SELECTED CHAPTERS OF PHYSICAL CHEMISTRY OF SOLUTIONS

Acid-base equilibria.
Polyprotic acids

$$H_nA^{z} \Leftrightarrow H_{n\text{-}1}A^{z\text{-}1} + H^{+}; n = 1, 2, 3.....$$

$$K_{a(1-z)} = a_{H^{+}} \frac{a_{H_{n\text{-}1}A^{z\text{-}1}}}{a_{H_nA^{z}}}$$

For polyprotic (or polybasic) acids, the ratio of the constants of the stepwise dissociation is very important:

$$\frac{K_{a(z\text{-}2)}}{K_{a(z\text{-}1)}} = ?$$

$$H_2A \Leftrightarrow HA^- + H^+;\ K_{a1}$$

$$HA^- \Leftrightarrow A^{2-} + H^+;\ K_{a2}$$

$$\boxed{\frac{K_{a1}}{K_{a2}} = ?}$$

Are there any regularities that describe this relationship?

Normally, $K_{a1} >> K_{a2}$

i.e, $pK_{a1} < pK_{a2}$

Analogously for:

$H_2A^+ \Leftrightarrow HA \Leftrightarrow A^-$ and $H_2A^{2+} \Leftrightarrow HA^+ \Leftrightarrow A$

But can it be that: $\mathrm{p}K_{\mathrm{a1}} > \mathrm{p}K_{\mathrm{a2}}$? **(inversion)**

Inorganic acids (small molecules): electrostatic factor results in

$$K_{\mathrm{a1}} \gg K_{\mathrm{a2}}$$

For example, the Pauling's rule:

$$\mathrm{H_3PO_4}:\quad \mathrm{p}K_{\mathrm{a1}} = 2.15;\quad \mathrm{p}K_{\mathrm{a2}} = 7.20;\quad \mathrm{p}K_{\mathrm{a3}} = 12.32$$

In general, since the molecules of inorganic acids are small, it is reasonable to assume a significant role of the electrostatic factor.

For example, the presence of one negative charge in the single charged anion should hinder the elimination of the next proton with the formation of the double charged anion.

But some exceptions are also known:

$$H_4SiO_4\text{:}\quad \mathrm{p}K_{a1} = \mathrm{p}K_{a2} = 11.7;\quad \mathrm{p}K_{a3} = \mathrm{p}K_{a4} = 12.00$$

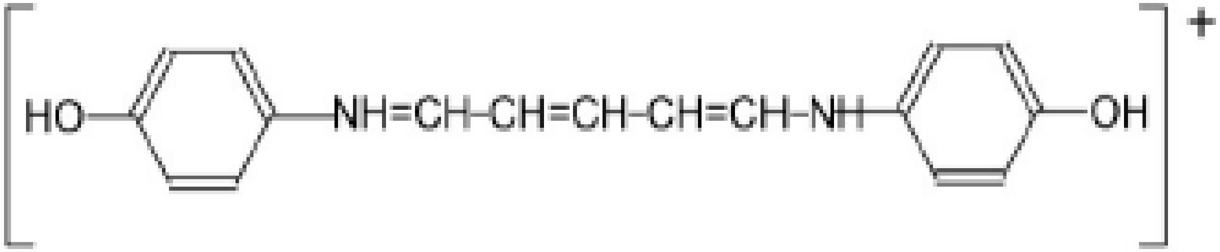
$$Hg\left(H_2O\right)_n^{\;2+} \Leftrightarrow HgOH^+ \Leftrightarrow Hg\left(OH\right)_2$$

$$\mathrm{p}K_{a1} = 3.70 \pm 0.07;\ \mathrm{p}K_{a2} = 2.60 \pm 0.09\ \text{(ionic strength 0.5 M)}$$

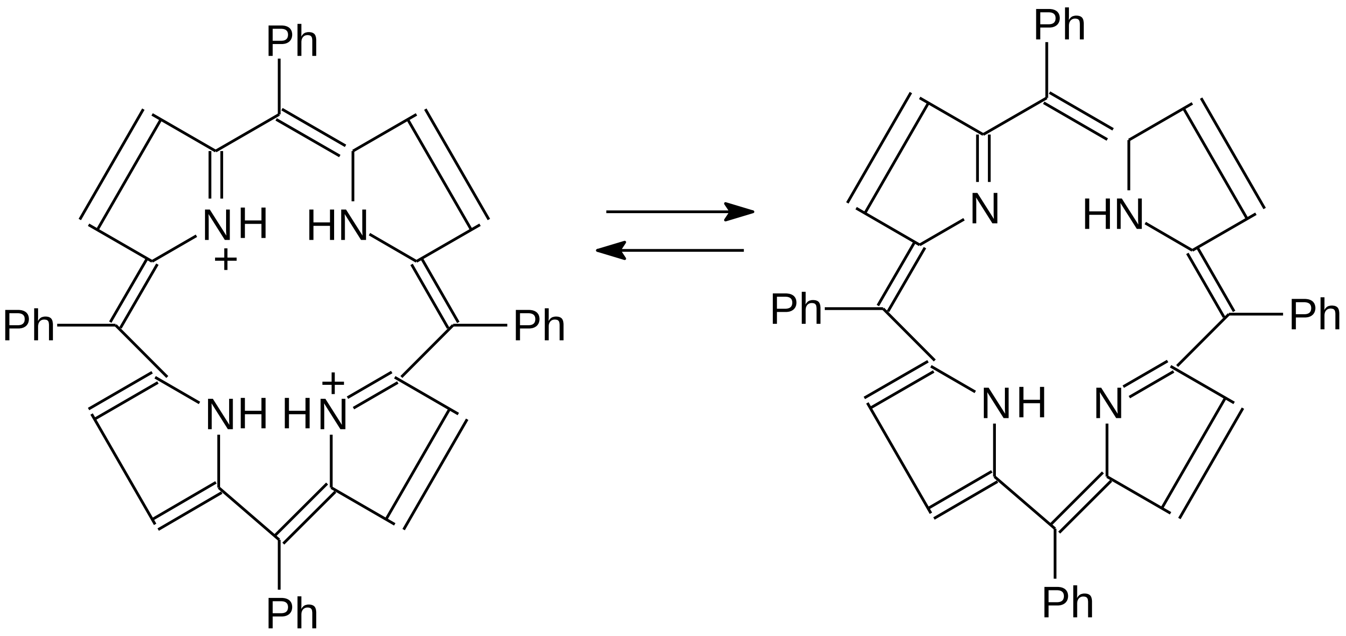
Organic acids: some unusual ratios of the dissociation constants: inversion or $K_{a1} = K_{a2}$

$$\mathrm{Ar-N{=}N^{+} \Leftrightarrow Ar-N{=}NOH \Leftrightarrow Ar-N{=}NO^{-}}$$

(diazonium cation in aqueous alkaline media)



(*p*-dihydroxyglutaconeanyl)



Double charged cation (H_4A^{2+}) and the neutral form (H_2A) of *meso*-tetraphenylporphyrin.

±

Sources of error:

Small fraction of the intermediate HA- form

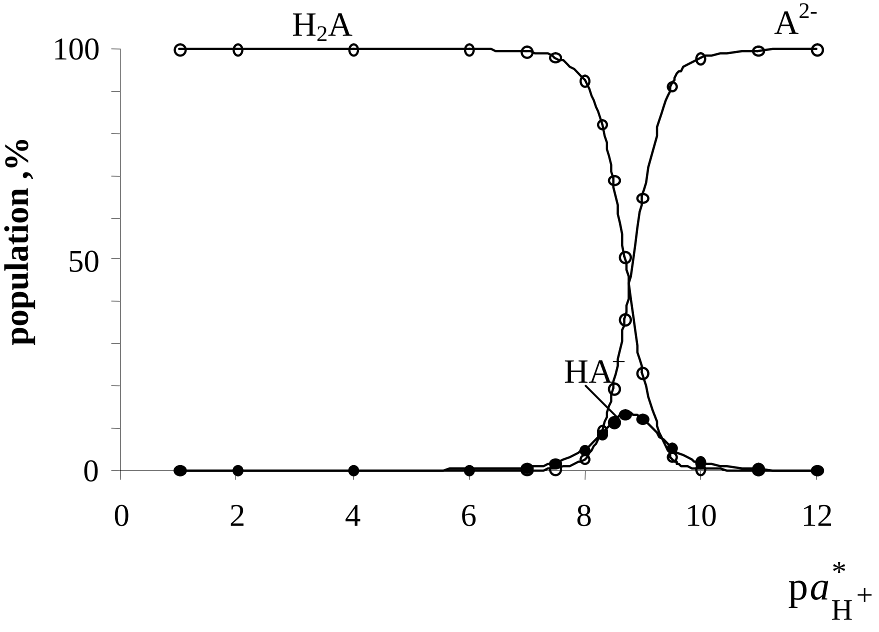
$$\alpha_{\mathrm{HA}^-} = \frac{100\%}{(K_{a1})^{-1} a_{\mathrm{H}^+} + 1 + K_{a2} (a_{\mathrm{H}^+})^{-1}}$$

Slow reactions, including intramolecular rearrangements

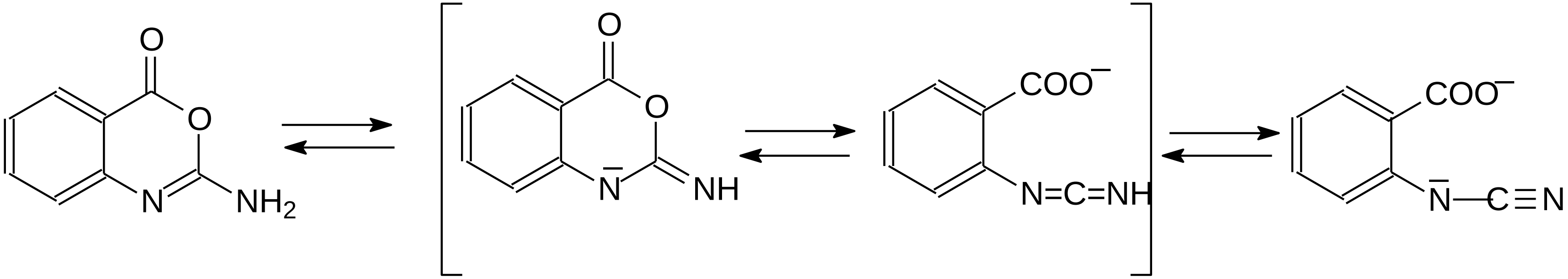
2,7-Dichlorofluorescein in 47% ethanol – 47 % benzene – 6 % water

$$\mathrm{p}K_{\mathrm{a1}} = 9.23 \pm 0.08;$$

$$\mathrm{p}K_{\mathrm{a2}} = 8.22 \pm 0.08$$



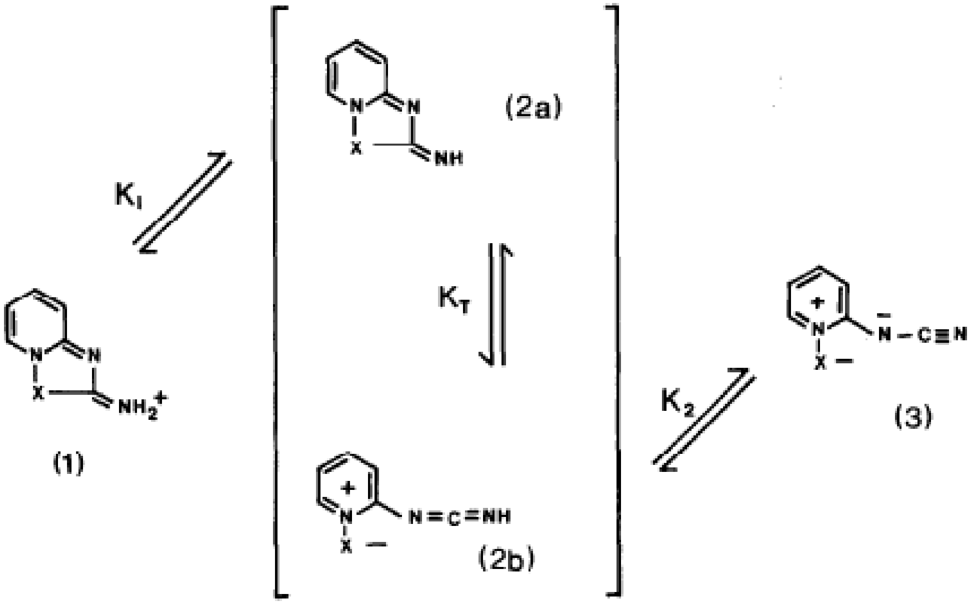
But inversion of the p*K*a may be NOT an error!



Inversion of the dissociation constants of 2-amino-4,5-benzo-6-oxo-1,3-oxasine

$$pK_{a1} = 10.61;\ \ pK_{a2} = 9.21$$

Hegarty A.F., *Bruice T.C.* Acyl Transfer Reactions from and to the Ureido Functional Group. I. The Mechanisms of Hydrolysis of an *O*-Acylisourea (2-Amino-4,5-benzo-6-oxo-1,3-oxazine) // J. Amer. Chem. Soc. -1970. -**92**, № 22. -P. 6561–6567.



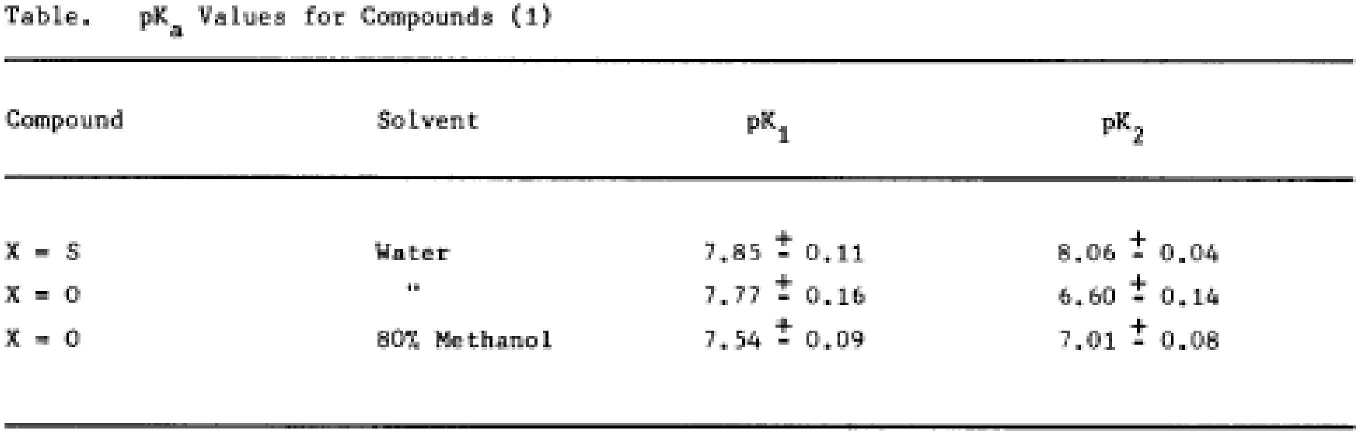
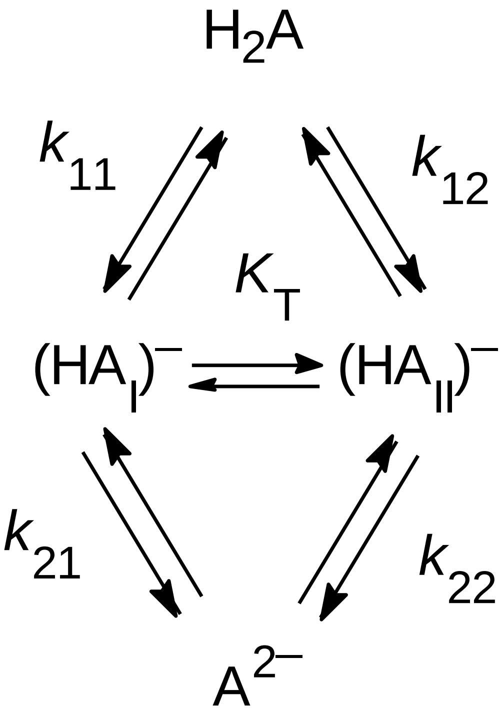


Table. pK_a Values for Compounds (1)

Compound	Solvent	pK_1	pK_2
X = S	Water	7.85 ± 0.11	8.06 ± 0.04
X = O	"	7.77 ± 0.16	6.60 ± 0.14
X = O	80% Methanol	7.54 ± 0.09	7.01 ± 0.08

Clarkson R., Dowell R.I., Taylor P.J. The reversible cation-anion isomerisation of 2-imino-2H-pyrido [1,2-b][1, 2, 4] thia(oxa)diazole hydrobromide // Tetrahedron Letters -1982. -**23**, № 4. –P.485–488.

“Microscopic” dissociation constants



$$K_{a1} = k_{11} + k_{12}$$

$$K_{a2}^{-1} = k_{21}^{-1} + k_{22}^{-1}$$

$$K_T = \frac{\left[HA_{II}^-\right]}{\left[HA_I^-\right]} = \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

If $k_{11} = k_{12} = k_{21} = k_{22} = k$, then $K_{a1} = 2k$

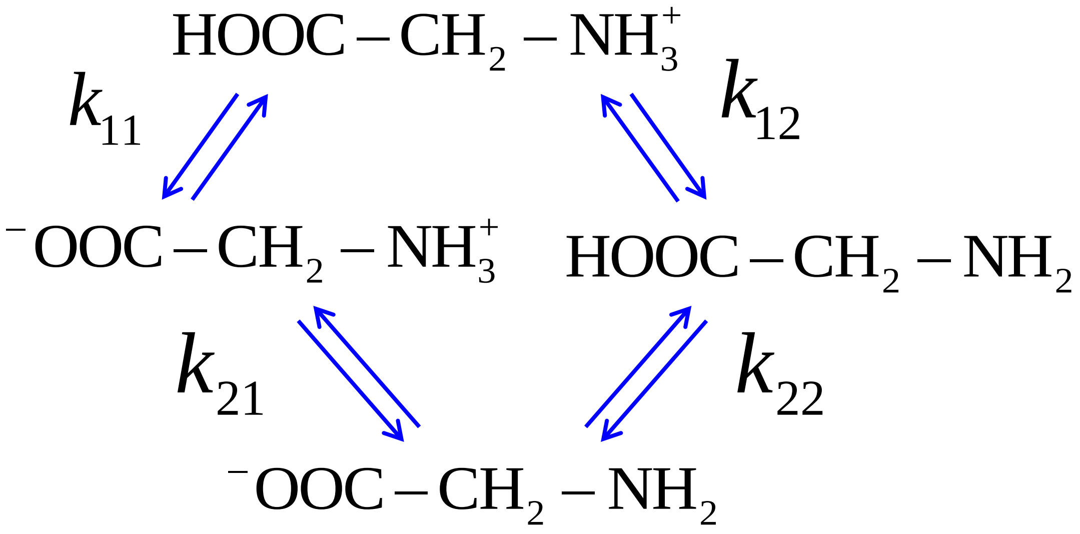
$$K_{a2} = \frac{k}{2}$$

$$pK_{a1} = pk - \log 2 = pk - 0.301$$

$$pK_{a2} - pK_{a1} = \log 4 = 0.602$$

Special case of aliphatic aminoacids

Glycine: $\mathrm{p}K_{\mathrm{a0}} = 4.3;\ \mathrm{p}K_{\mathrm{a1}} = 10.8$



$$\begin{tikzcd}
& \mathrm{HOOC-CH_2-NH_3^+} \arrow[dl, shift right, "k_{11}"'] \arrow[dr, shift left, "k_{12}"] & \\
\mathrm{{}^-OOC-CH_2-NH_3^+} \arrow[ur, shift right] \arrow[dr, shift left, "k_{21}"'] & & \mathrm{HOOC-CH_2-NH_2} \arrow[ul, shift left] \arrow[dl, shift right, "k_{22}"] \\
& \mathrm{{}^-OOC-CH_2-NH_2} \arrow[ul, shift left] \arrow[ur, shift right] &
\end{tikzcd}$$

$$K_{\mathrm{T}} = \frac{\left[\mathrm{HA}_{\mathrm{II}}^{-}\right]}{\left[\mathrm{HA}_{\mathrm{I}}^{-}\right]} = \frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}$$

How can we estimate the structure of the neutral form?

For $\mathrm{H_3COOC-CH_2-NH_3^+}:\ \mathrm{p}K_{\mathrm{a}} = 7.7;\ \ \mathrm{H_3C-NH_3^+}:\ \mathrm{p}K_{\mathrm{a}} = 10.7$

$\mathrm{HOOCCH_3}:\ \mathrm{p}K_{\mathrm{a}} = 4.76$

$$\boxed{K_{\mathrm{T}} = \frac{10^{-4.8}}{10^{-10.7}} \approx 10^{6}}$$

$$\mathrm{HOOC{-}(CH_2)_n{-}COOH} \Leftrightarrow \mathrm{HOOC{-}(CH_2)_n{-}COO^-} \Leftrightarrow \mathrm{{}^-OOC{-}(CH_2)_n{-}COO^-}$$

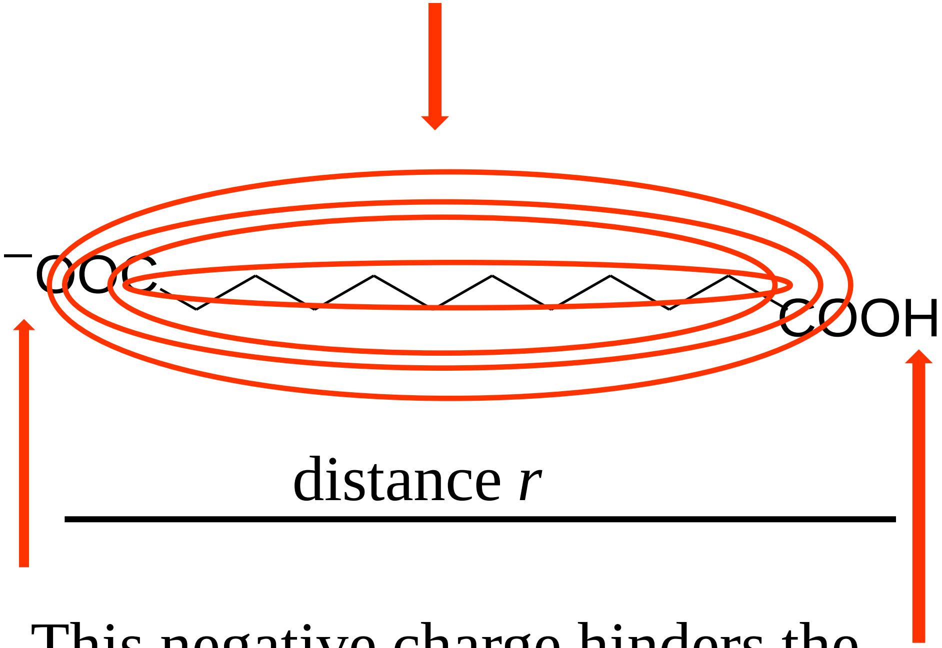
If $n \to \infty$:

$$k_{11} = k_{12} = k_{21} = k_{22} = k,$$

$$\mathrm{p}K_{\mathrm{a1}} = \mathrm{p}k - \log 2 = \mathrm{p}k - 0.301$$

$$\mathrm{p}K_{\mathrm{a2}} - \mathrm{p}K_{\mathrm{a1}} = \log 4 = 0.602$$

Electric field lines



This negative charge hinders the removal of the second proton

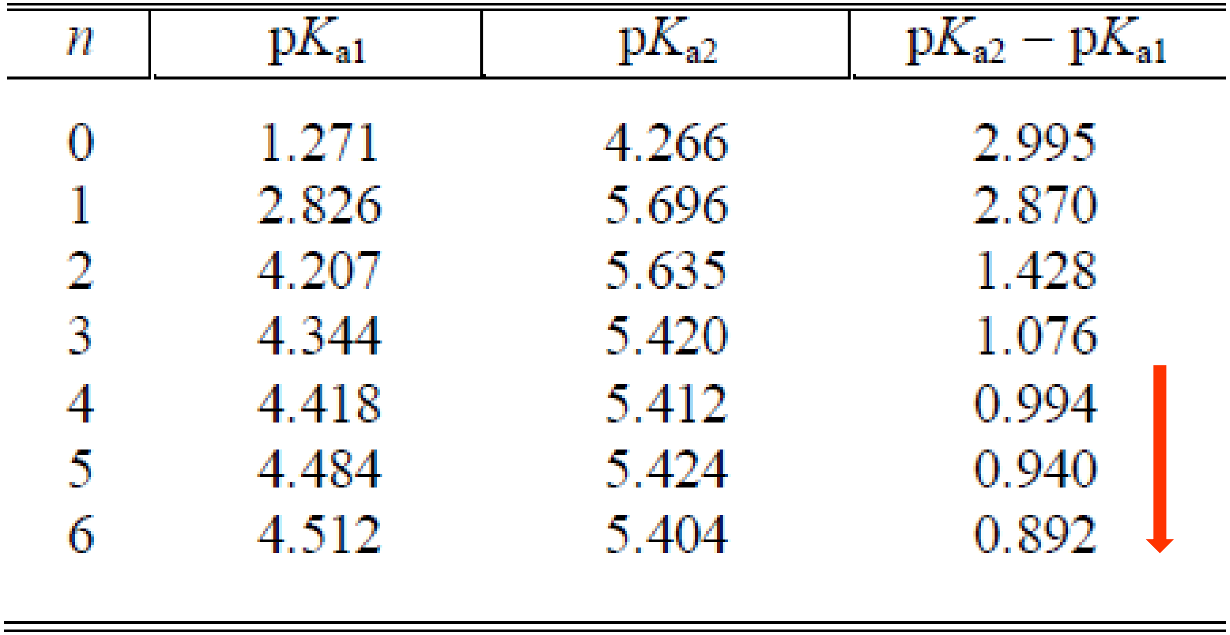
Bjerrum – Kirkwood – Westheimer:

$$\delta \mathrm{p}K_{\mathrm{a}} = \frac{e^{2} N_{A}}{2.302RT \times 4\pi \times 8.854 \times 10^{-12}} \times \frac{1}{\varepsilon_{eff}\, r}$$

effective relative permittivity

$$\mathrm{p}K_{\mathrm{a2}} - \mathrm{p}K_{\mathrm{a1}} = \log 4 + \delta \mathrm{p}K_{\mathrm{a}}^{\mathrm{el}}$$

$\mathrm{HOOC{-}(CH_2)_n{-}COOH}$ in water, 25 °C



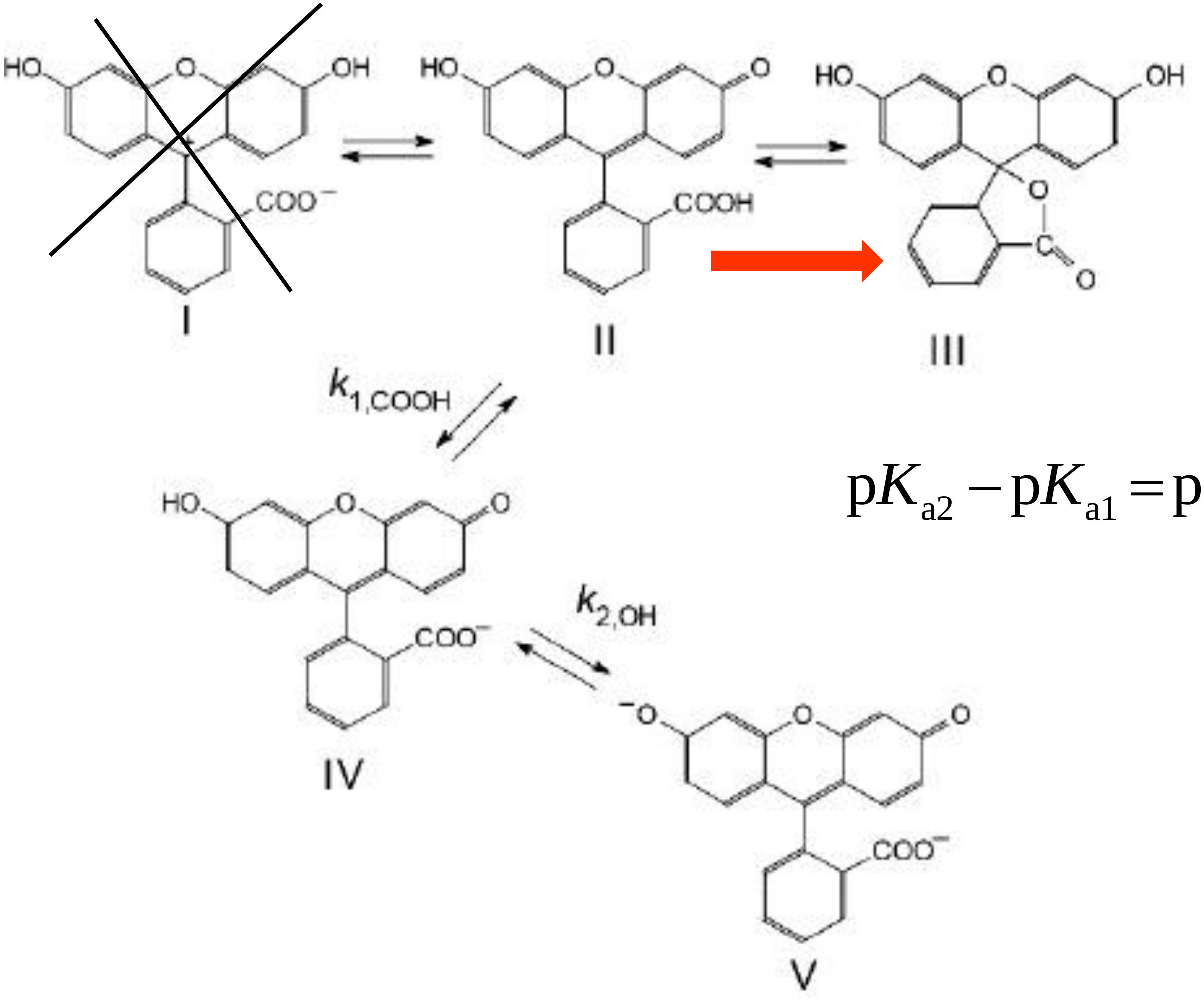
n	$\mathrm{p}K_{\mathrm{a1}}$	$\mathrm{p}K_{\mathrm{a2}}$	$\mathrm{p}K_{\mathrm{a2}} - \mathrm{p}K_{\mathrm{a1}}$
0	1.271	4.266	2.995
1	2.826	5.696	2.870
2	4.207	5.635	1.428
3	4.344	5.420	1.076
4	4.418	5.412	0.994
5	4.484	5.424	0.940
6	4.512	5.404	0.892

approach $\log 4 = 0.602$

Christensen J.J., Wrathall D.P., Izatt R.M., Tolman D.O. Christensen J.J., Izatt R.M., Hansen L.D. Thermodynamics of Proton Ionization in Dilute Aqueous Solution. VII. *J. Amer. Chem. Soc.* 1967. **89:** 213.

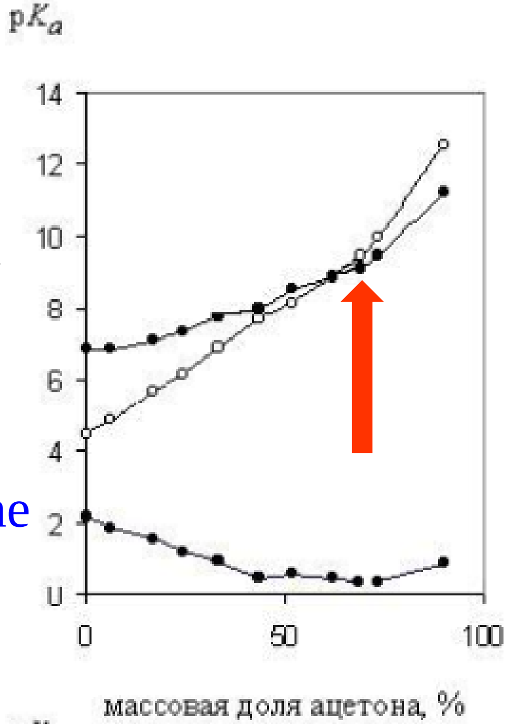
Hence: only the tautomeric transformations can result in the inversion of the dissociation constants ?!

As example: fluorescein

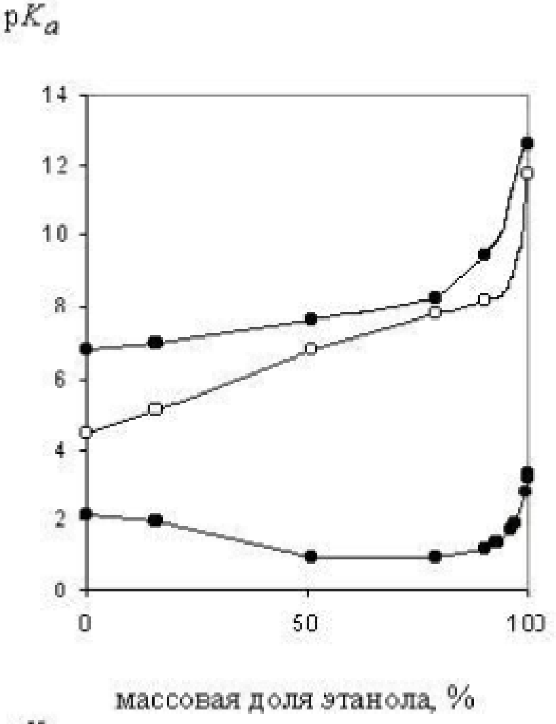


$$\mathrm{p}K_{\mathrm{a2}} - \mathrm{p}K_{\mathrm{a1}} = \mathrm{p}k_{2,\mathrm{OH}} - \mathrm{p}k_{1,\mathrm{COOH}} - \log\frac{[\mathrm{III}]}{[\mathrm{II}]}$$

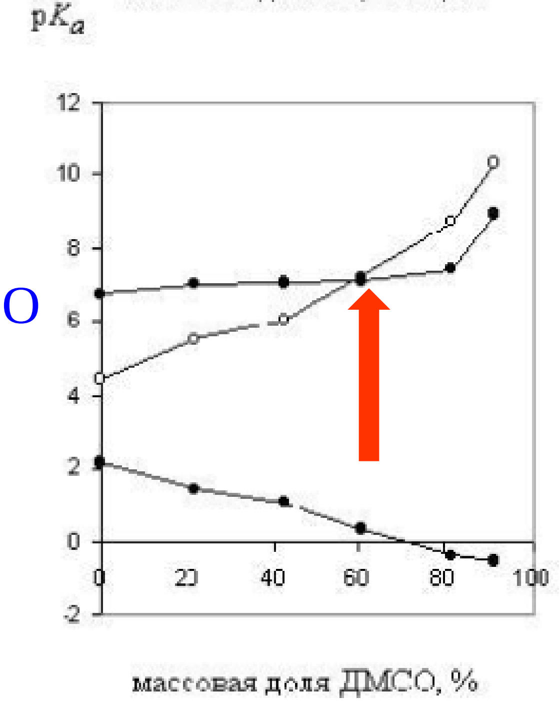
Fluorescein



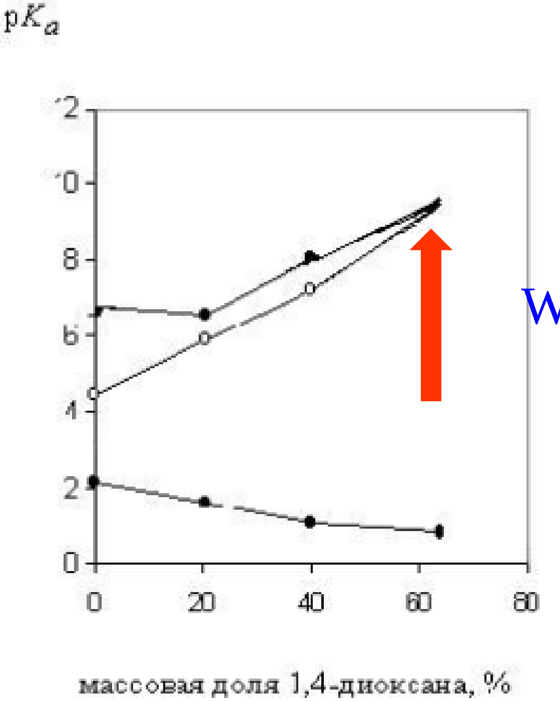
Water – acetone



Water – ethanol



Water – DMSO



Water – 1,4-dioxane

Selected pK_a values in water at 25 °C (from most reliable sources)

Acid		
Benzoic acid	4.201	4.204
Salicylic acid, pK_{a1}	2.996	2.98
Salicylic acid, pK_{a2}	—	12.38
Acetic acid	4.756	4.756
CO_2, pK_{a1}	6.352	6.352
CO_2, pK_{a2}	10.329	10.329
Phenol	9.998	9.99
4-Nitrophenol	7.149	7.150
2,4-Dinitrophenol	4.11	4.08
2,5- Dinitrophenol	5.216	5.216
2,6- Dinitrophenol	3.706	3.713
Phosphoric acid, pK_{a1}	2.148	2.148
Phosphoric acid, pK_{a2}	7.198	7.198
Phosphoric acid, pK_{a3}	—	12.32
Diethylbarbituric acid	7.98	8.020
Ammonium ion	9.245	9.246
Anilinium ion	4.596	4.60
Pyridinium ion	—	5.17

***Таблица 10.4.* Значения pK_s, $\lg {}^*\gamma_H^s$ и pK_a кислот в различных растворителях (шкала моль/л, 298 К)**

Растворитель	pK_s	$\lg {}^*\gamma_H^s$	pK_a			
			Пикриновая кислота	2,6-Динитрофенол	Салициловая кислота	Бензойная кислота
Вода	14,00	0	0,38; 0,43 *	3,71	2,99	4,199
Метанол	16,7—17,2	+1,52	3,55	*7,64* **	7,90	9,40
Этанол	18,9—19,5	+1,94	*4,10*	—	8,70	10,25
Пропанол-2	20,8—22,0	—	4,02	—	—	10,64;11,75
Бутанол-1	21,6	—	4,21; 4,35	—	9,61	11,48
2-Метил-пропанол-2	26,8—28,5	—	5,05; 5,35	—	—	15,0
Формамид	16,8	—	≈1,2	4,2	4,36	6,27
ДМСО	33,3	−3,40	−0,3; −0,5	4,9	6,8	11,1
ДМФА	29,4—31,6	−2,52	1,6	5,8	8,3	12,3
Ацетонитрил	≥33,3	+7,85	11,0	*16,2*	16,9	20,7
Ацетон	32,5	+(6—7)	9,2	13,8	*15,7*	*18,2*
Пропиленкарбонат	29	+(6,5—8,8)	9,3	—	15,2	19,7
Нитрометан	≥24		7,67; 8,02	16,0	—	*19,5*
Сульфолан	—	—	*17,4*	—	*23,6*	*26,3*
4-Метил-пентан-2-он	—	—	11,0	17,6	—	22,4

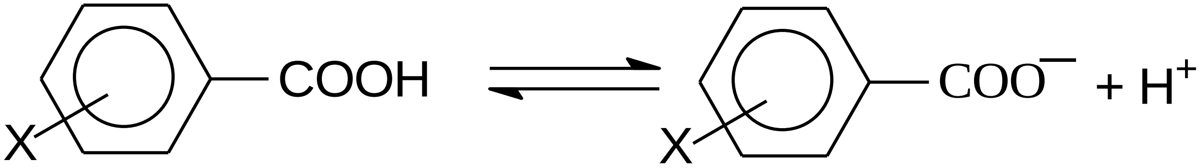
* Два значения pK_a приводятся в том случае, когда нет достаточных оснований отдать предпочтение одному из них.

** Курсивом набраны значения, являющиеся скорее ориентировочными.

Relation between the structure and p*K*a

Effects of substitution.

Aromatic compounds: Hammett's constants of para- and meta-substituents



$$\boxed{\log\frac{K_a^X}{K_a^H} = \mathrm{p}K_a^H - \mathrm{p}K_a^X = \rho\sigma}$$

(The same – for some rate constants of hydrolysis)

σ reflects the influence of the substituent

ρ characterizes the reaction series

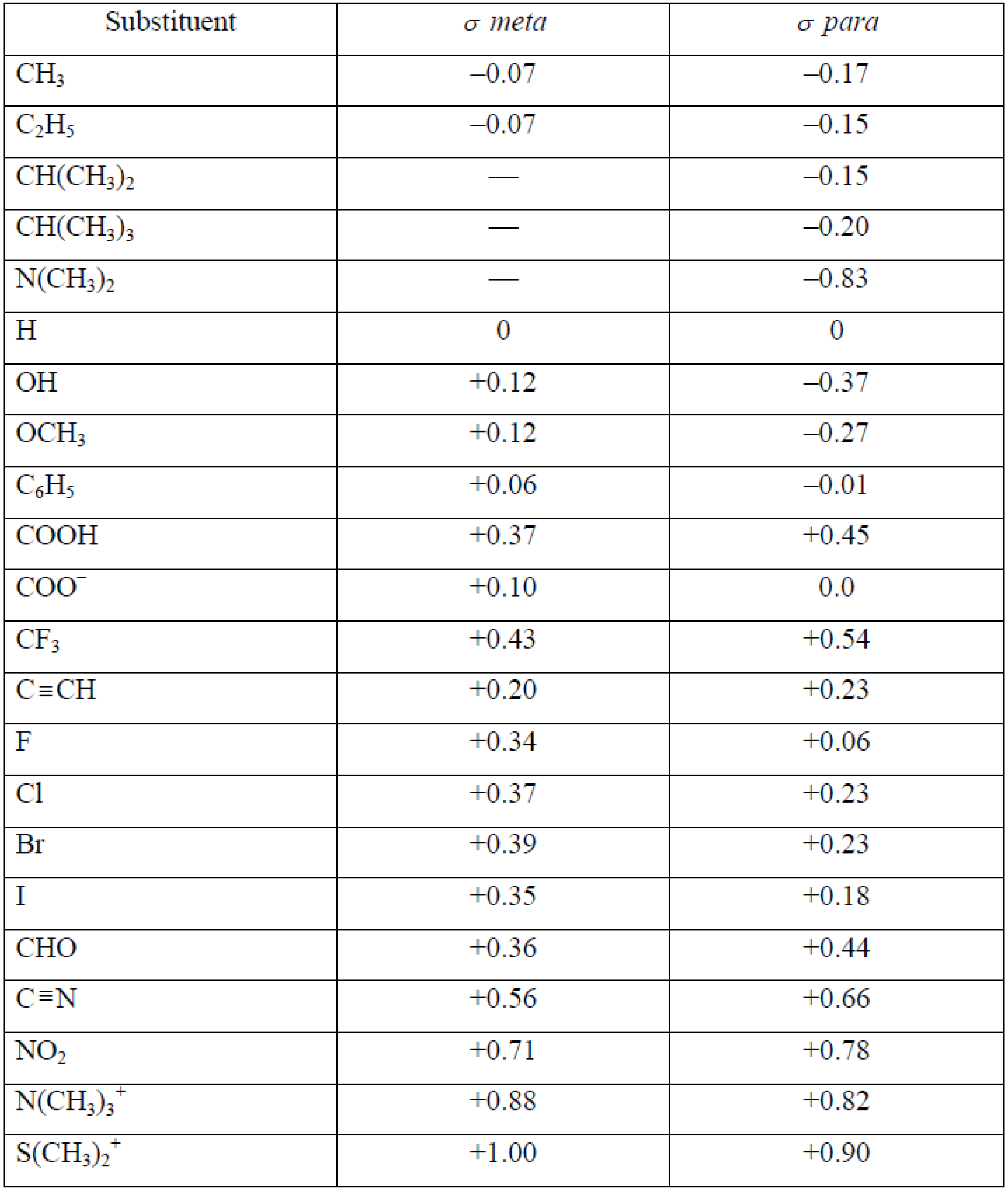
Benzoic acids, $XC_6H_4{-}COOH$ in water, 25 °C:

$\rho \equiv 1$

$$\sigma_X = \mathrm{p}K_a^H - \mathrm{p}K_a^X;$$

$$\sigma_H \equiv 0$$

$$\mathrm{p}K_{a1} = \mathrm{p}k - \log 2 = \mathrm{p}k - 0.301$$



Substituent	σ *meta*	σ *para*
CH_3	–0.07	–0.17
C_2H_5	–0.07	–0.15
$CH(CH_3)_2$	—	–0.15
$CH(CH_3)_3$	—	–0.20
$N(CH_3)_2$	—	–0.83
H	0	0
OH	+0.12	–0.37
OCH_3	+0.12	–0.27
C_6H_5	+0.06	–0.01
COOH	+0.37	+0.45
COO^-	+0.10	0.0
CF_3	+0.43	+0.54
$C{\equiv}CH$	+0.20	+0.23
F	+0.34	+0.06
Cl	+0.37	+0.23
Br	+0.39	+0.23
I	+0.35	+0.18
CHO	+0.36	+0.44
$C{\equiv}N$	+0.56	+0.66
NO_2	+0.71	+0.78
$N(CH_3)_3^+$	+0.88	+0.82
$S(CH_3)_2^+$	+1.00	+0.90

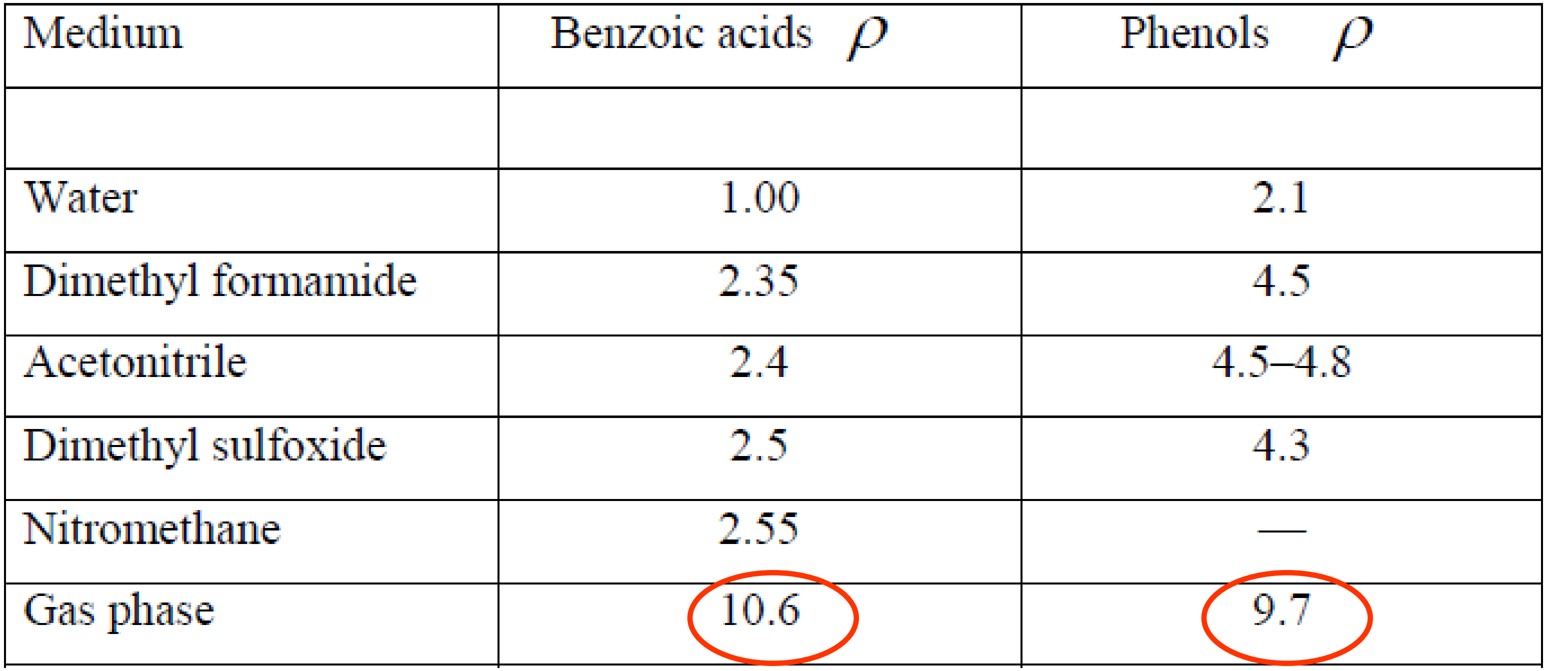
The problem of the ortho-substituents

Electronic interaction between the substituents

Two effects: conjugation ("mesomeric") and inductive effects

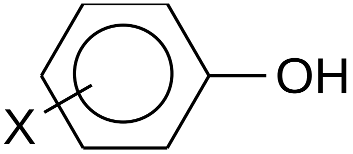
$$\rho = \frac{\mathrm{p}K_a^{\mathrm{H}} - \mathrm{p}K_a^{\mathrm{X}}}{\sigma}$$

Estimation of the "ro" constant in non-aqueous solvents



Medium	Benzoic acids ρ	Phenols ρ
Water	1.00	2.1
Dimethyl formamide	2.35	4.5
Acetonitrile	2.4	4.5–4.8
Dimethyl sulfoxide	2.5	4.3
Nitromethane	2.55	—
Gas phase	10.6	9.7

For



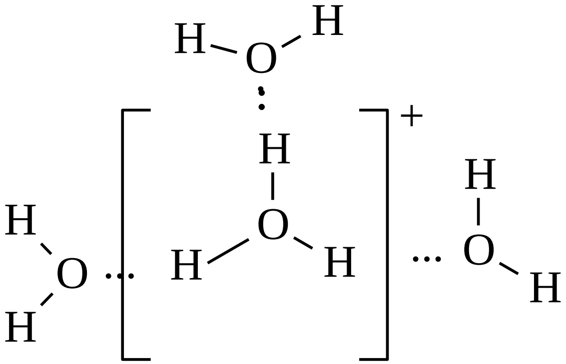
In water: $\rho = 2.1$

Proton in aqueous solutions:

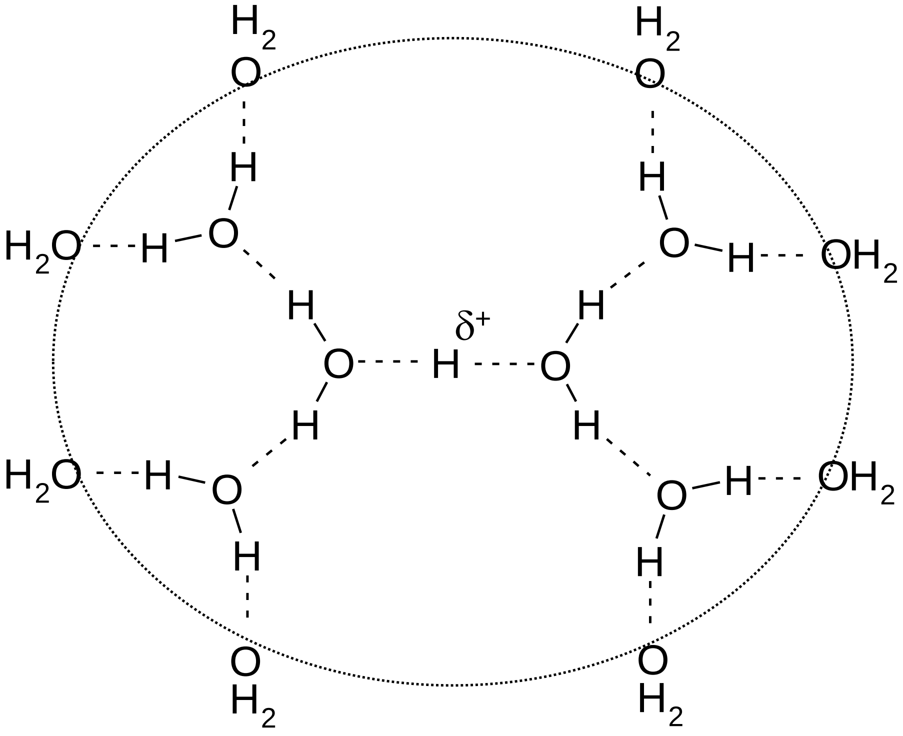
H_3O^+ hydronium ion;

$H_5O_2^+$ Zundel cation $[H_2O...H...OH_2]^+$

$H_9O_4^+$ Eigen cation

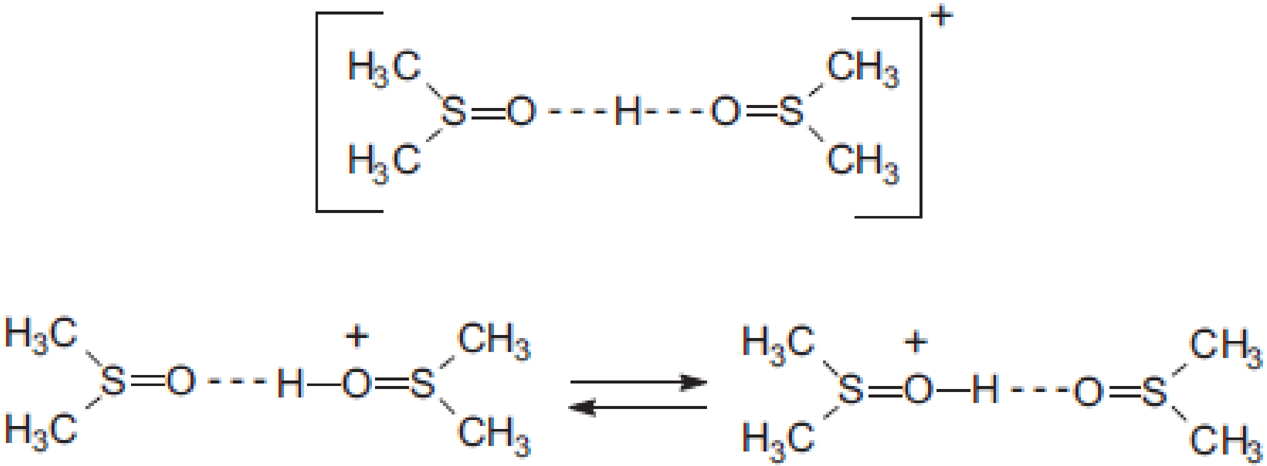


($H_7O_3^+$, $H_{11}O_5^+$) - ?!



$H_{13}O_6^+$ в водном растворе [Stoyanov et al., 2013)]

Proton in organic solutions



Acidity scales in solution

Cell without a liquid junction

$$\mathrm{Pt}\,|\,\mathrm{H_2}\,|\,\mathrm{H^+, Cl^-}\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag}$$ (Harned cell)

Cell with liquid junction

$$\text{glass electrode}\,(\mathrm{H^+})\,|\,\mathrm{H^+}\,|\,1\,\mathrm{M\ KCl}\,|\,\mathrm{AgCl}\,|\,\mathrm{Ag}$$

Standard pH solutions for water:

$$\mathrm{pH} = 1.68;\ 4.01;\ 6.86;\ 9.18;\ 12.45\ (25\ ^{\circ}\mathrm{C})$$

t, °C =	5	15	20	25	30	38	50
Composition, mol/kg:							
0.05 $KH_3(C_2O_4)\cdot 2H_2O$	1.668	1.672	1.675	1.679	1.683	1.691	1.707
0.05 $KH_2C_6H_5O_7$	3.840	3.802	3.788	3.776	3.766	—	3.749
$C_2H_4O_2(COOK)(COOH)$, satur. at 25 °C	—	—	—	3.557	3.552	3.548	3.549
0.05 $C_6H_4(COOK)(COOH)$	3.999	3.999	4.002	4.008	4.015	4.030	4.060
0.025 KH_2PO_4 + 0.025 Na_2HPO_4	6.951	6.900	6.881	6.865	6.853	6.840	6.833
0.008695 KH_2PO_4 + 0.03043 Na_2HPO_4	7.500	7.448	7.429	7.413	7.400	7.384	7.367
0.01 $Na_2B_4O_7\cdot 10H_2O$	9.395	9.276	9.225	9.180	9.139	9.081	9.011
0.025 $NaHCO_3$ + 0.025 Na_2CO_3	10.24 5	10.118	10.062	10.012	9.966	—	9.828
$Ca(OH)_2$, satur. at 25 °C	13.207	12.810	12.627	12.454	12.289	12.043	11.705

In aqueous solutions: $\mathrm{pH}_x = \dfrac{E^0 - E_x}{k}$ (**instrumental pH**)

The problem of ionic strength: the pH values refer to relatively low ionic strength. If the ionic strength of solutions *x* is much higher, a systematic error appears.

Another problem: determination of pH in organic solvents.

For water-organic solvents, **a correction may be made:**

$$\mathrm{pH}_s = \mathrm{pH}_x - \Delta$$

The values of Δ are known. For example, in 50 mass % ethanol in water, Δ = 0.20.

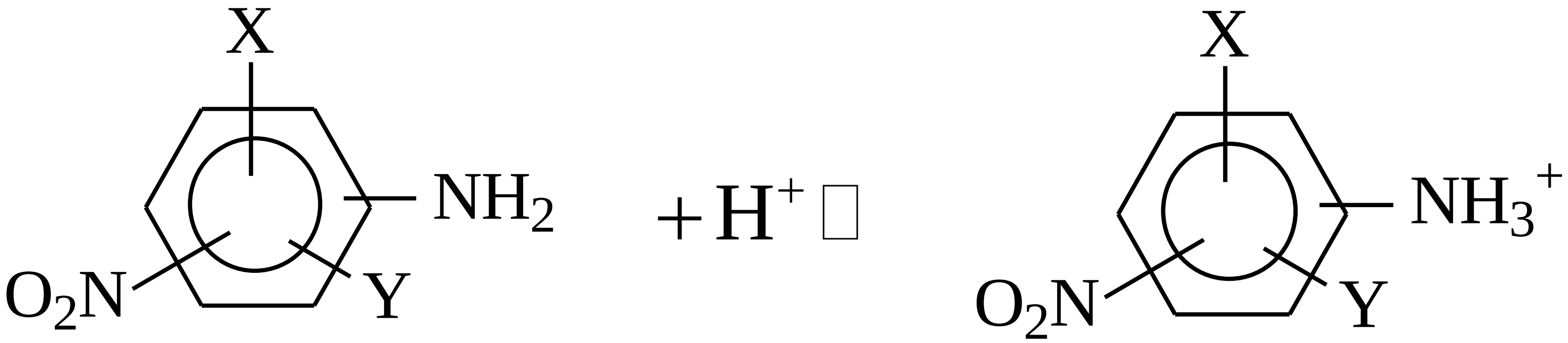
For heavy water: $\mathrm{pD} = \mathrm{pH} + 0.40$

Acidity function

The Hammett acidity function.

$$pK_{HB^+} = -\log\left(a_{H^+} \frac{[B]}{[HB^+]} \frac{f_B}{f_{HB^+}} \right) = -\log \frac{a_{H^+} f_B}{f_{HB^+}} - \log \frac{[B]}{[HB^+]}$$

$$pK_{HB^+} = H_0 + \log Q$$



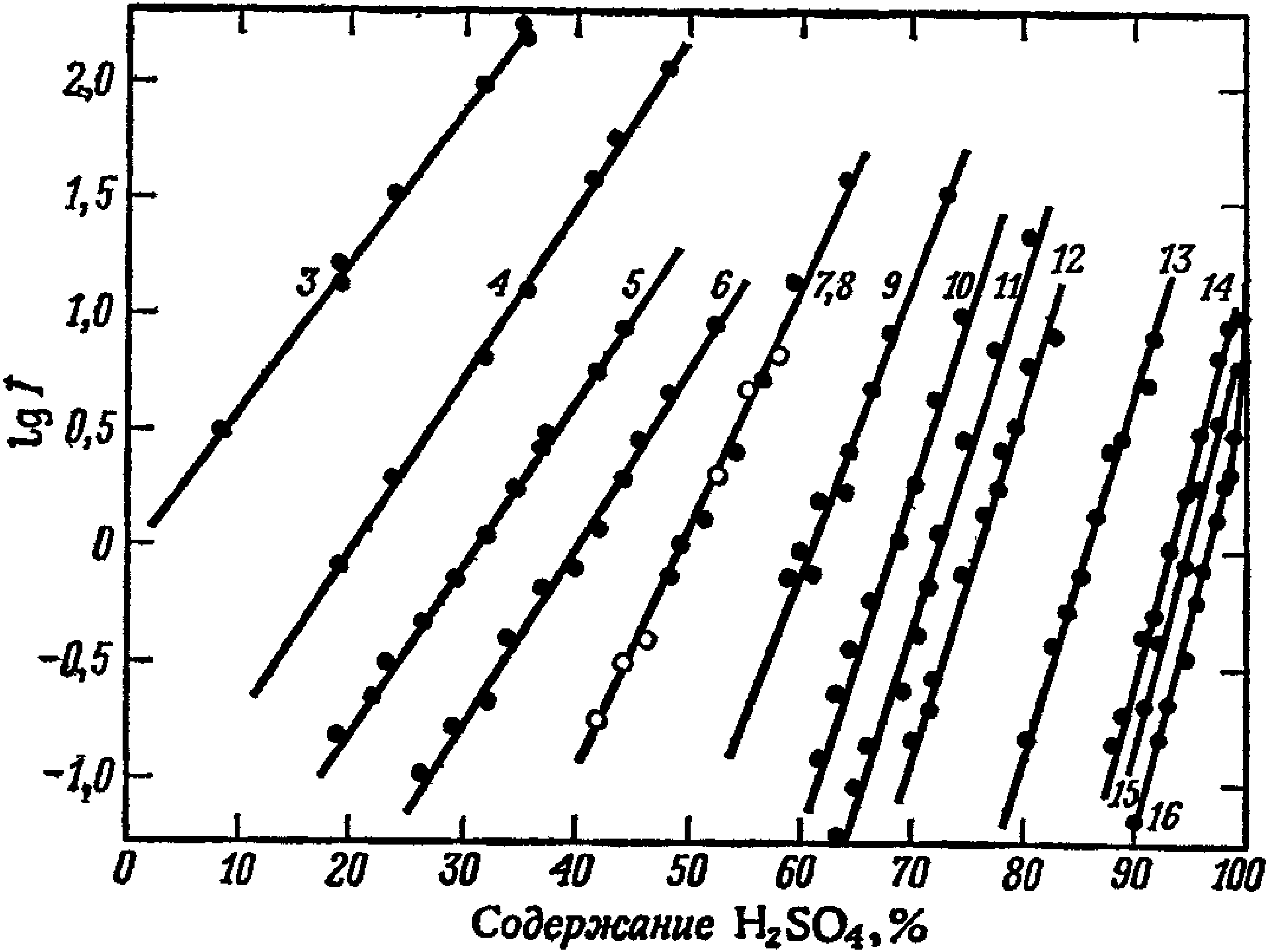


Рис. 9.1. Значения lg*I* для индикаторов типа H_0 в смесях серной кислоты с водой; обозначения соответствуют табл. 9.1 [10].

Таблица 9.1

$pK^{\circ\circ}$ индикаторов типа H_0 в смесях серная кислота—вода и хлорная кислота—вода

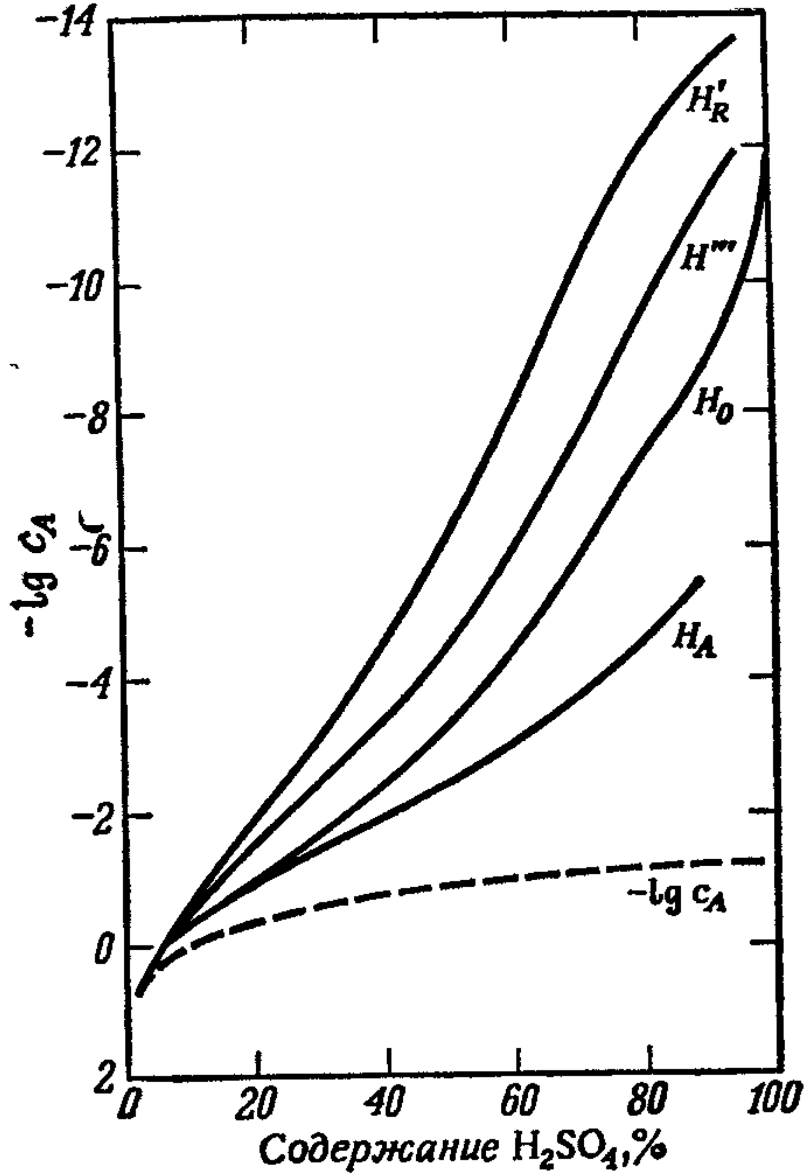
Номер	Индикатор	H_2SO_4[а]	$HClO_4$[б]
1	*м*-Нитроанилин	2,50	
2	*п*-Нитроанилин	0,99	
3	*о*-Нитроанилин	—0,29	—0,29
4	4-Хлор-2-нитроанилин	—1,03	—1,07
5	2,5-Дихлор-4-нитроанилин	—1,78	—1,79
6	2-Хлор-6-нитроанилин	—2,43	—2,41
7	2,6-Дихлор-4-нитроанилин	—3,27	—3,20
8	2,4-Дихлор-6-нитроанилин	—3,27	
9	2,4-Динитроанилин	—4,53	—4,26
10	2,6-Динитроанилин	—5,54	—5,25
11	4-Хлор-2,6-динитроанилин	—6,14	—6,12
12	2-Бром-4,6-динитроанилин	—6,68	—6,69
13	3-Метил-2,4,6-тринитроанилин	—8,22	—8,56
14	3-Бром-2,4,6-тринитроанилин	—9,46	—9,77
15	3-Хлор-2,4,6-тринитроанилин	—9,71	
16	2,4,6-Тринитроанилин	—10,10	

[а] Данные Гаммета и Дейрупа [9], пересмотренные Паулем и Лонгом [7], а также данные Иоргенсона и Хартера [10].

[б] Данные Эйтса и Уэя [11].

Функции кислотности и некоторые другие характеристики смесей серной кислоты с водой[а]

Содержание кислоты, %	H_0	H'''	H_I	H'_R	H_A	$\lg a_w$	$\lg c_A$	$H_0 + \lg c_A$
5	0,11	0,01	0,05	—0,06			—0,28	—0,17
10	—0,31	—0,53	—0,55	—0,69	—0,29	—0,026	0,03	—0,28
15	—0,66	—0,99	—0,97	—1,28	—0,70		0,228	—0,43
20	—1,01	—1,47	—1,42	—1,86	—1,00	—0,059	0,367	—0,64
25	—1,37	—1,96	—1,85	—2,46	—1,25	—0,086	0,479	—0,89
30	—1,72	—2,44	—2,35	—3,10	—1,50	—0,124	0,572	—1,15
35	—2,06	—2,93	—2,88	—3,82	—1,74	—0,175	0,653	—1,41
40	—2,41	—3,46	—3,42	—4,55	—2,00	—0,246	0,726	—1,68
45	—2,85	—4,01	—4,02	—5,31	—2,24	—0,341	0,782	—2,07
50	—3,38	—4,54	—4,65	—6,15	—2,51	—0,454	0,853	—2,53
55	—3,91	—5,11	—5,32	—7,07	—2,77	—0,604	0,910	—3,00
60	—4,46	—5,91	—6,06	—8,13	—3,10	—0,793	0,962	—3,50
65	—5,08	—6,73	—6,87	—9,13	—3,38	—1,040	1,014	—4,07
70	—5,80	—7,65	—7,79	—10,16	—3,74	—1,363	1,061	—4,74
75	—6,56	—8,53			—4,15	—1,765	1,106	—5,45
80	—7,34	—9,44		—11,84	—4,62	—2,282	1,148	—6,19
85	—8,14	—10,30			—5,02	—2,79	1,187	—6,95
90	—8,92	—11,14		—13,23	—5,57	—3,51	1,221	—7,70
95	—9,85	—11,89		—13,61		—4,47	1,249	—8,60
100	—12,2							

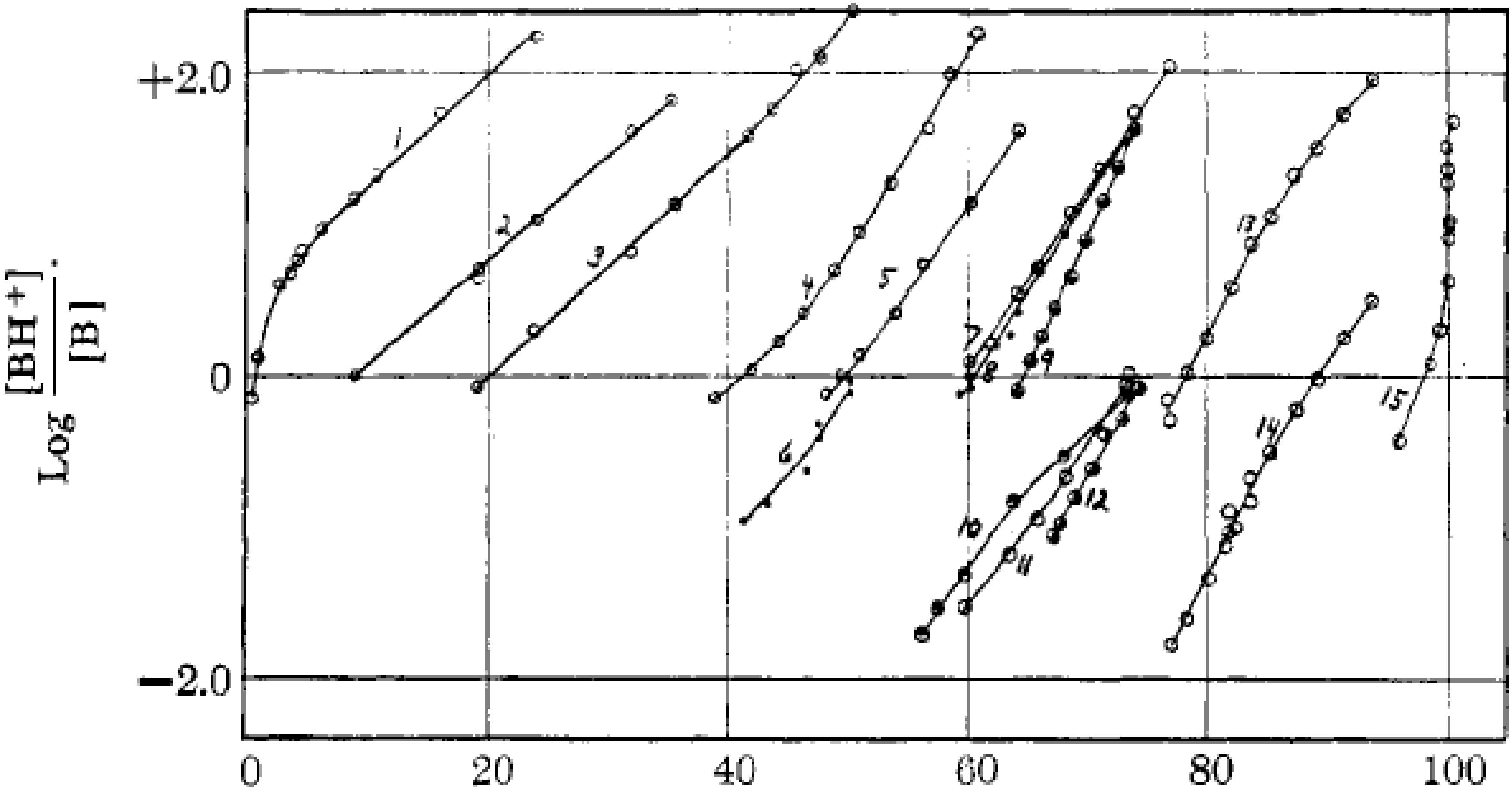


Функции кислотности для смесей серной кислоты с водой.

[Contribution from the Department of Chemistry, Columbia University]

A SERIES OF SIMPLE BASIC INDICATORS. I. THE ACIDITY FUNCTIONS OF MIXTURES OF SULFURIC AND PERCHLORIC ACIDS WITH WATER[1]

By Louis P. Hammett and Alden J. Deyrup[2]



УСПЕХИ ХИМИИ

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ФУНКЦИЯ КИСЛОТНОСТИ ВОДНЫХ РАСТВОРОВ СИЛЬНЫХ КИСЛОТ

М. И. Винник

ОГЛАВЛЕНИЕ

1. Шкала кислотности для водных растворов сильных кислот

При исследовании кинетики химических процессов в гомогенной жидкой фазе необходимо учитывать влияние растворителя на термодинамические свойства реагирующих веществ. Особенно сильно проявляются свойства среды в химических реакциях, протекающих в водных растворах сильных кислот и оснований. Большая склонность к образованию водородных связей и большие концентрации ионов в таких растворах способствуют образованию различных комплексов и ионов с участием реагентов.

REVIEW/SYNTHÈSE

Acidity functions: an update

ROBIN A. COX AND KEITH YATES
Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ont., Canada M5S 1A1

Received February 14, 1983

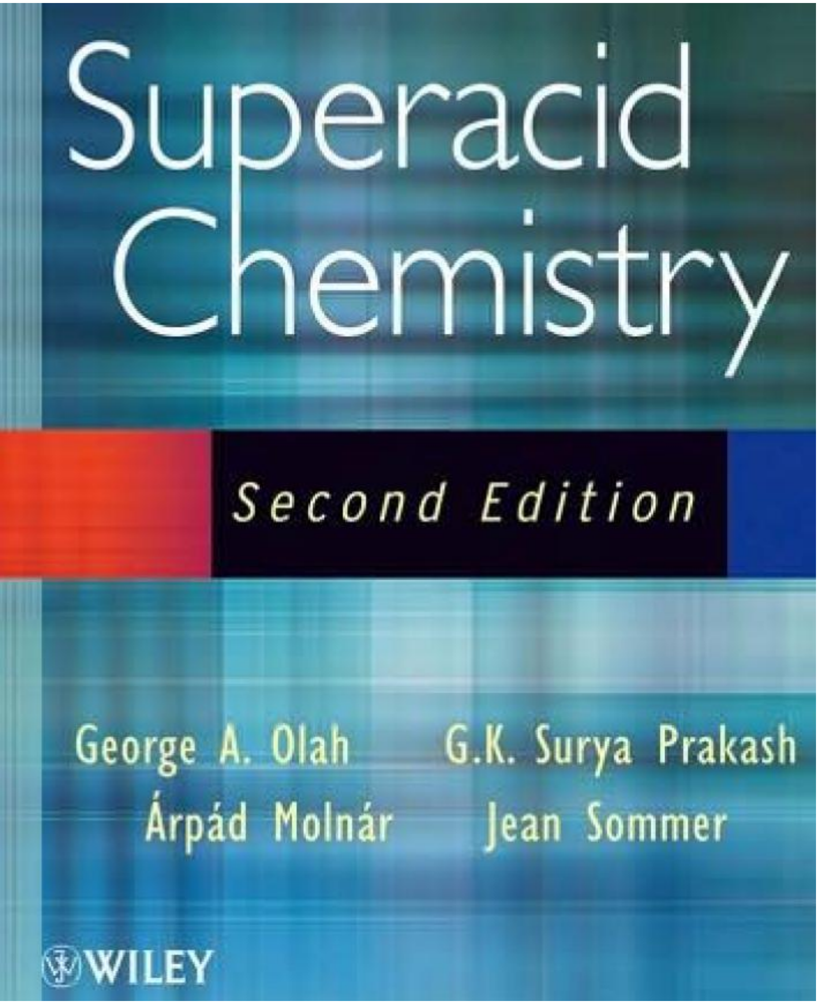
ROBIN A. COX and KEITH YATES. Can. J. Chem. **61**, 2225 (1983).

The subject of acidity functions is reviewed, with emphasis on modern developments. H_0 and other scales determined in acid media, using the Hammett cancellation assumption (zero'th order approximation) are discussed briefly. The extension to strongly basic systems is also documented. Literature references to acidity function scales in aqueous acid, aqueous acid/organic solvent, and aqueous base media are tabulated, together with those in aqueous base/organic solvent mixtures at both variable and fixed base concentration. Over 400 acidity functions are referenced, including several electrochemical scales. Various approaches to developing universal functions from the data are discussed. Proton activity scales, based on the Yates–McClelland method of pK_{BH^+} determination, and on electrochemical H_{GF} scales, are prominent among these. Carpentier's method is mentioned, and the first-order approximation, assumed linearity among log activity coefficient ratios, is used to introduce the Bunnett–Olsen and excess acidity (X-function) methods. A brief critical discussion of which method to use is provided. Future developments anticipate the second-order approximation, with a quadratic dependence of log ionization ratios upon X-functions. The review cites 337 individual references.

ROBIN A. COX et KEITH YATES. Can. J. Chem. **61**, 2225 (1983).

On étudie de nouveau les fonctions d'acidité en tenant compte des nouvelles théories. On discute brièvement des échelles H_0 et des autres échelles déterminées en milieu acide en utilisant l'hypothèse d'annulation de Hammett (approximation d'ordre zéro). On a également étudié les échelles en milieu fortement basique. On a compilé les références de la littérature portant sur les échelles de fonctions d'acidité en milieu acide, en milieu aqueux/solvant organique, et en milieu basique aqueux ainsi que celles portant sur les fonctions en milieu basique aqueux/mélanges de solvants organiques à des concentrations fixes et à des concentrations variables de bases. On a dressé une liste de plus de 400 fonctions d'acidité incluant plusieurs échelles électrochimiques. On discute des différentes approches utilisées pour développer des fonctions universelles à partir des données. Les échelles d'activité du proton basées sur la méthode de détermination du pK_{BH^+} de Yates–McClelland et sur les échelles électrochimiques H_{GF} tiennent la première place. On mentionne la méthode de Carpentier et on utilise l'approximation d'ordre un en supposant la linéarité du logarithme des rapports du coefficient d'activité pour introduire la méthode d'acidité en excès de Bunnett–Olsen (fonction X). On discute brièvement de l'utilisation de telle ou telle méthode. Les développements futurs anticipent une approximation d'ordre deux, avec une influence quadratique des fonctions X sur le logarithme des rapports d'ionisation. La nouvelle étude comporte 337 références.

[Traduit par le journal]


Superacid Chemistry

Second Edition

George A. Olah G.K. Surya Prakash

Árpád Molnár Jean Sommer

WILEY

Superacidic media

	H_0	
H_2SO_4	–12	
$HClO_4$	–13	
CF_3SO_3H	–14.1	
HF	–15.0	
FSO_3H	–15.1	
$FSO_3H – SbF_5$, 1 : 1	≈–23	“magic acid”
$HF – SbF_5$, 1 : 1	≈–28	

Formation of “non-classical” cations

CH_5^+, CH_6^{2+}, O_3H^+, H_3^+, etc. (Olah et al.)

Superbasic media

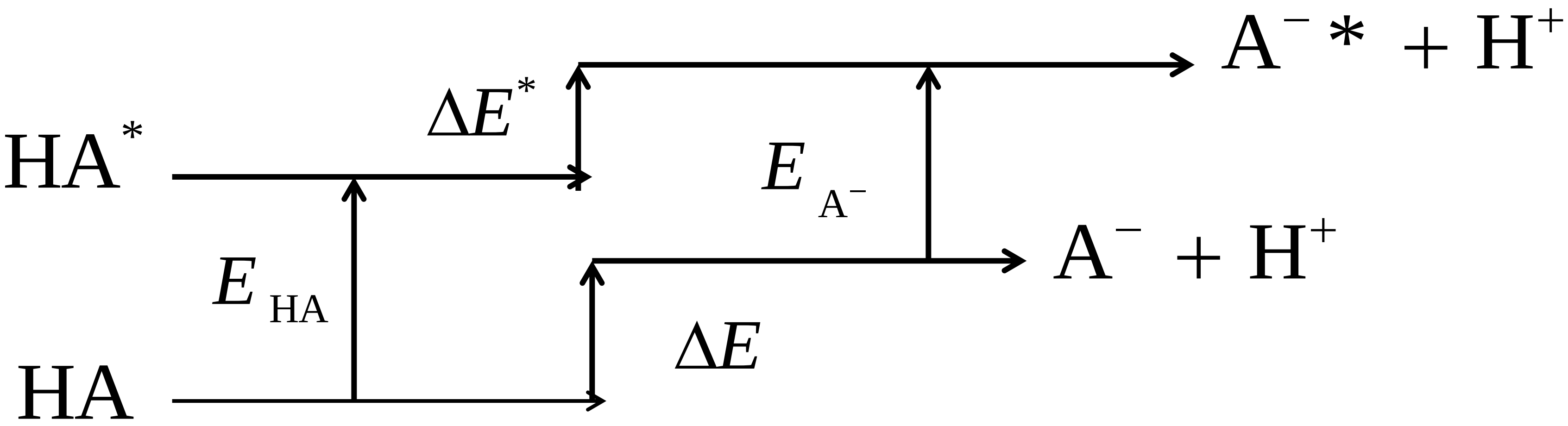
Dimethyl sulfoxide + methanol + KOH;

potassium dimsil in dimethyl sulfoxide

Even toluene may be ionized: $C_6H_5CH_3 \rightarrow C_6H_5CH_2^-$

Acid-base equilibrium in the excited state

Weller cycle:



$$E_{\mathrm{HA}} + \Delta E^{*} = \Delta E + E_{\mathrm{A}^{-}};$$

$$E_{\mathrm{HA}} = h\nu_{\mathrm{HA}}; E_{\mathrm{A}} = h\nu_{\mathrm{A}^{-}}$$

Acid-base equilibrium in the excited state

$$\Delta G^* = -RT\ln K_a^* = 2.303\,RT\,\mathrm{p}K_a^*;$$

$$\Delta G = 2.303\,RT\,\mathrm{p}K_a$$

$$\Delta G^* = \Delta H^* - T\Delta S^* = \Delta E^*;$$

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

$$\mathrm{p}K_a^* - \mathrm{p}K_a = \frac{h\left(\nu_{A^-} - \nu_{HA}\right)}{2.303\,RT}$$

$$\boxed{\mathrm{p}K_a^* - \mathrm{p}K_a = 2.096\times10^4\left(\frac{1}{\lambda_{A^-}} - \frac{1}{\lambda_{HA}}\right)}$$

$T = 298.15\,\mathrm{K}$; λ – in nanometers

Acid-base equilibrium in the excited state

$$\mathrm{p}K_\mathrm{a}^* - \mathrm{p}K_\mathrm{a} = 2.096 \times 10^4 \left(\frac{1}{\lambda_{\mathrm{A}^-}} - \frac{1}{\lambda_\mathrm{HA}} \right)$$

For example, if $\lambda_{\mathrm{A}^-} = 500\,\mathrm{nm},\ \lambda_\mathrm{HA} = 400\,\mathrm{nm},\quad \mathrm{p}K_\mathrm{a}^* - \mathrm{p}K_\mathrm{a} = -10.48$

if $\lambda_{\mathrm{A}^-} = 600\,\mathrm{nm},\ \lambda_\mathrm{HA} = 700\,\mathrm{nm},\quad \mathrm{p}K_\mathrm{a}^* - \mathrm{p}K_\mathrm{a} = +4.99$

Kinetics of protolytic reactions

$$\mathrm{H}^{+} + \mathrm{HO}^{-} \rightarrow \mathrm{H_2O};\ \ k = 1.4\times10^{11}\ M^{-1}s^{-1}$$

$$\mathrm{H}^{+} + e^{-} \rightarrow \mathrm{H};\ \ k = 2\times10^{10}\ M^{-1}s^{-1}$$

$$\mathrm{H}^{+} + \mathrm{CH_3COO}^{-} \rightarrow \mathrm{CH_3COOH};\ \ k = (1.1-5.2)\times10^{10}\ M^{-1}s^{-1}$$

(estimated by 8 different methods)

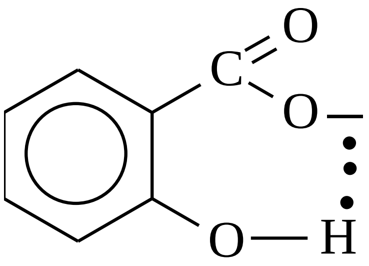
Diffusion-limited reactions

Kinetics of protolytic reactions

$$H^+ + RCOO^- \rightarrow RCOOH;\ k = (3.8 \pm 1.0) \times 10^{10}\ M^{-1}s^{-1}$$

(for 11 different carboxylic acids)

For salicylic acid, the intramolecular hydrogen bond decelerates the reaction



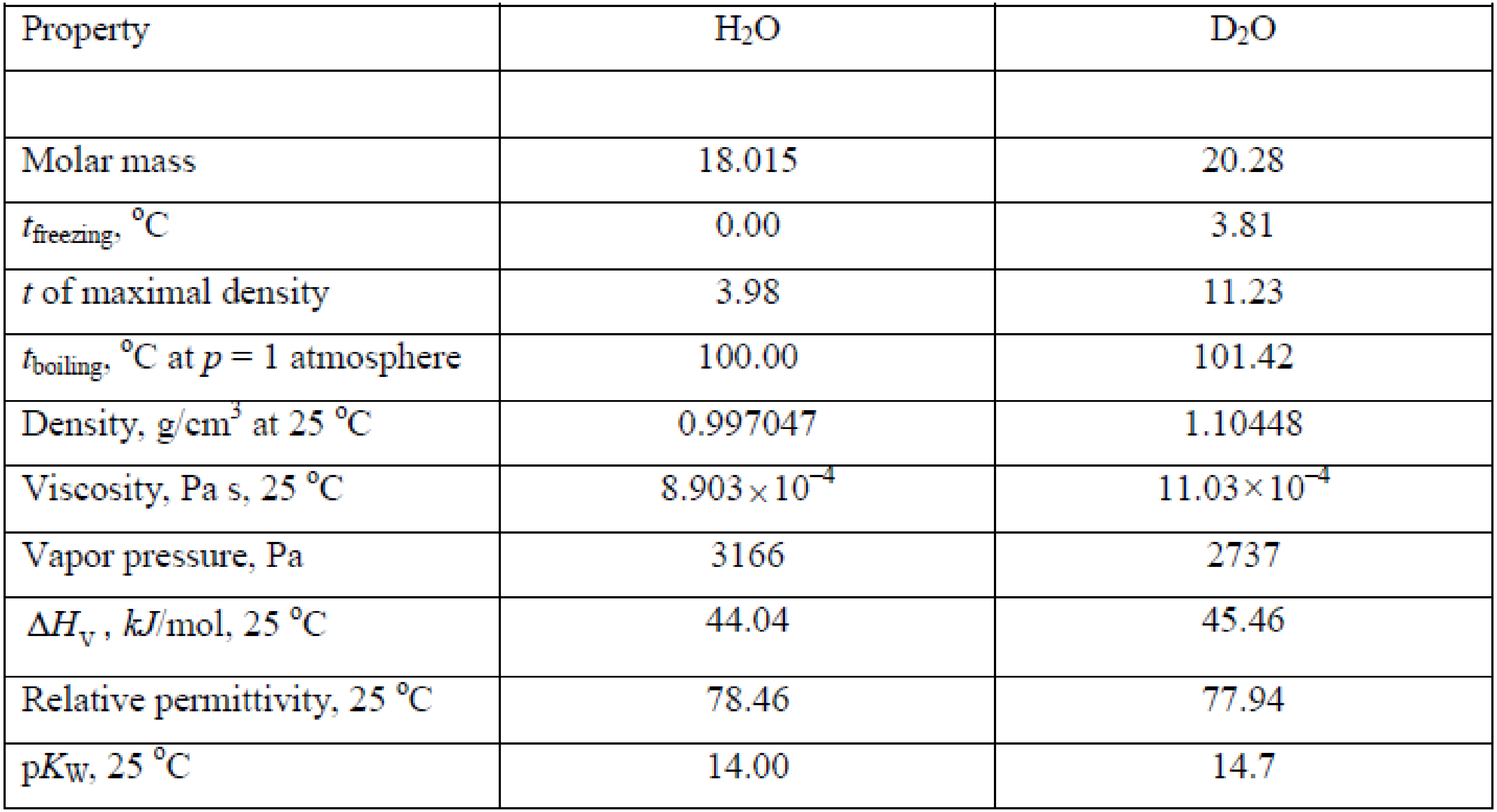
$$+ H^+ \rightarrow\ ;\ k = 6.4 \times 10^9\ M^{-1}s^{-1}$$

Slow reactions

$$CH_2NO_2^- + H^+ \rightarrow CH_3NO_2;\ k = 10^2\ M^{-1}s^{-1}; 25\ ^{o}C$$

Nitroparaffins can be titrated in water by NaOH

“Heavy water”: Deuterium oxide



Property	H_2O	D_2O
Molar mass	18.015	20.28
t_{freezing}, °C	0.00	3.81
t of maximal density	3.98	11.23
t_{boiling}, °C at $p = 1$ atmosphere	100.00	101.42
Density, g/cm^3 at 25 °C	0.997047	1.10448
Viscosity, Pa s, 25 °C	8.903×10^{-4}	11.03×10^{-4}
Vapor pressure, Pa	3166	2737
ΔH_V, kJ/mol, 25 °C	44.04	45.46
Relative permittivity, 25 °C	78.46	77.94
pKw, 25 °C	14.00	14.7

(C. Reichardt. Solvents and Solvent Effects in Organic Chemistry).

Medium effects: $\Delta \mathrm{p}K_{\mathrm{a}} = \mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}}$

$$\mathrm{HA} \Leftrightarrow \mathrm{A}^{-} + \mathrm{H}^{+}$$

Thermodynamic
dissociation constant →

$$K_{\mathrm{a}} = a_{\mathrm{H}^{+}} \frac{a_{\mathrm{A}}}{a_{\mathrm{HA}}}; \quad a_i \text{ are activities}$$

$$\mathrm{p}K_{\mathrm{a}} = -\log K_{\mathrm{a}}$$

$$K_a^w = a_{H^+}^w \frac{a_A^w}{a_{HA}^w}; \quad \text{in water}$$

$$K_a^s = a_{H^+}^s \frac{a_A^s}{a_{HA}^s}; \quad \text{in the non-aqueous solvent}$$

$$\frac{K_a^w}{K_a^s} = \frac{a_{H^+}^w}{a_{H^+}^s} \frac{a_A^w}{a_A^s} \frac{a_{HA}^s}{a_{HA}^w} = P_{H^+}^{-1} \times P_A^{-1} \times P_{HA} = \gamma_{H^+} \times \gamma_A \times \gamma_{HA}^{-1}$$

$$\boxed{\mathrm{p}K_a^s - \mathrm{p}K_a^w = \log \gamma_{H^+} + \log \gamma_A - \log \gamma_{HA}}$$

This approach is applicable to other equilibria as well.

$${}^{w}\gamma_i^s\,; \quad \text{hereafter: } \gamma_i$$

Estimation of the γ_i values

$$\gamma_i = \frac{\mu_i^{0s} - \mu_i^{0w}}{RT}$$

MOLECULES.

1. Solubility:

$$\boxed{\gamma_i = \frac{a_i^w}{a_i^s} \approx \frac{s_i^w}{s_i^s}}$$

Main condition: **the absence of crystal solvates**

Another problem: too high solubility, or even unlimited solubility.

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

$$\frac{a_i^s}{a_i^w} = P_i = \exp\frac{\mu_i^{0w} - \mu_i^{0s}}{RT}; \qquad \frac{a_i^s}{a_i^w} = P_i = \gamma_i^{-1}$$

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**.

Estimation of the γ_i values

ELECTROLYTES. IONS.

1. 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.

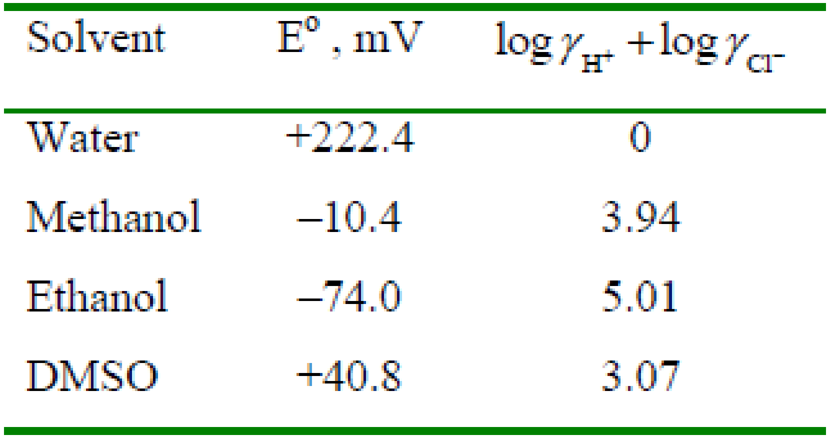
2. Electrochemical cells.

$$\mathrm{Pt}\left|\mathrm{H_2}\right|\mathrm{H^+,Cl^-}\left|\mathrm{AgCl}\right|\mathrm{Ag}$$

$$\frac{1}{2}\mathrm{H_2}+\mathrm{AgCl}\Box\quad \mathrm{Ag}+\mathrm{H^+}+\mathrm{Cl^-};$$

$$E=E^0-\frac{RT}{F}\ln(a_{\mathrm{H^+}}a_{\mathrm{Cl^-}})$$

$$\log\gamma_{\mathrm{H^+}}+\log\gamma_{\mathrm{Cl^-}}=\frac{E^{0\mathrm{w}}-E^{0\mathrm{s}}}{59.16}$$



Solvent	E°, mV	$\log\gamma_{\mathrm{H^+}}+\log\gamma_{\mathrm{Cl^-}}$
Water	+222.4	0
Methanol	–10.4	3.94
Ethanol	–74.0	5.01
DMSO	+40.8	3.07

3. Tetraphenylborate hypothesis.

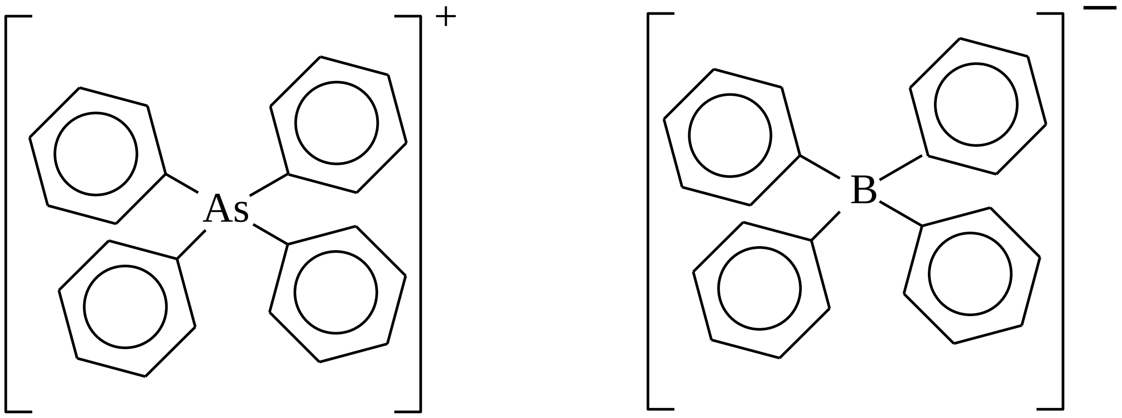
The main problem is as follows:

The transfer activity coefficients of single ions from one solvent to another **cannot be determined by thermodynamic methods.**

Contrary to the γ_i values of neutral molecules, only the $\gamma_+\gamma_-$ product may be obtained experimentally.

Therefore, the dividing of the corresponding products can be made using some **extrathermodynamic assumptions**.

Presently, the most accepted assumption is the so-called **tetraphenylborate hypothesis.**



The assumption consists in equating $\gamma_{\mathrm{B(C_6H_5)_4^-}}$ to $\gamma_{\mathrm{As(C_6H_5)_4^+}}$ or $\gamma_{\mathrm{P(C_6H_5)_4^+}}$

The ions can be considered as “pseudo-spherical”

If $$\log\gamma_{\mathrm{As(C_6H_5)_4^+}} = \log\gamma_{\mathrm{B(C_6H_5)_4^-}} = \frac{1}{2}(\mathrm{p}K_{\mathrm{sp}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{sp}}^{\mathrm{w}}),$$

where K_{sp} is the solubility product of $\mathrm{As(C_6H_5)_4^+B(C_6H_5)_4^-}$,

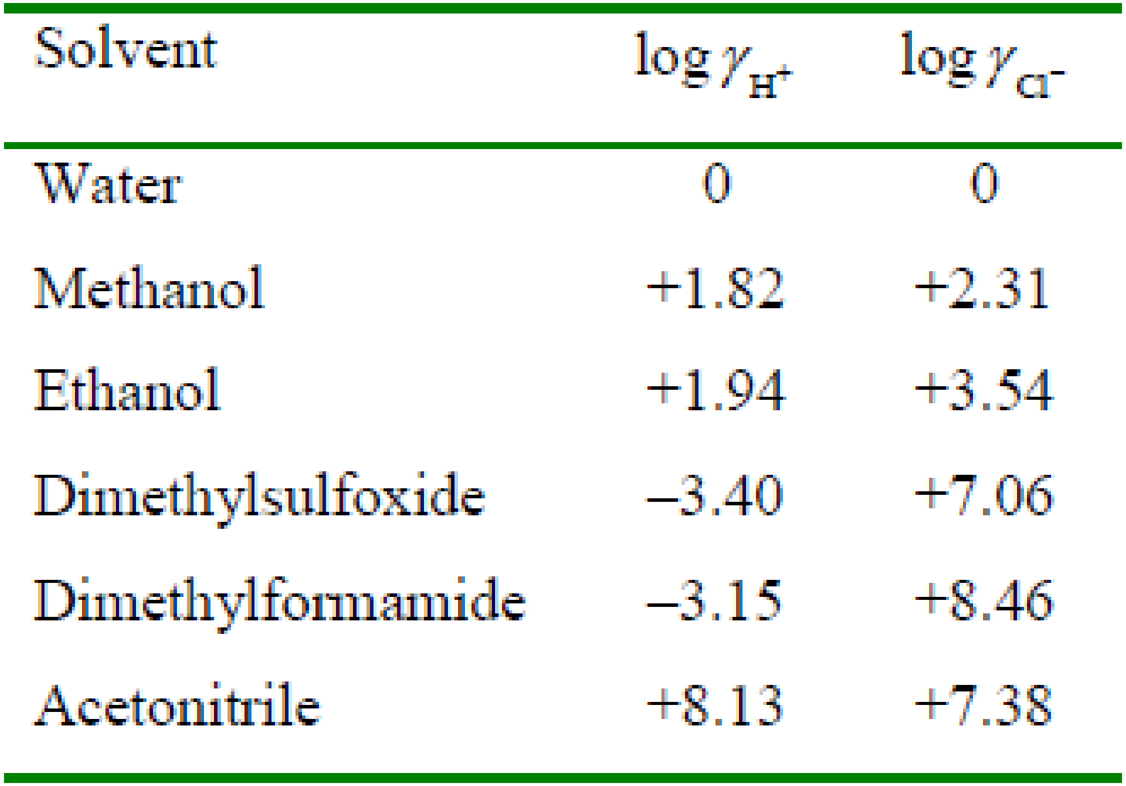
then the values for other ions may be calculated:

$\gamma_{\mathrm{Cl^-}}$ using the solubility products of $\mathrm{As(C_6H_5)_4^+Cl^-}$, in water and in a corresponding solvent;

$\gamma_{\mathrm{K^+}}$ using the solubility products of $\mathrm{K^+B(C_6H_5)_4^-}$, in water and in a corresponding solvent;

$\gamma_{\mathrm{H^+}}$ as $$= \frac{E^{0\mathrm{w}} - E^{0\mathrm{s}}}{59.16} - \log\gamma_{\mathrm{Cl^-}}$$

Some examples from a much larger body of data:

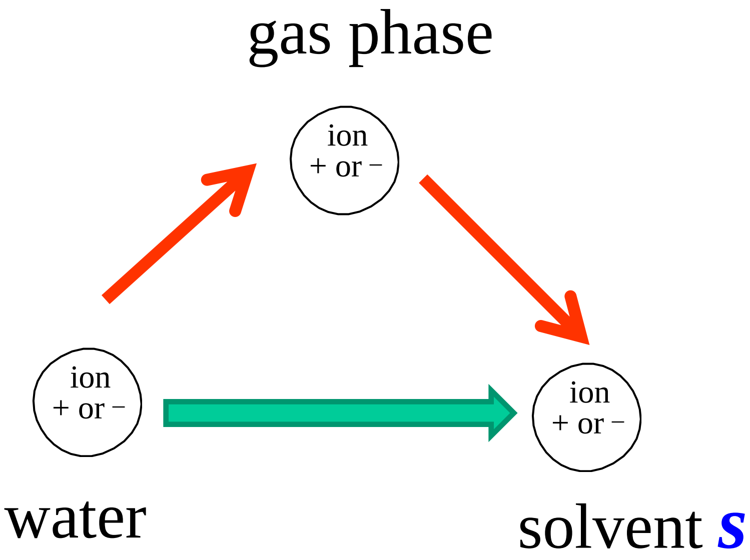


Solvent	$\log \gamma_{H^+}$	$\log \gamma_{Cl^-}$
Water	0	0
Methanol	+1.82	+2.31
Ethanol	+1.94	+3.54
Dimethylsulfoxide	–3.40	+7.06
Dimethylformamide	–3.15	+8.46
Acetonitrile	+8.13	+7.38

$\log \gamma_i < 0:$ profitable transfer

$\log \gamma_i > 0:$ unprofitable transfer

Attempts to estimate the transfer activity coefficients theoretically



Born's equation for a charged sphere:

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

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}} = \log \gamma_{\mathrm{H}^{+}} + \log \gamma_{\mathrm{A}} - \log \gamma_{\mathrm{HA}}$$

$$\log {}^{\mathrm{w}}\gamma_{\mathrm{i}}^{\mathrm{s}} = \frac{\Delta G_{\mathrm{tr}}(i)}{2.303RT} = \frac{e^{2} z_{\mathrm{i}}^{2} N_{\mathrm{A}}}{4.60\ RTr_{\mathrm{i}} \times 4\pi \times \varepsilon_{0}} \times \left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_{\mathrm{r,w}}} \right]$$

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}} = \frac{e^{2} N_{\mathrm{A}}}{4.60\ RT \times 4\pi \times \varepsilon_{0}} \times \left[\frac{1}{r_{\mathrm{H}^{+}}} + \frac{(z_{\mathrm{HA}} - 1)^{2}}{r_{\mathrm{A}}} - \frac{z_{\mathrm{HA}}^{2}}{r_{\mathrm{HA}}} \right] \times \left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_{\mathrm{r,w}}} \right]$$

(the so-called Bronsted equation)

$$\mathrm{p}K_\mathrm{a}^\mathrm{s} - \mathrm{p}K_\mathrm{a}^\mathrm{w} = \frac{e^2 N_\mathrm{A}}{4.60\,RT \times 4\pi \times \varepsilon_0} \times \left[\frac{1}{r_{\mathrm{H}^+}} + \frac{(z_\mathrm{HA} - 1)^2}{r_\mathrm{A}} - \frac{z_\mathrm{HA}^2}{r_\mathrm{HA}} \right] \times \left[\frac{1}{\varepsilon_{\mathrm{r,s}}} - \frac{1}{\varepsilon_{\mathrm{r,w}}} \right]$$

Comparison with the experiment

Poor agreement!

Solvent (ε_r)	$\Delta\mathrm{p}K_\mathrm{a}^\mathrm{el}$	Experimental values of $\mathrm{p}K_\mathrm{a}^\mathrm{s} - \mathrm{p}K_\mathrm{a}^\mathrm{w}$ for benzoic acid
Methanol (32.6)	1.03	5.20
Ethanol (24.4)	1.63	6.05
1-Butanol (17.5)	2.57	7.28
tert-Butanol (12.5)	3.90	10.8
Dimethylsulfoxide (46.5)	0.51	6.9
Dimethylformamide (36.7)	0.84	8.1
Acetonitrile (36.0)	0.87	16.5
Propylenecarbonate (65.0)	0.15	15.5

?

However, for the picric acid in acetone ($\mathrm{p}K\mathrm{a}$ = 9.2) and methylisobutylketone ($\mathrm{p}K\mathrm{a}$ = 11.0) the experimental and calculated differences coincide: = 1.8.

These two solvents are of the **same chemical nature**, but with different relative permittivity, 20.56 and 13.92 at 25 °C, respectively.

Therefore, more adequate is the so-called Bronsted–Izmailov equation:

$$\mathrm{p}K_{\mathrm{a}}^{\mathrm{s}} - \mathrm{p}K_{\mathrm{a}}^{\mathrm{w}} = \frac{e^{2} N_{\mathrm{A}}}{4.60\,RT \times 4\pi \times \varepsilon_{0}} \times \left[\frac{1}{r_{\mathrm{H}^{+}}} + \frac{(z-1)^{2}}{r_{\mathrm{B}}} - \frac{z^{2}}{r_{\mathrm{HB}}} \right] \times \left[\frac{1}{\varepsilon_{\mathrm{r},s}} - \frac{1}{\varepsilon_{\mathrm{r,w}}} \right] + \frac{\Delta G_{\mathrm{H}^{+}}^{\mathrm{solv}} + \Delta G_{\mathrm{B}}^{\mathrm{solv}} - \Delta G_{\mathrm{HB}}^{\mathrm{solv}}}{2.30\,RT}$$