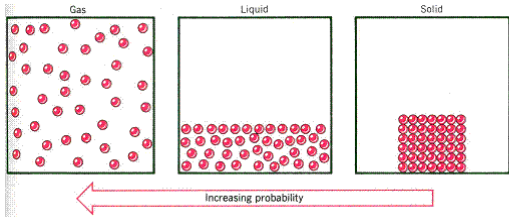# A folyamatok iránya, entrópia

Figure 14.7. *In the absence of attractive forces, the most likely distribution of molecules in a container corresponds to that of a gas. Less likely is the distribution in a liquid, which places all the molecules at one end of the container. Least likely is the highly ordered stacking of molecules that we find in a solid.*
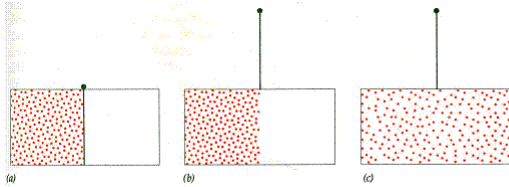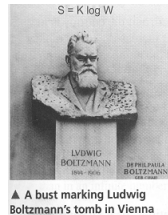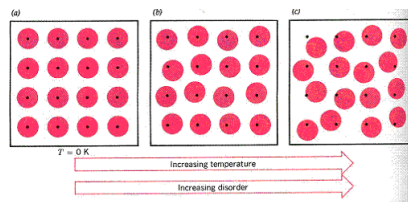
Általános megfontolás:

Entalpiaváltozás	Entrópiaváltozás	Spontán a reakció?
Exotem ($\Delta H < 0$)	$\Delta s > 0$	Igen, $\Delta G < 0$
Exotem ($\Delta H < 0$)	$\Delta s < 0$	Ha $\lvert T * \Delta S \rvert < \lvert \Delta H \rvert$
Endoterm ($\Delta H > 0$)	$\Delta s > 0$	Ha $T * \Delta S > \Delta H$
Endoterm ($\Delta H > 0$)	$\Delta s < 0$	Nem, $\Delta G < 0$

Figure 14.8. *The expansion of a gas into a vacuum. (a) A gas in a container separated from a vacuum by a removable wall. (b) At the moment the wall is removed, the gas finds itself in an improbable particle distribution within the now larger container. (c) The gas expands spontaneously to a more probable distribution of its molecules.*

Pl. szilárd anyag olvadásakor:

Figure 14.11. *The melting of a solid is accompanied by an enthalpy increase and an entropy increase, so both ΔH and ΔS are positive quantities.*

T nő, rendezetlenség nő

A bust marking Ludwig Boltzmann's tomb in Vienna

entrópia def.: $S = k_B \ln W$ Boltzmann

Néhány anyag standard moláris entrópiája 25°C-on

Anyag	S^0, J/(mol*K)	Anyag	S^0, J/(mol*K)	Anyag	S^0, J/(mol*K)
Gázok		**Folyadék**		C(gyémánt)	2,4
NH_3	192,5	C_6H_6(benzol)	173,3	C (grafit)	5,7
Cl_2	223	CH_3CH_2OH	160,7	Na	51
CO_2	213,7	H_2O	69,0	$MgCO_3$	65,7
He	126,2	**Szilárd**		MgO	26,9
H_2	130,7	$CaCO_3$	92,9	NaCl	72,1
N_2	191,6	CaO	39,8	Sn (fehér)	51,6
O_2	205,1	Cu	33,2	Sn(szürke)	44,1

Példa: $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$
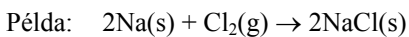
$\Delta S = 2*72 - (2*51 + 223) = -181$ J/K

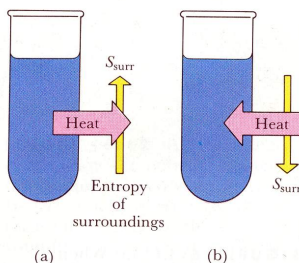A környezet entrópiaváltozását is figyelembe kell venni!

FIGURE 16.10 (a) In an exothermic process, heat escapes into the surroundings and increases their entropy. (b) In an endothermic process, the entropy of the surroundings decreases.
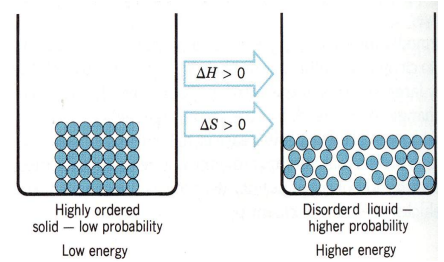
$\Delta S_{körny} = -\Delta H/T$

Visszatérve fenti NaCl-példánkra

$\Delta S_{körny} = -(-2*413000)$ J / 298 K = 2772 J/K

$\Sigma(\Delta S) = -181 + 2772 = 2591$ J/K

Így már, a teljes változás bőven pozitív ....

II főtétel: spontán változás akkor lehetséges, ha a teljes entrópia (rendszeré + környezeté) nő!

A szabadentalpia

Praktikus összevonásként bevezetjük a szabadentalpiát:

$G = H - TS$

G már formailag a rendszerre definiálható, változása negatív kell legyen. Spontán változás: $\Delta G < 0$

Képződési szabadentalpiák táblázatokban. Tképp nem független adatok, fenti H és S adatokból adódnak.

Egyensúlyban: a szabadenergiának MINIMUMA van.
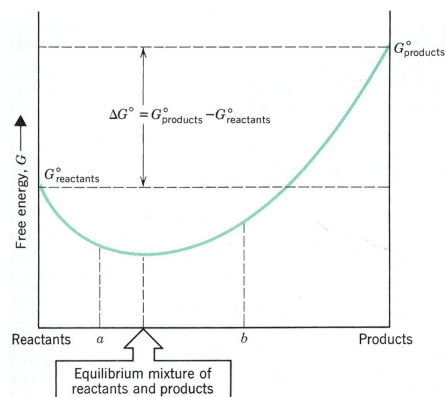
Figure 14.13. *The variation in the free energy of a homogeneous chemical system as the reaction proceeds from pure reactants on the left to pure products on the right. The minimum on the curve marks the position of equilibrium. If the system has a composition corresponding to point a, the reaction is spontaneous in the forward direction. If the composition corresponds to point b, the reaction is spontaneous in the reverse direction.*

Néhány anyag standard képződési szabadentalpiája (25⁰ C, 1 atm)

| Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)	Substance	ΔG_f° (kJ/mol)
$Al(s)$	0	$HCN(g)$	+124.7	$CuSO_4 \cdot 5H_2O(s)$	−1879.7	$N_2O_5(g)$	+115
$AlCl_3(s)$	−629	$CH_4(g)$	−50.6	$F_2(g)$	0	$HNO_3(l)$	−79.9
$Al_2O_3(s)$	−1577	$C_2H_2(g)$	+209	$HF(g)$	−273	$O_2(g)$	0
$Al_2(SO_4)_3(s)$	−3100	$C_2H_4(g)$	+68.2	$H_2(g)$	0	$O_3(g)$	+163
$As(s)$	0	$C_2H_6(g)$	−33	$H_2O(l)$	−237	$P(s, \text{white})$	0
$AsH_3(g)$	+68.9	$C_3H_8(g)$	−23	$H_2O(g)$	−228	$P_4O_{10}(s)$	−2698
$As_4O_6(s)$	−1153	$C_4H_{10}(g)$	−17.0	$H_2O_2(l)$	−120.3	$H_3PO_4(s)$	−1119
$As_2O_5(s)$	−782	$C_6H_6(l)$	+124.3	$I_2(s)$	0	$K(s)$	0
$Ba(s)$	0	$CH_3OH(l)$	−166	$I_2(g)$	+19.3	$KCl(s)$	−409.1
$BaCO_3(s)$	−1139	$C_2H_5OH(l)$	−175	$HI(g)$	+1.30	$Si(s)$	0
$BaCl_2(s)$	−810.8	$HCHO_2(g)$ (formic acid)	335	$Fe(s)$	0	$SiH_4(g)$	+52.3
$BaO(s)$	−525.1			$Fe_2O_3(s)$	−741.0	$SiO_2(s, \text{alpha})$	−856
$BaSO_4(s)$	−1353	$HC_2H_3O_2(l)$ (acetic acid)	−392	$Fe_3O_4(s)$	−1015.4	$Na(s)$	0
$Br_2(l)$	0			$Pb(s)$	0	$NaF(s)$	−545
$Br_2(g)$	+3.11	$HCHO(g)$ (formaldehyde)	−102.5	$PbO(s, \text{yellow})$	−187.9	$NaCl(s)$	−384
$HBr(g)$	−53.1			$PbO_2(s)$	−219	$NaBr(s)$	−349
$Ca(s)$	0	$CH_3CHO(g)$ (acetaldehyde)	−129	$Pb(OH)_2(s)$	−420.9	$NaI(s)$	−286
$CaCO_3(s)$	−1129			$PbSO_4(s)$	−811.3	$NaHCO_3(s)$	−852
$CaCl_2(s)$	−748.1	$(CH_3)_2CO(l)$ (acetone)	−155.4	$Li(s)$	0	$Na_2CO_3(s)$	−1048
$CaO(s)$	−604.2			$LiCl(s)$	−384.4	$Na_2O_2(s)$	−447.7
$Ca(OH)_2(s)$	−896.6	$C_6H_5CO_2H(s)$ (benzoic acid)	−245.3	$Mg(s)$	0	$NaOH(s)$	−379.5
$Ca_3(PO_4)_2(s)$	−3852			$MgCl_2(s)$	−592.5	$Na_2SO_4(s)$	−1270.2
$CaSO_4(s)$	−1320	$CO(NH_2)_2(s)$ (urea)	−197.3	$MgCl_2 \cdot 2H_2O(s)$	−1118	$S(s, \text{rhombic})$	0
$CaSO_3 \cdot 2H_2O(s)$	−1555			$Mg(OH)_2(s)$	−833.9	$SO_2(g)$	−300
$CaSO_4 \cdot \frac{1}{2}H_2O(s)$	−1435	$Cl_2(g)$	0	$Mn(s)$	0	$SO_3(g)$	−370
$CaSO_4 \cdot 2H_2O(s)$	−1796	$HCl(g)$	−95.4	$MnSO_4(s)$	−956	$H_2SO_4(l)$	−689.9
$C(s, \text{graphite})$	0	$HCl(aq)$	−131.2	$KMnO_4(s)$	−737.6	$Sn(s, \text{white})$	0
$C(s, \text{diamond})$	+2.9	$Cr(s)$	0	$N_2(g)$	0	$SnCl_4(l)$	−440.2
$CCl_4(l)$	−65.3	$Cr_2O_3(s)$	−1059	$NH_3(g)$	−17	$SnO_2(s)$	−519.6
$CO(g)$	−137	$K_2Cr_2O_7(s)$	−1864	$N_2H_4(l)$	+149.4	$Zn(s)$	0
$CO_2(g)$	−395	$Cu(s)$	0	$NH_4Cl(s)$	−202.9	$ZnO(s)$	−318.3
$CO_2(aq)$	−386.02	$CuCl_2(s)$	−131	$NO(g)$	+86.8	$ZnSO_4(s)$	−874.5
$H_2CO_3(aq)$	−623.16	$CuO(s)$	−127	$NO_2(g)$	+51.9		
$CS_2(l)$	+65.3	$Cu_2S(s)$	−86.2	$N_2O(g)$	+104		
$CS_2(g)$	+67.2	$CuS(s)$	−53.6	$N_2O_4(g)$	+97.9		
		$CuSO_4(s)$	−661.8				

Entrópia, szabadentalpia (összefogl.): www.chem.uncc.edu/faculty/murphy/1252/Chapter19B/sld016.htm

The Second Law of Thermodynamics

- For an isolated system, the First Law dictates that: $\Delta H = 0$
- For a spontaneous process, the system must evolve to a state with higher probability:
$$W_2 > W_1$$
- From Boltzmann's equation, $S_2 > S_1$ or $\Delta S > 0$
- The universe is an isolated system, so
  spontaneous process: $\Delta S_{univ} > 0$

Entropy of Solids, Liquids, and Gases

The entropy per mole of a substance depends on its physical state.
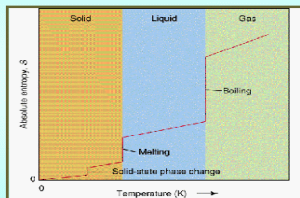
Estimating Entropy Changes

Entropy generally increases when -

- A substance goes from the solid to the liquid phase or liquid to gas:
  $H_2O(l) \rightarrow H_2O(g)$ $\Delta S^\circ = +119$ J/K
- A solution forms:
  $AgCl(s) \rightarrow Ag^+(aq) + Cl^-(aq)$ $\Delta S^\circ = +34$ J/K
- Number of moles of gas increases.
  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta S^\circ = +160$ J/K

Chemical Reactions and the Second Law

The Second Law states:
$$\Delta S_{sys} + \Delta S_{surr} > 0$$
Using the result from the previous slide:
$$\Delta S_{sys} - \frac{\Delta H_{sys}}{T} > 0$$
In terms of the system only, a spontaneous process must satisfy:
$$\Delta H - T\Delta S < 0$$

The Free Energy

The Gibbs Free Energy is defined as:
$$G = H - TS$$
At constant T and P, the change in free energy is:
$$\Delta G = G_2 - G_1 = H_2 - TS_2 - (H_1 - TS_1)$$
$$\Delta G = \Delta H - T\Delta S$$
For a spontaneous reaction: $\boxed{\Delta G < 0}$

Standard Free Energy of Reaction

The ΔG° of a reaction at 25° can be determined using Standard Free Energies of Formation:
$$\Delta G^\circ = \sum n\, \Delta G_f^\circ(\text{products}) - \sum n\, \Delta G_f^\circ(\text{reactants})$$
What is ΔG° at 25°C for the reaction:
$$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$$
$\Delta G^\circ = 2\, \Delta G_f^\circ(NH_3,g) - \Delta G_f^\circ(N_2,g) - 3\, \Delta G_f^\circ(H_2,g)$
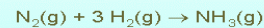$= 2(-16.66 \text{ kJ}) - 0 - 3(0) = -33.32 \text{ kJ}$

Temperature and Spontaneity

At temperatures other than 25°C, we use:
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
and assume: $\Delta H^\circ \approx \Delta H^\circ(25°)$; $\Delta S^\circ \approx \Delta S^\circ(25°)$

Determine ΔG° at 300°C for:
$$N_2(g) + 3 H_2(g) \rightarrow NH_3(g)$$
$\Delta H^\circ = -92.38$ kJ; $\Delta S^\circ = -198.3$ J/K
$\Delta G^\circ = -92.38$ kJ $- 573$ K$(-0.1983$ kJ/K$) = 22$ kJ

Free Energy and Equilibrium

The change in G during a reaction is related to the standard change, ΔG°, by
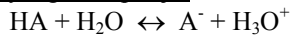$$\Delta G = \Delta G^\circ + RT \ln Q$$
where Q is the reaction quotient.

At equilibrium: $\Delta G = 0$ and $Q = K_{eq}$:
$$\Delta G^\circ = -RT \ln K_{eq} \quad \text{or} \quad K_{eq} = e^{-\Delta G^\circ / RT}$$

Egyensúly vizes elektrolitoldatokban

Gyenge sav pH-ja:

$HA + H_2O \leftrightarrow A^- + H_3O^+$

$x = H_3O^+ = A^-$; $K = x^2/(c_0-x) \approx x^2/c_0$ $x = \dots$

Néhány gyenge sav ionizációs állandója, ill. pKa értéke

http://www.cem.msu.edu/~reusch/VirtualText/acidity.htm

Ionization Constants of Inorganic Monoprotic Acids

Common Name	Formula	Acidity Constant	pKa
perchloric acid	$HClO_4$	*ca.* 10^{10}	*ca.* -10
hydrogen iodide	HI	*ca.* 10^9	*ca.* -9
hydrogen bromide	HBr	*ca.* 10^9	*ca.* -9
hydrogen chloride	HCl	*ca.* 10^7	*ca.* -7
nitric acid	HNO_3	*ca.* 200	*ca.* -2
thiocyanic acid	HSCN	70	-1.85
hydronium ion	H_3O^+	55	-1.74
chloric acid	$HClO_3$	10	-1.0
iodic acid	HIO_3	0.18	0.75
hypophosphorous acid	$H_2P(O)OH$	10^{-2}	2.0
hydrogen fluoride	HF	$6.6 * 10^{-4}$	3.2
nitrous acid	HNO_2	$5.0 * 10^{-4}$	3.3
cyanic acid	HOCN	$3.54 * 10^{-4}$	3.45
hypochlorous acid	HOCl	$2.95 * 10^{-8}$	7.53
hypobromous acid	HOBr	$2.3 * 10^{-9}$	8.65
hydrocyanic acid	HCN	$5.8 * 10^{-10}$	9.25
hypoiodous acid	HOI	10^{-10}	10
hydrogen peroxide	H_2O_2	$2.5 * 10^{-12}$	11.6
water	H_2O	$1.82 * 10^{-16}$	15.74
ammonia	NH_3	*ca.* 10^{-34}	*ca.* 34

Ionization Constants of Inorganic Polyprotic Acids

Common Name	Formula	Acidity Constant	pKa
sulfuric acid	H_2SO_4 HSO_4^{-1}	$K_1 = 2.4 * 10^6$ $K_2 = 1.0 * 10^{-2}$	-6.62 1.99
chromic acid	H_2CrO_4 $HCrO_4^{-1}$	$K_1 = 3.55$ $K_2 = 3.36 * 10^{-7}$	-0.55 6.47
sulfurous acid	H_2SO_3 HSO_3^{-1}	$K_1 = 1.71 * 10^{-2}$ $K_2 = 5.98 * 10^{-8}$	1.77 7.22
phosphoric acid	H_3PO_4 $H_2PO_4^{-1}$ HPO_4^{-2}	$K_1 = 7.1 * 10^{-3}$ $K_2 = 6.2 * 10^{-8}$ $K_3 = 4.6 * 10^{-13}$	2.15 7.21 12.34
phosphorous acid	H_3PO_3 $H_2PO_3^{-1}$	$K_1 = 1.6 * 10^{-2}$ $K_2 = 6.3 * 10^{-7}$	1.8 6.2
pyrophosphoric acid	$H_4P_2O_7$ $H_3P_2O_7^{-1}$ $H_2P_2O_7^{-2}$ $HP_2O_7^{-3}$	$K_1 = 3 * 10^{-2}$ $K_2 = 4.4 * 10^{-3}$ $K_3 = 2.5 * 10^{-7}$ $K_4 = 5.6 * 10^{-10}$	1.52 2.36 6.60 9.25
carbonic acid	H_2CO_3 HCO_3^{-1}	$K_1 = 4.35 * 10^{-7}$ $K_2 = 4.69 * 10^{-11}$	6.36 10.33
hydrogen sulfide	H_2S HS^{-1}	$K_1 = 9 * 10^{-8}$ $K_2 = ca.10^{-15}$	6.97 *ca.*15
boric acid	H_3BO_3 $H_2BO_3^{-1}$ HBO_3^{-2}	$K_1 = 7.2 * 10^{-10}$ $K_2 = 1.8 * 10^{-13}$ $K_3 = 1.6 * 10^{-14}$	9.14 12.7 13.8

Bázisok

Base	Conjugate Acid	Equilibrium Reaction	Kb
Ammonia (NH_3)	NH_4^+	$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$	1.8×10^{-5}
Pyridine (C_5H_5N)	$C_5H_5NH^+$	$C_5H_5N + H_2O \leftrightarrow C_5H_5NH^+ + OH^-$	1.7×10^{-9}
Hydroxylamine (H_2NOH)	H_3NOX^+	$H_2NOH + H_2O \leftrightarrow H_3NOH^+ + OH^-$	1.1×10^{-8}
Methylamine (NH_2CH_3)	$NH_3CH_3^+$	$NH_2CH_3 + H_2O \leftrightarrow NH_3CH_3^+ + OH^-$	4.4×10^{-4}

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FIGYELEM! Gyakori megadási mód:

A B bázishoz konjugált BH^+ sav savi állandójának megadása

common method for evaluating the strength of bases is to report the acidities of the conjugate acids of the bases (these conjugate acids are often "onium" cations). The resulting pKa's are proportional to the base strength of the base.

A useful rule is: $pK_a + pK_b = 14$.

Ionization Constants of B-H^+ Onium Acids

Common Name	Formula	Acidity Constant	pKa
carboxylic acids	$R-CO_2H$	*ca.* 10^6	*ca.* -6
alcohols	$R-CH_2-OH$	*ca.* 10^2	*ca.* -2
aniline	$C_6H_5NH_2$	$2.5 * 10^{-5}$	4.6
pyridine	C_5H_5N	$6.3 * 10^{-6}$	5.2
hydroxyl amine	$HONH_2$	$1.3 * 10^{-6}$	5.9
ammonia	NH_3	$5.62 * 10^{-10}$	9.25
ethyl amine	$C_2H_5NH_2$	$2.0 * 10^{-11}$	10.7
piperidine	$(CH_2)_5NH$	10^{-11}	11.0

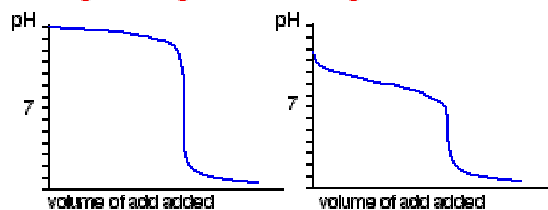Titration curves for strong acid v strong base
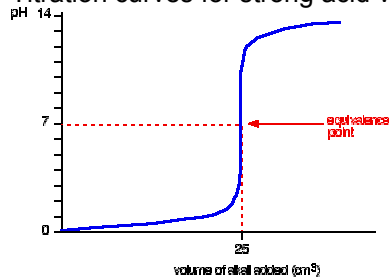
Hidrolízis láttuk: $K_aK_b = K_v = 10^{-14}$

Pl. NaA só: $A^- + H_2O \leftrightarrow HA + OH^-$ $K_h = K_v/K_a$
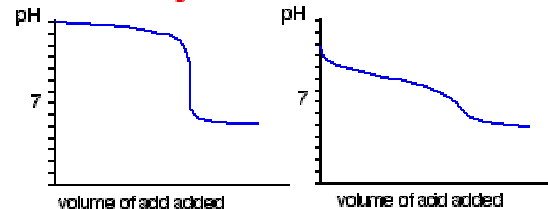
$[HA] = [OH^-] = x$; $[A^-] = c_{só} -x \approx c_{só}$

http://www.chemguide.co.uk/physical/acidbaseeqia/phcurves.html
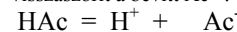

Pufferek Cél: pH-t stabilizálni.

Gyenge sav + erős bázis, ill. gyenge bázis + erős sav.

Pl. Na-Acetát + HAc

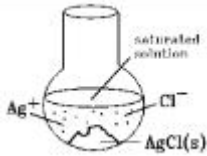Az egyensúly tképp csak az ecetsav disszociációja, melyet persze visszaszorít a bevitt Ac^- :

$HAc = H^+ + Ac^-$

c_{sav} (-x)   x $c_{só}$ (+x)

$$[H^+] = x = K_a\, c_{sav}/\, c_{só}$$

2005/29

Heterogén egyensúlyok
www.ucdsb.on.ca

Oldhatósági szorzat

Ha a csapadékban K_nA_m összetételű anyag van

K - kation, A - anion, akkor

$$L = [K]^n[A]^m;$$

pl. $[Ag^+][Cl^-]$, $[Fe^{3+}][OH^-]^3$; $[Ag^+]^2[CrO_4^{2-}]$

adatok:

Solubility Products of Slightly Soluble Salts

Compound	Ksp	Compound	Ksp	Compound	Ksp
AgBr	5.35 x 10-13	BaF2	1.84 x 10-7	KclO4	1.05 x 10-2
Ag2CO3	8.45 x 10-12	BaSO4	1.08 x 10-10	MgCO3	6.82 x 10-6
AgCl	1.76 x 10-10	CaCO3	4.96 x 10-9	MgF2	7.42 x 10-11
Ag2CrO4	1.12 x 10-12	CaF2	1.46 x 10-10	MgNH4PO4	2. x 10-13*
AgCN	5.97 x 10-17	CaSO4	7.10 x 10-5	Mg(OH)2	5.61 x 10-11
AgI	1.18 x 10-16	CdS	1.40 x 10-29	MnS	4.65 x 10-14
Ag3PO4	8.88 x 10-17	Ca(OH)2	4.68 x 10-6	NiS	1.07 x 10-21
Ag2SO4	1.20 x 10-5	CuC2O4	4.43 x 10-10	PbCl2	1.78 x 10-5
Ag2S	6.69 x 10-50	CuS	1.27 x 10-36	PbS	9.05 x 10-29
AgCNS	1.03 x 10-12	Fe(OH)3	2.79 x 10-39	PbSO4	1.82 x 10-8
Al(OH)3	2. x 10-32*	Hg2Br2	6.42 x 10-23	SnS	3.25 x 10-28
BaCO3	2.58 x 10-9	Hg2Cl2	6.24 x 10-13	Zn(OH)2	4.13 x 10-17
BaCrO4	1.17 x 10-10	HgS	1.55 x 10-52	ZnS	2.93 x 10-25

Komplexek stabilitási állandója

First Stability Constants (log K_1) of Various Metal Chelates

from Chapter 6 - Sequestrants in Foods, by Thomas E. Furia, in "CRC handbook of Food Additives", 2nd ed. 1972
as revised by cited authors (where data shows a letter corresponding to citation at bottom of table) *latest revision May 28, 2001*

	Ba	*Ca*	*Co(II)*	*Cu*	*Fe(II)*	*Fe(III)*	*Mg*	*Mn*	*Ni*	*Sr*	*Zn*
Acetic acid	0.39	0.53	2.24				0.51		0.74	0.43	1.03
Citric acid	2.3	3.5	4.4	6.1	3.2	11.85	2.8	3.2	4.8	2.8	4.5
EDTA	**7.78**	**10.70**	**16.21**	**18.8**	**14.3**	**25.7**	**8.69**	**13.56**	**18.56**	**8.63**	**16.5**
Glycine	0.77	1.43	5.23	8.22	4.3	10.0	3.45	3.2	6.1	0.91	5.16
Lactic acid	0.55	1.07	1.89	3.02		6.4	0.93	1.19	2.21	0.70	1.86
Maleic acid	2.26	2.43		3.90			1.68	2.0	1.1	2.0
Salicylic acid			6.72	10.60	6.55	16.35	4.7	2.7	6.95		6.85

Cu--ammónia komplex, többlépcsős egyensúly

$$K_1 = \frac{[Cu(NH_3)(H_2O)_5^{2+}]}{[Cu(H_2O)_6^{2+}][NH_3]}$$

$$= 1.78 \times 10^4 \ mol^{-1} \ dm^3$$

ion	K_n	value (mol^{-1} dm^3)	log K_n
$[Cu(NH_3)(H_2O)_5]^{2+}$	K_1	1.78×10^4	4.25
$[Cu(NH_3)_2(H_2O)_4]^{2+}$	K_2	4.07×10^3	3.61
$[Cu(NH_3)_3(H_2O)_3]^{2+}$	K_3	9.55×10^2	2.98