

DISSOCIATION CONSTANTS OF INORGANIC  
ACIDS AND BASES IN AQUEOUS SOLUTION

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DES ACIDES ET DES BASES INORGANIQUES  
EN SOLUTION AQUEUSE

DIVISION DE CHIMIE ANALYTIQUE  
COMMISSION DE CHIMIE ÉLECTROANALYTIQUE\*

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## INTRODUCTION

Most of the existing tables of dissociation constants of inorganic acids and bases in aqueous solution are fragmentary in character, include little or no experimental details, and give few references. Easily the most comprehensive of the previous collections is *Stability Constants of Metal-Ion Complexes*, compiled by L. G. Sillén and A. E. Martell, and published as Special Publication No. 17 of the Chemical Society, London, in 1964. However, because of the nature of this compilation, the  $pK$  values in it tend to be overlain by the much greater bulk of the stability constant data. In many cases, also, it is difficult to decide by inspection which of the  $pK$  values should be taken from the wide range sometimes given for a particular substance.

The present Table follows the pattern of the similar Tables for organic acids and organic bases, which were also prepared at the request of the International Union of Pure and Applied Chemistry as part of the work of the Commission on Electrochemical Data. The Table of organic acids, compiled by Kortum, Vogel, and Andrussov was published in *Pure and Applied Chemistry*, **1**, 187–536 (1960), and also separately as a book\*. The Table of organic bases, by the present author, was published in 1965 as a supplement to *Pure and Applied Chemistry*.†

For convenience, the dissociation constants of inorganic acids and bases have been given, in most cases, in the form of  $pK_a$  values, and the classes of compounds include not only conventional acids and bases such as boric acid and magnesium hydroxide, but also hydrated metal ions (which behave as acids when they undergo hydrolysis) and free radicals, such as the hydroxyl radical,  $\cdot\text{OH}$ . All of these reactions have in common the gain or loss of a proton or a hydroxyl ion. On the other hand, the hydrolyses of metal-complex ions such as the cobaltammines have been excluded, as being more appropriate to the stability constant compilation mentioned above.

In general, and largely because of the difficulties attending  $pK$  measurements on inorganic species, it is not possible to offer a critical assessment of most of the published values. In particular cases, such as water, highly precise constants are available over a range of temperatures, and the uncertainty is only of the order of 0.001 pH unit. More commonly, only a few, often widely discordant, values have been reported.

This is partly because of the chemical reactivity of the materials themselves. For example, nitrous acid readily decomposes to dinitrogen trioxide. At concentrations above 0.01 M, boric acid is appreciably polymerised to polyboric acids; molybdic acid solutions contain  $\text{Mo}_7\text{O}_{24}^{6-}$  and higher species; bisulphite ion is in equilibrium with pyrosulphite ion,  $\text{S}_2\text{O}_5^{2-}$ ; and many transition and higher-valent metal ions form polynuclear species on hydrolysis.

\* G. Kortum, W. Vogel and K. Andrussov. *Dissociation Constants of Organic Acids in Aqueous Solution*. Butterworth & Co. Ltd., London, 1961.

† D. D. Perrin. *Dissociation Constants of Organic Bases in Aqueous Solution*. Butterworth & Co. Ltd., London, 1965.

Often, too, unsatisfactory methods of determination have been used. Thus, pH titration measurements are seldom satisfactory if  $pK$  values lie below 2 or above 12, and in such circumstances can give quite misleading results. Again,  $pK$  values for the hydrolysis of metal ions have often been obtained from measurements of the pH values of solutions of their purified salts in water. As Sillén has pointed out (*Quart. Rev.*, **13**, 146 (1959)), inorganic salts often adsorb tenaciously onto their surfaces traces of acidic or basic impurities, which persist even on repeated recrystallization, so that the measured pH values of their solutions may be much higher or lower than expected.

Even with experimentally accurate results, extrapolation to thermodynamic  $pK$  values at  $I = 0$  is not always possible. The usual basis of such extrapolation is the Debye-Hückel equation,

$$-\log f_{\pm} = \frac{Z_i^2 AI^{\frac{1}{2}}}{1 + \kappa a I^{\frac{1}{2}}} - bI$$

which is used to calculate the activity coefficient term. For precise work, values of  $a$  (the "mean distance of nearest approach" of the ions) and  $b$  are chosen to fit the data over a range of ionic strengths, so that the value of the  $pK$ , extrapolated to  $I = 0$ , can be obtained. At low ionic strengths and where moderate accuracy (say  $\pm 0.05$  pH unit) is sufficient some simplifying assumptions can often be made. Thus, Davies' equation (*J. Chem. Soc.* **1938**, 2093) is obtained by taking  $Ka = 1$ ,  $b = 0.2$ ; Güntelberg's equation (*Z. physik. Chem. Leipzig*, **123**, 199 (1926)) sets  $Ka = 1$ ,  $b = 0$ ; and the approximation  $Ka = 0$ ,  $b = 0$  (*i.e.*  $-\log f = Z_i^2 AI^{\frac{1}{2}}$ ) is also used. However, with moderately strong acids and bases ( $pK$  values less than 2 or greater than 12), the numerical values of the thermodynamic  $pK$  constants depend in part on the assumptions made in deriving them, including the ion-size parameter  $a$  used in the extended Debye-Hückel equation (see, for example, R. G. Bates, V. E. Bower, R. G. Canham and J. E. Prue, *Trans. Faraday Soc.*, **55**, 2062 (1959); A. K. Covington, J. V. Dobson and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **61**, 2057 (1965), E. A. Guggenheim, *Trans. Faraday Soc.* **62**, 2750 (1966)). Thus, the  $pK$  of bisulphite ion at 25° varies from 1.927 to 1.967 as  $K_a$  is varied from 1.0 to 1.7. In the same way,  $pK_b$  for  $\text{Ca}(\text{OH})_2$  varies from 1.14 to 1.27 at 25°, depending on the choice of parameters.

A distinction must also be made between true and apparent  $pK$  values. The first  $pK$  of carbon dioxide in water as measured is about 6.4 at 20°, whereas the true  $pK$  of carbonic acid ( $\text{H}_2\text{CO}_3$ ) is 3.8. The difference between the apparent and the true  $pK$  values is due to the slight extent to which carbon dioxide is covalently hydrated in water. Similarly, periodic acid exists as  $\text{H}_5\text{IO}_6$  and  $\text{HIO}_4$  (mainly as the latter), so that its measured second  $pK$  (8.3) is very much higher than its first one (about 2).

In the absence of experimental values, especially for some of the oxyacids, attempts have been made to predict  $pK$  values, usually from similarities of structure. The more commonly used methods are those of J. E. Ricci (*J. Am. Chem. Soc.*, **70**, 109 (1948)), L. Pauling (*General Chemistry*, Freeman, San Francisco, 1947, p. 394), and A. Kossiakoff and D. Harker (*J. Am. Chem. Soc.*, **60**, 2047, (1938)). Even in apparently simple cases, there may be considerable uncertainty. For example different values would be predicted

## INTRODUCTION

for germanic acid depending on whether it existed mainly as  $\text{GeO}(\text{OH})_2$  or  $\text{Ge}(\text{OH})_4$ .

Because of the many different kinds of uncertainties inherent in the present  $\text{p}K$  compilation, no attempt has been made to assess the accuracy of each entry. Nevertheless, where possible, I have attempted to select what appear to be the best available values. The results for hydrogen sulphide illustrate this. Thus, several methods have indicated that the second  $\text{p}K$  of hydrogen sulphide is about 14, which is too high for potentiometric titration methods to be applicable. Hence the  $\text{p}K_2$  values that have been obtained by potentiometric titration are not set out in the Table. Instead, references to the papers where they are given are included under "other measurements". This heading also covers results where insufficient experimental details are given.

# I. HOW TO USE THE TABLE

## GENERAL ARRANGEMENT

The Table summarizes data recorded in the literature up to the end of 1967 for the dissociation constants of inorganic acids and bases in aqueous solution. It also includes references to acidity functions for strong acids and bases, and details about the formation of polynuclear species where this is relevant. The substances are listed alphabetically, with chemical formulae, so that the entries are self-indexing.

*Column 1* gives the name of the substance and the negative logarithm of the dissociation constant ( $pK_a$ ). Wherever possible, these values are thermodynamic ones obtained by extrapolation to ionic strength  $I = 0$ , generally by using some form of the Debye-Hückel equation such as that due to Davies. In all cases,  $pK$  values are listed in decreasing extent of protonation.

*Column 2* gives the temperature of measurements in °C.

*Column 3* lists details such as:

$I = \frac{1}{2}\sum C_i Z_i^2$  = ionic strength

$c$  = concentration in mole/l, or

$m$  = concentration in mole/1000 g. of water.

It also records any other details relating to the  $pK$  value quoted. Designation of a constant as "practical" implies that it includes both the activity of the hydrogen ion (usually as measured by pH meter) and the concentrations of the other species.

*Column 4* summarises the method of measurement, the procedure used in evaluating the constants, and any corrections that were taken into consideration; the symbols have the meanings set out under "Methods of Measurement", page 7. Because different investigators rarely use identical procedures, these symbols can only serve as guides: for fullest details the original papers should be consulted.

*Column 5* gives the literature references which are listed alphabetically at the end of the Table.



## II. METHODS OF MEASUREMENT AND CALCULATION

The abbreviations in *Column 4* of the Table are, with only minor differences, the same as those used in "Dissociation Constants of Organic Bases in Aqueous Solution".

### CONDUCTOMETRIC METHODS

- C1            Measurements in solutions of salt and acid  
C2            Measurements in solution of base only

### ELECTROMETRIC METHODS

#### [i] Cells without diffusion potentials

- Ela            Method of Harned and Ehlers (*J. Am. Chem. Soc.* **54**, 1350 (1932))  
(Cell of type Pt (H<sub>2</sub>)|B, BCl, NaCl||B, BCl, NaCl|AgCl|Ag, for which  $E - E_0 + (RT/F) \ln [\text{BH}^+] [\text{Cl}^-]/[\text{B}] = - (RT/F) \ln K'$ , and extrapolate to  $I = 0$ )
- Elb            Method of Harned and Owen (*J. Am. Chem. Soc.* **52**, 5079 (1930)) ,Pt(H<sub>2</sub>)|B, NaCl|AgCl|Ag, where molality of B is  $M$ ,  $E = E_0 - (RT/F) \ln ([m_{\text{H}^+}] [m_{\text{Cl}^-}] f_{\pm}^2)$ . Extrapolate to  $I = 0$  at constant  $M$ , then to  $M = 0$ )
- Elcg            Determination of [H<sup>+</sup>] from cells of the type, Glass|solution, Cl-|AgCl|Ag
- Elch            Determination of [H<sup>+</sup>] from the cell, Pt(H<sub>2</sub>) solution, Cl-|AgCl|Ag
- Eld            Method of Bates (*J. Am. Chem. Soc.* **70**, 1579 (1948)). Determination of  $K_1$  and  $K_2$  for dibasic acids
- Ele            Method of Bates and Pinching (*J. Res. Natl. Bur. Std.* **43**, 519 (1949)). A particular case of method Elcg in which the solution is a buffer comprising a weak base and a weak acid

#### [ii] Approximately symmetrical cells with diffusion potentials

- E2a            Method of Owen (*J. Am. Chem. Soc.* **60**, 2229 (1938))
- E2b            Method of Larsson and Adell (*Z. Physik. Chem.* **156**, 352, 381 (1931)) (Uses cell Pt(H<sub>2</sub>)|B, NaCl|sat. KCl|NaOH, NaCl|(H<sub>2</sub>)Pt and an approx.  $K$  to adjust to equal ionic strengths in the half-cells. From  $E$  obtain [H<sup>+</sup>] and hence  $K'$ : extrapolation to  $I = 0$  gives  $K$ )
- E2c            Method of Everett and Landsman (*Proc. Roy. Soc. London*, **A215**, 403, (1952))  
(This is like E2b but uses a second weak base of known  $pK$  instead of a strong base. The method gives the ratio of the two constants)

**[iii] Unsymmetrical cells with diffusion potentials**

E3ag	pH measurements in buffer solutions of weak electrolytes using glass electrodes
E3ah	Similar measurements using hydrogen electrodes
E3bg	Measurements of pH changes during titrations using glass electrodes
E3bh	Similar measurements using hydrogen electrodes
E3b, quin	Similar measurements using quinhydrone electrodes
E3c	Differential potentiometric methods
E3d	pH measurements at equal concentrations of salt and base

**OPTICAL METHODS**

01	Direct determination of the degree of dissociation by extinction coefficient measurements in solutions of weak bases and salts
02	Colorimetric determination with an indicator of known $pK$
03	Colorimetric determination with an indicator calibrated with a buffer solution of known pH
04	Method of von Halban and Brüll ( <i>Helv. Chim. Acta</i> <b>27</b> , 1719 (1944)) (Solutions of the base being studied, plus indicator, are compared with similar solutions containing alkali and indicator)
05	Light absorption measurements combined with electrometric measurements
06	Light absorption measurements using solutions of mineral acids of known concentrations and (usually) Hammett's acidity function, $H_0$
07	Similar to 06 but using solutions of alkalis

**OTHER METHODS**

ANALYT	Constants derived from chemical analysis
CALORIM	Calorimetric measurements
CAT	Constants estimated from catalytic coefficients
CRYOSC	Cryoscopic measurements
DISTRIB	Distribution between solvents
FP	Constants derived from freezing-point data
ION	Ion-exchange studies
KIN	Constants estimated from kinetic measurements
NMR	Nuclear magnetic resonance measurements
POLAROG	Polarographic measurements
RAMAN	Measurements of Raman spectra
REDOX	Oxidation-reduction potentials
SOLY	Solubility measurements
VAP	Vapour pressure measurements

## CALCULATIONS

**[i] Conductance measurements**

R1a Method of Davies (*The Conductivity of Solutions*, Chapman Hall, London 1930)

(By successive approximations,  $f_A$  is calculated from the Debye-Hückel-Onsager equation in the form

$$f_A = 1 - A(\alpha c_0)^{\frac{1}{2}}/\Lambda_0$$

which assumes that  $\Lambda_0$  can be obtained from Kohlrausch's law of independent ionic mobilities)

R1b Method of MacInnes (*J. Am. Chem. Soc.* **48**, 2068 (1926))

(The quantity  $\Lambda_e = f_A \Lambda_0$  is determined directly, where  $\Lambda_e$  is the conductance of the weak electrolyte if it were completely dissociated at the ionic strength studied: it is necessary to know  $\Lambda$  for strong electrolytes as a function of  $I$ )

R1c Method of Fuoss and Krauss (*J. Am. Chem. Soc.* **55**, 476 (1933))

(The Debye-Hückel-Onsager equation is used in the form,  $\Lambda_c = \alpha(\Lambda_0 - A(\alpha c_0)^{\frac{1}{2}})$  to derive an equation relating  $\Lambda_0$ ,  $c$  and  $K$ , which is solved by successive approximation until  $\Lambda_0$  is constant at all values)

R1d Method of Shedlovsky (*J. Franklin Inst.* **225**, 739 (1938))

(This is like R1c but a different equation is used)

R1e Method of Fuoss (*J. Am. Chem. Soc.* **79**, 3301 (1957))

**[ii] Differential potentiometric measurements**

R2a Method of Kilpi (*Z. Physik. Chem.* **173**, 223, 427 (1935); **175**, 239 (1936) (at point of inflection).

### III. TABLE

Nos. 1-2

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
<b>1. (Aquo) Aluminium ion, Al<sup>3+</sup></b>				
3.00	15	pK for hydrolysis of Al <sup>3+</sup> , $\epsilon = 0.0005 - 0.01$ M in AlCl <sub>3</sub> , extrapolated against <i>I</i> <sub>±</sub>	E3ag	S17
5.15	20			
4.98	25	pK for hydrolysis of Al <sup>3+</sup> , <i>I</i> varied from 0.0025 to 0.019, extrapolated to <i>I</i> = 0	E3ag	H41
4.96	25	pK for hydrolysis of Al <sup>3+</sup> , $\epsilon = 10^{-5} - 10^{-2}$ M in Al(ClO <sub>4</sub> ) <sub>3</sub> , extrapolated to <i>I</i> = 0	E3ag	F33
5.02	25		E3,quin	K12
4.96	25	pK for hydrolysis of Al <sup>3+</sup> ; also log <i>K</i> = 7.55 for 2Al(OH) <sub>2</sub> <sup>+</sup> ⇌ Al <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup> , and log <i>K</i> = 6.89 for 2Al <sub>2</sub> (OH) <sub>4</sub> <sup>2+</sup> + 2H <sub>2</sub> O ⇌ Al <sub>4</sub> (OH) <sub>10</sub> <sup>2+</sup> + 2H <sup>+</sup>	E3ag	K67
5.03	25	pK for hydrolysis of Al <sup>3+</sup>	E3AG	I19
5.10	25	pK for hydrolysis of Al <sup>3+</sup>	KIN	H64a
4.49	25	pK for hydrolysis of Al <sup>3+</sup> , from dissociation field effect relaxation times	KIN	K69
2.88	100	pK for hydrolysis of Al <sup>3+</sup>	C1	M9
11.22	25	pK for Al(OH) <sub>3</sub> + H <sub>2</sub> O ⇌ Al(OH) <sub>4</sub> <sup>-</sup> + H <sup>+</sup> Hydrolysis of Al <sup>3+</sup> in 2 M NaClO <sub>4</sub> at 40° gives, mainly, one or more polynuclear complexes Other measurements: B94, D23, F5, I20, L1, T7, W25.		B97
<b>2. Amidophosphoric acid, NH<sub>2</sub>PO<sub>3</sub>H<sub>2</sub></b>				
3.00	25	<i>I</i> = 0.2 (KCl), "practical" constants	E3bg	C13
8.15	25	<i>I</i> = 1(NMMe <sub>4</sub> Br), concentration constants, <i>f</i> <sub>±</sub> assumed same as for HBr	E3bg	I12
3.3		Titration of 0.1 M solution; pK of +NH <sub>3</sub> PO <sub>3</sub> H <sub>2</sub> given as 2.1		
3.8	20		E3b	R41
2.92			E,Sb	K29
7.86			E,h	M26
2.8	10			H15
4.6	25	Other measurements: C19		R10

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
<b>3. Aminodisulphonic acid, NH(HSO<sub>3</sub>)<sub>2</sub></b>				
8-50	25	pK <sub>3</sub> ; I = 1.0 (NaCl)	E3ag	D37a
<b>4. Aminophosphazenes, see Hexaminotriphosphazene, Octaminotetraphosphazene.</b>				
<b>5. Aminophosphoric acid, see Amidophosphoric acid.</b>				
<b>6. Ammonia, NH<sub>3</sub></b>				
10-081	0			
9-903	5			
9-730	10			
9-564	15			
9-401	20			
9-246	25			
9-093	30			
8-947	35			
8-805	40			
8-671	45			
8-540	50			
10-081	0			
9-904	5			
9-731	10			
9-564	15			
9-400	20			
9-245	25			
9-093	30			
8-947	35			
8-805	40			
8-670	45			
8-539	50			
9-555	15			
9-240	25			
8-946	35			
8-670	45			
		Equal concentrations of NH <sub>3</sub> and KH phenol sulphonate, <i>c</i> varied from 0.011 to 0.104 M, activity coefficients calculated from Debye-Hückel equation, pK plotted against <i>I</i>	E1ch	B20
			E1a	B19
		Thermodynamic quantities are derived from these values. <i>I</i> varies from 0.06 to 0.20. Extrapolated to zero concentration of NH <sub>4</sub> <sup>+</sup> at each <i>I</i> , then extrapolated against <i>I</i>	E2b	E23
		Thermodynamic quantities are derived from these values.		

9.867	5	$c = 0.02$ to $0.08$ ; $I = 0.07$ to $0.2$ , extrapolated to $I = 0$ , $c = 0$	E2b	E25
9.529	15			
9.215	25			
8.923	35			
8.645	45			
10.19	0		C1	N24
9.58	18			
9.35	25			
7.45	100			
6.45	156			
5.60	218			
5.74	306			
4.68	49			
4.83	93			
5.04	138			
5.36	182			
5.76	227			
6.21	271			
6.62	293			
7.58	100			
p <i>K</i> <sub>b</sub> values				
taking p <i>K</i> <sub>w</sub> = 12.38; inversion of sucrose				
Ref. H49a gives an equation fitting literature values of p <i>K</i> from 0° to 300°.				
p <i>K</i> <sub>b</sub> values 1000 atmospheres pressure				
	2000			
4.29	25		CAT	K69
3.91	25			
3.61	25			
4.32	45			
3.95	45			
3.65	45			
4.71	45			
4.30		1 atmosphere pressure		
3.74	1100			
3.32	2500			
2.95	4000			
2.68	5400			
2.42	6800			
2.21	8200			
2.11	9600			
2.00	11000			
32.72	12000			
Self-ionization of liquid ammonia, from cell potential data				
	-50			P30

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
32.49 27.66 29.8 40	-33.2 24.8 25	Self-ionization of liquid ammonia, from thermodynamic data		C32
		Self-ionization of liquid ammonia, from thermodynamic data		J13
		Approximate pK of NH <sub>2</sub> <sup>-</sup> , theoretical calculation		S29
		A value of 4.20 at 25° has been claimed from high field conductance measurements to be the true pK <sub>b</sub> of NH <sub>4</sub> <sup>+</sup> + OH <sup>-</sup> ⇌ NH <sub>4</sub> OH		B35
		A similar value, 4.28 at 20°, has been estimated from published data		M43
		For pK values in methanol-water mixtures, see E26, P1.		
		Other measurements: B51, F41, H26, H37, K3, K26, L49, M44, N25, O16, P13, S31, W22.		
<b>7. (Aquo) Antimony III ion, Sb<sup>3+</sup></b>				
1.4 11.8 0.87 11.0	25 25 25 25	pK for SbOH <sup>2+</sup> ⇌ SbO <sup>+</sup> + H <sup>+</sup> pK for SbO <sup>+</sup> + H <sub>2</sub> O ⇌ HSbO <sub>2</sub> + H <sup>+</sup> pK for SbO <sup>+</sup> + H <sub>2</sub> O ⇌ HSbO <sub>2</sub> + H <sup>+</sup> pK for HSbO <sub>2</sub> + 2H <sub>2</sub> O ⇌ Sb(OH) <sub>4</sub> <sup>-</sup> + H <sup>+</sup>	SOLY SOLY SOLY SOLY	K5 P29
<b>8. Antimony pentoxide, Sb<sub>2</sub>O<sub>5</sub></b> See also Dodeca-antimonic acid.				
2.55 25		pK for HSb(OH) <sub>6</sub> ⇌ Sb(OH) <sub>6</sub> <sup>-</sup> + H <sup>+</sup> ; I = 0.5(NM <sub>2</sub> Cl); Sb concentration ≤ 10 <sup>-3</sup> M; at higher concentrations polynuclear complexes are also formed.	E3b	L17
<b>Aquo metal ion, See entry under appropriate metal ion</b>				
<b>9. Arsenic acid, H<sub>3</sub>AsO<sub>4</sub></b>				
2.089 2.114 2.138 2.163 2.194 2.223 2.265 2.296 2.332	7.054 7.032 7.015 6.999 6.990 6.980 6.974 6.973 6.973	I varied from 0.007 to 0.096 (for K <sub>1</sub> ) and 0.010 to 0.21 (for K <sub>2</sub> ); extrapolated to I = 0	E1a,quin	A10

Thermodynamic quantities are derived from the results.

2-383	6-973	45			
2-420	6-980	50			
	$pK_1 = 2.014 + 5 \times 10^{-5} (t - 40.0)^2$				
	$pK_2 = 6.971 + 5 \times 10^{-2} (t - 39.4)^2$ , $t$ in °C.				
2-49	7-05	10			F19
2-19	6-94	25			
1-95	6-87	35			
2-15	6-80	50			
2-301	7-08	25			
		25			

Taking  $pK_2$  of  $H_3PO_4$  as 7.16

For values of  $pK_1$  in  $D_2O/H_2O$  mixtures, see S3  
Other measurements: B58, B86, C23, K48, L50, M8, S54, W4, W5

**10. Arsenious acid,  $H_3AsO_3$  ( $HAsO_2$ )**

9-295	15				
9-265	20				
9-18	25				
9-09	30				
8-97	35				
8-885	40				
8-81	45				
9-294	25				
9-22	25				
9-26	18				
9-08	25				
9-4	Room				
	13.5				
	13.8				
	32				

Molal scale;  $\epsilon = 0.008$ ,  $I = 0.1$  (KCl)

In KCl solutions, extrapolated to  $I = 0$

Taking  $pK$  of boric acid as 9.19

“Practical” constant, titration of 0.017 M  $H_3AsO_3$

$pK_2$  obtained from ultraviolet spectra

Other measurements: B58, C11, G5, K36, K48, T15, W5, W25, Z2

**11. Azido-dithiocarbonic acid,  $HSCSN_3$**

1-67	25				
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Free acid readily decomposes

**12. (Aquo) Barium ion,  $Ba^{2+}$**

0-62	5				
0-60	15				

$pK_1$  of  $BaOH^+$ ;  $I = 0.1$ ;  $f_{\pm}$  calculated by Davies' equation, for extrapolation to  $I = 0$ ; from c.m.f. data of H.S. Harned and



Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
0.64	25	C. G. Geary, <i>J. Am. Chem. Soc.</i> <b>59</b> 2032 (1937)		
0.69	25			
0.72	45			
0.64	25	Thermodynamic quantities are derived from the results. pK <sub>b</sub> of BeOH <sup>+</sup> ; $I = 0.04$ to 0.17; using Davies' equation and activity measurements of H. S. Harned and C. M. Mason, <i>J. Am. Chem. Soc.</i> <b>54</b> , 1441 (1932)		D7
0.85	25	$\epsilon = 0.02 - 0.05$ (Ba(OH) <sub>2</sub> ), $I = 0.23$ to 0.6 (Ba(OH) <sub>2</sub> + BaCl <sub>2</sub> ); extrapolation to $I = 0$ , using Davies' equation	KIN	B30
0.62	25	$I = 0.1$ to 0.45	CAT, KIN	B31
0.72	25	Concentration constant; 0.2 - 1 N BaCl <sub>2</sub> ; salt effect on indicator	O3	K39
0.00	25	$I = 3$ (NaClO <sub>4</sub> ) Other measurements: B32, K64	E2ah	C7
<b>13. (Aquo) Beryllium ion, Be<sup>2+</sup></b>				
5.7	~7	Beryllium ions readily hydrolyze in solution and form condensed species containing more than one beryllium atom. See, for example, C8 and K1. Successive pK values for hydrolysis of Be <sup>2+</sup> ; $I = 0.1$ (NaClO <sub>4</sub> ); rapid-reaction measurements; BeOH <sup>+</sup> quickly forms trimer Be <sub>3</sub> (OH) <sub>3</sub> <sup>3+</sup>	E3ag	S30
6.5	25	pK for Be <sup>2+</sup> $\rightleftharpoons$ BeOH <sup>+</sup> + H <sup>+</sup> ; $I = 1$ (NaClO <sub>4</sub> ); Be <sub>2</sub> OH <sup>3+</sup> also formed	E3bg	M21
>6.1	25	pK for Be <sup>2+</sup> $\rightleftharpoons$ BeOH <sup>+</sup> + H <sup>+</sup> ; $I = 3$ (NaClO <sub>4</sub> ); recalculation of data from refs. C8 and K1 using a computer; also -log $K = 10.87$ for Be <sup>2+</sup> + 2H <sub>2</sub> O $\rightleftharpoons$ Be(OH) <sub>2</sub> + 2H <sup>+</sup> ; constants given for Be <sub>3</sub> (OH) <sub>3</sub> <sup>3+</sup> and Be <sub>2</sub> OH <sup>3+</sup>		H56
10.82		pK <sub>b</sub> for Be(OH) <sub>2</sub> $\rightleftharpoons$ BeOH <sup>+</sup> + OH <sup>-</sup> ; $\epsilon = 0.01$ ; between pH 6.2 - 5.4; at lower pH values di- and tri-nuclear complexes are formed; constants are given	E3b	A9
10.46		pK for Be(OH) <sub>2</sub> + H <sub>2</sub> O $\rightleftharpoons$ Be(OH) <sub>3</sub> <sup>-</sup> + H <sup>+</sup> ; tracer concentrations; also -log $K = 13.65$ for Be <sup>2+</sup> + 2H <sub>2</sub> O $\rightleftharpoons$ Be(OH) <sub>2</sub> + 2H <sup>+</sup>	DISTRIB	G39

14. (Aquo) Bismuth(III) ion, Bi<sup>3+</sup>

1-58

25

E3bg

O6

$pK$  for  $Bi^{3+} \rightleftharpoons Bi(OH)^{2+} + H^+$ ;  $I = 3(NaClO_4)$ ;  $[Bi^{3+}]$  determined by Bi-Hg electrode; main equilibrium is  $6Bi^{3+} + H_2O \rightleftharpoons Bi_6(OH)_{12}^{6+} + 12H^+$ , with  $\log K = 0.33$   
 Hydrolysis of  $Bi^{3+}$  gives  $Bi_6O_6^{6+} + 12H^+$ , with  $-\log K = 0.53$  at 25° and  $I = 1(NaClO_4)$ , and at higher pH values  $Bi_6O_6(OH)_3^{3+}$ , with  $\log K = -8.1$   
 Hydrolysis of  $Bi_6O_6^{6+}$  ( $= Bi_6(OH)_{12}^{6+}$ ) gives  $Bi_9(OH)_{20}^{7+}$ ,  $Bi_9(OH)_{21}^{6+}$  and  $Bi_9(OH)_{22}^{5+}$ ; constants are listed

K1

$-\log K = 8.81$  for  $3Be^{2+} \rightleftharpoons Be_3(OH)_3^{3+} + 3H^+$ ;  $-\log K = 3.24$  for  $2Be^{2+} \rightleftharpoons Be_2OH^{3+} + H^+$ ;  $-\log K = 11.0$  for  $Be^{2+} \rightleftharpoons Be(OH)_2 + 2H^+$ ; all for  $I = 0.5(NaClO_4)$ ,  $c$  0.001 to 0.08 M in  $Be^{2+}$   
 $-\log K = 10.9$  for  $Be^{2+} \rightleftharpoons Be(OH)_2 + 2H^+$ , at 25° and  $I = 3(NaClO_4)$ ; constants also given for di- and tri-nuclear species.  
 Other measurements: L40, W26.

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15. Boric acid, H<sub>3</sub>BO<sub>3</sub>

9-5078  
 9-4374  
 9-3785  
 9-3255  
 9-2780  
 9-2340  
 9-1947  
 9-1605  
 9-1282  
 9-1013  
 9-0766  
 9-0537  
 9-0310

0  
 5  
 10  
 15  
 20  
 25  
 30  
 35  
 40  
 45  
 50  
 55  
 60

E1ch

M11

Molal scale; equimolar concentrations (0.003 to 0.03 M) of NaCl, borax and boric acid; extrapolated to  $I = 0$  using extended Debye-Hückel equation

9-440  
 9-380  
 9-327  
 9-280

5  
 10  
 15  
 20

E1ch

O18

$pK = 2237.94/T + 0.016883T - 3.305$  ( $T$  in °K)  
 Thermodynamic quantities are derived from the results. Molal scale.  $I$  varied from 0.02 to 3 by adding NaCl; extrapolated to zero boric acid concentration at constant  $I$ , then to  $I = 0$

Name, Formula and p <i>K</i> value	T(°C)	Remarks	Methods	Reference
9·237	25			
9·198	30			
9·164	35			
9·132	40			
9·080	50			
9·380	10	Thermodynamic quantities are derived from the results		
9·327	15	<i>I</i> varied from 0·01 to 0·12; constants corrected using Debye-Hückel equation and extrapolated to <i>I</i> = 0	E1a	O15
9·280	20			
9·236	25			
9·197	30			
9·132	40			
9·080	50			
9·21	20	$pK = 9·023 + 8 \times 10^{-5} (76·7 - t)^2$ ( <i>t</i> in °C)		
8·98	25	<i>I</i> = 0·04. The second p <i>K</i> of boric acid is greater than 14	E3ah	F31
9·00	25	<i>I</i> = 0·1 (NaClO <sub>4</sub> )	E3bh	I4
	25	<i>I</i> = 3(NaClO <sub>4</sub> )		
9·00	25	At boric acid concentrations above 0·4 M, higher than trimeric complexes are also formed		
		<i>I</i> = 3(NaClO <sub>4</sub> ); boric acid concentrations varied from 0·01 to 0·60 M. Other equilibria were:		
		3H <sub>3</sub> BO <sub>3</sub> ⇌ H <sub>4</sub> B <sub>3</sub> O <sub>7</sub> <sup>-</sup> + H <sup>+</sup> + 2H <sub>2</sub> O, log <i>K</i> = - 6·84,		
		3H <sub>3</sub> BO <sub>3</sub> ⇌ H <sub>5</sub> B <sub>3</sub> O <sub>8</sub> <sup>2-</sup> + 2H <sup>+</sup> + H <sub>2</sub> O, log <i>K</i> = - 15·44		
		Polymeric species are important at concentrations above about 0·01 M		
		Other measurements: B71, B88, E6, F9, H10, H25, I5, I6, K42, K48, L15, L41, M24, O17, P39.	E3bh	I9
<b>16. (Aquo) Cadmium ion, Cd<sup>2+</sup></b>				
10·2	25	p <i>K</i> for hydrolysis of Cd <sup>2+</sup> ; <i>I</i> = 3(NaClO <sub>4</sub> + Cd(ClO <sub>4</sub> ) <sub>2</sub> ); <i>c</i> = 0·1 to 1·45 (Cd(ClO <sub>4</sub> ) <sub>2</sub> ); Cd <sub>2</sub> OH <sup>3+</sup> and Cd <sub>4</sub> (OH) <sub>4</sub> <sup>4+</sup> are also formed	E3bg, quin	B44
9·0	25	p <i>K</i> for hydrolysis of Cd <sup>2+</sup> ; <i>I</i> = 3(NaClO <sub>4</sub> + Cd(ClO <sub>4</sub> ) <sub>2</sub> ); <i>c</i> = 0·01 to 0·9 (Cd(ClO <sub>4</sub> ) <sub>2</sub> )	E3bg	M12

KIN K69  
SOLY G14  
DISTRIB D46  
POLAROG L3

pK for hydrolysis of  $\text{Cd}^{2+}$ ;  $c = 0.02$  ( $\text{CdCl}_2$ )  
pK for hydrolysis of  $\text{Cd}^{2+}$   
pK<sub>b</sub> for  $\text{HCdO}_2^+ + \text{H}_2\text{O} \rightleftharpoons \text{Cd}(\text{OH})_2 + \text{OH}^-$   
 $I = 3(\text{NaClO}_4)$ , pK<sub>b</sub> for  $\text{CdOH}^+ \rightleftharpoons \text{Cd}^{2+} + \text{OH}^-$   
pK<sub>b</sub> for  $\text{Cd}(\text{OH})_2 \rightleftharpoons \text{CdOH}^+ + \text{OH}^-$   
pK<sub>b</sub> for  $\text{Cd}(\text{OH})_3^- \rightleftharpoons \text{Cd}(\text{OH})_2 + \text{OH}^-$   
pK<sub>b</sub> for  $\text{Cd}(\text{OH})_4^{2-} \rightleftharpoons \text{Cd}(\text{OH})_3^- + \text{OH}^-$   
on assumption that  $\log K_a = \frac{1}{4} \log K_1 K_2 K_3 K_4 + ((5 - 2n)/2)$   
 $\log (K_n/K_{n+1})$   
 $\log K$  for  $\text{Cd}^{2+} + 4\text{OH}^- \rightleftharpoons \text{Cd}(\text{OH})_4^{2-}$  is about 9.7 at 25°  
Other measurements: C12, G38, L39

### 17. Caesium hydroxide, CsOH

For alkalinity function for CsOH solutions, see L12a, M40.

### 18. (Aquo) Calcium ion, $\text{Ca}^{2+}$

9.49	100	pK <sub>b</sub> for $\text{CaOH}^+$ ; $m = 0.002 - 0.02$ $\text{Ca}(\text{OH})_2$ in 0.003 - 0.01 M $\text{CaCl}_2$ or 0.006 - 0.02 M KCl; values of pK <sub>b</sub> depend on choice of $\gamma_{\text{Cl}}/\gamma_{\text{OH}}$ used to evaluate molality of hydroxyl ion.	E1b	B17
9.3	10	pK <sub>b</sub> for $\text{CaOH}^+$ ; $I = 0.02$ to 0.1 ( $\text{Ca}(\text{OH})_2 + \text{CaCl}_2$ ); $f \pm$ calculated assuming Davies' equation	E1ch	G26
0.7	25	pK <sub>b</sub> for $\text{CaOH}^+$ ; $I = 0.007$ to 0.08	SOLY	B29
4.30	25	$I = 0.02$ to 0.08		
3.44	40	$I = 0.04$ to 0.10		
2.58	15	extrapolated to $I = 0$ assuming Davies' equation;		
1.72	25	$\text{Ca}(\text{IO}_3)_2$ in KOH solutions.	SOLY	D9
	0	pK <sub>b</sub> for $\text{CaOH}^+$ ; $\text{Ca}(\text{IO}_3)_2$ in $\text{Ca}(\text{OH})_2$ solutions; extrapolated using Davies' equation.	KIN	B32
	0	pK <sub>b</sub> for $\text{CaOH}^+$ ; $I = 0.18$ to 0.30; value sensitive to choice of activity coefficient	SOLY	D6
	25	$I = 0.025$ to 0.08		
	25	calculation of data of G. Kilde, <i>Z. Anorg. Allgem. Chem.</i> , <b>218</b> 113 (1934)		
	25	Recalculation of data of F. M. Lea and G. E. Bessey, <i>J. Chem. Soc.</i> <b>1937</b> 1612	C2	B30

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
1-46	25	$I = 0.13$ to $0.24$ ( $\text{Ca}(\text{OH})_2 + \text{CaCl}_2$ ); $\epsilon = 0.02 - 0.03$	KIN	B30
1-29	25	$\text{Ca}(\text{OH})_2$ ; extrapolated using Davies' equation		
1-03		$I = 0.02$ to $0.05$ ; $f$ $\pm$ calculated from Guggenheim's equation ( <i>Phil. Mag.</i> , <b>19</b> , 588 (1935))	CAT, KIN	B31
0-64	25	Concentration constant; $0.2 - 1N$ $\text{CaCl}_2$ ; from salt effect on indicator $I = 3(\text{NaClO}_4)$ For the acidity function of $\text{Ca}(\text{OH})_2$ solutions from $0.95^\circ$ and $I = 0.01$ to $0.20$ , see B18 Other measurements; G42	O3 E2ah	K39 C7
<b>19. Carbonic acid, <math>\text{H}_2\text{CO}_3</math></b>				
6-577	0	Apparent pK values; double extrapolation procedure to eliminate effect of added NaCl and to obtain values at zero bicarbonate concentration	E1ch	H29
6-517	5			
6-465	10			
6-420	15			
6-382	20			
6-351	25			
6-327	30			
6-309	35			
6-296	40			
6-289	45			
6-287	50			
6-579	0	$\text{p}K_1 = 3404.71/T - 14.8435 + 0.032786T$ ( $T$ in $^\circ\text{K}$ ) Thermodynamic quantities are derived from the results. Apparent pK values; $I = 0.004 - 0.2$ , extrapolated to $I = 0$	E1ch	H31
6-517	5			
6-464	10			
6-419	15			
6-381	20			
6-352	25			
6-327	30			
6-309	35			
6-298	40			
6-290	45			

6-285	50					
6-514	5	Apparent p <i>K</i> values; $I = 0.003 - 3$ ; extrapolated to $I = 0$ by fitting to an extended Debye-Hückel equation		E3bh		N7
6-421	15					
6-349	25					
6-310	35					
6-294	45					
6-583	0	$pK_1 = 6.572 - 0.012173t + 0.00013329t^2$ ( $t$ in °C)				
6-429	15	Apparent p <i>K</i> values; 0.001 N in KHCO <sub>3</sub> , KCl, HCl, and saturated CO <sub>2</sub> solutions		C1,R1d		S40
6-366	25					
6-317	38					
6-35	25	Apparent p <i>K</i> value		E2b, quin		A45
6-35	25	Apparent p <i>K</i> value		E1c, quin		A44
6-38	25	Apparent p <i>K</i> values, molal scale, $I$ varied from 0.0001 to 0.1, 1035 atmosphere, 2050 atmosphere, 2930 atmosphere, 1 atmosphere		C1		E10
5-90						
5-48						
5-15						
6-32						
5-85	35					
5-45						
5-12						
6-32	45					
5-89						
5-50						
5-16						
6-30	55					
5-86						
5-49						
5-17						
6-31	65					
5-88						
5-51						
5-26						
10-625	0	$I$ varied from 0.02 to 0.16; extrapolated to $I = 0$ using extended Debye-Hückel equation		E3ah		H39
10-557	5					
10-490	10					
10-430	15					
10-377	20					
10-329	25					

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
10·290	30	$pK_2 = 2902.39/T - 6.4980 + 0.02379T$ ( $T$ in °K) Thermodynamic quantities are derived from the results. $I$ varied from 0.005 to 0.1; extrapolated against $I$	E.g	C45
10·250	35			
10·220	40			
10·195	45			
10·172	50			
10·179	60	$pK_2 = 2909.10/T - 6.119 + 0.02272T$ ( $T$ in °K) Double extrapolation, first to values in pure aqueous NaCl solutions, then against $I$ to $I = 0$ $I = 0$ $I = 1(\text{NaCl})$	E3ah	W9
10·153	70			
10·142	80			
10·140	90			
10·641	0			
10·397	18	$I$ varied from 0.01 to 0.2; extrapolated against $I^{\ddagger}$ $I$ varied from 0.01 to 0.2; extrapolated against $I^{\ddagger}$ True pK for $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ; high field conductivity measurements	VAP	N6 E9
10·32	25			
10·33	25			
6·35	50			
6·29	100			
6·24	100			
6·33	150			
6·55	200			
6·42	100			
6·77	150			
7·27	200			
7·89	250			
8·70	300			
6·46	100			
6·81	156			
7·14	200			
10·96	218	$I$ varied from 0.01 to 0.2; extrapolated against $I^{\ddagger}$ $I$ varied from 0.01 to 0.2; extrapolated against $I^{\ddagger}$ True pK for $\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$ ; high field conductivity measurements	CI	R48
6·34	25			
6·31	38			
3·81	5			
3·75	15			
3·76	25			
3·78	35			

3.80	38				
3.80	45				
3.68	0.5				D31
3.88	25				B34
3.75	23.5				S13
3.82	30.2				
3.89	35.6				
3.80	4				L38
<b>20. Caro's acid, see Peroxymonosulphuric acid</b>					
<b>21. (Aquo) Cerium(III) ion, Ce<sup>3+</sup></b>					
	25				M38
					B49
<b>22. (Aquo) Cerium(IV) ion, Ce<sup>4+</sup></b>					
	5				R20a
	15				
	25				
	35				
	25				O1a
	1.6				B8
	25				
	25				S42
<b>23. Chloramine, see Monochloramine</b>					

True  $pK$  for  $H_2CO_3$ , calculated from apparent  $pK$ , using rates of hydration and dehydration  
 True  $pK$  for  $H_2CO_3$ ; from high field conductivity measurements, taking  $pK_{obs} = 6.352$   
 True  $pK$  for  $H_2CO_3$ ; from rapid-reaction measurements  
 True  $pK$  for  $H_2CO_3$ ; 150 atmospheres; pressure jump method. Other measurements: B79, B101, B111, C40, C41, F6, F34, H42, K6, K7, K8, K9, K10, K28, K43, M22, M28, M45, N12, R37, S1, S69.

$pK$  for hydrolysis of  $Ce^{3+}$ ; from hydrolysis of "pure" salts;  $\epsilon = 0.001 - 0.5 M Ce_2(SO_4)_3$   
 $Ce_3(OH)_5^{4+}$  was formed at 25° by hydrolysis of 0.05 M  $Ce^{3+}$  in 3 M  $LiClO_4$   
 Other measurements: R8, S72

$I = 1.1 - 4(HClO_4, NaClO_4)$ ;  $\epsilon = 1 - 14 \times 10^{-3} M$ ; dimerization was important  
 $I = 0.9$  to  $1.7(HClO_4)$   
 $\epsilon = 1 \times 10^{-3} M Ce(IV)$ ; polymerisation was negligible.  
 $pK$  values for hydrolysis to  $CeOH^{3+}$  and  $Ce(OH)_2^{2+}$ ;  
 $I = 2(HClO_4, NaClO_4)$ ;  $\epsilon = 3.5 \times 10^{-3} M Ce(IV)$ ; from pH-dependence of redox potential  
 $pK$  for  $CeOH^{3+} \rightleftharpoons Ce(OH)_2^{2+} + H^+$ ;  $HClO_4$  concentration from 0.2 - 0.4 M; from pH-dependence of redox potential  
 Other measurements: D2a

Other measurements: R8, S72

Other measurements: D2a



<i>Name, Formula and pK value</i>	<i>T(°C)</i>	<i>Remarks</i>	<i>Methods</i>	<i>Reference</i>
<b>24. Chloric acid, HClO<sub>3</sub></b> ~ - 2.7		Theoretical prediction, based on structure		K52
<b>25. Chlorosulphuric acid, HClSO<sub>3</sub></b> For pK in sulphuric acid, see B11				
<b>26. Chlorous acid, HClO<sub>2</sub></b>				
1.94	25	Spectral differences extrapolated to zero time; $\epsilon = 0.001$ to $0.003$ M NaClO <sub>2</sub> , acidified with HClO <sub>4</sub> ; activity coefficients from Debye-Hückel equation	O6	L18
1.97	19-20	$\epsilon = 0.001 - 0.1$ M NaClO <sub>2</sub> ; extrapolation against $I^{\frac{1}{2}}$	E3bg	D5
1.96	20		E3bg, R2a	H66
1.99	23	"Practical" constant; concentration of HClO <sub>2</sub> ~ 0.25 M Other measurements: L20, T1		L36
<b>27. Chromic acid, H<sub>2</sub>CrO<sub>4</sub></b>				
6.444	5		E3bg	L35a
6.478	15			
6.488	25			
6.524	35			
6.569	45			
6.642	60			
6.472	15			
6.500	25			
6.533	35			
6.593	45			
6.40	18			
6.47	18			
6.52	25			
6.52	25			
6.50	25			
0.74	25			
6.60	20 ± 2			
		Titration of 0.025 M H <sub>2</sub> CrO <sub>4</sub> Titration of 0.04 M K <sub>2</sub> CrO <sub>4</sub> $I = 0.0018$ to $0.0028$ ; $f \pm$ calculated from Davies' equation $I = 0.002$ to $0.004$ $I = 0.01$ to $0.16$ ; extrapolated to $I = 0$ ; $K = 0.023$ for Cr <sub>3</sub> O <sub>7</sub> <sup>2+</sup> + H <sub>2</sub> O $\rightleftharpoons$ 2HCrO <sub>4</sub> <sup>-</sup> $I$ about 0.16; HCl/KCl solutions $I = 0.1$ ; corrected to $I = 0$ by Davies' equation, tracer concentrations	O5	L35a
			E3bg	B81
			E3bg	B88
			E3bg	H72
			O5	
			E3ag	N16
			E3ch	
			DISTRIB	H13

15	Concentration constants corrected for formation of $\text{CrO}_3\text{Cl}^-$ ; $I = 1(\text{LiClO}_4, \text{LiCl}, \text{HClO}_4, \text{HCl})$	O6	T11b
25			
35		O5	B5
25	$c = 2.5 \times 10^{-5} \text{ M}$		
25	In $\text{HClO}_4$ solutions	O6	L14
25	In $\text{H}_2\text{SO}_4$ solutions, using $\text{H}_L$ scale	O6	
25	In $\text{HCl}$ solutions, using $\text{H}_L$ scale	O6	
25	In $\text{HNO}_3$ solutions, using $\text{H}_0$ scale	O6	
25	In $\text{H}_3\text{PO}_4$ solutions, using $\text{H}_0$ scale	O6	
25	In $\text{HClO}_4$ solutions, using $\text{H}_L$ scale		
25	$pK_1$ varies with the proton source because of the formation of species such as $\text{HCrO}_3\text{Cl}$ and $\text{HCrO}_3(\text{OSO}_3\text{H})$		
25	$I = 1.0$ ; in $\text{HCl}$ solutions, correcting for the formation of $\text{CrO}_3\text{Cl}^-$	O6	H12
	The equilibrium constant for $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$ is 0.0265 at $20^\circ$ and 0.0303 at $25^\circ$		D13
	Other measurements: B24, B100, H78, J1a, J6, M18, S7, S41, S43a, S66, T11a, T12		

25	$pK$ for hydrolysis of $\text{Cr}^{3+}$ ; $I = 0.0014 - 0.04$ ; extrapolated to $I = 0$	E3ag	H41
25	$pK$ for hydrolysis of $\text{Cr}^{3+}$ ; corrected for $\text{Cr}^{3+} - \text{SO}_4^{2-}$ ion-pair formation; $I = 0$	C1	T19
46.2	$pK$ for hydrolysis of $\text{Cr}^{3+}$ ; $I = 0.068 (\text{LiClO}_4)$ ; from variation of apparent stability constant of $\text{CrNCS}^{2+}$ with pH	O5	P36
63.6			
73.7			
2.83			
2.65			
2.49			
94.6			
15	$I = 0.068 (\text{LiClO}_4)$ ; extrapolation from results at 46-95°		P36
25	$pK$ for hydrolysis of $\text{Cr}^{3+}$	C1	B53
0			
25			
50			
3.47			
75			
2.99			
2.58			
4.26			
15	$pK$ for hydrolysis of $\text{Cr}^{3+}$ ; $I = 0.5 (\text{NaNO}_3)$	E3bg	J15
	$pK$ for hydrolysis of $\text{Cr}^{3+}$ ; $I = 0$	KIN	B94

Name, Formula and p <i>K</i> value	T(°C)	Remarks	Methods	Reference
4-1 ~5.6	20	Successive p <i>K</i> values for hydrolysis of Cr <sup>3+</sup> ; <i>I</i> = 0.1 (NaClO <sub>4</sub> ); rapid-flow measurements	E3ag	S30
4-10 5.55	25	Successive "practical" p <i>K</i> values for hydrolysis of Cr <sup>3+</sup> ; <i>I</i> = 0.04 to 0.4	E3ag	E18
3-96	25	Other measurements: B54, C15, D23, L4	O5	
<b>29. (Aquo) Cobalt(II) ion, Co<sup>2+</sup></b>				
9-96	15	p <i>K</i> for hydrolysis of Co <sup>2+</sup> at <i>I</i> = 0.25 and 0.75 (NaClO <sub>4</sub> )	E3bg	B64
9-85	25			
9-62	35			
9-50	45			
8-9	30	p <i>K</i> for hydrolysis of Co <sup>2+</sup> ; <i>I</i> = 0.1 (KCl)	E3bg	C12
8-7	100	p <i>K</i> for hydrolysis of Co <sup>2+</sup> Other measurements: A7, D23, G12, F31	KIN	K68
<b>30. (Aquo) Cobalt(III) ion, Co<sup>3+</sup></b>				
2-10	12.5	p <i>K</i> for hydrolysis of Co <sup>3+</sup> ; <i>I</i> = 1 (NaClO <sub>4</sub> )	O6	S79
1-98	18.5			
1-78	23.6			
1-71	28.2			
The above values are uncertain because high cobaltic concentrations and low acidities favour formation of polynuclear species				
<b>31. (Aquo) Copper(II) ion, Cu<sup>2+</sup></b>				
8-0	25	The p <i>K</i> for Cu <sup>2+</sup> is not known; hydrolysis of Cu <sup>2+</sup> gives almost entirely polynuclear complexes of the type, Cu <sub>n</sub> (OH) <sub>2n-2</sub> <sup>2+</sup> ; formation constants for Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> from 15-42° are given. p <i>K</i> for Cu <sup>2+</sup> ⇌ CuOH <sup>+</sup> + H <sup>+</sup> ; <i>I</i> = 3 (NaClO <sub>4</sub> ): the major species formed is Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> , with -log <i>K</i> = 10.6	E3bg	B33
7-97	18	p <i>K</i> for Cu <sup>2+</sup> ⇌ CuOH <sup>+</sup> + H <sup>+</sup> ; the major species formed is Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> , with -log <i>K</i> = 10.89 Hydrolysis of Cu <sup>2+</sup> gives Cu <sub>2</sub> (OH) <sub>2</sub> <sup>2+</sup> , with -log <i>K</i> at 25° ranging from 10.5 to 10.9	E3bg	P15
				H4

~10					M3
13-1		Prediction of p <i>K</i> for $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{HCuO}_2^- + \text{H}^+$			
<12.8	25	p <i>K</i> for $\text{HCuO}_2^- \rightleftharpoons \text{H}^+ + \text{CuO}_2^{2-}$		SOLY	J11
	25	p <i>K</i> for $\text{Cu}(\text{OH})_2 \rightleftharpoons \text{HCuO}_2^- + \text{H}^+$		SOLY	
		Other measurements: A5, C12, C36, D8, F35, K5, K69, Q3			
<b>32. Cyanic acid, HCNO</b>					
3.76	0	Corrected to <i>I</i> = 0 by extended Debye-Hückel equation;		E3ag	C5
3.64	10	extrapolated to zero time to allow for decomposition			
3.57	18				
3.46	25				
3.37	35				
3.48	45	<i>I</i> varied from 0.06 to 0.2; ionic strength correction doubtful;		E3ag	J4
3.54	18	extrapolated to zero time			
3.47	25	<i>I</i> = 0		E3ag	M60
		Other measurements: A19, B67a, T4			
<b>33. Decahydrodecaboric acid, H<sub>2</sub>B<sub>10</sub>H<sub>10</sub></b> For acidity function, see M50					
<b>34. Decavanadic acid, H<sub>6</sub>V<sub>10</sub>O<sub>28</sub></b>					
3.65	20	p <i>K</i> <sub>5</sub> ; <i>I</i> = 0.2; also log <i>K</i> = -7.50 for $10\text{VO}_2^+ + 8\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{V}_{10}\text{O}_{28}^{4-} + 14\text{H}^+$ ; and log <i>K</i> = -23.5 for $2.5\text{V}_4\text{O}_{12}^{4-} + 3\text{H}_2\text{O} \rightleftharpoons \text{HV}_{10}\text{O}_{28}^{5-} + 5\text{OH}^-$		E3ag	S5
3.6	25	p <i>K</i> <sub>6</sub> ; p <i>K</i> <sub>7</sub> ; <i>I</i> = 1(NaClO <sub>4</sub> ); total vanadium concentrations $2 \times 10^{-3}$ - $2 \times 10^{-2}$ M; also log <i>K</i> = -6.75 for $10\text{VO}_2^+ + 8\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{V}_{10}\text{O}_{28}^{4-} + 14\text{H}^+$		E3ag	R32
3.5	25	<i>I</i> = 3(NaClO <sub>4</sub> )		O5	
3.70		<i>I</i> = 1(NaClO <sub>4</sub> ); 0.025 - 0.1 M in vanadate		E	C17
4.45	20	<i>I</i> = 1(NaClO <sub>4</sub> ); rapid titration		E	S32
		<i>I</i> = 0.1(NM <sub>2</sub> Cl); rapid-reaction studies; complex formation occurs with alkali cations		O5	
2.19	33	Saturated Na <sub>2</sub> SO <sub>4</sub> solution; up to 0.1 M Na <sub>3</sub> VO <sub>4</sub> solutions; also log <i>K</i> = 2.4 for $\text{H}_2\text{V}_{10}\text{O}_{28}^{4-} + 14\text{H}^+ \rightleftharpoons 10\text{VO}_2^+ + 8\text{H}_2\text{O}$		CRYOSG	N13
		Other measurements: C16			
<b>35. Deuterium chloride, DC1</b> For Hammett acidity function in D <sub>2</sub> O, see H63					
<b>36. Deuterium oxide, D<sub>2</sub>O</b>					
15.526	10	Molal scale; extrapolated to <i>I</i> = 0		E1ch	C32a,
15.136	20				C34a
14.955	25				

Name, Formula and p <i>K</i> value	<i>T</i> (°C)	Remarks	Methods	Reference
14-784	30			
14-468	40			
14-182	50			
15-439	10	Molar scale		
15-049	20			
14-869	25			
14-699	30			
14-385	40			
14-103	50	Mole fraction scale		
17-224	10			
16-834	20			
16-653	25			
16-482	30			
16-166	40			
15-880	50			
15-08	15	$pK_m = 4913.14/T - 7.5117 + 0.0200854T$ ( <i>T</i> in °K) Thermodynamic quantities are derived from the results. Molar scale; <i>I</i> = 0.04 to 0.10, extrapolated to <i>I</i> = 0	E2bh	W35
14-71	25			
14-37	35			
14-807	20	Molal scale, taking $pK_w = 14.073$ for H <sub>2</sub> O	E3ah	S31
14-812	25	Molal scale	ANALYT	K24
14-81	25	Using 0.01 M Ba(OH) <sub>2</sub> in H <sub>2</sub> O/D <sub>2</sub> O mixtures; molal scale.	E3ag	S3
14-86	25	Molar scale, <i>I</i> = 0	E3bh	G31
14-856	25	Molar scale, <i>I</i> = 0	E3bh	G31a
14-80	25	<i>I</i> = 0	E1cd	A2
		For p <i>K</i> values of H <sub>2</sub> O/D <sub>2</sub> O mixtures, see G31, G31a		
<b>37. Deuterio-ammonia, ND<sub>3</sub></b>				
9-757	20	<i>I</i> = 0; in D <sub>2</sub> O; taking p <i>K</i> of NH <sub>3</sub> in H <sub>2</sub> O as 9.265	E3ah	S31
4-9		p <i>K</i> <sub>b</sub> ; rough estimate		L24
<b>38. Deuterio-arsenic acid, D<sub>3</sub>AsO<sub>4</sub></b>				
2-596	25	p <i>K</i> <sub>1</sub> in D <sub>2</sub> O; <i>I</i> = 0; from measurements in D <sub>2</sub> O/H <sub>2</sub> O mixtures	E3ag	S3

<b>39. Deuteriocarbonic acid, D<sub>2</sub>CO<sub>3</sub></b>								
6-77	10-96	25	Apparent p <i>K</i> in D <sub>2</sub> O; taking p <i>K</i> <sub>1</sub> for CO <sub>2</sub> in H <sub>2</sub> O = 6.35	E3a,quin	C40			
	10-93	25	In D <sub>2</sub> O; meter standardized in H <sub>2</sub> O; p <i>K</i> <sub>2</sub> for H <sub>2</sub> CO <sub>3</sub> in H <sub>2</sub> O taken as 10.33	E3ag	G29			
		25	In D <sub>2</sub> O; taking p <i>K</i> <sub>2</sub> for H <sub>2</sub> CO <sub>3</sub> in H <sub>2</sub> O as 10.33	E3ag	C41			
<b>40. Deuteriodisulphuric acid, D<sub>2</sub>S<sub>2</sub>O<sub>7</sub></b>			For p <i>K</i> <sub>a</sub> in concentrated H <sub>2</sub> SO <sub>4</sub> , see F21					
<b>41. Deuteriohydrazine, N<sub>2</sub>D<sub>4</sub></b>								
	9-08	17	“Practical” constant; in D <sub>2</sub> O; <i>I</i> = (KCl)	E3dg	F12			
	8-69	30						
	9-11	18	“Practical” constant, in D <sub>2</sub> O; <i>I</i> = 1 (KCl)	E3dg	B102			
<b>42. Deuteriohydrazoic acid, DN<sub>3</sub></b>								
	5-01	20	In D <sub>2</sub> O; <i>I</i> = 0	E3bg	B108			
<b>43. Deuterio-iodic acid, DIO<sub>3</sub></b>								
	1-15	25	In D <sub>2</sub> O; taking p <i>K</i> of HIO <sub>3</sub> in H <sub>2</sub> O = 0.85	C1,R1d	M2			
<b>44. Deuteriophosphoric acid, D<sub>3</sub>PO<sub>4</sub></b>								
	2-350	25	In D <sub>2</sub> O; <i>I</i> = 0; extrapolated from measurements in D <sub>2</sub> O/H <sub>2</sub> O mixtures	E3ag	S3			
	2-362	25	In D <sub>2</sub> O; taking p <i>K</i> <sub>1</sub> for H <sub>3</sub> PO <sub>4</sub> in H <sub>2</sub> O as 2.128	C	M2			
	2-31	25	In D <sub>2</sub> O; meter standardised in H <sub>2</sub> O; taking p <i>K</i> <sub>1</sub> for H <sub>3</sub> PO <sub>4</sub> in H <sub>2</sub> O as 2.11	E3ag	G29			
	7-8846	5	In D <sub>2</sub> O; using KD <sub>2</sub> PO <sub>4</sub> /Na <sub>2</sub> DPO <sub>4</sub> mixtures from 0.005 to 0.025 m, and NaCl 0.005 m; extrapolated to <i>I</i> = 0	E1a	G8			
	7-8499	10						
	7-8233	15						
	7-7986	20						
	7-7796	25						
	7-7667	30						
	7-7547	35						
	7-7484	40						
	7-7433	45						
	7-7435	50						

$pK_2 = 2202.11/T - 5.9823 + 0.021388T$  ( $T$  in °K)  
Thermodynamic quantities are derived from the results.

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
7-750	25	In D <sub>2</sub> O; extrapolated from measurements in D <sub>2</sub> O/H <sub>2</sub> O mixtures; taking pK <sub>2</sub> for H <sub>3</sub> PO <sub>4</sub> in H <sub>2</sub> O as 7.290; $I = 0$	E, quin	R38
2-188	20	In D <sub>2</sub> O; $I = 0$ ; taking pK <sub>1</sub> and pK <sub>2</sub> for H <sub>3</sub> PO <sub>4</sub> in water as 1.983, 7.207	E3ah	S31
<b>45. Deuteriosulphuric acid, D<sub>2</sub>SO<sub>4</sub></b>				
2-33	25	In D <sub>2</sub> O; pK <sub>2</sub> ; $I = 0$ , from plot of solubility of Ag <sub>2</sub> SO <sub>4</sub> in dilute D <sub>2</sub> SO <sub>4</sub> in D <sub>2</sub> O as function of $I$ from 0.1 to 1.0 M	SOLY	L30
2-69	50			
2-98	75			
3-29	100			
3-59	125			
3-91	150			
4-21	175			
4-52	200			
4-84	225			
		$pK_2 = 0.0123175T - 22.86565/T - 1.253986$ ( $T$ in °K) Thermodynamic quantities are derived from the results. Other measurements of pK <sub>2</sub> , see B7, D39 For Hammett acidity function in D <sub>2</sub> O, see H63 For self-dissociation constant of D <sub>2</sub> SO <sub>4</sub> see F21		
<b>46. Diamidophosphoric acid, (NH<sub>2</sub>)<sub>2</sub>PO<sub>2</sub>H</b>	18		C1	K29
4-92	25			
4-83				
<b>47. Difluorophosphoric acid, HPO<sub>2</sub>F<sub>2</sub></b>				
		For basic pK in sulphuric acid, see B11		
<b>48. Diimidotriphosphoric acid, H<sub>2</sub>O<sub>3</sub>P.NH<sub>2</sub>.PO<sub>2</sub>H.NH<sub>2</sub>.PO<sub>3</sub>H<sub>2</sub></b>				
~1	9.84	Concentration constants, $I = 0.1$ (NMe <sub>4</sub> Br)	E3bg	I12
~0	3-03	$I = 0.2$ (NMe <sub>4</sub> Br)		
~0	3-83	$I = 0.3$ (NMe <sub>4</sub> Br)		
~0	3-94	$I = 1$ (MNMe <sub>4</sub> Br)		
~1	3-36	$f \pm$ assumed same as for HBr		
	10.00			

~1	~2.2	3.24	6.80	9.50	37	Values of $pK_1$ and $pK_2$ could be seriously in error because of experimental limitations $I = 0.1$ ; same remarks as above $I = 0.1$	E3bg	I11
~1	~2.4	3.59	7.02	9.28	50			
<b>49. Diperosmic acid, See Osmic(VIII) acid</b>								
<b>50. Diperruthenic acid, (hydrated <math>RuO_4</math>)</b>								
11.17					20?	Distribution between $CCl_4$ and water	DISTRIB	M15
14.24						$pK_b$ for $H_2RuO_5 \rightleftharpoons HRuO_4^+ + OH_2^-$		S48
11.9								
<b>51. Disulphuric acid, <math>H_2S_2O_7</math></b>								
-12	-8					Theoretical predictions (Ricci's method) of $pK_1$ and $pK_2$		G24
-13	-8					Theoretical predictions (Pauling's method) of $pK_1$ and $pK_2$		B13
1.85					10	$pK$ in concentrated $H_2SO_4$ ; molal scale	FP	B74
2.52					20	$pK$ in concentrated $H_2SO_4$ ; molal scale		
<b>52. Dithionic acid, <math>H_2S_2O_6</math></b>								
-3.4	-0.2					Theoretical predictions of $pK_1$ and $pK_2$ from structure		K52
<b>53. Dithionous acid, see Hyposulphurous acid</b>								
<b>54. Dodeca-antimonic acid, <math>H_{12}(Sb(OH)_6)_{12}</math></b>								
<1.55	<1.55	<1.55			25	$pK_1, pK_2, pK_3$	E3b	L17
1.55	2.95	4.35				$pK_4, pK_5, pK_6$		
5.75	7.15					$pK_7, pK_8$ , all at $I = 0.5$ (NMe <sub>4</sub> Cl); this acid exists in equilibrium with mononuclear antimony species at Sb(V) concentrations above $10^{-3} M$		
<b>55. Dodecahydrododecaboric acid, <math>H_2B_{12}H_{12}</math></b>								
For acidity function, see M50								
<b>56. Dodecatungstic acid, <math>H_{10}W_{12}O_{41}</math></b>								
~3.6	5.27	6.28			20	$pK_8, pK_9, pK_{10}$ ; $I = 0.1$ (NaCl); rapid-reaction technique	E3ag	S83



Name, Formula and $pK$ value	$T$ ( $^{\circ}\text{C}$ )	Remarks	Methods	Reference
57. (Aque) Dysprosium(III) ion, $\text{Dy}^{3+}$ 8-10	25	$pK_a$ for hydrolysis of $\text{Dy}^{3+}$ ; titration of 0.004-0.009 M $\text{Dy}(\text{ClO}_4)_3$ with 0.02 M $\text{Ba}(\text{OH})_2$ ; $I = 0.3(\text{NaClO}_4)$	E3b	F33a
58. (Aque) Erbium(III) ion, $\text{Er}^{3+}$ 7-99	25	$pK_a$ for hydrolysis of $\text{Er}^{3+}$ ; titration of 0.004-0.009 M $\text{Er}(\text{ClO}_4)_3$ with 0.02 M $\text{Ba}(\text{OH})_2$ ; $I = 0.3(\text{NaClO}_4)$	E3b	F33a
59. (Aque) Europium(III) ion, $\text{Eu}^{3+}$ 8-31	25	$pK_a$ for hydrolysis of $\text{Eu}^{3+}$ ; titration of 0.004-0.009 M $\text{Ba}(\text{OH})_2$ ; $I = 0.3(\text{NaClO}_4)$	E3b	F33a
~8-8	25	$pK$ for hydrolysis of $\text{Eu}^{3+}$ ; hydrolysis of "pure" salt; $c = 0.001$ - $0.01$ M $\text{Eu}_2(\text{SO}_4)_3$	E3ag	M38
60. Ferric ion, see Iron(III) ion				
61. Ferricyanic acid, $\text{H}_3\text{Fe}(\text{CN})_6$ <1	25	$pK_3$ ; $c \approx 10^{-3}$	E3bg	J14
62. Ferrocyanic acid, $\text{H}_4\text{Fe}(\text{CN})_6$ 2.2 4.17 2.57 3 4.3 4.17 2.3 4.28 4.25	25 25 17 25 25 25	$pK_3, pK_4$ ; $c \approx 10^{-3}$ ; $I = 0.01$ to 0.5; extrapolated to $I = 0$ $pK_3, pK_4$ ; $I = 0$ $pK_3, pK_4$ ; $I = 0$ $pK_4$ ; $I = 0.001$ to 0.25; extrapolated against $I$ $pK_3, pK_4$ variation of redox potential with pH; extrapolated to $I = 0$ $pK_4$ ; variation of redox potential with pH Other measurements: K37	E3bg E3bg E3bg E3bg REDOX REDOX	J14 H74 N14 L7 H20a K46
63. Ferrous ion, see Iron(II) ion				
64. Fluorophosphoric acid, $\text{H}_2\text{PO}_3\text{F}$ ~0.5 4.80 5.12	40 25	"Practical" constants	E3b E	D32 R47

65. Fluorosulphuric acid,  $\text{HFSO}_3$

For  $pK_a$  in sulphuric acid, see B11

66. (Aquo) Gadolinium(III) ion,  $\text{Gd}^{3+}$

25	$pK$ for hydrolysis of $\text{Gd}^{3+}$ ; hydrolysis of "pure" salt; $c = 0.001 - 0.01 \text{ M}$ $\text{Gd}_2(\text{SO}_4)_3$	E3ag	M38
25	$pK_a$ for hydrolysis of $\text{Gd}^{3+}$ ; titration of $0.004 - 0.009 \text{ M}$ $\text{Gd}(\text{ClO}_4)_3$ with $0.02 \text{ M}$ $\text{Ba}(\text{OH})_2$ ; $I = 0.3(\text{NaClO}_4)$	E3b	F33a

67. (Aquo) Gallium(III) ion,  $\text{Ga}^{3+}$

25	$pK$ for hydrolysis of $\text{Ga}^{3+}$ ; $c = 0.004 - 0.25 \text{ M}$ in $\text{Ga}^{3+}$	E3bg	M39
25	$pK$ for hydrolysis of $\text{Ga}^{3+}$ ; $I = 0.5(\text{NaClO}_4)_4$	O6	W20
18	Successive $pK$ values for hydrolysis of $\text{Ga}^{3+}$	E3ah	F32
18	Successive $pK$ values for hydrolysis of $\text{Ga}(\text{OH})_4^-$ to $\text{Ga}(\text{OH})_5^{2-}$ and $\text{Ga}(\text{OH})_6^{3-}$		
20	$pK$ for $\text{Ga}(\text{OH})_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ga}(\text{OH})_4^- + \text{H}^+$ ; $c = 0.005 - 0.025 \text{ M}$ in $\text{Ga}(\text{OH})_4^-$ ; from pH of hydrolysed alkali-metal salts		I22
20	Successive $pK$ values for hydrolysis of $\text{Ga}^{3+}$ to $\text{GaOH}^{2+}$ , $\text{Ga}(\text{OH})_2^+$ and $\text{Ga}(\text{OH})_3$ ; $I = 1(\text{NaCl})$	DISTRIB	A17

68. Germanic acid,  $\text{H}_4\text{GeO}_4$  ( $\text{H}_2\text{GeO}_3$ )

9.02	$pK_1, pK_2, pK_3$ ; $I = 0.5(\text{NaClO}_4)$	E3bg	H1
8.98	$I = 1(\text{NaClO}_4)$		
9.03	Below $0.004 \text{ M}$ , germanic acid is mainly monomeric; at higher concentrations an octagermanic anion is also formed		
8.98	$pK_1, pK_2$ ; $I = 0.5(\text{NaCl})$ ; $\log K = 29.14$ for $8\text{Ge}(\text{OH})_4 + 3\text{OH}^- \rightleftharpoons (\text{Ge}(\text{OH})_4)_8(\text{OH})_3^{3-}$	E3bg,h	I7
8.92	$I = 0$	E3cg	A25
8.73			
8.62			
9.1	$I = 2(\text{KCl})$	E3b	C9
9.08	In $0.5 \text{ M}$ $\text{Na}_2\text{SO}_4$	E	L42
12.43	$I = 3(\text{NaCl})$	E3bh	I10
12.31	In saturated $\text{Na}_2\text{SO}_4$ solution	CRYOSC	K63
	Other measurements: G15, G52, P43, R35, S26		

69. Gold(III) hydroxide,  $\text{Au}(\text{OH})_3$

25	Successive $K_p$ values for ionization to $\text{H}_2\text{AuO}_3^{2-}$ , $\text{HauO}_3^-$ and $\text{AuO}_3^{3-}$ ,	SOLY	J11
<11.7	$13.36 > 15.3$		

Name, Formula and $pK$ value	$T(^{\circ}C)$	Remarks	Methods	Reference
<b>70. (Aquo) Hafnium (IV) ion, <math>Hf^{4+}</math></b> -0.12    0.23    0.42    0.52	25	Successive $pK$ values for hydrolysis of $Hf^{4+}$ ; $I = 1(HClO_4)$ ; using low (radio-isotope) $Hf^{4+}$ concentrations; at concentrations above $10^{-3}$ M polymers (mainly trimers and tetramers) are also formed	DISTRIB	P24
<b>71. Heptamolybdic acid, <math>H_6Mo_7O_{24}</math></b> ~3.7    4.33	25	$pK_5, pK_6$ ; $I = 3(NaClO_4)$ ; concentration constants; also log $K = 57.7$ for $7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O$	E1cg,h	S8
<b>72. Hexadecapolyphosphoric acid, <math>H_{13}P_{16}O_{49}</math></b> ~2    2.92    6.48    6.08 ~2    2.64    6.48    8.02 ~2    2.52    6.50    8.18	25 37 50	Concentration constants: $I = 1(NMMe_4Br)$ ; $f_{\pm}$ assumed same as for $HBr$ ; first two of these $pK$ values may be seriously in error because of experimental difficulties	E3bg	I11
<b>73. Hexametaphosphoric acid, <math>H_6P_6O_{18}</math></b> 2    5.60    7.82		No details		K3a
<b>74. Hexaminotriphosphazene, <math>N_3P_3(NH_2)_6</math></b> <3.2    7.65    7.70	25 25	$pK_1, pK_2$ ; $I = 0$ $pK_3$ ; $I = 0$	E E	F10 F11
<b>75. Hexapolyphosphoric acid, <math>H_6P_6O_{19}</math></b> ~2.1    2.19    5.98    8.13	25	Concentration constants; $I = 1(NMMe_4Br)$ ; $f_{\pm}$ assumed same as for $HBr$ ; lowest two $pK$ values uncertain because of experimental difficulty	E3bg	I12
~1.3    2.22    5.83    8.02 ~1.3    2.22    5.81    8.00	37 50	Concentration constants, as above	E3bg	I11
<b>76. (Aquo) Holmium (III) ion, <math>Ho^{3+}</math></b> 8.04	25	$pK_9$ for hydrolysis of $Ho^{3+}$ ; titration of 0.004-0.009 M $Ho(ClO_4)_3$ with 0.02 M $Ba(OH)_2$ ; $I = 0.3(NaClO_4)$	E3b	F33a

77. Hydrazine, N<sub>2</sub>H<sub>4</sub>

-0.88	8.11	O2.E	S28
0.27	7.94	E3bg	Y15
	8.24	E3dg	W2
	7.99		
	7.82		
	8.60	E3dg	B102
	8.40		
	8.20		
	8.15	E3bg	J5
	8.07	E3dg	H59

$I = 0$   
 $I = 0$   
 $I$  from 0.01 to 0.15; extrapolated to  $I = 0$

“Practical” constant;  $I = 1$  (KCl)

“Practical” constant;  $I = 0.3$  (NaClO<sub>4</sub>)

“Practical” constant; 0.02–0.05 M hydrazine

Other measurements; B78, G21, H78

For H<sub>2</sub> acidity function of hydrazine see D26, F8, S12, S73

78. Hydrazinosulphuric acid, <sup>+</sup>NH<sub>3</sub>NHSO<sub>3</sub><sup>-</sup>  
 3.85

E3bg

A39

0.0075 M solution

79. Hydrazoic acid, HN<sub>3</sub>

4.72		E1cg	Y16
4.65, 4.68		E3bg	
4.62		O5	B110
4.59		E3ag	H78
4.68		E3bg	B108
4.692		E3cg	S36
4.686			
4.684			
4.682			
4.680			
4.680			
4.680			
4.70			
4.64		E3bg	B67a
4.58			
4.55		E3b	Q4
-6.21		DISTRIB	B6
-10.1			

$I = 0$   
 $I = 0.01$  to 0.03  
 $I = 0.03$  to 1.0; p*K* corrected using Debye-Hückel equation and extrapolated against  $I$

$I = 0$   
 $I = 0.02$

$I = 0.01$  to 0.04, extrapolated to  $I = 0$

$I = 0.1$  to 1.3 (KCl); extrapolated against  $I^{\frac{1}{2}}$

p*K* of monocation, H<sub>2</sub>N<sub>3</sub><sup>+</sup>, using H<sub>0</sub> function for H<sub>2</sub>SO<sub>4</sub>

p*K* of dication, H<sub>3</sub>N<sub>3</sub><sup>2+</sup>, using H<sub>0</sub> function for H<sub>2</sub>SO<sub>4</sub> and data

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Other measurements: B88, H21, H64, O9, W15

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
<b>80. Iodiodic acid, HI</b>				
~-9	25	Using Raoult's law	VAP	B25
~-9.5	25	Calculation from thermodynamic data		MI
<b>81. Hydrobromic acid, HBr</b>				
~-8	25	Using Raoult's law	VAP	B25
~-9	25	Calculation from thermodynamic data For Hammett acidity function of HBr, see P11, V8		MI
<b>82. Hydrochloric acid, HCl</b>				
-7.3	0		VAP	R21
-6.8	10			
-6.4	20			
-6.1	25			
-5.9	30			
-5.4	40			
-5.1	50			
~-7.4	0			
~-7	25	Assuming free HCl is like free HCN	VAP	W33
~-7	25	Calculation from thermodynamic data	B25	B25
~-7	25	Calculation from thermodynamic data		MI
~-7		Assuming solubilities of free HCl and RCl (where R = CH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> , etc.) in water fall in regular sequence		E2
~-7		Assuming $K_{HF}/K_{HCl} \approx K_{H_2O}/K_{H_2S} \approx 10^{-9}$		S22
~-6		I = 0; in superheated steam, density 0.525 g/ml	C1	P12
3.26	360			
3.42	373			
3.47	378			
4.11	370			
4.14	373			
4.24	378			
4.32	383			
4.61	373			
4.74	378			

$\sim$ -10  
 $\sim$ -3  
 pK of  $\text{H}_2\text{Cl}^+$ ; theoretical prediction  
 pK of HCl; theoretical prediction  
 For pK values of HCl in superheated steam between 400 and 700°, with densities from 0.3 to 0.8 g/cm<sup>3</sup>, see F26  
 For pK value in absolute ethanol, see S22  
 For Hammett acidity function of HCl see B27, B75, D21 (in the presence of LiCl and NaCl), G17 and G18 (temperature range), P10 (in the presence of added salts), P11, V8.  
 For  $\text{H}_\text{A}$  acidity function, see Y5  
 For  $\text{H}_\text{L}$  acidity function, see P27  
 For  $\text{H}_\text{O}'$ ,  $\text{H}_\text{O}''$ ,  $\text{H}_\text{R}$  and  $\text{H}_\text{R}'$  acidity functions of HCl, see A36

### 83. Hydrocyanic acid, HCN

9-216	25	Taking pK of <i>m</i> -bromophenol as 9.004; 0.01-0.05 M borax buffers; extrapolation to $I = 0$ , using extended Debye-Hückel equation; freshly prepared cyanide solutions	O2	A22
9-63	10	$I = 0.002$ to 0.024; extrapolation to $I = 0$ using extended Debye-Hückel equation, freshly prepared cyanide solutions	E3bg	I23
9-49	15			
9-36	20			
9-21	25			
9-11	30			
8-99	35			
8-88	40			
8-78	45			
9-36	20	Thermodynamic quantities are derived from the results	E3bg	B67a
9-19	26	$I = 0.01$ to 0.04, extrapolated to $I = 0$		
9-05	33			
9-30	28	Other measurements: A20, B84, B87, B88, H28, K36:	E3b	G10

### 84. Hydrofluoric acid, HF ( $\text{H}_2\text{F}_2$ )

3-18	25	for $I = 0$ ; 0.01-0.1 M in HF, 0.002-0.01 M in KF; over these temperatures, $K_1$ for $\text{F}^- + \text{HF} \rightleftharpoons \text{HF}_2^-$ is 3.4, 4.0, 4.7, 4.8, 4.9, 5.7, 5.8, 8, respectively	C1, R1b	E11
3-40	50			
3-64	75			
3-85	100			
4-09	125			
4-34	150			

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
4.58	175			
4.89	200	Data fit $pK = 2.75 + 295/T - 1.91 \log T + 0.014 T$ ( $T$ in °K) †		
3.21	25	Thermodynamic quantities are derived from the results for $I = 0$ ; 0.001 M in NaF; dilute HF solutions	C1	E21
3.10	15	for $I = 0$ ; using Pb-Hg/PbF <sub>2</sub> instead of Ag/AgCl. 0.001-1.0 M in	E1ch	B90
3.17	25	HF, $K_1$ for $F^- + HF \rightleftharpoons HF_2^-$ was 3.94, 3.86, 4.32 at 15, 25, 35°		
3.25	35			
2.96	0	Recalculation of data by E. Deussen	C	W28
3.16	25	( <i>Z. Anorg. Allgem. Chem.</i> , <b>44</b> 312 (1905)); $K_1$ for $F^- + HF \rightleftharpoons HF_2^-$ was 2.43, 2.70 at 0, 25°		
3.16	25	Taking $a_{HF_2^-}/(a_{HF} a_{F^-}) = 5.4$	E	B95
~9		pK of $H_2F^+$ ; theoretical prediction		S29
		Other measurements: A15, A41, B67, B98, B99, C24, C30, C31, D10, D41, F3, F29, P28, R33, R34, R50 (at 100, 156, 218°), S78		
		For Hammett acidity function of HF, see B26, H80, N2 (in ethanol-water mixtures), P11		
<b>85. Hydrogen peroxide, H<sub>2</sub>O<sub>2</sub></b>				
11.86	15	$I = 0.05$ to $4.8(NaClO_4)$ ; extrapolated against $I^{1/2}$ ; $c = 0.55$ M	E3ag	E22
11.75	20	H <sub>2</sub> O <sub>2</sub>		
11.65	25			
11.55	30			
11.45	35			
11.81	20			
11.92	10			
11.62	25			
11.34	35			
11.21	50			
12.11	0			
12.23	0			
12.19	0			
11.85	19			
			E3bg	K4
			CALOR	S2
			KIN	J22
			DISTRIB	
			C1	
			O1	J17

11-58		30	$I = 0.1$ (phosphate buffers) corrected to $I = 0$ by Debye-Hückel equation In strong hydrogen peroxide solutions (above several per cent $H_2O_2$ in water), superacidity is observed, giving lower values of $pK$ which pass through a flat minimum (8.7) near 50% Other measurements: E24	O1	M51 M34, K32
<b>86. Hydrogen polysulphide</b> 3-8 6-3		20	For $H_2S_4$ ; $I = 0.1$ ( $NaClO_4$ ); rapid-flow measurements; 3.4 and 5.6 for $H_2S_5$	E3ag	S30
<b>87. Hydrogen selenide, <math>H_2Se</math></b> 15.0		22	Estimated uncertainty $\pm 0.6$ pH units; the direct titration of $H_2Se$ with $KOH$ gives low $pK_2$ values because of aerial oxidation	SOLY	W27
	14	25	Value needed to fit experimental $E_4/pH$ plot	POLAROG	L35
	3-89 3-73 3-77	25 25-9	$I \sim 0.03$ ; titration of $H_2Se$ in the dark $c = 0.008-0.1 M H_2Se$	E3bg C1	H9 H61 B104
<b>88. Hydrogen sesquioxide, <math>H_2O_3</math></b> 9-10			Theoretical prediction		C46
<b>89. Hydrogen sulphide, <math>H_2S</math></b> 7-33 7-24 7-13 7-05 6-97 6-90 6-79 6-69 6-62 7-57 7-06 6-82 7-02		5 10 15 20 25 30 40 50 60 0 25 50 25		C1	W30
		20	$c = 0.001$ to $0.017 M$ in $H_2S$	C1,R1b	L44
		25	$I$ varied from 0.01 to 0.17, phosphate buffers	O1	E14
		25	Extrapolation of measured $pK$ versus alkali concentration	O7 FP,C O5	J3a M54
	14.0 14.7 13-85	0 30			



Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
7-26	10	Values of $pK_2$ (obtained from titrations) given in this reference are probably too low	E3bg	T20
7-07	25			
6-99	35			
6-91	50			
6-96	18	$\epsilon = 0.001-0.04$ M in H <sub>2</sub> S	E3ag, VAP	G35
6-87	20			
6-79	25			
6-66	35			
6-54	45			
6-91	25			
6-81	25	1 atmosphere pressure	E3bg	Y17
6-68	25	500 atmosphere pressure	Cl	E13
6-56	25	1000 atmosphere pressure		
6-45	25	1500 atmosphere pressure		
6-37	25	2000 atmosphere pressure		
	0	Calculated from thermodynamic data and potential measurements		M13
	14-75			
	13-90			
6-88	25	$I = 1(KCl)$ ; Hg electrode versus calomel		W18
6-99	20	Calculated from published thermodynamic data	E	P32
6-89	25			
12-24	40			
6-81	80			
6-54	10-68			
6-52	90			
6-59	9-27			
	120			
	8-55			
<b>90. Hydrogen telluride, H<sub>2</sub>Te</b>				
2-64	18	$\epsilon = 0.003-0.09$ M H <sub>2</sub> Te	Cl	H61
2				BI04
11	25	Value of $pK_2$ needed to fit E <sub>1</sub> /pH plot		POLAROG L35
12-16	25	Value of $pK_3$ needed to fit E <sub>1</sub> /pH plot		POLAROG P7

<b>91. Hydroperoxy radical, HO<sub>2</sub></b>					
4-4	23	pK for HO <sub>2</sub> ⇌ H <sup>+</sup> + O <sub>2</sub> <sup>-</sup> ; from pH-dependence of reaction with tetramethane; species generated by electron irradiation	KIN	C46	
4-45	23	pH-dependence of rate of reaction with tetranitromethane	O	R1a	
4-5		pulsed radiolysis experiments	O	C46a	
~2		estimate		UI	
~6	20	estimate		W11	
<b>92. Hydrosulphuric acid, see Hydrogen sulphide</b>					
<b>93. Hydroxylamine, NH<sub>2</sub>OH</b>					
6-186	15	$I = 0.25, 1, 2.25(\text{NaClO}_4)$ ; extrapolated to $I = 0$	E3bg	L47	
6-063	20	using Debye Hückel equation			
5-948	25				
5-730	35	$pK = 2775.7/T - 5.8899 + 0.0084782T$ ( $T$ in °K)			
		Thermodynamic quantities are calculated from the results for $I = 0$ ; taking pK of 3,4-dinitrophenol as 5.46, 5.42, and 5.38	O2	R22	
6-04	20	For $I = 0$	E3ag	H8	
5-96	25	$I = 0.0023$ to $0.023$ ; extrapolated against $I^\ddagger$	DISTRIB		
5-84	30	"Practical" constant; $I = 1(\text{KCl})$	E3bg	B51	
5-98	25	"Practical" constant; $I = 1(\text{KCl})$ ; in D <sub>2</sub> O	E3ag	B103	
5-93	25	Other measurements: F28, I15, M16, M52, M53, R28, S83, W21	E3ag		
5-97	30				
6-04	30				
6-49	30				
<b>94. Hydroxylamine-<i>N,N</i>-disulphonic acid, HON(HSO<sub>3</sub>)<sub>2</sub></b>					
11-85	25	$pK_3; I = 1.6(\text{K}_2\text{SO}_4?)$	E3ag	A8a	
<b>95. Hydroxylamine-<i>N</i>-sulphonic acid, HO.NH.OSO<sub>2</sub>H</b>					
~12-5	Room	$pK_3; I = 1.5(\text{K}_2\text{SO}_4)$	E3ag	A8a	
12-38	64-2	$I = 1.6(\text{Na}_2\text{CO}_3 \text{ or } \text{Na}_2\text{SO}_4)$			
12-20	73-8				
12-10	83-5				
<b>96. Hydroxylamine O-sulphonate, <sup>+</sup>NH<sub>3</sub>OSO<sub>3</sub><sup>-</sup></b>					
1-48	45	$I = 1(\text{NaClO}_4)$	E3ag	C3	

Name, Formula and pK value	T(°C)	Remarks	Methods	Reference
<b>97. Hydroxyl radical, ·OH</b>	23	Pulse radiolytic method		R1
11·9	~23	Pulse radiolysis; pK obtained from pH-dependence of rate of formation of radical ion, ·CO <sub>3</sub> <sup>-</sup>		W9a
11·8				
<b>98. Hypobromous acid, HOBr</b>	10		O	F 18
8·66	25			
8·49	25			
8·23	50		E3bg	K11
8·80	15·65			
8·60	25·28			
8·47	35·55			
8·36	45·55			
8·68	22	$I = 0·02$ to $0·1$	E3bg	S44
8·69	20	$c = 0·01-0·02$ M BrO <sup>-</sup>	E3bg	S45
		Other measurements: C14, F2, K16, L29, S53, S64		
<b>99. Hypochlorous acid, HOCl</b>	0	Measured relative to pK <sub>2</sub> of HgPO <sub>4</sub> ;	O3	M46a
7·825	5	$I = 0·05$ to $0·2$ ; extrapolated to $I = 0$		
7·754	10			
7·690	15			
7·633	20			
7·582	25			
7·537	30			
7·497	35			
7·463	10	For $I = 0$ ; $c = 0·01$ M HOCl	E3bg	F16
7·49	25			
7·30	35			
7·18	50			
7·05	10	For $I = 0$ ; $c = 0·003$ M HOCl	O5	O13
7·50	25			
7·31	35			
7·19	50			
7·06				

7.82	0	Extrapolated to zero time, and to $I = 0$ using Debye-Hückel equation	E3ag	C4
7-72	10			
7-65	15			
7-53	25			
7-49	35			
7-46	45			
7-53	25		E3bg	H7
7-50	20		E3bg	S45
7-49	20		E3bg	M59
7-66	25		E3bg	A38
7-55	0-6	For $I = 0$ ; using Debye-Hückel equation		
7-42	27	"Practical" constant; $c = 0.25$ M HOCl Other measurements: B85, D4, G2, G27, H65, H73, I2, K17, S4, S46, S52, S53, S58, Y11	E3bg, R2a	L36
<b>100. Hypoiodous acid, HOI</b>				
10-64	25	Also $pK = 14.48$ for $I_2OH^- \rightleftharpoons I_2O^{2-} + H^+$	E,h	C21
9-7	22		E3bg	J19
~11	25		KIN	F39
12.4	20		E	S51
9-49	25	$pK_b$ for $HOI \rightleftharpoons I^- + OH^-$ ; iodine electrode	O5	M57
1-35	25	$pK$ of $H_2OI^+$	E	A18
1-54	25	$pK$ of $H_2OI^+$ ; cells of type $Pt, I_2, Ag^+, H^+/Sat.KNO_3/I^-, I_2, H^+, Pt$	E	B28
<b>101. Hyponitrous acid, <math>H_2N_2O_2</math></b>				
7-51	0	$I \leq 0.06$ ; from rates of decomposition	KIN	P34
7-22	20			
7-09	30			
	25			
11-35	50			
11-09	55			
10-97	18			
11-1	15			
	25			
7-32	25		E3ag	H79
7-21	35		KIN	
7-17	45			
6-92	45	Using borate buffers in determining $K_2$ Using NaOH solutions		

Name, Formula and p <i>K</i> value	<i>T</i> (°C)	Remarks	Methods	Reference
7.05	25	For <i>I</i> = 0	E3bg	L10
11.4	25		O3	
6.75	25	<i>I</i> = 1 Other measurements: A3, P33	KIN	B106
<b>102. Hypophosphoric acid, H<sub>4</sub>P<sub>2</sub>O<sub>6</sub></b>				
<2	20	"Practical" constants; <i>I</i> = 0.1 (KCl) Concentration constants; titration of 0.01 M Na <sub>4</sub> P <sub>2</sub> O <sub>6</sub> in 0.049 M HCl with 0.1 M NaOH	E3bh E3bh	S35 T16
<b>103. Hypophosphorous acid, H<sub>3</sub>PO<sub>2</sub></b>				
1.23	25	For <i>I</i> = 0	C1, R1c	P8
1.07	18	"Practical" constant; titration of 0.11 N HgPO <sub>2</sub> with 0.11 N NaOH	E3bg	M48
1.02	16	<i>I</i> = 0.16	E3a	G44a
1.12	30	<i>I</i> = 0.16		
1.2	45	<i>I</i> = 0.57		
1.03	16	<i>I</i> = 1.13 (KCl); concentration constant Other measurements: B89, G43, K41, M33, N26		
<b>104. Hyposulphurous acid, H<sub>2</sub>S<sub>2</sub>O<sub>4</sub></b>				
0.35	25		C1	J3
<b>105. Imidodiphosphoric acid, H<sub>2</sub>O<sub>3</sub>P.NH. PO<sub>3</sub>H<sub>2</sub></b>				
~1.5	2.66	7.32	10.22	25
~2	2.85	7.08	9.72	25
~2	2.81	7.05	9.77	25
~1.5	3.05	7.62	10.36	25
~1.8	2.60	7.16	9.79	37
~1.8	2.68	6.99	9.52	37
~1.8	2.81	6.90	9.41	50
~1.8	2.83	6.88	9.32	50
Concentration constants; <i>I</i> = 0.1 (NM <sub>4</sub> Br); <i>f</i> ± assumed same as for HBr; p <i>K</i> <sub>1</sub> may be seriously in error because of experimental difficulties				
		<i>I</i> = 0.2		
		<i>I</i> = 0.3		
		<i>I</i> = 1.0		
		<i>I</i> = 0.1; as above		
		<i>I</i> = 0.3		
		<i>I</i> = 0.1		
		<i>I</i> = 0.3		
			E3bg	I12
				I11

<b>106. (Aquo) Indium(III) ion, <math>\text{In}^{3+}</math></b>					
4.43	3.9		25	Successive pK values for hydrolysis of $\text{In}^{3+}$ to $\text{In}(\text{OH})_2^+$ and $\text{In}(\text{OH})_3$ ; $I = 3(\text{NaClO}_4)$ ; using In-Hg electrode; above 0.001 M, indium forms $\text{In}[(\text{OH})_2\text{In}]_n^{(3+n)+}$	B41
4.4	4.4		25	Successive pK values for hydrolysis of $\text{In}^{3+}$ ; $I = 3(\text{NaClO}_4)$ ; tracer amounts of $\text{In}^{3+}$	DISTRIB R31
11.89	11.55	11.32	20 ± 2	Successive pK <sub>b</sub> values for hydrolysis of $\text{In}^{3+}$ to $\text{In}(\text{OH})_2^+$ and $\text{In}(\text{OH})_3$ ; $I = 1$	DISTRIB H19
6.95			25	pK for hydrolysis of $\text{In}^{3+}$ to form a mixed hydroxy-chloro complex; $I = 3(\text{NaCl})$ ; $\epsilon = 0.001-0.04$ M $\text{In}^{3+}$ ; a binuclear $\text{In}_2(\text{OH})_2$ chloro complex is also formed Other measurements: H43, H51, M36, M37	E3ag B48
<b>107. Iodic acid, <math>\text{HIO}_3</math> (<math>\text{H}_5\text{IO}_6</math>)</b>					
0.804			25	Obtained by three independent methods, taking ion-size parameter of 5Å; value depends on ion-size assumed; cmf method due to A. K. Covington and J. E. Prue, <i>J. Chem. Soc.</i> <b>1955</b> , 3701	Cl, E, and KIN P26a
0.785			25	Solubility of $\text{AgIO}_3$ in $\text{HNO}_3$ and $\text{KNO}_3$ , extrapolated against $I^{\frac{1}{2}}$ ; $I = 0.008 - 0.5$	SOLY L25
0.815			30		
0.84			35		
0.788			25	Solubility of $\text{Ba}(\text{IO}_3)_2$ in 1:1 electrolyte solutions, extrapolated against $I^{\frac{1}{2}}$ ; $I = 0.0025$ to 1	SOLY N3
0.773			25	$I = 0.0026$ to 0.01; extrapolated against $I^{\frac{1}{2}}$	O4 H14
0.773			25	Calculated from data of C. A. Kraus and H. C. Parker, <i>J. Am. Chem. Soc.</i> , <b>44</b> , 2429 (1922)	Cl, R1c F38
0.807			25	Calculated from data of C. A. Kraus and H. C. Parker, <i>J. Am. Chem. Soc.</i> <b>44</b> , 2429 (1922), taking an ion size of 3Å	Cl, R1c L17a
0.58			0		FP A4
0.72			18		Cl NMR
0.74			30	For $I = 0$ Other measurements: D44a, K18, K60, M2, O12, R36. For $\text{H}_0$ acidity function of aqueous $\text{HIO}_3$ , see D18	H67
<b>108. (Aquo) Iron(II) ion, <math>\text{Fe}^{2+}</math></b>					
6.93			20	pK for hydrolysis of $\text{Fe}^{2+}$ ; $I = 0.5-2(\text{NaClO}_4)$	E3bg B65
6.74			25		
6.49			35		

Name, Formula and p <i>K</i> value	T(°C)	Remarks	Methods	Reference
6-34	40			
7-15	20	p <i>K</i> for hydrolysis of Fe <sup>2+</sup> ; <i>I</i> = 1(NaClO <sub>4</sub> )	E3bg	B63
6-8	25	p <i>K</i> for hydrolysis of Fe <sup>2+</sup>	SOLY	L19
8-3	25	p <i>K</i> for hydrolysis of Fe <sup>3+</sup> ; <i>c</i> = 0.02-0.08 M FeCl <sub>3</sub> ; hydrolysis of "pure" salts	E3ag	G13
7-9	25	Concentration constants; <i>I</i> = 0.5(KCl)		
7-2	25	p <i>K</i> for hydrolysis of Fe <sup>2+</sup> , from rate of H <sub>2</sub> O <sub>2</sub> decomposition as function of pH in presence of Fe <sup>2+</sup> ; <i>I</i> = 1(NaClO <sub>4</sub> )	KIN	W14
3-3	25	log <i>K</i> for Fe <sup>2+</sup> + 3OH <sup>-</sup> ⇌ Fe(OH) <sub>3</sub> ; is estimated from polarography to be 7.85 in 1.375 N NaOH		S21
		Other measurements: H45, I34		
<b>109. (Aquo) Iron(III) ion, Fe<sup>3+</sup></b>				
2-71	15	p <i>K</i> for hydrolysis of Fe <sup>3+</sup> ; concentration constant; <i>I</i> = 0.01	O5	T21
2-46	25			
2-29	35			
2-30	20	p <i>K</i> for hydrolysis of Fe <sup>3+</sup> ; <i>I</i> = 0.025 to 0.15 (NaClO <sub>4</sub> , HClO <sub>4</sub> ); extrapolated to <i>I</i> = 0	O6	R16
2-34	25			
2-38	18	p <i>K</i> for hydrolysis of Fe <sup>3+</sup> ; <i>I</i> = 0.01 to 0.03; extrapolated to <i>I</i> = 0	O6	M30
2-19	25			
2-02	32			
2-96	18	<i>I</i> = 1(NaClO <sub>4</sub> ); constants are also given for 2FeOH <sup>2+</sup> ⇌ Fe <sub>2</sub> (OH) <sub>4</sub> <sup>4+</sup>		
2-79	25			
2-61	32			
2-17	25	p <i>K</i> for hydrolysis of Fe <sup>3+</sup> ; <i>I</i> = 0.015 to 3.0; extrapolated to <i>I</i> = 0 using Debye-Hückel equation; constants are also given for 2FeOH <sup>2+</sup> ⇌ Fe <sub>2</sub> (OH) <sub>4</sub> <sup>4+</sup>	O6	M31
2-19	25	For <i>I</i> = 0		
2-63	20-22	<i>I</i> = 0.1(KNO <sub>3</sub> )	O6	S47
2-80	25	<i>I</i> = 0.5(NaClO <sub>4</sub> )	O5	P35
2-92	21	<i>I</i> = 0.55; in D <sub>2</sub> O	O6	W20
2-74	20	Successive p <i>K</i> values for hydrolysis of Fe <sup>3+</sup> ; <i>I</i> = 1(NaClO <sub>4</sub> ); -log <i>K</i> = 2.85 for 2Fe <sup>3+</sup> + 2H <sub>2</sub> O ⇌ Fe <sub>2</sub> (OH) <sub>2</sub> <sup>4+</sup> + 2H <sup>+</sup>	REDOX	H75 P18
2-83	25	Successive p <i>K</i> values for hydrolysis of Fe <sup>3+</sup>	E	I18
2-83	25		C	

3-05	3-26	25	Successive $pK$ values for hydrolysis of $Fe^{3+}$ ; $I = 3(NaClO_4)$ ; also $-\log K = 2.91$ for $2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$ . Values of $-\log K$ for $2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+$ , from 15-41, are estimated from magnetic measurements. Other measurements: A31, B10, B52, B53, B76, B91, B94, C30, I20, L5, L33, O10, S81	REDOX	H46 M56
<b>110. Isohyppophosphoric acid, <math>H_4P_2O_6</math></b>					
4-5	8-5	25	$pK_2$ , $pK_3$ ; $c = 0.02 M$	E3bg	B60
1-67	6-26	25	$pK_2$ , $pK_3$ ; $I = 0.1$ to $1.0 (Et_4NCl)$ ; extrapolated to $I = 0$ ; $pK_1$ estimated as 0.6	E3bg	C10a
<b>111. (Aquo) Lanthanum(III) ion, <math>La^{3+}</math></b>					
~10		25	$pK$ for hydrolysis of $La^{3+}$ ; from hydrolysis of "pure" salt; $c = 0.001-0.01 M La_2(SO_4)_3$	E3ag	M38
9-06		25	$pK_6$ for hydrolysis of $La^{3+}$ ; titration of $0.004-0.009 M La(ClO_4)_3$ with $0.02 M Ba(OH)_2$ ; $I = 0.3 (NaClO_4)$	E3b	F33a
8-98		25	ditto, using $0.02 M NaOH$	E3bg	B43
10-1		25	$pK$ for hydrolysis of $La^{3+}$ ; $I = 3(LiClO_4)$ ; $c = 0.1-1.0 M La(ClO_4)_3$ ; also $-\log K = 9.95$ for $2La^{3+} + H_2O \rightleftharpoons La_2OH^{5+} + H^+$ ; other species include $La_5(OH)_9^{6+}$ and $La_6(OH)_{10}^{6+}$	E3bg	W17
5-6		20	$pK_6$ ; $c = 0.01 M LaCl_3$	E3bg	D8
3-3		25	$pK_6$ ; estimated from solubility measurements of I. M. Kolthoff and R. Elmquist, <i>J. Am. Chem. Soc.</i> , <b>53</b> , 1217 (1931)		
~5		18	$pK_6$	DISTRIB	V6
<b>112. (Aquo) Lead(II) ion, <math>Pb^{2+}</math></b>					
7-78		18	$pK$ for hydrolysis of $Pb^{2+}$ ; for $I = 0$ ; $c = 0.005-0.4 M (PbNO_3)_2$ ; also $\log K = -7.30$ for $2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+$ , and $\log K = -20.93$ for $4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$	E3bg	P16
8-66		20	$pK$ for hydrolysis of $Pb^{2+}$ ; $Pb_4(OH)_4^{4+}$ is also formed	E3bg	F4
7-93		25	$pK$ for hydrolysis of $Pb^{2+}$ ; $I = 2(NaClO_4)$ ; also $\log K = -19.35$ for $4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$	H76	
8-84		25	$pK$ for hydrolysis of $Pb^{2+}$ ; $I = 2(NaNO_3)$ ; also $\log K = -7.11$ for $2Pb^{2+} + H_2O \rightleftharpoons Pb_2OH^{3+} + H^+$ ; $\log K = -21.72$ for $4Pb^{2+} + 4H_2O \rightleftharpoons Pb_4(OH)_4^{4+} + 4H^+$	E3ag	H77
7-1	10-1	25	$pK$ values for stepwise hydrolysis of $Pb^{2+}$ to $PbOH^+$ , $(PbOH)_2$ and $(Pb(OH))_3$ ; $I = 1 (KNO_3)$		POLAROG G38



$pK$	Name, Formula and $pK$ value	$T(^{\circ}C)$	Remarks	Methods	Reference
7.8	9.4 10.8	25	$pK$ values for stepwise hydrolysis of $Pb^{2+}$ ; $I = 0.3(NaClO_4)$ ; Pb-Hg electrode		C6
7.9	9.6 11.5	25	$I = 3(NaClO_4)$		
7.8		25	$pK_b$ for $PbOH^+ \rightleftharpoons Pb^{2+} + OH^-$	SOLY	C7
5.99		100	$pK$ for hydrolysis of $Pb^{2+}$ At high lead concentrations, $Pb^{2+}$ also hydrolyses to $Pb_2OH^{3+}$ and $Pb_4(OH)_4^{4+}$ (constants are given) At $25^{\circ}$ and $I = 2(NaClO_4)$ , $\log K = 12.62$ for $Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$ At $25^{\circ}$ and $I = 0$ , $\log K = 13.90$ for $Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$ At $25^{\circ}$ and $I = 0$ , $\log K = 13.95$ for $Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$ At $20^{\circ}$ , $\log K = 12.15$ for $Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$ Other measurements: C36, G49, G51, T14, W26	KIN	C69 O8, P4
				POLAROG	O11
				POLAROG	N27
				POLAROG	V9
				POLAROG	H52
		5	$pK_b$ ; $I = 0.02$ to $0.1$ ; $f \pm$ calculated using Davies' equation; e.m.f. data from H. S. Harned and H. R. Copson, <i>J. Am. Chem. Soc.</i> , <b>55</b> , 2206 (1933), and H. S. Harned and J. G. Donelson, <i>J. Am. Chem. Soc.</i> , <b>59</b> , 1280 (1937)	Elch	G26
		15			
		25			
		35			
		45			
		25	$pK_b$ ; $f \pm$ from Davies' equation	C2, R1b	D3
		25	$pK_b$	C2, R1d	S65
		25	$pK_b$	C2, R1e	O2
		25	$pK_b$ ; concentration constant; $I = 3(NaClO_4)$ ; taking $fOH^- = fCl^-$	O3	K38
		25	$pK_b$ ; concentration constant; from salt effect on indicator; $I = 1(LiCl)$		
			$I = 0.2(LiCl)$		
		49	$pK_b$ ; for $I = 0$	C2	W29
		93			
		138			

113. (Aquo) Lithium ion,  $Li^+$ 

0.26

1.42  
1.59  
1.76

182  
227  
271

For alkalinity function of LiOH solutions, see L12a, M40, S73

**114. (Aquo) Lutecium(III) ion, Lu<sup>3+</sup>**

20 pK<sub>b</sub> for LuOH<sup>2+</sup> ⇌ Lu<sup>3+</sup> + OH<sup>-</sup>; *c* = 0.01 M LuCl<sub>3</sub>  
 25 pK<sub>a</sub> for hydrolysis of Lu<sup>3+</sup>; titration of 0.004–0.009 M Lu(ClO<sub>4</sub>)<sub>3</sub>  
 with 0.02 M Ba(OH)<sub>2</sub>; *I* = 0.3(NaClO<sub>4</sub>)  
 25 ditto, using 0.02 M NaOH

E3bg

F33a

**115. (Aquo) Magnesium ion, Mg<sup>2+</sup>**

25 pK<sub>b</sub>; for *I* = 0; *c* = 0.03 M MgCl<sub>2</sub>  
 18 pK<sub>b</sub>  
 25 pK<sub>b</sub>; *I* = 0  
 18 pK<sub>b</sub>; concentration constant; *c* = 0.1–0.5 N MgCl<sub>2</sub>; salt effect  
 on indicator  
 25 pK for hydrolysis of Mg<sup>2+</sup>; *I* = 3(NaCl, MgCl<sub>2</sub>)  
 30 pK for hydrolysis of Mg<sup>2+</sup>; *I* = 0.1(KCl); *c* = 0.01 M  
 100 pK for hydrolysis of Mg<sup>2+</sup>; taking pK<sub>w</sub> = 12.38; *c* = 0.06 M  
 MgCl<sub>2</sub>; rate of inversion of sucrose

E3bg

S74

G28

H71

K39

E3bg, h

L22

Cl2

K69

**116. (Aquo) Manganese(II) ion, Mn<sup>2+</sup>**

15 pK for hydrolysis of Mn<sup>2+</sup>; *I* = 0.002 to 0.04; extrapolated to  
*I* = 0 by fitting extended Debye-Hückel equation  
 20  
 25  
 30  
 36  
 42  
 30  
 100

E3bg

P20

pK for hydrolysis of Mn<sup>2+</sup>; *I* = 0.1(KCl)  
 pK for hydrolysis of Mn<sup>2+</sup>

Cl2

K69

**117. (Aquo) Manganese(III) ion, Mn<sup>3+</sup>**

25 pK for hydrolysis of Mn<sup>3+</sup>; *I* = 4(Mn(ClO<sub>4</sub>)<sub>2</sub>.HClO<sub>4</sub>)  
 23 *I* = 5.3 to 6.1 (Mn(ClO<sub>4</sub>)<sub>2</sub>.HClO<sub>4</sub>)  
 23 *I* = 6(HClO<sub>4</sub>, NaClO<sub>4</sub>)

O6

W13

F1

D34

**118. Manganic acid, H<sub>2</sub>MnO<sub>4</sub>**

35 pK<sub>3</sub>; *I* ≈ 0.1

KIN

L37