COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9]	H. Miyamoto Department of Chemistry Niigata University Niigata, Japan and M. Salomon US Army ET & DL Fort Monmouth, NJ, USA
(2) Water; H_2O; [7732-18-5]	July, 1984

CRITICAL EVALUATION:

THE BINARY SYSTEM

Data for the solubility of potassium chlorate in water have been reported in 23 studies (1-23). Five studies (2, 5, 9, 15, 16) deal solely with the binary system, three studies (3, 7, 11) report solubilities in water-organic solvent mixtures, and the remaining studies deal with multicomponent systems. Most studies are based on isothermal measurements with chemical analyses either gravimetrically (3, 5, 7, 11) or by titration of chloride after reduction of the chlorate (6, 11-13, 20-23). One high temperature study by Benrath et al. (15) used the synthetic method.

Mellor (24) has cited a number of studies which are unavailable to the compilers and evaluators, and hence have not been included in this volume. The studies cited by Mellor are: Gay Lussac (25), Mulder (26), Geradin (27), Nordenshjold (28), Schlosing (29) Blarez (30), Arrhenius (31), Etarde (32) and Calvert (33).

In all studies including those for multicomponent systems, no hydrates of $KClO_3$ were reported. It is therefore concluded that the anhydrous salt is the solid phase over the temperature range of 273 - 578 K. A summary of all the binary solubility data is given in Table 1. In this table we list the solubilities in mole fraction units (calculated by the evaluators), and the solubilities in mol kg^{-1} units can be found in the compilations. Also included in Table 1 are the weighting factors used in fitting the data to the smoothing equations. A weight of (1) or (0) was given depending whether the specified result was included or omitted, respectively. We considered giving higher weight factors to data of higher precision (13, 14, 17-19, 22), but doing so would have resulted in the rejection of important data of less precision, mainly those of Pawlewsky (1). Data were rejected from the smoothing equation fit when the difference between the calculated and observed mole fraction solubilities exceeded twice the standard error of estimate: i.e. when

$$\text{abs}\,[\chi_{obsd} - \chi_{calcd}] > 2\sigma_x$$

Two smoothing equations were used. For mole fractions we used

$$Y_x = A/(T/K) + B\ell n(T/K) + C + D(T/K) \qquad [1]$$

and for molalities we used

$$Y_m = A/(T/K) + B\ell n(T/K) + C \qquad [2]$$

The complex Y terms in eqs. [1] and [2] are defined in the PREFACE to this volume and in the $LiClO_3$-H_2O and $RbClO_3$-H_2O critical evaluations. The resulting smoothing equations based on fitting only those solubilities between 273-373 K are given in eqs. [3] and [4] below. The smoothed solubilities at rounded temperatures are given in Table 2 and are designated as *recommended* values.

$$Y_x = -60986.171/(T/K) - 328.4915\ell n(T/K) + 1925.070 + 0.4819091(T/K) \qquad [3]$$

$$\sigma_y = 0.023 \qquad \sigma_x = 0.00023$$

$$Y_m = -6472.065/(T/K) - 11.3302\ell n(T/K) + 86.2555 \qquad [4]$$

$$\sigma_y = 0.020 \qquad \sigma_m = 0.049$$

COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9]	H. Miyamoto Department of Chemistry Niigata University Niigata, Japan and M. Salomon US Army ET & DL Fort Monmouth, NJ, USA
(2) Water; H_2O; [7732-18-5]	July, 1984

CRITICAL EVALUATION:

Table 1. Summary of Experimental Solubilities in the Binary System[a]

T/K	χ	(weight)	ref.	T/K	χ	(weight)	ref.
273.2	0.004594	(1)	1	313.2	0.01902	(0)	12
273.2	0.004603	(1)	12	313.2	0.01919	(1)	1
278.2	0.005584	(1)	1	313.2	0.02007	(1)	3
278.2	0.005810	(1)	19	318.2	0.02153	(0)	1
281.2	0.006543	(1)	5	318.2	0.02318	(1)	13
283.2	0.006499	(0)	1	323.2	0.02482	(0)	12
288.2	0.007803	(0)	1	323.2	0.02571	(1)	1
288.2	0.008769	(1)	13	323.2	0.02692	(0)	20
288.2	0.008871	(1)	9	326.2	0.02998	(0)	2
290.8	0.00953	(1)	11	328.2	0.02894	(1)	1
293.0	0.01040	(1)	5	333.2	0.03328	(1)	1
293.2	0.01034	(0)	16	338.2	0.03613	(1)	1
293.2	0.01053	(1)	1	341.2	0.04263	(0)	2
293.2	0.01048	(1)	7	343.2	0.04111	(1)	1
293.2	0.01053	(1)	8	348.2	0.04625	(1)	1
293.2	0.01055	(1)	10[b]	353.2	0.05149	(1)	1
293.2	0.01058	(1)	12	354.2	0.04328	(0)	2
293.2	0.01060	(1)	9	358.2	0.05730	(1)	1
298.2	0.01187	(0)	1	359.2	0.06050	(0)	2
298.2	0.01219	(1)	6	363.2	0.06348	(1)	1
298.2	0.01240	(1)	22	368.2	0.07024	(1)	1
298.2	0.01244	(1)	17	372.2	0.07769	(0)	5
298.2	0.01245	(1)	13	373.2	0.07656	(0)	7
298.2	0.01246	(1)	14	373.2	0.07548	(0)	1
298.2	0.01247	(1)	21	450.2	0.2152	---	15
298.2	0.01249	(1)	21	468.2	0.2618	---	15
298.2	0.01250	(1)	23	476.2	0.2854	---	15
298.2	0.01261	(1)	20	485.2	0.3153	---	15
298.2	0.01262	(1)	9	495.2	0.3533		15
303.2	0.01343	(0)	1	515.2	0.4266	---	15
303.2	0.01473	(1)	3	550.2	0.5891	---	15
303.2	0.01475	(1)	12	557.2	0.6347	---	15
303.2	0.01487	(1)	5	578.2	0.7659	---	15
308.2	0.01658	(0)	1				

[a] Original units were mainly mass %, and conversions to mole fractions were calculated by the evaluators.

[b] See Volume 14 for the compilations of Mazzetti's paper.

COMPONENTS:	EVALUATOR:
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(2) Water; H_2O; [7732-18-5]	July, 1984

CRITICAL EVALUATION:

Table 2. Recommended Solubilities at Rounded Temperatures Calculated from the Smoothing Equations [3] and [4].

T/K	m/mol kg^{-1}	χ
273.2	0.259	0.00457
278.2	0.323	0.00576
283.2	0.397	0.00715
288.2	0.485	0.00873
293.2	0.585	0.01051
298.2	0.699	0.01250
303.2	0.828	0.01470
308.2	0.973	0.01712
313.2	1.134	0.01976
318.2	1.311	0.02265
323.2	1.505	0.02578
328.2	1.716	0.02918
333.2	1.944	0.03287
338.2	2.188	0.03688
343.2	2.449	0.04126
348.2	2.725	0.04604
353.2	3.016	0.05128
358.2	3.322	0.05704
363.2	3.641	0.06341
368.2	3.972	0.07049
373.2	4.314	0.07839

The data of Benrath et al. (15) were also fitted to the smoothing eq. [1]:

$$Y_x = -6275.39/(T/K) - 6.4129\ell n(T/K) + 49.9386 + 0.0024454(T/K) \quad [5]$$

$$\sigma_y = 0.009 \qquad \sigma_x = 0.003$$

We tried to extrapolate eq. [5] to the melting point of $KClO_3$ (i.e. calculate the temperature for $\chi = 1.00$), but found a value of 608.4 K. The literature value of the melting point of $KClO_3$ is 641.6 K (45). The solubility at 373.2 K calculated from eq. [5] is $\chi = 0.0749$ which is much too low (see Table 2), and again suggests caution in using eq. [5] to compute solubilities outside the range of temperatures used in the least squares fit to this equation. As indicated in Table 1, the temperature range used to derive eq. [5] is 450-578 K.

COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9]	Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan
(2) Water; H_2O; [7732-18-5]	July, 1984

CRITICAL EVALUATION:

TERNARY SYSTEMS

Many studies for solubilities of potassium chlorate in aqueous ternary systems with saturating inorganic compounds have been reported. Some studies for solubilities in aqueous-organic solvent mixtures and in the presence of non-saturating components have also been reported. A summary of studies on aqueous ternary systems is given in Table 3. In general, the solubility of potassium chlorate is depressed by the addition of other potassium salts or by the addition of other chlorates.

1. One Saturating Component

Bronsted (5) measured solubilities in aqueous potassium hydroxide solutions over the KOH concentration range from 4.71 to 15.02 mol dm^{-3}. The solubility of potassium chlorate in aqueous KOH solution decreases with increasing concentration of KOH.

The solubility of potassium chlorate in ethanol-water mixtures has been measured by Taylor (10) at 303 and 313 K, and by Wright (7) at 293 and 373 K. The solubility in acetone-water mixtures have been studied by Taylor (3) at 303 and 313 K, and by Hartley (11) at 298 K. The solubility in glycerol containing low concentrations of water at 292 K was reported by Holms (33). The solubility of potassium chlorate in these mixtures decreases with increasing concentration of organic solvent.

Schnellbach and Rosin (37) measured the solubility of potassium chlorate in aqueous glycine solution. The solubility of potassium chlorate in aqueous solution containing glycine is higher than that of potassium chlorate in water.

2. Two Saturating Components

Systems with halides. The data for the aqueous ternary systems have been reported in 12 publications (4, 8, 10, 12, 14, 20, 23, 39-41, 42, 45) (see Table 3).

Solubilities in the NaCl - $KClO_3$-H_2O system were reported by Di Capua and Scaletti (8) and Nallet and Paris (42). Only one point at each temperature investigated was reported in both papers. Above 283 K the composition of the solid phase was pure $KClO_3$ and NaCl.

Solubilities in the ternary $KClO_3$-KCl-H_2O system have been reported in 9 publications (4, 8, 12, 20, 23, 39-41). Neither double salts nor solid solutions are formed.

Donald (39), Munter and Brown (41), and Nallet and Paris (42) studied the compositions of the solutions only at the ternary isothermally invariant point. These results and those of other investigators (8, 12, 20, 23) are summarized in Table 4. Mutter and Brown (41) stated that the result of Di Capua and Scaletti (8) have mistaken the sharp curvature of the potassium chlorate solubility isotherm in the range of low potassium chloride concentration as an indication of the location of the invariant point. The evaluators agree that there is a serious error in (8), and the data for this system have been rejected and the paper was not compiled.

Benrath and Braun (40) measured solubility in the ternary $KClO_3$-KCl-H_2O system at 473, and 523 K. The solid phases at these temperatures were similar to those at temperatures of 373 K or below.

Ricci (14) measured solubilities in the ternary systems $KClO_3$-KBr-H_2O and $KClO_3$-KI-H_2O at 298 K. The only solid phases in these systems are the pure anhydrous salts.

Systems with other halates. Mazzetti (10) measured solubilities for the ternary $KClO_3$-$Ca(ClO_3)_2$-H_2O system at 293 K, and Kirgintsev, Kashina, Vulikh and Korotkevich (21) for the ternary systems $KClO_3$-$RbClO_3$-H_2O and $KClO_3$-$CsClO_3$-H_2O at 298 K. Neither double salts nor solid solutions form in these systems.

COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9]	Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan
(2) Water; H_2O; [7732-18-5]	July, 1984

CRITICAL EVALUATION:

Table 3. A Summary of Solubility Studies in the Ternary Systems with Halides

Ternary system	T/K	Solid phase	Reference
$KClO_3 + NaCl + H_2O$	293	Not given	8
"	251.2, 254.0 263.4	$KClO_3$; $NaCl.2H_2O$; Ice	42
"	269	$KClO_3$; Ice	42
"	271.8	$KClO_3$; $NaCl.2H_2O$; NaCl	42
"	283, 303, 323, 343, 373	$KClO_3$; NaCl	42
$KClO_3 + KCl + H_2O$	293	Not given	4
"	293	Not given	8
"	293	$KClO_3$; KCl	10
"	273, 293, 303 313, 323	$KClO_3$; KCl	12
"	298, 323	$KClO_3$; KCl	20
"	298	$KClO_3$; KCl	23
"	273, 323, 348	Not given	39
"	423, 448, 473	$KClO_3$; KCl	40
"	273	Not given	39
"	262.3, 263.3	$KClO_3$; KCl; Ice	42
"	269	$KClO_3$; Ice	42
"	283, 303, 323, 343, 373	$KClO_3$; KCl	42
"	323	$KClO_3$; KCl	45
$KClO_3 + KBr + H_2O$	298	$KClO_3$; KBr	14
$KClO_3 + KI + H_2O$	298	$KClO_3$; KI	14

Swenson and Ricci (17) studied solubilities in the ternary system $KClO_3$-$KBrO_3$-H_2O at 298 K. In the system two salts dissolve to a limited extent in each other, forming two solid solutions containing up to 3 % $KClO_3$ in $KBrO_3$ and up to 5% $KBrO_3$ in $KClO_3$.

Karnakhov, Lepeshkov and Fursova (44) measured solubilities in the ternary $KClO_3$-$KClO_4$-H_2O system at 298 K. Potassium perchlorate has a great tendency to form solid solutions with potassium chlorate.

Table 4. Composition at Isothermally Invariant Points in the System $KClO_3$-KCl-H_2O

T/K	Composition at isothermally invariant point (mol %)		Reference
	KCl	$KClO_3$	
273	6.135	0.13	12
273	6.204	0.13	41
283	7.004	0.197	42
293	7.430	0.285	12
293	7.58	0.288	39
298	7.901	0.444	20
298	8.025	0.361	23

COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9] (2) Water; H_2O; [7732-18-5]	Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan July, 1984

CRITICAL EVALUATION:

Table 4. Composition at Isothermally Invariant Point in the System $KClO_3$-KCl-H_2O (Continued)

T/K	Composition at isothermall invariant point (mol %)		Reference
	KCl	$KClO_3$	
303	7.959	0.429	26
303	8.14	0.431	42
313	8.281	0.600	12
323	8.800	0.870	12
323	9.204	0.983	20
323	9.14	0.848	39
323	9.21	0.840	42
343	9.94	1.51	42
348	9.99	1.68	42
373	10.8	3.38	42

MULTICOMPONENT SYSTEMS

Although Di Capua and Scaletti (8) studied solubility in the quaternary system $KClO_3$-KCl-NaCl-H_2O at 298 K, they reported only one value.

Mazzetti (10) studied the $KClO_3$-KCl-$Ca(ClO_3)_2$-H_2O system at 293 K, but solubility data were only reported for ternary and quaternary systems. In these systems, the solid phases found were the pure components $KClO_3$, KCl, $Ca(ClO_3)_2.2H_2O$, $CaCl_2.6H_2O$ and $CaCl_2.4H_2O$.

Arkhipov, Kashina and Kuzina (23) studied the $KClO_3$-KCl-$RbClO_3$-RbCl-H_2O system at 298 K but only reported solubility data for the quaternary systems $KClO_3$-KCl-$RbClO_3$-H_2O, $KClO_3$-KCl-RbCl-H_2O and KCl-RbCl-$RbClO_3$-H_2O, and for the ternary systems $KClO_3$-KCl-H_2O, $KClO_3$-$RbClO_3$-H_2O and RbCl-$RbClO_3$-H_2O. In the 5 component system, there were three fields on the solubility diagram for the crystallization of the salts $KClO_3$, $RbClO_3$, and for the solid solution of potassium and rubidium chloride.

Karnaukhov, Lepeshkov and Fursova (44) studied solubilities in the quaternary $KClO_3$-KCl-$KClO_4$-H_2O system, and also for the ternary systems KCl-$KClO_4$-H_2O, $KClO_3$-KCl-H_2O and $KClO_3$-$KClO_4$-H_2O. Solid phases found are the pure components KCl, $KClO_3$ and $KClO_4$, and the solid solutions $nKCl.mKClO_4$ and $nKClO_4.mKClO_3$.

COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9]	Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan
(2) Water; H_2O; [7732-18-5]	July, 1984

CRITICAL EVALUATION:

REFERENCES:

1. Pawlewsky, B. *Ber. Dtsch, Chem. Ges.* 1899, *32*, 1040.
2. Tschungaeff, L.; Chlopin, W. *Z. Anorg. Allg. Chem.* 1914, *45*, 154.
3. Tayler, A. E. *J. Phys. Chem.* 1897, *1*, 718.
4. Winteler, F. *Z. Electrochem.* 1900, *7*, 360.
5. Calzolari, F. *Gazz. Chim. Ital.* 1912, *42*, 85.
6. Toda, S. *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.)* 1922, *43*, 320; *Coll. Sci. Kyoto Imp. Univ.* 1922, 377.
7. Wright, R. *J. Chem. Soc.* 1927, 1334.
8. Di Capua, C.; Scaletti, U. *Gazz. Chim. Ital.* 1927, *27*, 391.
9. Flottman, F. *Z. Anal. Chem.* 1928, *73*, 1.
10. Mazzetti, C. *Ann. Chim. Appl.* 1929, *19*, 273. (see Volume 14).
11. Hartley, G. S. *Trans. Faraday Soc.* 1931, *27*, 10.
12. Fleck, J. *Bull. Soc. Chem. Fr.* 1937, Ser. 5, *4*, 558; *Bull. Soc. Chem. Fr.* 1936, Ser. 5, *3*, 350.
13. Ricci, J. E.; Yanick, N. S. *J. Am. Chem. Soc.* 1937, 59, 491.
14. Ricci, J. E. *J. Am. Chem. Soc.* 1937, 59, 866.
15. Benrath, A.; Gjedebo, F.; Schiffer, B.; Wunderlich, H. *Z. Anorg. Allg. Chem.* 1937, *231*, 285.
16. Treadweel, W. D.; Ammann, A. *Helv. Chim. Acta* 1938, *21*, 1249.
17. Swenton, T.; Ricci, J. E. *J. Am. Chem. Soc.* 1939, *61*, 1974.
18. Chang, T. L.; Hsieh, Y. Y. *Sci. Repts. Natl. Tsing Hua Univ.* 1948, A5, 252.
19. Noonan, E. C. *J. Am. Chem. Soc.* 1948, *70*, 2915.
20. Turnetskaya, A. F.; Lepeshkov, I. *Zh. Neorg. Khim.* 1965, *10*, 2163; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1176.
21. Kirgintsev, A. N.; Kashina, N. I.; Vulikh, A. I.; Korotkevich, B. I. *Zh. Neorg. Khim.* 1965, *10*, 1225; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 662.
22. Kirgintsev, A. N.; Kozitskii, V. P. *Zh. Neorg. Khim.* 1968, *13*, 3342; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 1723.
23. Arkhipov, S. M.; Kashina, N. I.; Kuzina, V. A. *Zh. Neorg. Khim.* 1969, *14*, 567; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1969, *14*, 294.
24. Mellor, J. W. *A Comprehensive Treaties on Inorganic and Theoretical Chemistry Vol. II* Longmans, Green and Co., London, 1937, p324-70.
25. Gay Lussac, J. L. *Ann. Chim. Phys.* 1819, (2) *11*, 314.
26. Mulder, G. J. *Bijdragen tot de geschieden van het scherkunding gebonder water*, Rotterdam, 1864, 143.

COMPONENTS:	EVALUATOR:
(1) Potassium chlorate; $KClO_3$; [3811-04-9] (2) Water; H_2O; [7732-18-5]	Hiroshi Miyamoto Department of Chemistry Niigata University Niigata, Japan July 1984

CRITICAL EVALUATION:

REFERENCES: (Continued)

27. Gerardin, C. A. *Ann. Chim. Phys.* 1865, (4) 5, 148.

28. Nordenskjold, N. G. *Pogg. Ann.* 1869, *136*, 213.

29. Schlosing, T. C. R. *Hebd. Seances Acad. Sci.* 1871, *73*, 1271.

30. Blarez, C. C. R. *Hebd. Seances Acad. Sci.* 1891, *112*, 1213.

31. Arrhenius, S. *Z. Physik. Chem.* 1893, *11*, 397.

32. Etard, A. C. R. *Hebd. Seances Acad. Sci.* 1899, *108*, 176.

33. Calvert, H. T. *Z. Physik. Chem.* 1901, *38*, 513.

34. Dean, R. B.; Dixon, W. J. *Anal. Chem.* 1951, *23*, 636.

35. Bronsted, J. N. *J. Am. Chem. Soc.* 1920, *42*, 1448.

36. Holm, K. *Pharm. Weekblad* 1921, *58*, 1033; *Pharm. Weekblad* 1921, *58*, 860.

37. Schnellbach, W.; Rosin, J. *J. Am. Pharm. Assoc.* 1931, *20*, 227.

38. Shineider, H. *Z. Anal. Chem.* 1953, *135*, 191.

39. Donald, M. B. *J. Chem. Soc.* 1937, 1325.

40. Benrath, A.; Braun, A. *Z. Anorg. Allg. Chem.* 1940, *244*, 348.

41. Munter, P. A.; Brown, R. L. *J. Am. Chem. Soc.* 1945, *65*, 2456.

42. Nallet, A.; Paris, R. A. *Bull. Soc. Chim. Fr.* 1956, 488.

43. Nallet, A.; Paris, R. A. *Bull. Soc. Chim. Fr.* 1956, 494.

44. Karnakhov, A. S.; Lepeshkov, I. N.; Fursova, A. F. *Zh. Neorg. Khim.* 1969, *14*, 2211; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) 1969, *14*, 1160.

45. J. A. Dean, Ed. *Lange's Handbook of Chemistry: Twelfth Edition.* McGraw-Hill, NY. 1979.