

Reálné roztoky aneb aktivity na druhý pohled

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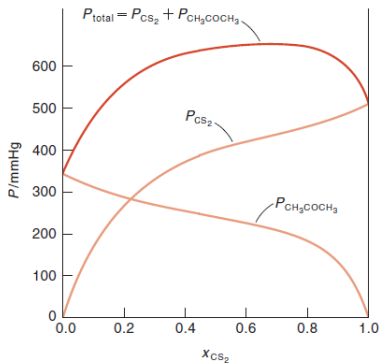
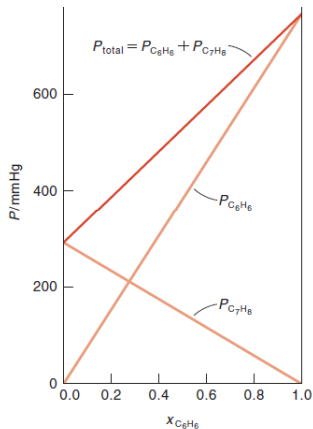
- 1 Reálné roztoky (neelektrolytů): Aktivity rozpouštědla a rozpuštěné látky
- 2 Reálné roztoky elektrolytů:
 - 1 Molární vodivost
 - 2 Aktivita iontů
 - 3 Hydrodynamický poloměr
 - 4 Iontová atmosféra
 - 5 Iontová síla
 - 6 Debyho-Hückelovův limitní zákon

Literatura:

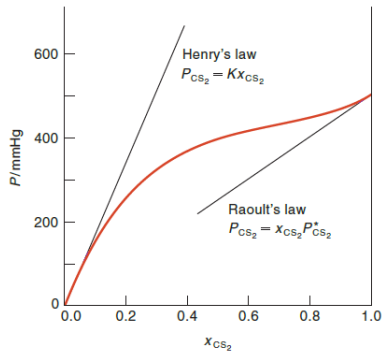
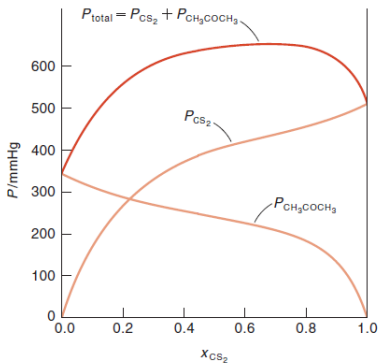
Raymond Chang: Physical Chemistry for the Chemical Sciences (ch. 6-7)

Peter Atkins: Fyzikální chemie (5.1.3, 5.4, 20.2)

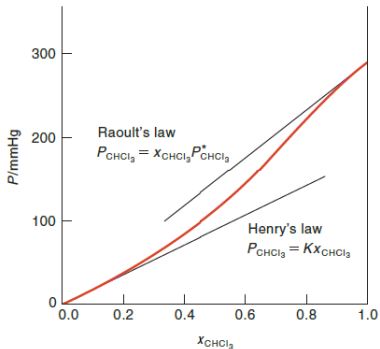
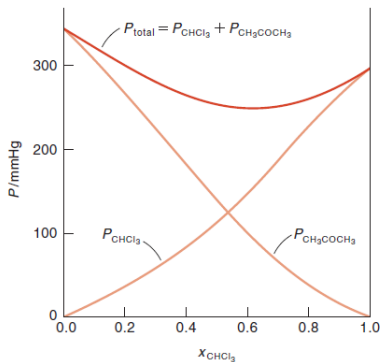
Ideální a neideální roztoky



Neideální roztoky: kladná odchyłka of Raultova zákona



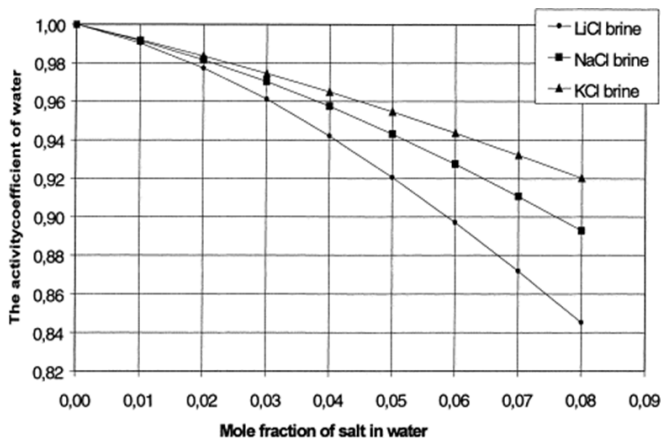
Neideální roztoky: záporná odchyłka of Raultova zákona



Aktivita vody ve směsi s močovinou

			measured		
Urea	Water, x	p_w_ideal	p_w/atm	a_w	activ_coeff
0	1.000	0.006025	0.006025	1.000	1.000
1	0.982	0.005917	0.005933	0.985	1.003
2	0.965	0.005814	0.005846	0.970	1.005
4	0.933	0.005621	0.005672	0.941	1.009
6	0.902	0.005435	0.005501	0.913	1.012
10	0.847	0.005103	0.005163	0.857	1.012

Aktivní koeficienty vody v roztocích elektrolytů

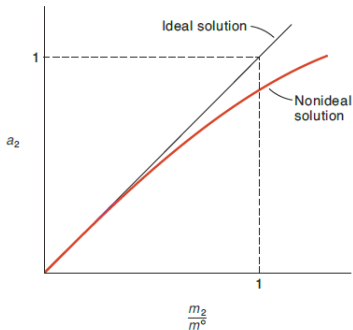
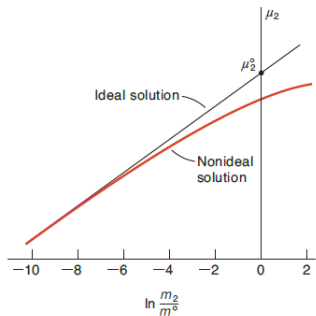


Henryho konstanty rozpustnosti plynů ve vodě

Table 6.1
Henry's Law Constants for Some Gases in Water at 298 K

Gas	K/torr	$K'/\text{atm mol}^{-1} \text{ kg H}_2\text{O}$
H ₂	5.54×10^7	1311
He	1.12×10^8	2649
Ar	2.80×10^7	662
N ₂	6.80×10^7	1610
O ₂	3.27×10^7	773
CO ₂	1.24×10^6	29.3
H ₂ S	4.27×10^5	10.1

Standardní stav pro rozpuštěnou látku v roztoku



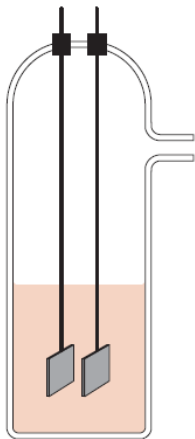
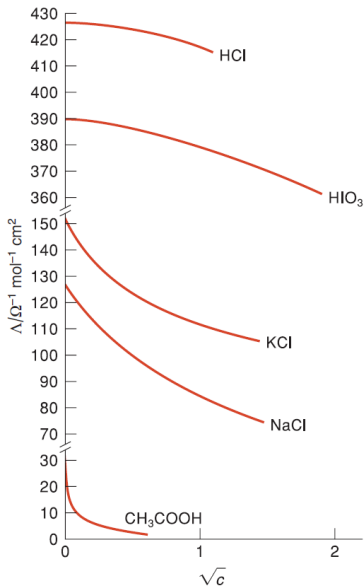


Figure 7.1

A conductance cell. The electrodes are made of

Molární vodivost Λ



Limitní molární vodivost Λ_0 pro elektrolyty ve vodě při 298 K

Table 7.1
Molar Conductance at Infinite Dilution for Some Electrolytes in Water at 298 K^a

Electrolyte	$\Lambda_0/\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$
HCl	426.16
CH ₃ COOH	390.71
LiCl	115.03
NaCl	126.45
AgCl	137.20
KCl	149.85
LiNO ₃	110.14
NaNO ₃	121.56
KNO ₃	144.96
CuSO ₄	267.24
CH ₃ COONa	91.00

^a To express Λ_0 as $\Omega^{-1} \text{ mol}^{-1} \text{ m}^2$, multiply each number by 10^{-4} . Thus, Λ_0 for HCl is $426.16 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$ or $4.2616 \times 10^{-2} \Omega^{-1} \text{ mol}^{-1} \text{ m}^2$.

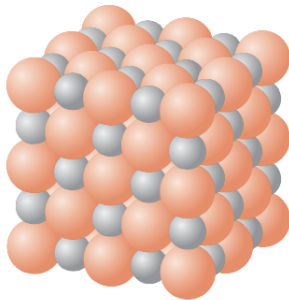
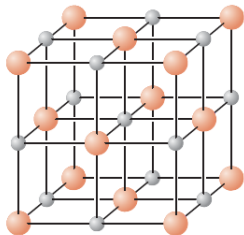
Molární iontová vodivost λ_0

Ion	$\frac{\lambda_0^a}{\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2}$
H ⁺	349.81
Li ⁺	38.68
Na ⁺	50.10
K ⁺	73.50
Rb ⁺	77.81
Cs ⁺	77.26
NH ₄ ⁺	73.5
Mg ²⁺	106.1
Ca ²⁺	119.0
Ba ²⁺	127.3
Cu ²⁺	107.2
OH ⁻	198.3
F ⁻	55.4
Cl ⁻	76.35
Br ⁻	78.14
I ⁻	76.88
NO ₃ ⁻	71.46
HCO ₃ ⁻	44.50
CH ₃ COO ⁻	40.90
SO ₄ ²⁻	160.0

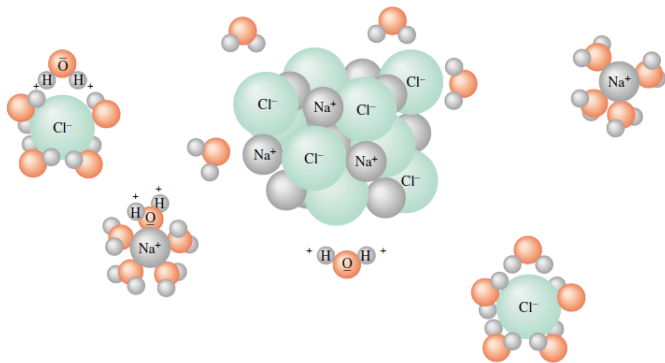
Molární iontová vodivost λ_0 a iontová pohyblivost $u_{+/-}$

Ion	λ_0^a $\Omega^{-1} \text{ mol}^{-1} \text{ cm}^2$	Ionic mobility ^b $10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$
H ⁺	349.81	36.3
Li ⁺	38.68	4.01
Na ⁺	50.10	5.19
K ⁺	73.50	7.62
Rb ⁺	77.81	7.92
Cs ⁺	77.26	7.96
NH ₄ ⁺	73.5	7.62
Mg ²⁺	106.1	5.50
Ca ²⁺	119.0	6.17
Ba ²⁺	127.3	6.59
Cu ²⁺	107.2	5.56
OH ⁻	198.3	20.50
F ⁻	55.4	5.74
Cl ⁻	76.35	7.91
Br ⁻	78.14	8.10
I ⁻	76.88	7.95
NO ₃ ⁻	71.46	7.41
HCO ₃ ⁻	44.50	4.61
CH ₃ COO ⁻	40.90	4.24
SO ₄ ²⁻	160.0	8.29

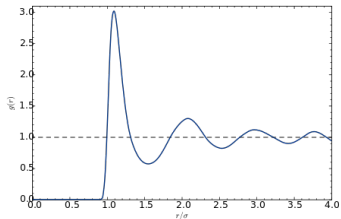
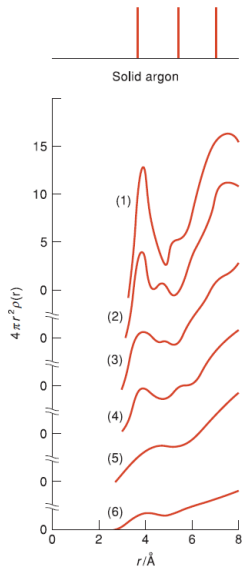
Krystalová struktura NaCl



Rozpouštění NaCl



Roztoky: Radiální distribuční funkce kapalného argonu



Hydratace iontů, hydratační číslo, hydratační sféra

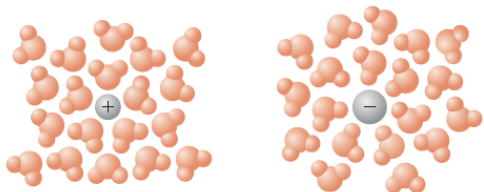
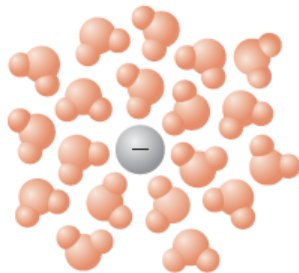
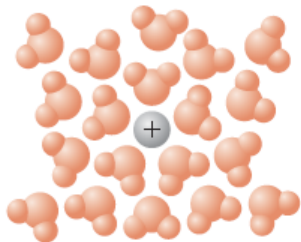


Figure 7.5

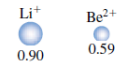
Hydration of a cation and an anion. In general, each cation and each anion has a specific number of water molecules associated with it in the hydration sphere.

Hydratace iontů, hydratační číslo, hydratační sféra



iont	τ /s
Br^-	10^{-11}
Na^+	10^{-9}
Cu^{2+}	10^{-7}
Fe^{2+}	10^{-5}
Al^{3+}	7
Cr^{3+}	$1,5 \times 10^5$

Lontové poloměry



Ionic radii



2 Å

Tlumení meziontové síly dielektrickou interakcí solventu

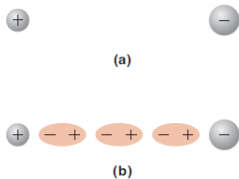


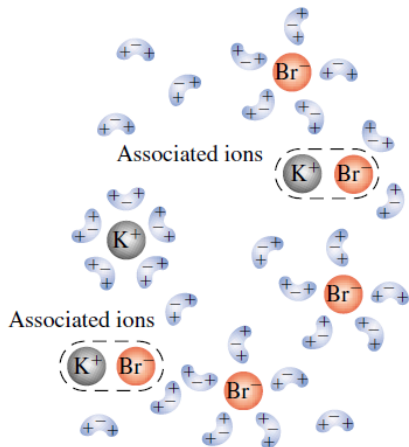
Table 7.3

Dielectric Constants of Some Pure Liquids at 298 K

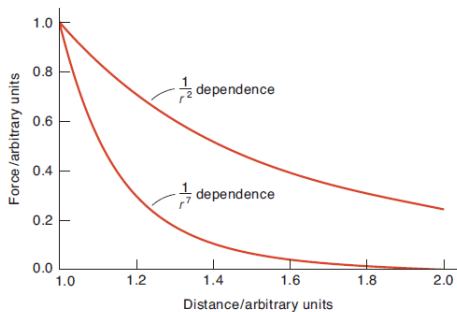
Liquid	Dielectric constant, ϵ^a
H ₂ SO ₄	101
H ₂ O	78.54
(CH ₃) ₂ SO (dimethylsulfoxide)	49
C ₃ H ₈ O ₃ (glycerol)	42.5
CH ₃ NO ₂ (nitromethane)	38.6
HOCH ₂ CH ₂ OH (ethylene glycol)	37.7
CH ₃ CN (acetonitrile)	36.2
CH ₃ OH	32.6
C ₂ H ₅ OH	24.3
CH ₃ COCH ₃ (dimethyl ether)	20.7
CH ₃ COOH	6.2
C ₆ H ₆	4.6
C ₂ H ₅ OC ₂ H ₅ (diethyl ether)	4.3
CS ₂	2.6

^a The dielectric constant is a dimensionless quantity.

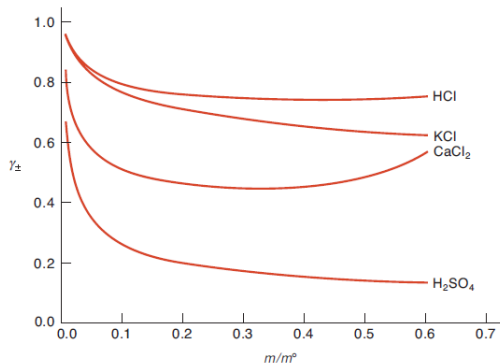
Volné solvatované ionty a iontové páry



Srovnání dosahu působení van der Waalsovských a elektrostatických sil



Střední aktivitní koeficienty iontů, závislost na iontové síle



Střední aktivitní koeficienty iontů, závislost na iontové síle

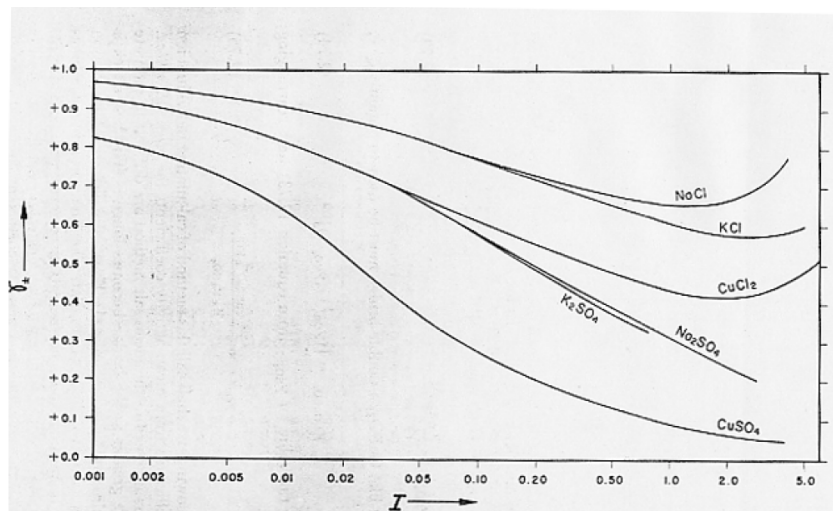
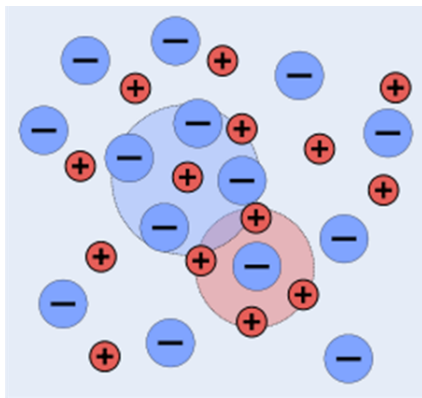
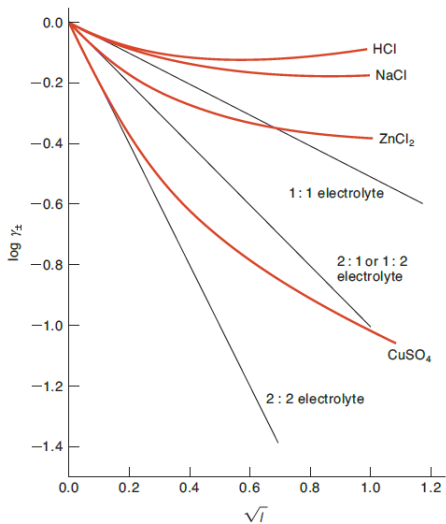


FIG. 2.14. Mean activity coefficients of typical salts plotted against the ionic strength (log scale). Note the similarity of the behavior of salts of the same valence type at ionic strengths below 0.1. [Data from W. M. Latimer, *op. cit.*, p. 354.]

Lontová atmosféra



Debyho-Hückelův *limitní* zákon, použitelný pro $I < 0,01$



Rozšířený Debyho-Hückelův zákon, použitelný pro $I < 0,1$

TABLE 3.4 PARAMETER a AND INDIVIDUAL ION ACTIVITY COEFFICIENTS

Ion Size Parameter, a (Å) ^a	Ion	Activity Coefficients Calculated with (2) of Table 3.3 for Ionic Strength				
		10 ⁻⁴	10 ⁻³	10 ⁻²	0.05	10 ⁻¹
9	H ⁺	0.99	0.97	0.91	0.86	0.83
	Al ³⁺ , Fe ³⁺ , La ³⁺ , Ce ³⁺	0.90	0.74	0.44	0.24	0.18
8	Mg ²⁺ , Be ²⁺	0.96	0.87	0.69	0.52	0.45
6	Ca ²⁺ , Zn ²⁺ , Cu ²⁺ , Sn ²⁺ , Mn ²⁺ Fe ²⁺	0.96	0.87	0.68	0.48	0.40
5	Ba ²⁺ , Sr ²⁺ , Pb ²⁺ , CO ₃ ²⁻	0.96	0.87	0.67	0.46	0.39
4	Na ⁺ , HCO ₃ ⁻ , H ₂ PO ₄ ⁻ , CH ₃ COO ⁻	0.99	0.96	0.90	0.81	0.77
	SO ₄ ²⁻ , HPO ₄ ²⁻	0.96	0.87	0.66	0.44	0.36
	PO ₄ ³⁻	0.90	0.72	0.40	0.16	0.10
3	K ⁺ , Ag ⁺ , NH ₄ ⁺ , OH ⁻ , Cl ⁻	0.99	0.96	0.90	0.80	0.76
	ClO ₄ ⁻ , NO ₃ ⁻ , I ⁻ , HS ⁻					

^a After J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937). Reproduced with permission from American Chemical Society.

Přesnější přiblížení aktivitních koeficientů než Debyho-Hückelův *limitní* zákon

TABLE 3.3 INDIVIDUAL ION ACTIVITY COEFFICIENTS

Approximation	Equation ^a	Approximate Applicability [ionic strength (<i>M</i>)]
Debye-Hückel	$\log f = -Az^2\sqrt{I}$ (1)	$<10^{-2.3}$
Extended Debye-Hückel	$= -Az^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}}$ (2)	$<10^{-1}$
Güntelberg	$= -Az^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$ (3)	$<10^{-1}$ useful in solutions of several electrolytes
Davies	$= -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right)$ (4) ^b	<0.5

^a *I* (ionic strength) = $\frac{1}{2} \sum C_i z_i^2$; $A = 1.82 \times 10^6 (\epsilon T)^{-3/2}$ (where ϵ = dielectric constant); $A \approx 0.5$ for water at 25°C; z = charge of ion; $B = 50.3 (\epsilon T)^{-1/2}$; $B \approx 0.33$ in water at 25°C; a = adjustable parameter (angstroms) corresponding to the size of the ion. (See Table 3.4.)

^b Davies has proposed 0.3 (instead of 0.2) as a coefficient for the last term in parentheses.

Viskozita roztoků klesá s teplotou Arheniovsky. Proč?

Rozpouštědlo není spojitě - molekuly přeskakují po děrách mezi ostatními molekulami - na to potřebují energii E_V .

$$\eta = \eta_0 e^{-E_V/k_B T}$$