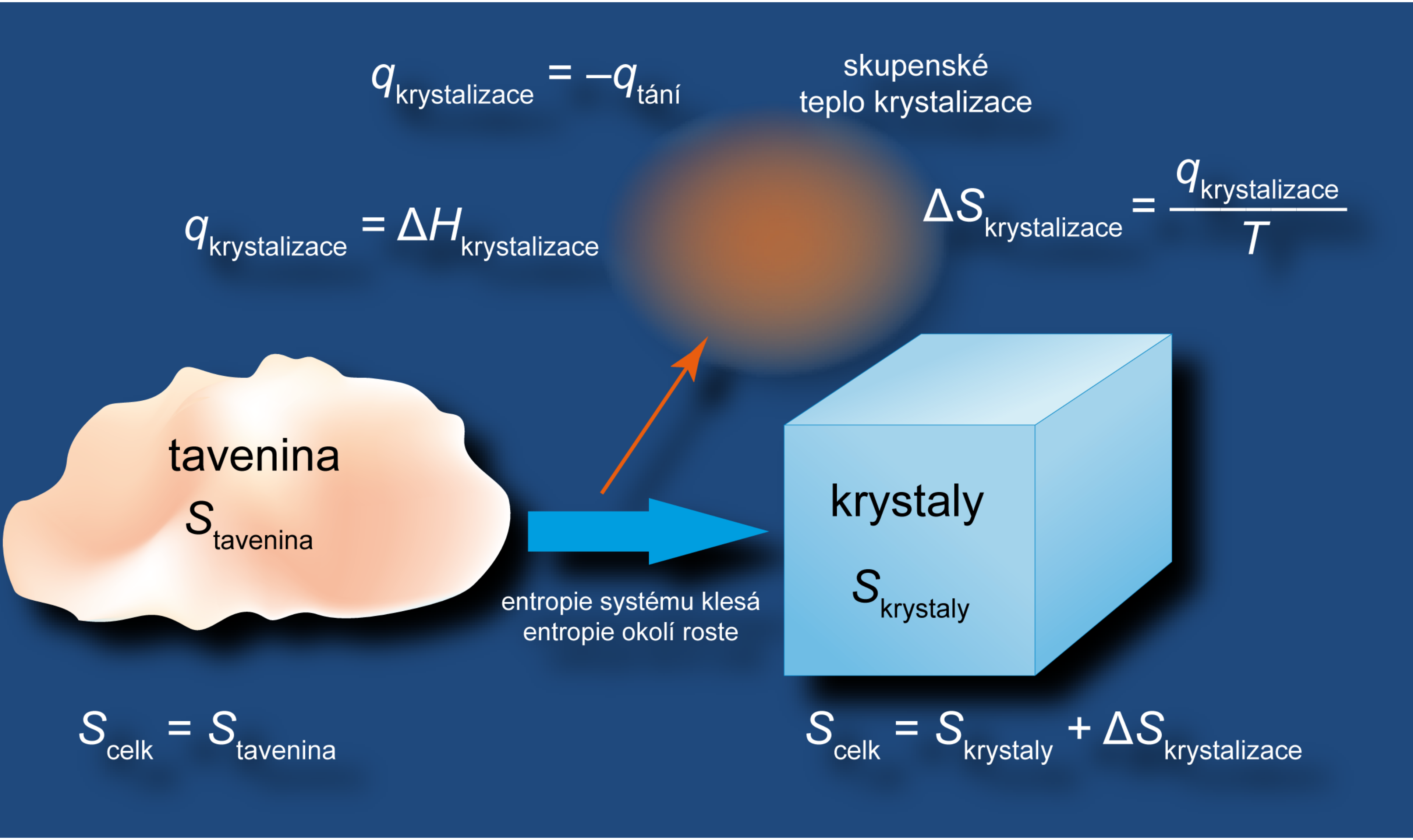
Total entropy of the system with H_2O



Comparison of total entropies of the system with H_2O in different states at different temperatures.

For the sake of illustration, the temperature dependence of the entropies of ice, water, steam and the heats of melting and boiling on the temperature was neglected. These changes in entropies depending on the temperature would slightly modify the individual values, but the basic relationships between the total entropies of the system in individual states would remain the same.

Comparison of system entropy during crystallization



$q_{\text{krystalizace}} = -q_{\text{tání}}$

skupenské
teplo krystalizace

$q_{\text{krystalizace}} = \Delta H_{\text{krystalizace}}$

$\Delta S_{\text{krystalizace}} = \dfrac{q_{\text{krystalizace}}}{T}$

tavenina

S_{tavenina}

krystaly

S_{krystaly}

entropie systému klesá
entropie okolí roste

$S_{\text{celk}} = S_{\text{tavenina}}$

$S_{\text{celk}} = S_{\text{krystaly}} + \Delta S_{\text{krystalizace}}$

Dependence of phase stability on temperature and pressure

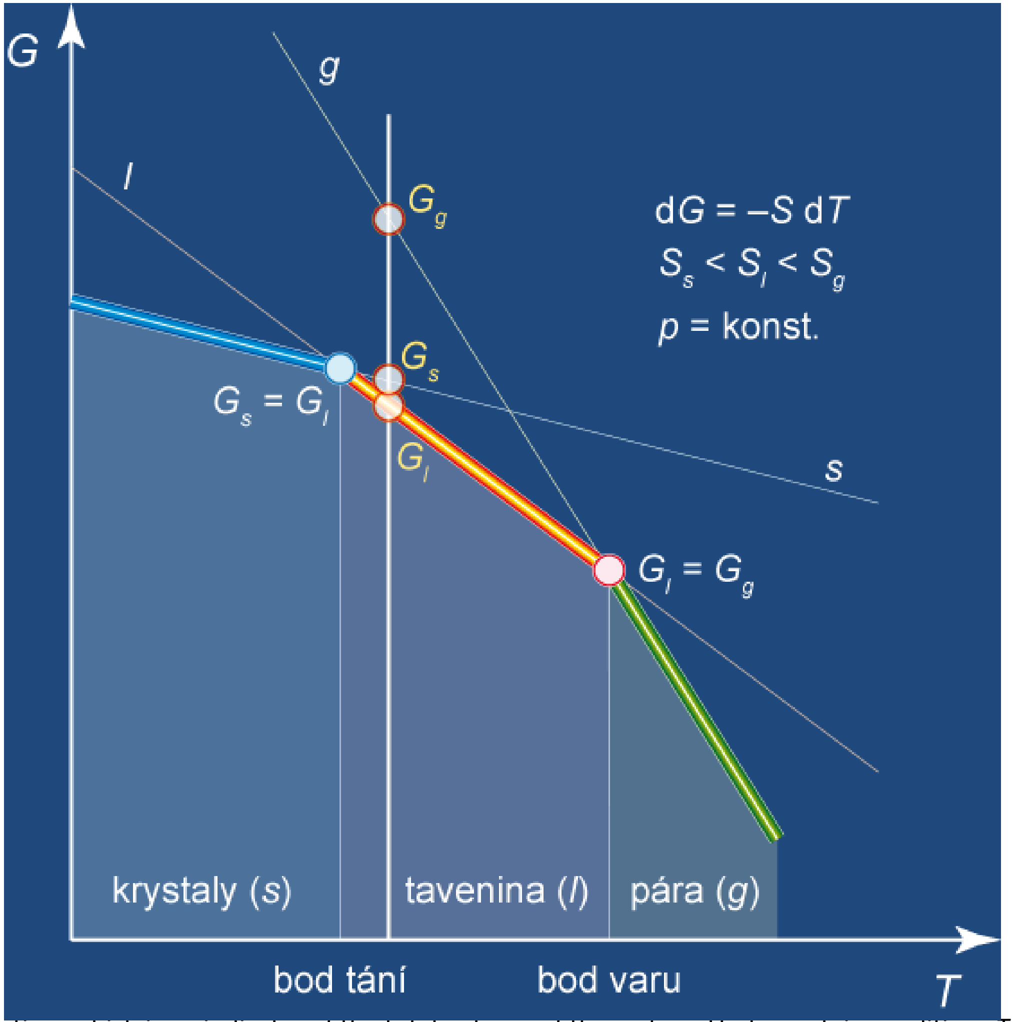
Temperature can be changed, pressure and composition remain constant.

T

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

$$\mathrm{d}G = -S\mathrm{d}T$$

$$G = G^{\circ} - S\left(T - T^{\circ}\right)$$



Stability is determined by the value of the Gibbs function, which is an indicator of the total entropy of the system. Under certain conditions *T* and *p*, the system chooses the state with the lowest value of the Gibbs function (highest total entropy).

As the temperature increases, the Gibbs function decreases in direct proportion to the negative value of the system's own entropy. For crystalline phases it decreases the slowest (low entropy value), for gaseous phases it decreases the fastest (highest entropy value). Therefore, at high temperatures, the least ordered phase is preferred.

Dependence of phase stability on temperature and pressure

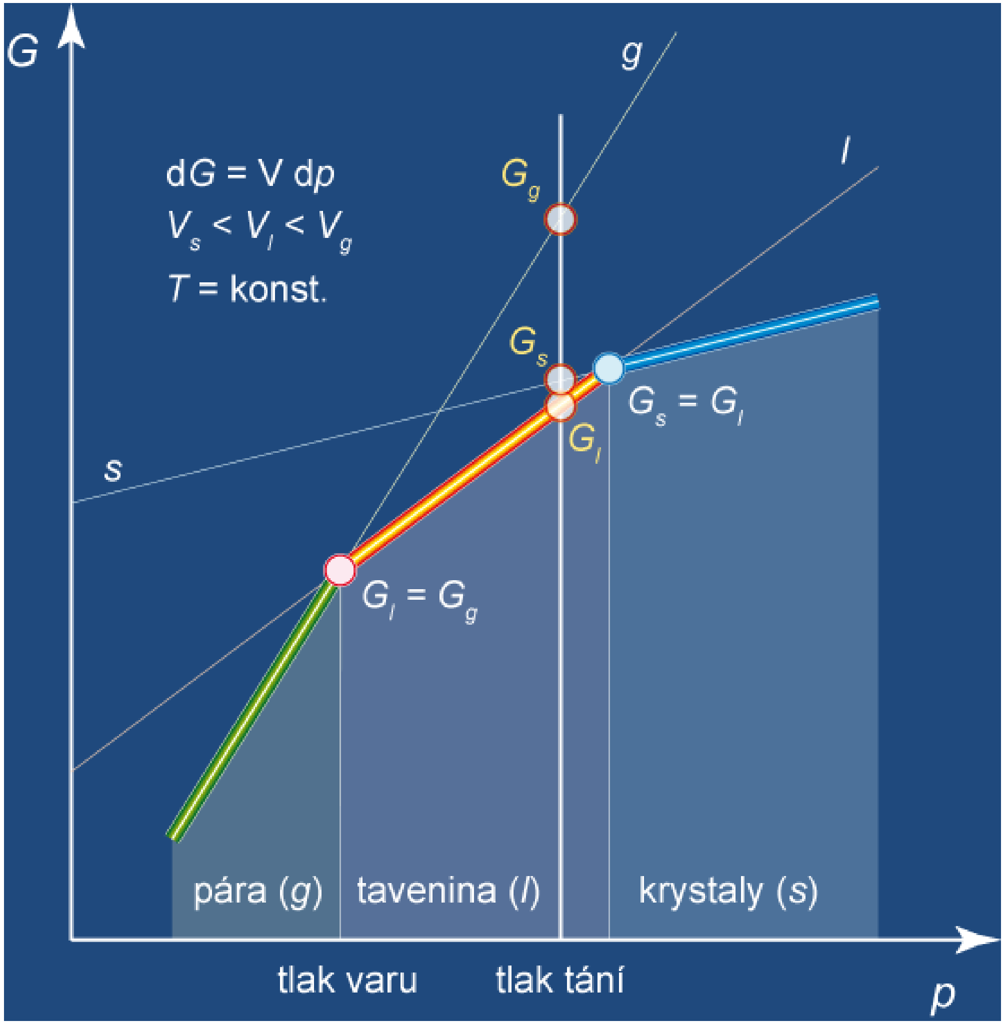
Pressure can be varied, temperature and composition remain constant.

P

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p$$

$$\mathrm{d}G = V\mathrm{d}p$$

$$G = G^{\mathrm{o}} + V\left(p - p^{\mathrm{o}}\right)$$



Stability is determined by the value of the Gibbs function, which is an indicator of the total entropy of the system. Under certain conditions *T* and *p,* the system chooses the state with the lowest value of the Gibbs function (highest total entropy).
With increasing pressure, the Gibbs function grows directly proportional to the volume of substances. It grows fastest for gases, slowest for solids. Therefore, at high pressures, the state with the smallest volume (the lowest value of the Gibbs function) is preferred.

Systems with variable phase composition

- chemical reactions
- melting in a multi-component system
- dissolution in water

Changes in the value of the chemical potentials of individual components and the values of the Gibbs function of individual phases occur not only as a result of changes in temperature and pressure, but also as a result of changes in the concentration of components in some or all phases.
Temperature and pressure are usually determined from outside the system, the concentration of components in individual phases can change not only by supplying components from outside the system and removing components from the system, but also by transitioning components between individual phases.

Derivation of basic relations

$$\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{C} + 2\mathrm{D}$$

For a model reaction that takes place at a certain temperature and pressure, it is possible to follow the evolution of the value of the Gibbs function depending on how "far" the reaction proceeds. The pressure and temperature do not change during the reaction and therefore the change in the value of the Gibbs function depending on the temperature and pressure will be zero. In the model course, only pure starting substances A and B are present in the system at the beginning, only pure products C and D are present in the system at the end of the reaction.
The course of the values of the Gibbs function, depending on how much of the starting substances have been transformed into products, also shows how the total entropy of the system changes.
According to the second law of thermodynamics, changes in the system will tend to achieve the lowest value of the Gibbs function and thus to achieve the maximum total entropy.

$$\mathrm{A} + 2\mathrm{B} \rightarrow 3\mathrm{C} + 2\mathrm{D}$$

To express the degree of transformation of starting substances into products, it is possible to use the so-called progress of the reaction (extent of reaction), which indicates how much of the path the system has traveled from starting substances to products.

$$\begin{aligned} &\text{na počátku:} && \xi = 0 \\ &\text{na konci:} && \xi = 1 \end{aligned}$$

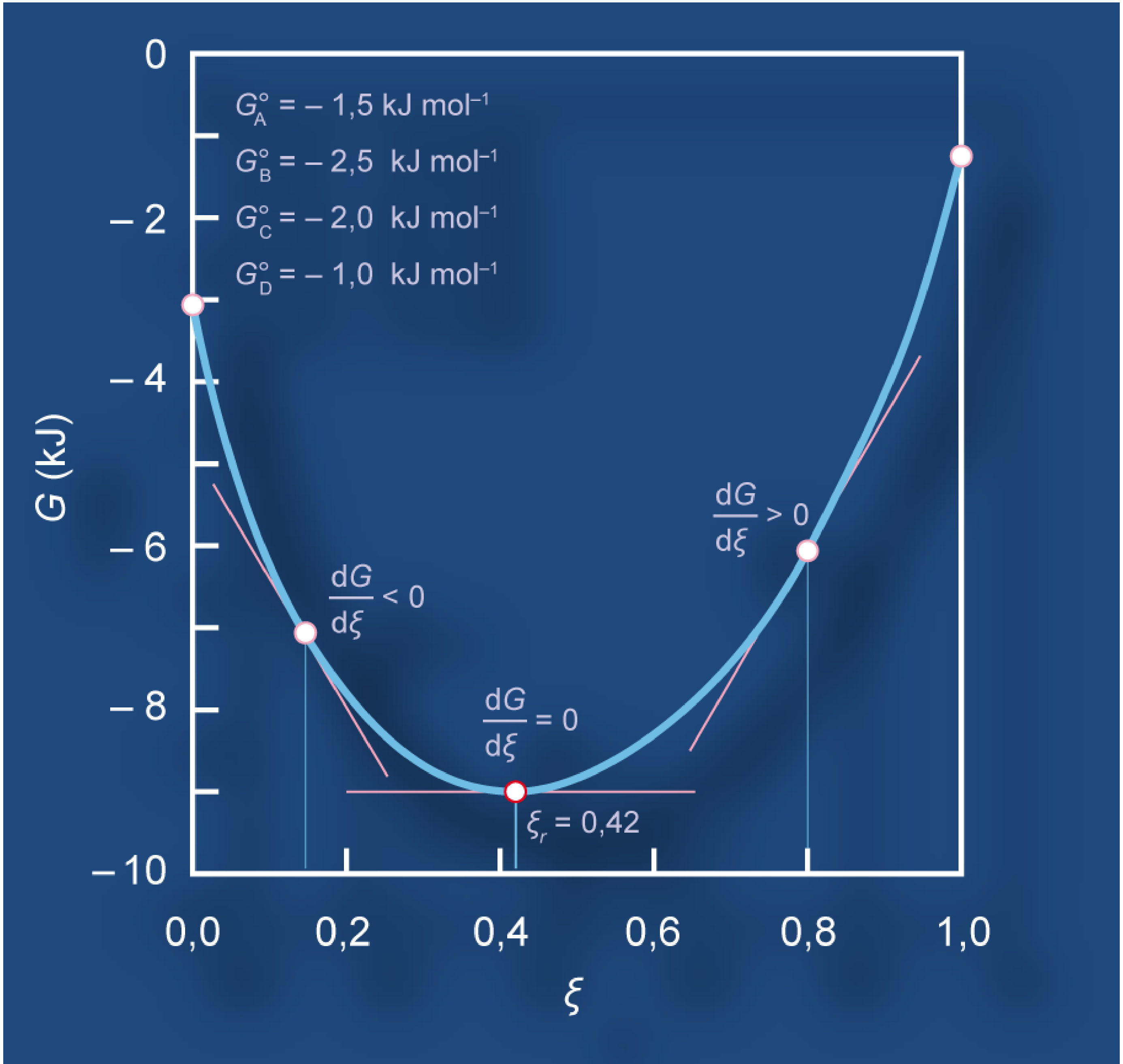
The change in the representation of the components in the system depending on the progress of the reaction ξ is then given by the relations

$$\begin{aligned} \mathrm{d}n_{\mathrm{A}} &= -\mathrm{d}\xi \\ \mathrm{d}n_{\mathrm{B}} &= -2\mathrm{d}\xi \\ \mathrm{d}n_{\mathrm{C}} &= +3\mathrm{d}\xi \\ \mathrm{d}n_{\mathrm{D}} &= +2\mathrm{d}\xi \end{aligned}$$

The value of the Gibbs function of the system at any moment is given by the sum of the values of the Gibbs function of the individual components

$$G_{\mathrm{syst}} = G_{\mathrm{A}} + G_{\mathrm{B}} + G_{\mathrm{C}} + G_{\mathrm{D}}$$

Dependence of the Gibbs function on the progress of the reaction



For the dependence of the Gibbs function on the progress of the reaction , we obtain

$$\frac{\mathrm{d}G}{\mathrm{d}\xi} = 3\mu_C + 2\mu_D - \mu_A - 2\mu_B$$

The value d *G* /d *ξ* represents the direction of the tangent to the dependence of the value of the Gibbs function on the progress of the reaction. If this direction is negative, then the further continuation of the reaction from left to right will lead to a decrease in the Gibbs function and the reaction will tend to continue. If the slope is positive, then the further continuation of the reaction would increase the value of the Gibbs function of the system. On the contrary, the reaction will tend to proceed from right to left.

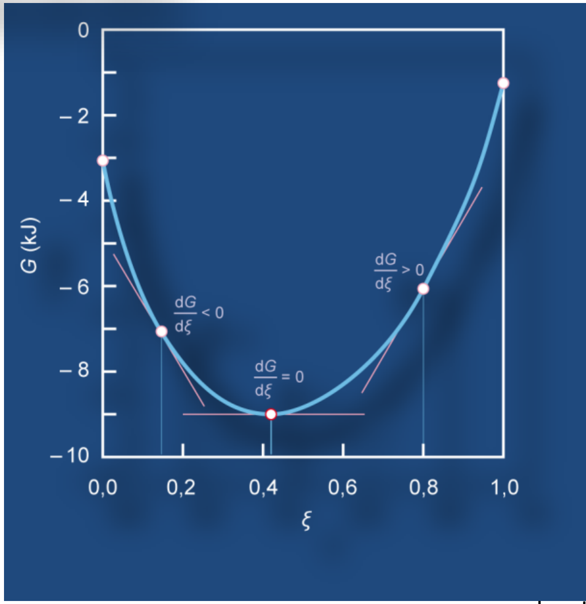
The minimum of the Gibbs function and thus the equilibrium will be reached at the point where this slope has a zero value.

$$\frac{\mathrm{d}G}{\mathrm{d}\xi} < 0 \quad \text{z leva do prava} \qquad \frac{\mathrm{d}G}{\mathrm{d}\xi} > 0 \quad \text{z prava do leva}$$

$$\frac{\mathrm{d}G}{\mathrm{d}\xi} = 0 \quad \text{rovnováha}$$

The direction of the dependence of the value of the Gibbs function on the progress of the reaction is referred to as the reaction Gibbs function ΔG_r

$$\Delta G_r = \frac{\mathrm{d}G}{\mathrm{d}\xi} = 3\mu_\mathrm{C} + 2\mu_\mathrm{D} - \mu_\mathrm{A} - 2\mu_\mathrm{B}$$



about

By substituting for chemical potentials and further modification

$$\Delta G_r = 3\left(\mu_{\mathrm{C}}^{\circ} + RT\ln a_{\mathrm{C}}\right) + 2\left(\mu_{\mathrm{D}}^{\circ} + RT\ln a_{\mathrm{D}}\right) - \left(\mu_{\mathrm{A}}^{\circ} + RT\ln a_{\mathrm{A}}\right) - 2\left(\mu_{\mathrm{B}}^{\circ} + RT\ln a_{\mathrm{B}}\right)$$

$$\Delta G_r = 3\mu_{\mathrm{C}}^{\circ} + 2\mu_{\mathrm{D}}^{\circ} - \mu_{\mathrm{A}}^{\circ} - 2\mu_{\mathrm{B}}^{\circ} + 3RT\ln a_{\mathrm{C}} + 2RT\ln a_{\mathrm{D}} - RT\ln a_{\mathrm{A}} - 2RT\ln a_{\mathrm{B}}$$

$$\Delta G_r = 3G_{\mathrm{C}}^{\circ} + 2G_{\mathrm{D}}^{\circ} - G_{\mathrm{A}}^{\circ} - 2G_{\mathrm{B}}^{\circ} + 3RT\ln a_{\mathrm{C}} + 2RT\ln a_{\mathrm{D}} - RT\ln a_{\mathrm{A}} - 2RT\ln a_{\mathrm{B}}$$

$$\Delta G_r = \Delta G_r^{\circ} + RT\ln a_{\mathrm{C}}^{3} + RT\ln a_{\mathrm{D}}^{2} - RT\ln a_{\mathrm{A}} - RT\ln a_{\mathrm{B}}^{2}$$

$$\Delta G_r = \Delta G_r^{\circ} + RT\ln\frac{a_{\mathrm{C}}^{3}a_{\mathrm{D}}^{2}}{a_{\mathrm{A}}a_{\mathrm{B}}^{2}}$$

$$\Delta G_r = \Delta G_r^{\circ} + RT\ln Q$$

$\Delta G^{\circ}{}_r$ is the **standard reaction Gibbs function** (or the standard value of the reaction Gibbs function) and is equal to the difference of the standard values of the Gibbs function of the substances on the right side and the substances on the left side of the chemical reaction. The coefficient *Q* is referred to as **the reaction quotient** and is equal to the product of the instantaneous activities (concentrations) of the products multiplied by the respective coefficients, divided by the product of the activities (concentrations) of the reactants multiplied by the respective coefficients.

$$\Delta G_r^{\circ} = 3G_{\mathrm{C}}^{\circ} + 2G_{\mathrm{D}}^{\circ} - G_{\mathrm{A}}^{\circ} - 2G_{\mathrm{B}}^{\circ}$$

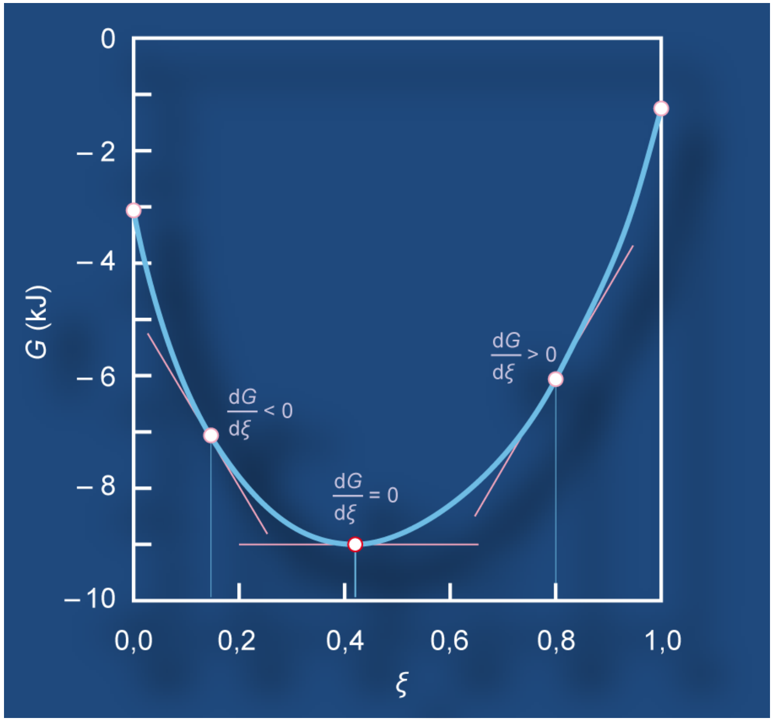
$$Q = \frac{a_{\mathrm{C}}^{3}a_{\mathrm{D}}^{2}}{a_{\mathrm{A}}a_{\mathrm{B}}^{2}}$$

For balance

$$\frac{\mathrm{d}G}{\mathrm{d}\xi} = \Delta G_r = 0$$

$$0 = \Delta G_r^{\mathrm{o}} + RT\ln\frac{a_{\mathrm{C}}^{3}a_{\mathrm{D}}^{2}}{a_{\mathrm{A}}a_{\mathrm{B}}^{2}} = \Delta G_r^{\mathrm{o}} + RT\ln K$$

$$\ln K = \frac{-\Delta G_r^{\mathrm{o}}}{RT}$$



At equilibrium, the reaction Gibbs function is equal to zero, the system tends to remain in this state with the lowest value of the Gibbs function. The reaction quotient *Q* under these conditions becomes the equilibrium constant *K* . The equilibrium constant is uniquely determined by the difference in the standard values of the Gibbs function of the substances that participate in the reaction.
This key relationship applies to any transformations that result in a change in the concentrations of some or all components of the system. In essence, the change in the value of the Gibbs function of the system is not the "connecting" and "disconnecting" of the components of the system (atoms, ions, molecules), but the change in their concentrations as a result of this "connecting" and "disconnecting", i.e. the change in dilution and the associated change in the Gibbs function relevant components in the form of a *RT member* ln *and* .

If the model reaction did not take place in an environment where at least some components form a solution - there would be no change in concentration, the values of the Gibbs function would remain constant. Under the given conditions of temperature and pressure, the combination of substances that have a lower value of the Gibbs function (A and B or C and D) at the given temperature and pressure would clearly be preferred . Only by changing the external conditions (temperature, pressure or both) can a state be reached where the mentioned substances can be in equilibrium with each other. If the given substances form a solution, then the system can reach the minimum of the Gibbs function also by internal changes in the system by changing the concentration of the components due to chemical reactions, dissolution or melting and crystallization.

Dependence of the equilibrium constant on temperature

$$\ln K = \frac{-\Delta G_r^{\circ}}{RT}$$

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\mathrm{d}}{\mathrm{d}T}\left(\frac{-\Delta G_r^{\circ}}{RT}\right)$$

$$\mathrm{d}\ln K = \frac{\Delta H_r^{\circ}}{R}\frac{\mathrm{d}T}{T^2}$$

The given relationship shows how the equilibrium constant *K* (more precisely , ln *K*) when the temperature changes by d *T* . The value Δ *H* ° *r* is the standard reaction enthalpy – the difference in the enthalpies of the substances on the right and left side of the reaction.

$$K_T = K_{T^{\circ}} e^{-\frac{\Delta H_r^{\circ}}{R}\left(\frac{1}{T}-\frac{1}{T^{\circ}}\right)}$$

Van't Hoff's equation

To express the change in K with temperature change

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta H_r}{RT^2}$$

We can integrate on

$$\log K_{T_1} - \log K_{T_2} = \frac{-\Delta H_r^0}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Example 3.8

- What is the value of the solubility product (= equilibrium dissolution constant) of calcite at 25 °C and 1 atm ?

$$\Delta G^0_{f\,\mathrm{CaCO_3}} = -1128.8\ \mathrm{kJ/mol}$$

$$\Delta G^0_{f\,\mathrm{Ca^{2+}}} = -553.6\ \mathrm{kJ/mol}$$

$$\Delta G^0_{f\,\mathrm{CO_3^{2-}}} = -527.8\ \mathrm{kJ/mol}$$

Example 3.9

- In underground karst systems, the average temperature is 10 °C. What will be the corresponding dissociation constant for calcite?

$$\Delta H^0_{f\,\mathrm{CaCO_3}} = -1206.9 \text{ kJ/mol}$$

$$\Delta H^0_{f\,\mathrm{Ca^{2+}}} = -542.8 \text{ kJ/mol}$$

$$\Delta H^0_{f\,\mathrm{CO_3^{2-}}} = -677.1 \text{ kJ/mol}$$

Summary

Basic principles applicable to the assessment of system stability and transformations:

1. in any process, energy is conserved
2. in any process the total entropy increases

It then follows from these two principles

$$dS_{celk} > 0 \text{ a tedy } dG < 0$$

It then holds for the Gibbs function and related quantities

$$dS_{celk} = -\frac{dG}{T} \qquad G = H - TS$$

$$dG = Vdp - SdT + \mu dn \qquad \mu = \mu^\circ + RT \ln X$$

$$\ln K = \frac{-\Delta G_r^\circ}{RT} \qquad K_T = K_{T^\circ} e^{\frac{-\Delta H_r^\circ}{R}\left(\frac{1}{T} - \frac{1}{T^\circ}\right)}$$

With the help of these relationships, any problem of balance and transformations can be solved.

EVROPSKÁ UNIE
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MINISTERSTVO ŠKOLSTVÍ,
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