SELECTED CHAPTERS OF PHYSICAL CHEMISTRY OF SOLUTIONS

Equilibrium between phases

Partition of compounds between two phases. Extraction of molecules

Partition between two phases (water/organic solvent, practically immiscible with water)

$$\frac{a_{\mathrm{i}}^{s}}{a_{\mathrm{i}}^{\mathrm{w}}} = P_i = \exp\frac{\mu_{\mathrm{i}}^{0\mathrm{w}} - \mu_{\mathrm{i}}^{0\mathrm{s}}}{RT}; \qquad \frac{a_{\mathrm{i}}^{s}}{a_{\mathrm{i}}^{\mathrm{w}}} = P_{\mathrm{i}} = \gamma_{\mathrm{i}}^{-1}$$

Two limitations:

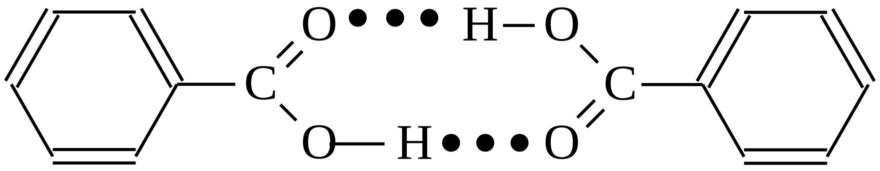
(1) many organic solvents are **unlimitedly miscible** with water;

(2) in any case, the partition constants and transfer activity coefficients reflect the equilibrium between the two **mutually saturated solvents**.

If we consider the partition of an acid HA, following interfering equilibria should be taken into account first:

in water: $\mathrm{HA} \rightleftharpoons \mathrm{H}^{+} + \mathrm{A}^{-}$

in the organic phase: $2\mathrm{HA} \rightleftharpoons (\mathrm{HA})_2$

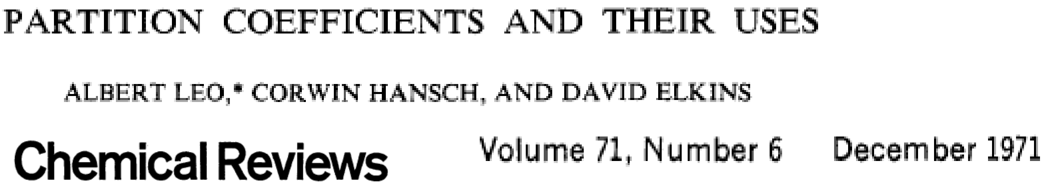


Association (dimerization) through hydrogen bonds

If we consider the partition of an acid HA, following interfering equilibria should be taken into account first:

Association constant in benzene:

Benzoic acid	295
Valeric acid	140
Acetic acid	28
Picric acid	0.6



PARTITION COEFFICIENTS AND THEIR USES

ALBERT LEO,* CORWIN HANSCH, AND DAVID ELKINS

Chemical Reviews Volume 71, Number 6 December 1971

Linear **F**ree-**E**nergy **R**elationships = LFER

$$\pi_{\mathrm{X}} = \log P_{\mathrm{RX}} - \log P_{\mathrm{RH}}$$

$$\pi_{\mathrm{CH_3}} = 0.50$$

These increments are ca. constant in the absence of steric hindrance and additional electronic effects

Comparison of Aromatic and Aliphatic π Values

Function	*Aromatic* π *Log* $P_{C_6H_5X}$ – *log* $P_{C_6H_6}$	*Aliphatic* π *Log* P_{RX} – *log* P_{RH}	$\Delta\pi$ $\pi_{ar} - \pi_{al}$
NH_2	−1.23	−1.19	−0.04
I	1.12	1.00	0.12
$S\text{–}CH_3$	0.61	0.45	0.16
$COCH_3$	−0.55	−0.71	0.16
$CONH_2$	−1.49	−1.71	0.22
$COOCH_3$	−0.01	−0.27	0.26
Br	0.86	0.60	0.26
CN	−0.57	−0.84	0.27
F	0.14	−0.17	0.31
Cl	0.71	0.39	0.32
COOH	−0.28	−0.67	0.39
OCH_3	−0.02	−0.47	0.45
OC_6H_5	2.08	1.61	0.47
$N(CH_3)_2$	0.18	−0.30	0.48
OH	−0.67	−1.16	0.49
NO_2	−0.28	−0.85	0.57

Influence of the structure of the solute: amphiphiles

For example, **water – *iso*-octane system**

$$C_8H_{17}-C_6H_4-O-(CH_2CH_2O)_nCH_2CH_2OH$$

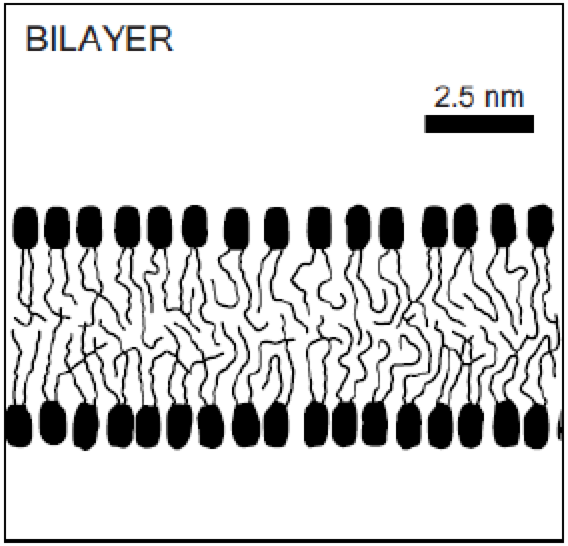
$$\log P = 3.836 - 0.442n$$

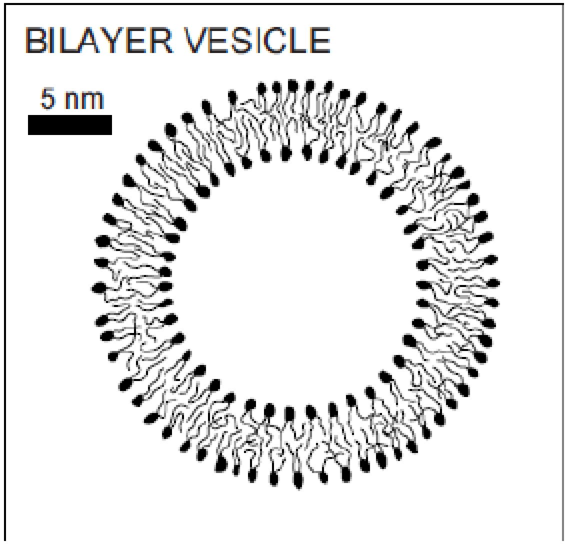
Why water/1-octanol ?

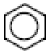
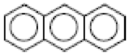
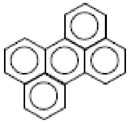
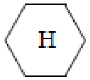
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-OH$

hydrophobic portion

hydrophilic group





Compound		log P_{ow}
CH_2Cl_2		1.25
$CHCl_3$		1.96
CCl_4		2.83
Benzene		2.13
Naphthalene		3.35
Anthracene		4.54
Perylene		6.50
Phenol		1.46
1-Butanol		0.88
1-Pentanol		1.56
1-Hexanol		2.03
1-Heptanol		2.41
CH_4		1.12
C_2H_6		1.78
C_3H_8		2.36
C_4H_{10}		2.92
C_5H_{12}		3.62
n-C_6H_{14}		4.11
Cyclohexane		3.44

Extraction of ionic associates

Water/benzene; water/dichloromethane; water/trichloromethane; water/nitrobenzene; water/1-octanol; water/iso-butylmethylketone

$$\mathrm{Ct}^{+}_{\mathrm{w}} + \mathrm{An}^{-}_{\mathrm{w}} \Leftrightarrow \mathrm{Ct}^{+}\mathrm{An}^{-}_{\mathrm{org}};\ K_{\mathrm{ex}}$$

In water, cation-anion association is less probable, except the cases of some specific interactions or high hydrophobicity of ions.

By contrast, in the organic phase the polarity is as a rule low enough for ion association.

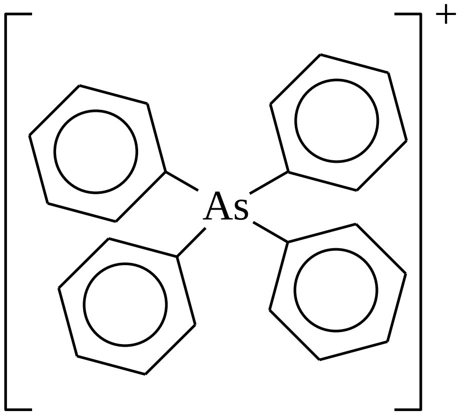
Previously we have considered:

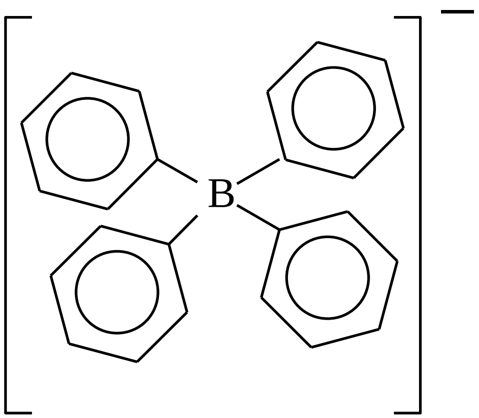
Estimation of the γ_{i} values of ions

Solubility. $\mathrm{Ct}^{+} + \mathrm{An}^{-} \Leftrightarrow \mathrm{CtAn}\downarrow;\ K_{\mathrm{sp}}$ (solubility product)

$$\gamma_{+}\gamma_{-} = \frac{K_{\mathrm{sp}}^{\mathrm{w}}}{K_{\mathrm{sp}}^{\mathrm{s}}}$$

This approach works for limitedly soluble salts.





Now we are going to discuss a similar, but different problem.

Extraction of ionic associates is widely used in chemical analysis and in various chemical operations.

Therefore it is useful to develop some methods, which allow predicting the values of extraction constants.

The abovementioned extraction constant is a combination of two constants:

$$K_{\mathrm{ex}} = \frac{\left[\mathrm{Ct^{+}An^{-}_{org}}\right]}{\left[\mathrm{Ct^{+}_{w}}\right]\left[\mathrm{An^{-}_{w}}\right]} = \frac{\left[\mathrm{Ct^{+}An^{-}_{w}}\right]}{\left[\mathrm{Ct^{+}_{w}}\right]\left[\mathrm{An^{-}_{w}}\right]} \times \frac{\left[\mathrm{Ct^{+}An^{-}_{org}}\right]}{\left[\mathrm{Ct^{+}An^{-}_{w}}\right]} = K^{\mathrm{w}}_{\mathrm{ass}} \times P_{\mathrm{Ct^{+}An^{-}}}$$

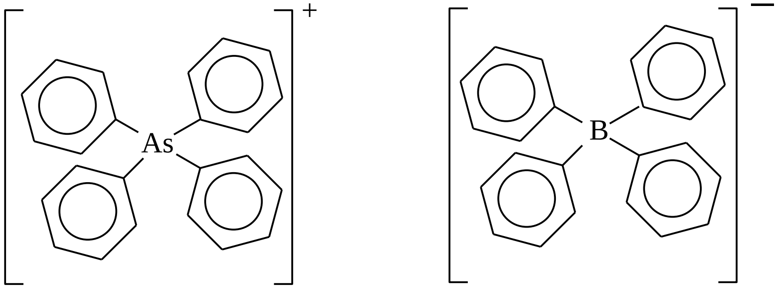
As the concentration of ion associates in water is negligible, the separate estimation of the last constants is impossible.

K. KASAHARA, N. OGAKI, K. MATSUI, K. KANO, S. TAGUCHI, K. GOTO, Nippon Kagaku Zasshi, (1986) 894:

An assumption was made about the additive contributions:

$$\log K_{ex} = \log K_{Ct^+} + \log K_{An^-} + \log K_{solvent}$$

and: $$K_{Ph_4As^+} = K_{Ph_4B^-}; \quad \log K_{benzene} = 0$$

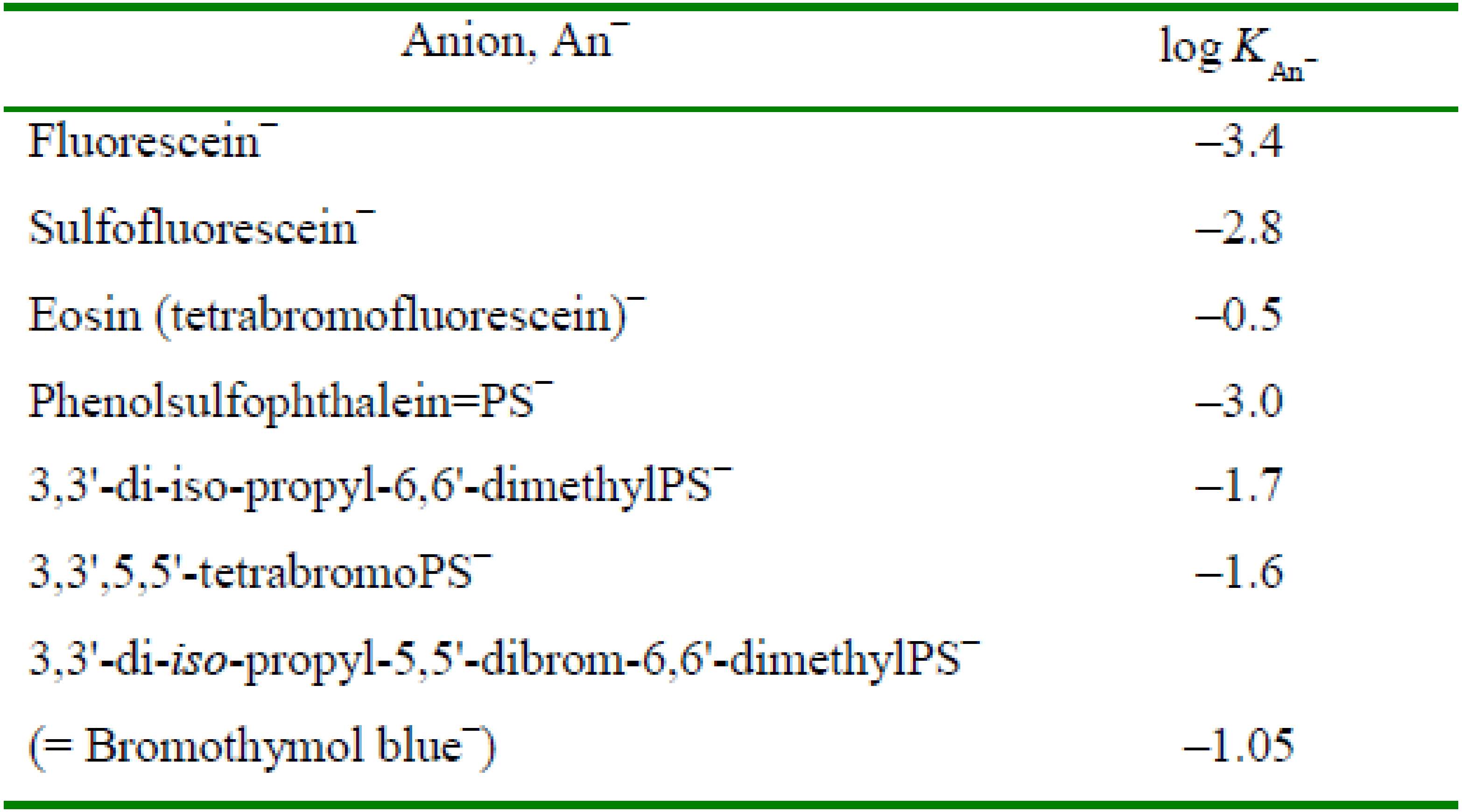


This allows estimating the separate values for single cations, anions, and solvents.

Cation	$\log K_{\mathrm{Cr^+}}$	Anion	$\log K_{\mathrm{An^-}}$	Solvent	$\log K_{\mathrm{Solvent}}$
Ph_4As^+	+2.9	Ph_4B^-	+2.9	Benzene	0
$N(CH_3)_4^+$	−3.5	Br^-	−5.6	CCl_4	−1.3
$N(C_2H_5)_4^+$	−1.3	NO_3^-	−4.3	Toluene	−0.6
$N(C_3H_7)_4^+$	+0.2	I^-	−3.1	C_6H_5Cl	+2.3
$N(C_4H_9)_4^+$	+1.8	SCN^-	−2.5	CH_2Cl_2	+4.1
$N(C_5H_{11})_4^+$	+3.9	BF_4^-	−2.0	$CHCl_3$	+(3.4–4.2)
		ClO_4^-	−1.5	$ClCH_2CH_2Cl$	+4.5
		$C_{12}H_{25}OSO_3^-$	+1.5	*iso*-$C_4H_9COCH_3$	+6.5
$NC_6H_{13}(CH_3)_3^+$	−0.8	$C_6H_{13}SO_3^-$	−4.2		
$NC_8H_{17}(CH_3)_3^+$	+0.2	$C_8H_{17}SO_3^-$	−2.8		
$NC_{10}H_{21}(CH_3)_3^+$	+1.6	$C_{10}H_{21}SO_3^-$	−1.3		
$NC_{12}H_{25}(CH_3)_3^+$	+2.9	$C_{12}H_{25}SO_3^-$	−0.2		
$NC_{14}H_{29}(CH_3)_3^+$	+3.9	$C_{14}H_{29}SO_3^-$	+0.9		
		$C_{11}H_{23}COO^-$	−2.5		
Malachite green$^+$	+4.6				
Crystal violet$^+$	+5.0	Thymol blue$^-$	−0.8		

K. KASAHARA, N. OGAKI, K. MATSUI, K. KANO, S. TAGUCHI, K. GOTO, Nippon Kagaku Zasshi, (1986) 894

Our data for anionic dyes



Anion, An$^-$	log K_{An^-}
Fluorescein$^-$	–3.4
Sulfofluorescein$^-$	–2.8
Eosin (tetrabromofluorescein)$^-$	–0.5
Phenolsulfophthalein=PS$^-$	–3.0
3,3'-di-iso-propyl-6,6'-dimethylPS$^-$	–1.7
3,3',5,5'-tetrabromoPS$^-$	–1.6
3,3'-di-*iso*-propyl-5,5'-dibrom-6,6'-dimethylPS$^-$ (= Bromothymol blue$^-$)	–1.05

Another approach [Schmidt (Шмидт)et al.]:

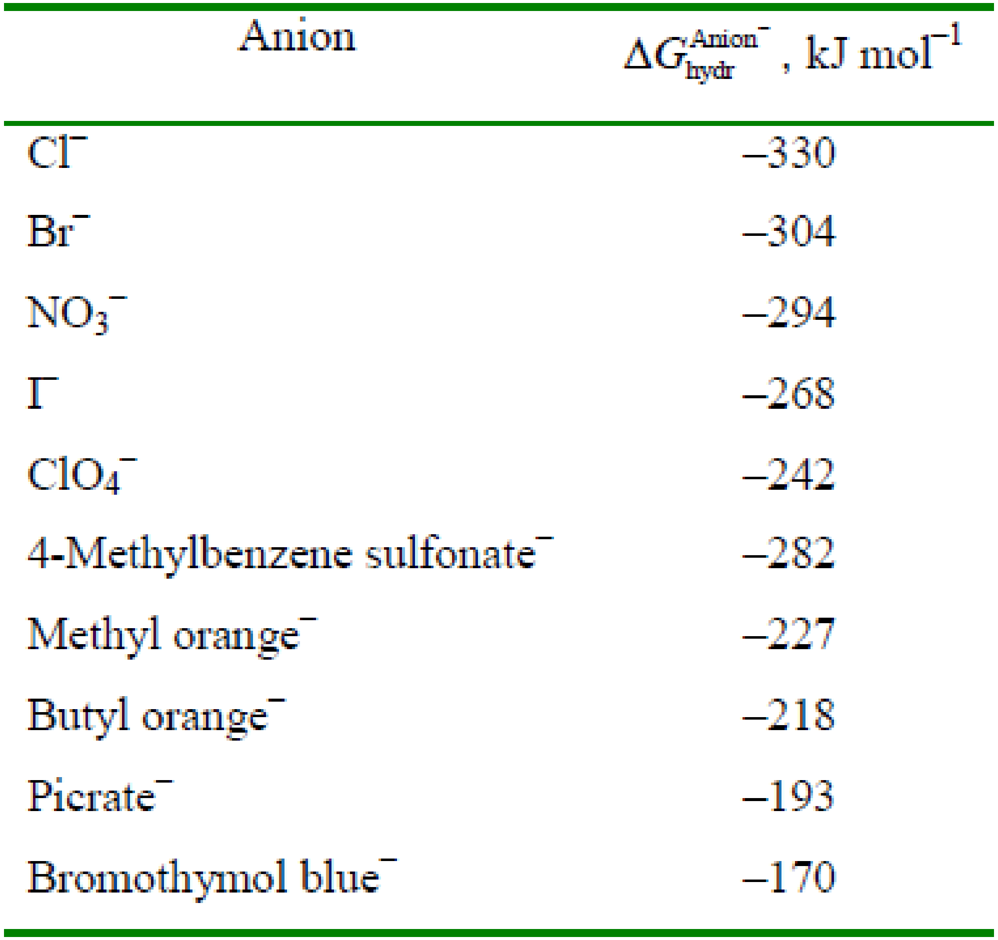
$$\left(\mathrm{Ct^{+}X^{-}}\right)_{\mathrm{org}} + \mathrm{Y_{w}^{-}} \Leftrightarrow \left(\mathrm{Ct^{+}Y^{-}}\right)_{\mathrm{org}} + \mathrm{X_{w}^{-}}; \quad K_{\mathrm{X,Y}}$$

$$\log K_{\mathrm{X,Y}} = \chi\left(\Delta G_{\mathrm{hydr}}^{\mathrm{Y^{-}}} - \Delta G_{\mathrm{hydr}}^{\mathrm{X^{-}}}\right)$$

For example:

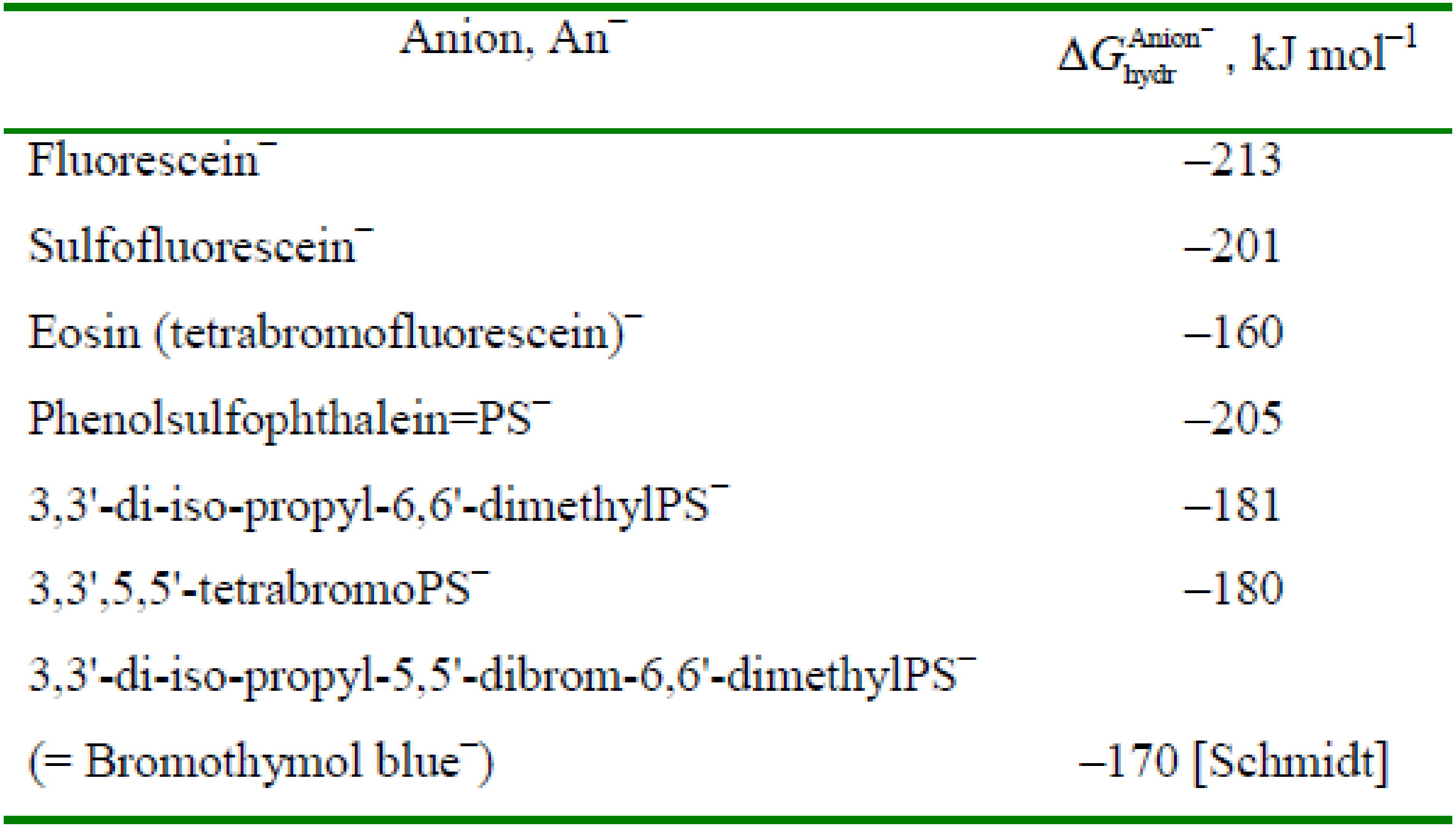
Cation	Solvent	χ
$N(C_4H_9)_4^+$	$CHCl_3$	0.051
$N(C_4H_9)_4^+$	toluene	0.058
$C_{16}H_{33}\,N(CH_3)_3^+$	$CHCl_3$	0.032
Ph_4As^+	$CHCl_3$	0.055

The Gibbs hydration energies of anions



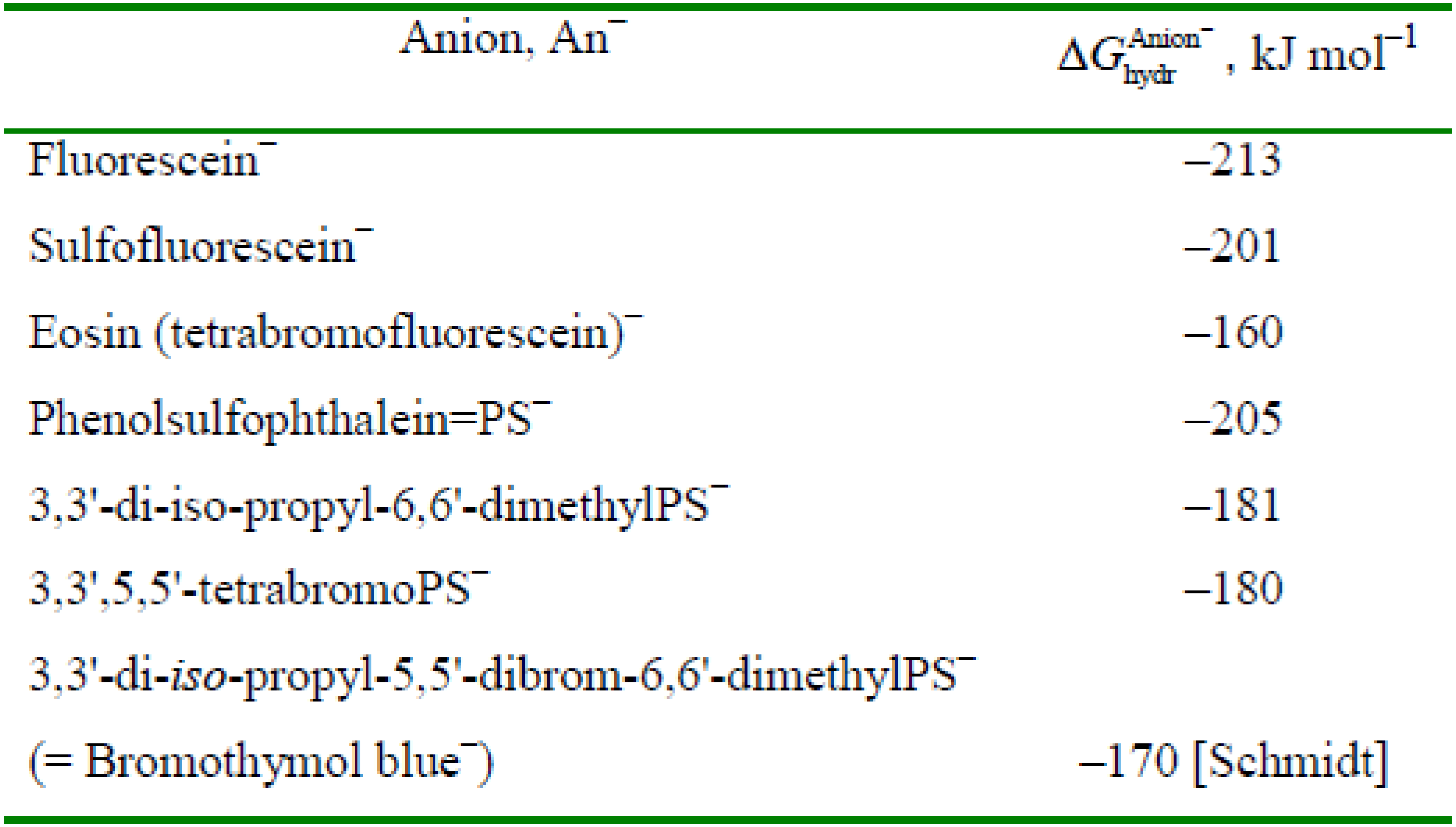
Anion	$\Delta G_{\text{hydr}}^{\text{Anion}^-}$, kJ mol^{-1}
Cl^-	–330
Br^-	–304
NO_3^-	–294
I^-	–268
ClO_4^-	–242
4-Methylbenzene sulfonate$^-$	–282
Methyl orange$^-$	–227
Butyl orange$^-$	–218
Picrate$^-$	–193
Bromothymol blue$^-$	–170

The Gibbs hydration energies of dye anions



Anion, An^-	$\Delta G_{hydr}^{Anion^-}$, kJ mol^{-1}
Fluorescein$^-$	–213
Sulfofluorescein$^-$	–201
Eosin (tetrabromofluorescein)$^-$	–160
Phenolsulfophthalein=PS$^-$	–205
3,3'-di-iso-propyl-6,6'-dimethylPS$^-$	–181
3,3',5,5'-tetrabromoPS$^-$	–180
3,3'-di-iso-propyl-5,5'-dibrom-6,6'-dimethylPS$^-$ (= Bromothymol blue$^-$)	–170 [Schmidt]

Our data for anionic dyes



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3,3'-di-*iso*-propyl-5,5'-dibrom-6,6'-dimethylPS$^-$ (= Bromothymol blue$^-$)	–170 [Schmidt]

Solvation and solubility of non-electrolytes

Alchemists stated: **Similia similibus solventur**

Solubility of: (i) gases; (ii) liquids; (iii) solids

Ideal solutions: Raoult's law $p_2 = p_2^{\mathrm{o}} x_2$

Positive deviations: $\Delta H_{\mathrm{mix}} > 0$

Negative deviations: $\Delta H_{\mathrm{mix}} < 0$

Henry's law: $p_2 = k x_2$

Растворимость некоторых газов в разных растворителях при 20 °С и 1 *атм*

Растворитель	Растворимость (мольные доли$\cdot 10^4$) газов									
	He	H_2	N_2	CO	O_2	CH_4	C_2H_4	CO_2(0°)	NH_3(0°)	Cl_2(0°)
Идеальная ($1/f_2^\circ$)	—	8	10	12,8	13,2	35	152	257	2380	2900
н-Гексан	—	6,5	12,5	—	19,3	42,4	161	—	—	—
Этиловый эфир	—	5,52	12,52	16,9	19,8	45,3	—	—	790	—
Циклогексан	1,22	3,80	7,22	—	—	28,3	—	—	—	—
Четыреххлористый углерод	—	3,27	6,42	8,86	12,0	28,6	147	100	—	2980
Ксилол	—	4,13	6,14	9,12	—	25,8	—	102		
Ацетон	1,08	2,31	5,92	8,54	9,25	22,3	75	211		
Бензол	0,77	2,61	4,40	6,24	8,16	20,7	107	91	—	—
Хлороформ	—	2,20	4,45	6,45	7,38	—	—	121	—	—
Нитробензол	—	1,56	2,63	3,94	—	—	—	113	—	—
Метиловый спирт	0,60	1,57	2,35	3,25	3,18	7,1	—	70	4390	—
Вода	0,070	0,15	0,12	0,13	0,23	0,24	0,33	7	4810	38

Konovalov's rules: liquid – vapor equilibrium

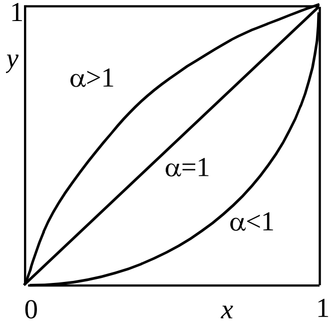
$$P = p_1 + p_2 = p_1^o x_1 + p_2^o x_2 = p_1^o(1-x) + p_2^o x$$

$$y = p_2/P = p_2^o x/P; \qquad y_1 = (1-y) = p_1^o(1-x)/P$$

$$\boxed{\frac{y}{1-y} = \frac{p_2^o x/P}{p_1^o(1-x)/P} = \frac{\alpha x}{1-x}} \qquad \alpha = p_2^o/p_1^o$$

$$\alpha = 1 \quad y = x; \qquad \alpha > 1 \quad y > x; \qquad \alpha < 1 \quad y < x;$$

First rule



Second rule:

azeotrope

Solubility of solids

$$\mu_2^{\text{satur.}} = \mu_2^{\text{solid}}$$

$$\mu_2^{\text{o}} + RT\ln a_2^{\text{satur.}} = \mu_2^{\text{solid}}$$

$$\Delta G^{\text{o}} = \mu_2^{\text{o}} - \mu_2^{\text{solid}} = -RT\ln a_2^{\text{satur.}}$$

$$\Delta G^{\text{o}} = \Delta H - T\Delta S = \Delta H + T\left(\frac{\partial \Delta G^{\text{o}}}{\partial T}\right)_p$$

$$-RT\ln a_2^{\text{satur.}} = (\Delta H_{\text{melt}} + \Delta H_{\text{mixing}}) + T\left(-R\ln a_2^{\text{satur.}} - RT\left(\frac{\partial \ln a_2^{\text{satur.}}}{\partial T}\right)_p\right)$$

Two stages: (i) melting of the solid;
(ii) mixing of the melt with the solvent.

Solubility of solids

$$RT^2\left(\frac{\partial \ln a_2^{\text{satur.}}}{\partial T}\right)_p = (\Delta H_{\text{melt}} + \Delta H_{\text{mixing}})$$

Already Lavoisier noted that easily melting compounds usually dissolve more easily.

Ideal solubility of solids in liquids: **Schroeder equation**

Two stages: (i) melting of the solid;

(ii) mixing of the melt with the solvent as formation of ideal solution: $\underline{\Delta H_{\text{mixing}} = 0.}$

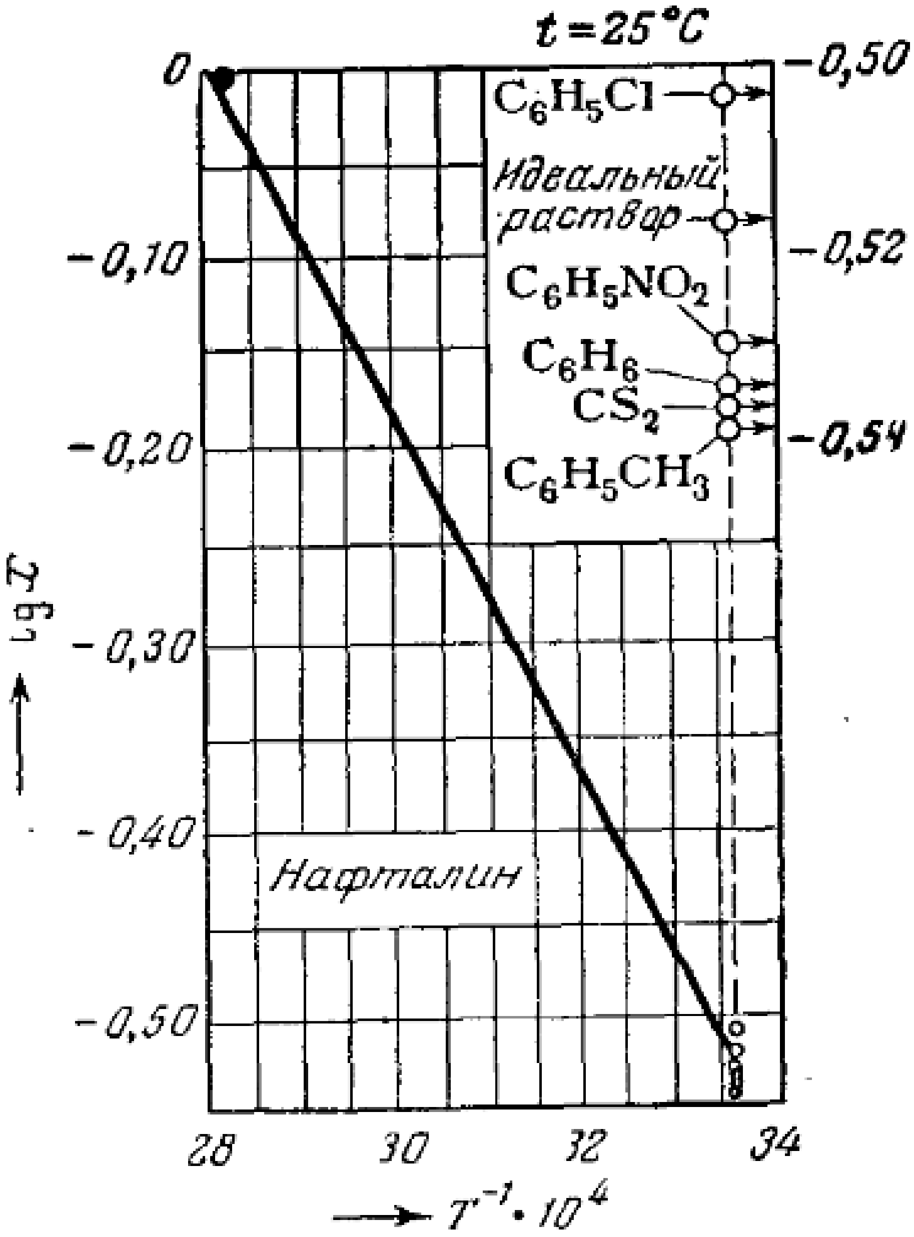
$$\left(\frac{\partial \ln a_2^{\text{satur.}}}{\partial T}\right)_p = \frac{\Delta H_{\text{melt}}}{RT^2}$$

$$\ln a_2^{\text{satur.}} = -\frac{A}{T} + B$$

Solubility of solids

Validation of the equation

$$\ln a_2^{\text{satur.}} = -\frac{A}{T} + B$$



Solubility of solids

Applications of the Schroeder's equation

Van't Hoff: solubility of succinic acid in water increases on going from 0 to 8.5 ^{o}C. This leads to a value of ΔH_{melt} = **28.45** kJ/mole. Calorimetric method gives a value of **27.2** kJ/mole for dilution of 1 mole succinic acid in a large volume of water (close value!).

Another example. According to Bronsted, for dissolution of sulfur in benzene and CS_2 the ΔH_{melt} values practically coincide (**21.8** kJ/mole). They are calculated using the Schroer's equation.

However, calorimetry leads to a value of **2.7** kJ/mole. Such a discrepancy can be easily explained because sulfur forms species S_8

$$21.8 / 2.7 = 8.07$$

Solubility of solids

Temperature dependence of solubility and the Le Chatelier principle

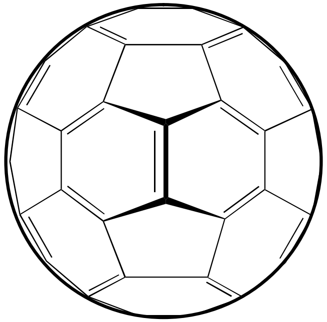
$$\left(\frac{\partial \ln a_2^{\text{satur.}}}{\partial T}\right)_p = \frac{\Delta H_{\text{solub.}}}{RT^2} \qquad \left(\frac{\partial \ln a_2^{\text{satur.}}}{\partial (1/T)}\right)_p = -\frac{\Delta H_{\text{solub.}}}{R}$$

(Van’t Hoff equations)

Presently, the solubility values of various compounds both in water and in other solvents can be found in numerous databases now easily available in the cyberspace.

Solubility of solids

An interesting example is the data on the solubility of fullerenes in solvents of various nature.



One of the most complete summaries of data:

Semenov K. N., Charykov N. A., Keskinov V. A., Piartman A. K., Blokhin A. A., Kopyrin A. A. Solubility of light fullerenes in organic solvents // J. Chem. Eng. Data. – 2010. – V. 55, N. 1 – P. 13-36.

solvent (ε_r at 298 K)	s/M (T = 298 ± 0.5 K, if not otherwise specified)	
	C_{60}	C_{70}
1-chloronaphthalene (5.00)	0.070[a]	–
1-phenylnaphthalene (2.50)	0.069[a]	–
1-methylnaphthalene (2.92)	0.046,[a] 0.046[b]	–
1,2-dichlorobenzene (9.93)	0.037,[a] 0.034,[b] 0.037,[c] 0.0318[d]	0.0303,[e] 0.043[f]
tetralin (2.76)	0.022,[a] 0.017,[g] 0.020,[h] 0.0218[i]	0.014[h]
o-xylene (2.57)	0.012,[b] 0.013,[j] 0.011,[k]	00185[j]
carbon disulfide (2.64 at 293 K)	0.011,[a] 0.011,[j] 7.2×10^{-3},[l] 9.5×10^{-3},[m] 0.016[n]	0.0117,[f] 6.3×10^{-3},[j] 0.01
chlorobenzene (5.62)	9.7×10^{-3},[a] 7.9×10^{-3} [b]	–
toluene (2.38)	4.0×10^{-3},[b] 3.3×10^{-3},[i] 4.0×10^{-3},[j] 2.98×10^{-3},[l] 3.18×10^{-3},[m] 4.4×10^{-3},[n] 3.88×10^{-3},[o] 3.39×10^{-3},[p] 3.61×10^{-3},[r] 4.16×10^{-3} [q]	1.67×10^{-3},[f] 1.8×10^{-3}, 1.27×10^{-3} [m]
benzene (2.27)	2.4×10^{-3},[a] 2.1×10^{-3},[b] 1.9×10^{-3},[i] 2.0×10^{-3},[l] 2.6×10^{-3} [n]	1.55×10^{-3} [f]
tetrachloromethane (2.24)	4.4×10^{-4},[a] 3.88×10^{-4},[c,p] 6.2×10^{-4} [l]	1.44×10^{-4} [f]
benzonitrile (25.20)	5.7×10^{-4} [a]	–
n-hexane (1.88)	6.0×10^{-5},[a] $<1.4 \times 10^{-4}$,[i] 5.6×10^{-5},[l] 5.1×10^{-5},[r] 6.4×10^{-5} [n]	1.5×10^{-5} [f]
n-octane (1.95)	4.2×10^{-4},[i] 3.5×10^{-5},[l] 3.5×10^{-5},[n] 2.8×10^{-5} [r]	5.0×10^{-5} [f]
1-octanol (10.34)	6.5×10^{-5},[r] 5.4×10^{-5},[q] 2.1×10^{-4} [s]	5.5×10^{-5},[r] 3.2×10^{-5} [t]
ethanol (24.55)	1.4×10^{-6},[a] 1.1×10^{-6},[r] 1.9×10^{-6},[q] 1.7×10^{-6} [s]	9.3×10^{-7},[r] 8.3×10^{-7} [u]
methanol (32.66)	0,[a] 4.8×10^{-8},[r] 3.7×10^{-8},[q] 3.3×10^{-8} [s]	4.5×10^{-8},[r] 4.8×10^{-7} [u]
tetrahydrofuran (7.58)	0,[a] 1.5×10^{-5},[q] 1.3×10^{-5},[v] 5.13×10^{-5},[n] 8.3×10^{-4} [i]	2.7×10^{-5} [v]
acetic acid (6.17)	9.4×10^{-6} [w]	–
enanthic acid (2.6)	3.56×10^{-4} [w]	–
acetone (20.56)	1.4×10^{-6} [a]	2.2×10^{-6} [f]
acetonitrile (35.94)	0,[a] 5.6×10^{-8} [q]	–
	"Reactive" Solvents	
piperidine (5.8 at 293 K)	0.074[i]	–
pyrrolidine	0.065[i]	–
quinoline (8.95)	0.010[b]	–
N-methyl-2-pyrrolidone (32.2)	1.2×10^{-3} [a]	–
pyridine (12.91)	1.2×10^{-3},[a] 4×10^{-4},[b] 4.2×10^{-4} [i]	–

“Good” (or “strong”) solvents and “poor” (or “weak”) solvents.

Attempts to find correlations between the solubility and solvent parameters (only few examples).

$$\log x_2 = -11.1 + 30.1\frac{n^2 - 1}{n^2 + 2} - 2.75\frac{\varepsilon_r - 1}{\varepsilon_r + 2} - 0.00194\delta_H{}^2$$

(81 solvents, $r = 0.935$)

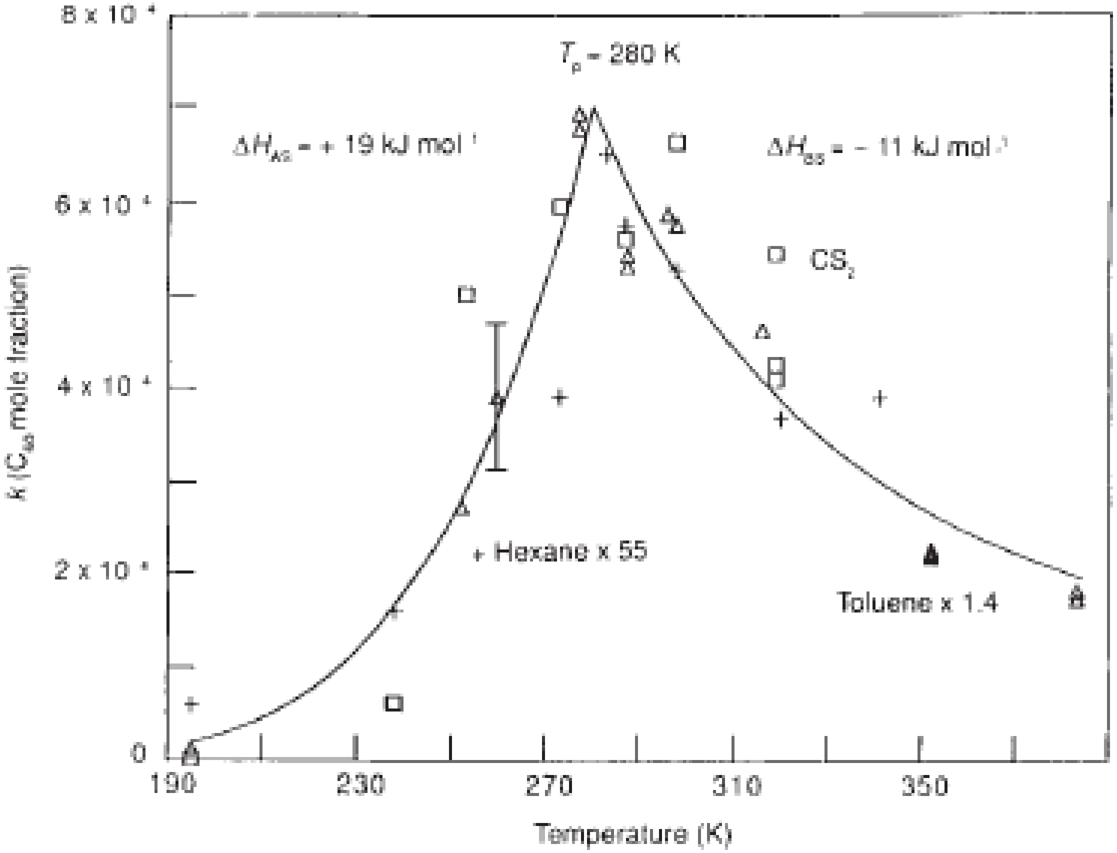
$$\log x_2 = -0.1298E_T(30) + 0.2264\mathcal{R} - 0.0592V_m + 0.729\beta$$

(95 solvents, $r = 0.996$)

Interfering factors: crystal solvates formation in good solvents and (partial!) transformation of molecular solutions in colloidal systems, i.e., organosols.

Application of the **Q**uantitative **S**tructure-**P**roperty **R**elationships, or QSPR.

Influence of crystal-solvate formation, which melt incongruently.



Fullerene solubility in toluene, *n*-hexane, CS$_2$

LETTERS TO NATURE

Anomalous solubility behaviour of C_{60}

Rodney S. Ruoff, Ripudaman Malhotra, David L. Huestis, Doris S. Tse & Donald C. Lorents

Solvophobic solvation

$$\Delta G^{\mathrm{o}}_{\mathrm{solut}} = \Delta H^{\mathrm{o}}_{\mathrm{solut}} - T\Delta S^{\mathrm{o}}_{\mathrm{solut}}; \qquad \Delta S^{\mathrm{o}}_{\mathrm{solut}} = \frac{\Delta H^{\mathrm{o}}_{\mathrm{solut}} - \Delta G^{\mathrm{o}}_{\mathrm{solut}}}{T}$$

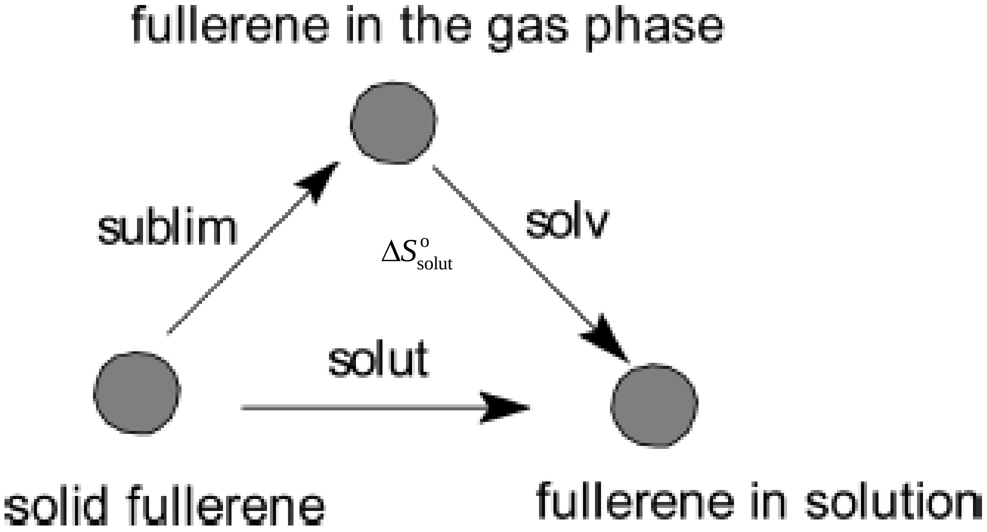


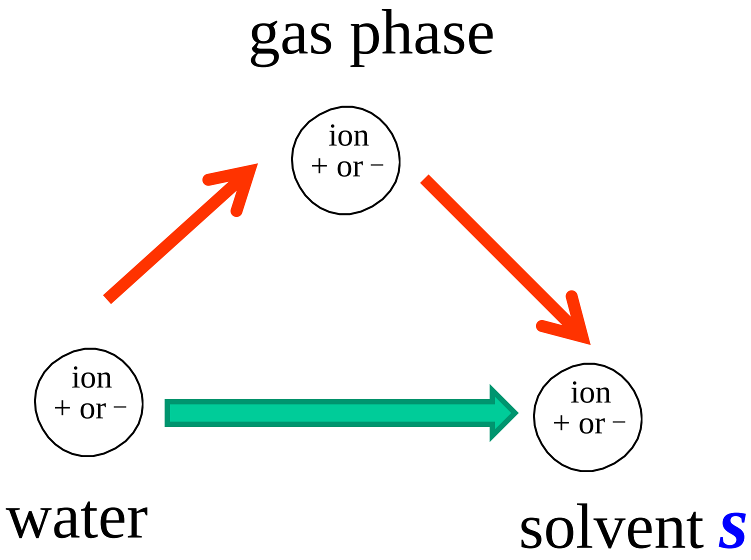
Figure 7. The Born–Haber cycle for fullerene dissolution and solvation.

$$\Delta G^{\mathrm{o}} > 0; \quad \Delta H^{\mathrm{o}} < 0$$

$$\Delta S^{\mathrm{o}}_{\mathrm{solut}} = -(83-109)\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

$$\Delta S^{\mathrm{o}}_{\mathrm{solv}} = -(201-208)\,\mathrm{J\,mol^{-1}\,K^{-1}}$$

Solvation energies of ions


gas phase

ion
+ or −

water

ion
+ or −

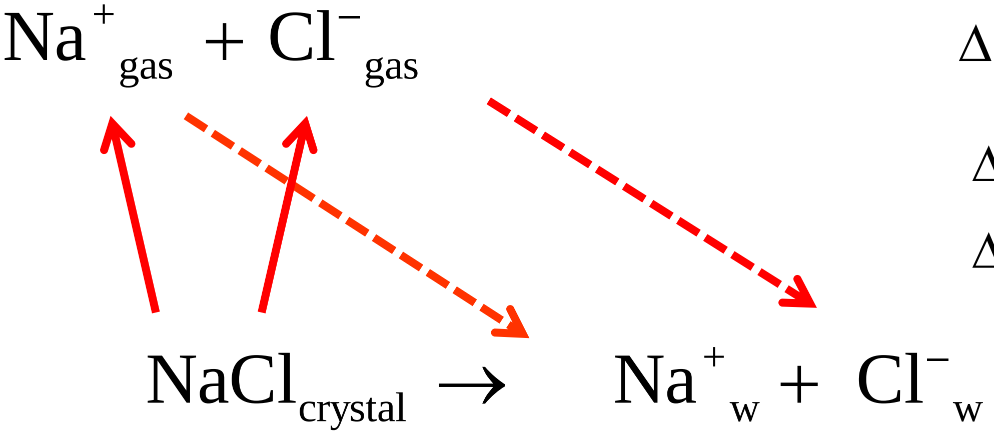
solvent ***s***

ion
+ or −

Born's equation for a charged sphere:

$$\log {}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}} = \frac{\Delta G_{\mathrm{tr}}(i)}{2.303RT} = \frac{e^2 z_{\mathrm{i}}^2 N_{\mathrm{A}}}{4.60\ RTr_{\mathrm{i}} \times 4\pi \times \varepsilon_0} \times \left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_{\mathrm{r,w}}} \right]$$

Dissolution of crystal lattice



$$Na^{+}_{gas} + Cl^{-}_{gas}$$

$$NaCl_{crystal} \rightarrow Na^{+}_{w} + Cl^{-}_{w}$$

$$\Delta G_{lattice} >> 0;$$

$$\Delta G_{hydr}(Na^{+}) << 0;\ \Delta G_{hydr}(Cl^{-}) << 0$$

$$\Delta H_{lattice} >> 0;$$

$$\Delta H_{hydr}(Na^{+}) << 0;\ \Delta H_{hydr}(Cl^{-}) << 0$$

$$\Delta H_{lattice} + \Delta H_{hydr}(Na^{+}) + \Delta H_{hydr}(Cl^{-}) = \Delta H_{dissolut}$$

$$\Delta G_{lattice} + \Delta G_{hydr}(Na^{+}) + \Delta G_{hydr}(Cl^{-}) = \Delta G_{dissolut}$$

Calculations of the lattice energy: Kapustinskiy – Yatsimirskiy formula

$$\Delta H_{\mathrm{lattice}} = 287.2\,\frac{\Sigma\,\nu_{\mathrm{C}t}\nu_{\mathrm{An}}}{r_{\mathrm{Ct}}+r_{\mathrm{An}}}\left[1-\frac{0.345}{r_{\mathrm{Ct}}+r_{\mathrm{An}}}+0.0087(r_{\mathrm{Ct}}+r_{\mathrm{An}})\right]$$

r – crystallographic radii, Å

ν – number of ions

$\Delta H_{\mathrm{lattice}}$ – in kcal/mole

For NaCl: 186 kcal/mole =

778 kJ/mole

$$\Delta H_{\mathrm{hydr}}(\mathrm{Na}^{+}) + \Delta H_{\mathrm{hydr}}(\mathrm{Cl}^{-}) = -\Delta H_{\mathrm{lattice}} + \Delta H_{\mathrm{dissolut}}$$

Another approach; another Born – Haber cycle

$$\begin{tikzcd}
\mathrm{Na}^{+}{}_{\mathrm{gas}} + \mathrm{Cl}^{-}{}_{\mathrm{gas}+} & \mathrm{Na}_{\mathrm{gas}} + \arrow[l, "I_{\mathrm{Na}} - E_{\mathrm{Cl}}"'] & \mathrm{Cl}_{\mathrm{gas}} \\
\mathrm{NaCl}_{\mathrm{crystal}} \arrow[u, "\Delta H_{\mathrm{lattice}}"] \arrow[r, "-\Delta H_{\mathrm{form}}"] & \mathrm{Na}_{\mathrm{solid}} + \frac{1}{2} \arrow[u, "\Delta H_{\mathrm{subl}}"] & \mathrm{Cl}_2 \arrow[u, "\frac{1}{2} D_{\mathrm{diss}}"']
\end{tikzcd}$$

$$\Delta H_{\mathrm{lattice}} = -\Delta H_{\mathrm{form}} + \Delta H_{\mathrm{subl}} + \frac{1}{2} D_{\mathrm{diss}} + I_{\mathrm{Na}} - E_{\mathrm{Cl}}$$

$$\Delta H_{\text{lattice}} = -\Delta H_{\text{form}} + \Delta H_{\text{subl}} + \frac{1}{2} D_{\text{diss}} + I_{\text{Na}} - E_{\text{Cl}}$$

$$= -(-410.9) + 108.7 + 121.38 + 482.2 - 365.3$$

$$= 771.7 (\text{kJ/mole})$$

	$-\Delta G^\circ_{\text{hydr}}$	$-\Delta H^\circ_{\text{hydr}}$
H^+	1066.1	1104.1
Li^+	487.4	528.4
Na^+	387.4	419.2
K^+	313.8	334.7
Rb^+	292.9	309.6
Cs^+	260.5	277.2
Ag^+	455.6	489.1
Ba^{2+}	1272.3	1329.7
Zn^{2+}	1981.5	2071.5
F^-	456.9	497.5
Cl^-	339.7	363.6
Br^-	325.9	349.4
I^-	279.5	291.6
SCN^-	—	322
ClO_4^-	218	238