”Working up phosphate from ashes”
ForskEL project no. 2008-1-0111
Report concerning the fourth project contribution from Aqueous Solutions Aps:

Modeling systems containing copper (II) and iron (III) in addition to H_2O – (K^+, Na^+, H^+, Ca^{2+}, Al^{3+}) – (F^-, Cl^-, HSO_4^-, SO_4^{2-}, OH^-, CO_2, HCO_3^-, CO_3^{2-}, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-})

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Abstract

In the first three parts of this project, a thermodynamic model for the description of phase relations in systems containing the components H_2O, – (K^+, Na^+, H^+, Ca^{2+}, Al^{3+}) – (F^-, Cl^-, HSO_4^-, SO_4^{2-}, OH^-, CO_2, HCO_3^-, CO_3^{2-}, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) was developed. In this fourth report, it is described how the modeling was extended to include copper (II) ions and iron (III) ions.

In this report it is also shown how the calculation of pH was improved in the model by the introduction of a correction function. An empirical correction term valid at ionic strengths below 10 mol/(kg H2O) is added.

Model parameters for the above system have not previously been published in the open literature. The modeling presented in this report can therefore not be compared to previous modeling projects. The system is very difficult to model and the modeling is impeded by the fact that the experimental data available in the open literature are very scarce and often contradictory.

Experimental data were found in CERE/IVC-SEP's data bank for electrolyte solutions. This data bank was available for the project due to Kommunekemi's membership of the CERE/IVC-SEP consortium.

Experimental data valid at temperatures from the freezing point of the solutions and up to 200 °C were used for determining parameters in the model. Most of the applied data are only valid at temperatures below the normal boiling points of the solutions. The model is therefore valid in the temperature range from the freezing point of the solutions and up to 100 - 120 °C.

The thermodynamic model used for the modeling is the Extended UNIQUAC model. The model was described in the first two reports of this project.

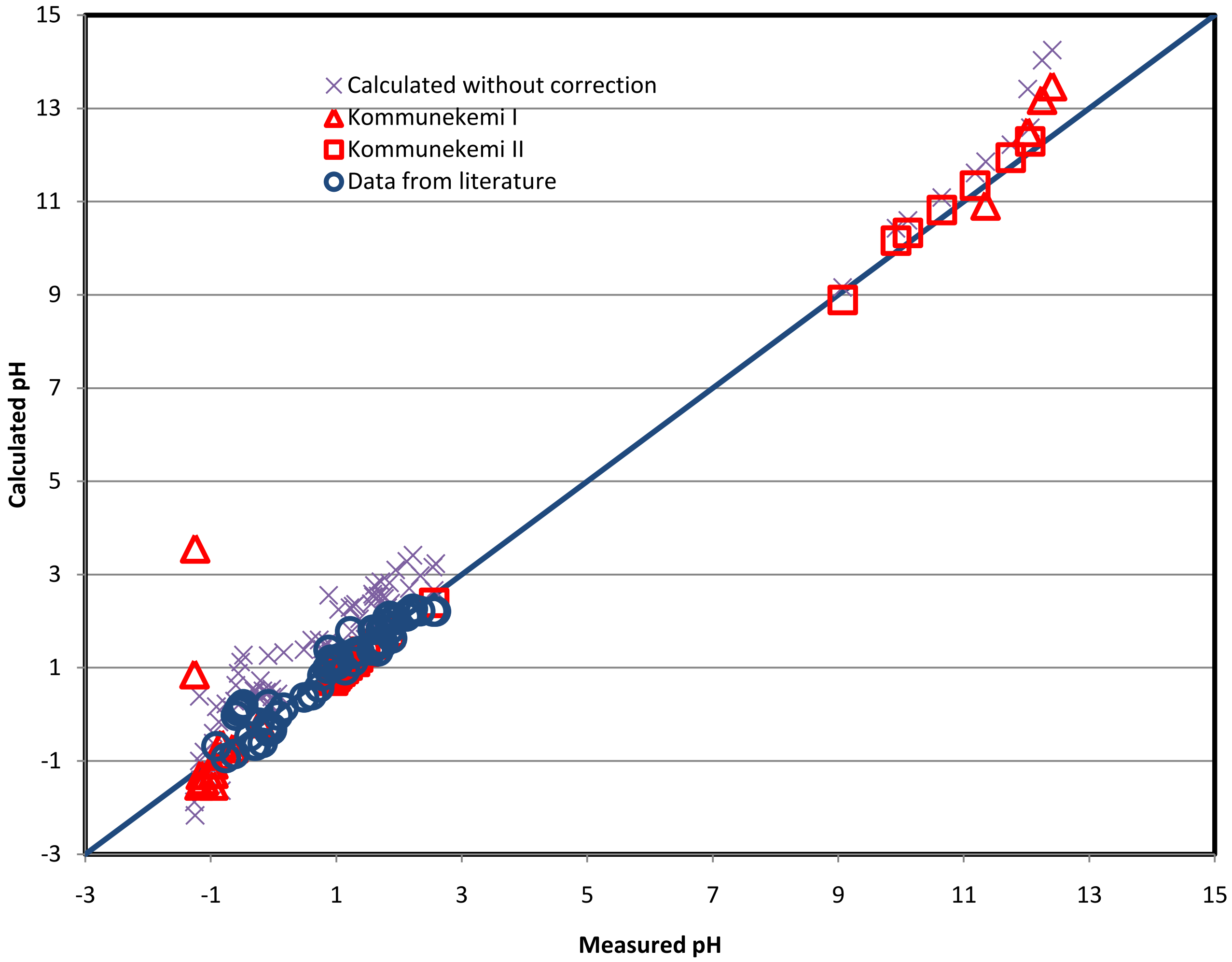

Figure 1: Calculated versus measured pH. By introducing a correction term, the calculated pH in most cases becomes almost identical with the measured value. Two values at very low pH were not used for determining the parameters of the correction term because the quality of the general fit then became significantly lowered.

Calculation of pH

pH is only defined for very dilute solutions[1]. In a thermodynamic model such as the Extended UNIQUAC model, pH can be calculated as minus the logarithm base 10 of the hydrogen ion activity on the molal scale. But this value will differ from measured pH values in concentrated solutions due to liquid junction potentials in the pH meter not accounted for. In order to enable the model to calculate a pH value similar to the measured value, a correction term was introduced. This correction term does not take the difference of the ions into account but only the ionic strength, as a measure of the concentration in the solution.

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[1] RP Buck; S Rondinini; AK Covington; FGK Baucke; CMA Brett; MF Camoes; MJT Milton; T Mussini; R Naumann; KW Pratt; P Spitzer; GS Wilson, Measurement of pH. Definition, Standards, and Procedures, Pure Appl. Chem., 74(2002)2169-2200(11)

The correction term was tested on solutions containing sodium, potassium, and hydrogen ions in addition to chloride, sulfate and hydroxide ions. The correction term can only be used for the Extended UNIQUAC model as each thermodynamic model has its own reference state for pH.

The effect of the correction term is shown in Figure 1. pH for all the experimental data were calculated without the correction term and these pH values are marked with crosses in Figure 1. When calculated with the correction term, the data came much closer to the diagonal, meaning much better agreement between experimental and calculated values.

Two datapoints from the series "Kommunekemi I" have a large deviation, even when calculated with the correction term. These two experimental points were not included when the parameters of the correction term were determined as they had a significant negative effect on the quality of the fit. These two data points had very large ionic strengths, 12.9 and 10.6 molal. It was found that the correction term is only valid up to an ionic strength of 10 molal. Above this concentration, the correction term will give wrong results.

The program will now output pH as calculated from the model as well as a corrected pH. The ionic strength will also be output so that the user can determine which of the values to use. The term is only valid at ionic strengths up to 10 molal and should not be used at higher ionic strengths.

At very high pH, according to Figure 1, there is some deviation, especially for the two points with largest pH. In these two points, the ionic strength is only 5.6 and 5.8. The deviation is therefore not caused by some extreme concentration.

Chemistry of copper (II) and iron (III) systems

The copper (II) ion or cupric ion has a tendency to form complexes like $CuCl^+$. The iron (III) ion or ferric ion forms complexes like $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$ (neutral molecule), $FeCl_4^-$, $FeCl_5^{2-}$, and $FeCl_6^{3-}$. Iron (III) systems with chloride and with sulfate were particularly difficult to model. It was attempted to improve the modeling of iron (III) chloride systems by introducing some of the above mentioned complex species. It was found however that the modeling could not be improved by introducing these species. These species were therefore left out in order to avoid making the model more complicated than necessary.

The introduction of the complex species mentioned above was made more difficult by the fact that experimental data documenting the speciation are insufficient and data from different sources often contradictory. An example is the recommended value for the gibbs energy of formation and the enthalpy of formation of the $FeCl^{2+}$ complex. These two standard state property values are of key importance for calculating the amount of the species. The National Institute of Science and Technology, NIST, recommends a certain value of the gibbs energy of formation and the enthalpy of formation[2] of this species. Other values were published by Rabinowitch and Stockmayer[3] in 1942 and by Vasil'ev and Lobanov[4]. The three sets of values are shown in Table 1. The equilibrium constant for the formation of the complex is strongly dependent on these values.

Table 1: Standard state property values for $FeCl^{++}$ from three different sources

	$\Delta_f G$ kJ/mol	$\Delta_f H$ kJ/mol
NIST (1982)	-143.9	-180.3
Rabinowitch and Stockmayer (1942)	-144.3	-180.078
Vasil'ev and Lobanov (1967)	-149.733	-191.133

The modeling of iron (III) sulfate solutions also causes problems. There is no agreement on the type of solid formed in these solutions. Cameron and Robertson[5] mentioned 30 different ferric sulfates reported by previous investigators. Ferric sulfate precipitating at relatively high pH can be expected to be a mixture of different combinations of the three oxides, Fe_2O_3, SO_3, and H_2O.

In addition to the problems with the ferric chlorides and sulfates, $Fe(OH)_3$ or its anhydrous form Fe_2O_3 are very sparingly soluble in water and will usually precipitate is the pH is not very low.

Experimental data for the solubility of copper hydroxide and copper phosphates are very scarce and data from different sources are not in agreement.

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[2] Wagman DD, Evans WH, Parker VB, Schumm RH, Halow I, Bailey SM, Churney KL, Nutall RL, The NBS tables of chemical thermodynamic properties, J. Phys. Chem. Ref. Data 11(1982) Supplement No. 2

[3] E Rabinowitch, WH Stockmayer, Association of ferric ions with chloride, bromide and hydroxyl ions (a spectroscopic study), J. Am. Chem. Soc. 64(1942)335-347

[4] VP Vasil'ev and GA Lobanov, : Effect of temperature and ionic strength on the heat of formation of the hydrated complex FeCl2+ in aqueous solution, Russian Journal of Physical Chemistry, 41(1967)1053-1053(8)

[5] F. K. Cameron, W. O. Robinson, Ferric Sulphates, The Journal of Physical Chemistry, 11(1907)641-650(9)

Modeling of systems with copper (II) ions (cupric ions)

Experimental data used for modeling copper (II) species

The experimental data used for determining model parameters for copper species are listed in Table 2. The types of data are mainly vapor pressure measurements of some sort (osmotic coefficients) and solid-liquid equilibrium (SLE) measurements.

Table 2: Sources and types of data used for determining model parameters for copper salts.

Source	Type of data
Downes, C.J. and Pitzer, K.S., Thermodynamics of Electrolytes. Binary Mixtures Formed from Aqueous NaCl, Na2SO4, CuCl2, and CuSO4 at 25°C J. Sol. Chem., 5(1976)389-398(6)	Osmotic coefficients of solutions with $CuCl_2$, $CuSO_4$, mixtures of $CuCl_2$ and NaCl, mixtures of $CuSO_4$ and Na_2SO_4 and mixtures of $CuCl_2$ and $CuSO_4$.
Vasil'ev V.A., Karapet'yants M.Kh., Sanaev E.S., Novikov S.N., Heat Capacities of Copper(II) Chloride Solutions at 25°C, Russ. J. Phys. Chem., 48(1974)1398-1399	Heat Capacities of Copper(II) Chloride Solutions at 25°C
Kopecky F., Dymes A., Osmometry in vapor phase. I, Osmotic coefficients of some electrolytes at 40°C, Chem. Zvesti., 26(1972)327-332	Osmotic coefficients of $CuSO_4$ solutions at 40 °C
Plake E., Siedepunktserhöhungen von wässerigen Lösungen starker Elektrolyte, Z. Phys. Chem.(Leipzig), A172(1935)113-128	Osmotic coefficients of $CuSO_4$ solutions at 100 °C
Plake E., Verdünnungswärmen von Lösungen starker Elektrolyte und die Assoziationshypothese von Nernst, Z.Phys.Chem.(Leipzig), A162(1932)257-80	Heat of dilution of $CuSO_4$ solutions
Marignac C., Sur les chaleurs spécifique des solutions salines, Ann.Chim.Phys., 8(1876)410-430	Heat capacity of $CuSO_4$ solutions
Lange E., Monheim J., Robinson A.L., The heats of dilution of aqueous solutions of Zinc, Cadmium and Copper Sulfates and Sulfuric Acid at 25°C, Journal of the American Chemical Society 55(1933)4733-4745	Heat of dilution of $CuSO_4$ solutions
Awakura, Y., Kawasaki, Y., Uno, A., Sato, K., Majima, H., Activities of water and hydrochloric acid in aqueous solution systems of hydrochloric acid-MCln including copper, Hydrometallurgy,	Water activity of aqueous solutions of HCl – $CuCl_2$ solutions

19(1987)137-57	
Robinson, R. A., Stokes, R. H., Part VI. The activity coefficients of manganese, cobalt, nickel and copper chloride in aqueous solution at 25°, Trans. Faraday Soc., 36(1940)1137-8	Mean ionic activity coefficients for $CuCl_2$ solutions
Robinson, R. A., Jones, R. S., The activity coefficients of some bivalent metal sulfates in aqueous solution from vapor pressure measurements, J. Am. Chem. Soc., 58(1936)959-961	Osmotic coefficients of $CuSO_4$ solutions at 25 °C
Brown, J. B., The constitution of cupric chloride in aqueous solution, Trans. Roy. Soc. N. Z., 77(1948)19-23	Osmotic coefficients of $CuCl_2$ solutions at 25 °C
M.EL Guendouzi, A. Mounir, A. Dinane, Water activity, osmotic and activity coefficients of aqueous solutions of Li_2SO_4, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$ at T = 298,15K, J. Chem. Thermodynamics, 35(2003)209-220	Water activity of $CuSO_4$ solutions at 25 °C
Schreinemakers, F.A.H. and de Baat, W.C., Gleichgewichte in quaternaren Systeme, Z. Physik. Chem., 65(1909)586-594	SLE of NaCl-$CuCl_2$-H_2O system at 30°C
Schreinemakers, F.A.H., Equilibria in the system: Water - Sodium Sulphate - Sodium Chloride - Copper sulphate - Cupric Chloride, Koninklijke Akademie van wetenschappen Te Amsterdam, Proceeding of the section of sciences 13(1911)1163-1177	SLE of NaCl-$CuCl_2$-Na_2SO_4-$CuSO_4$-H_2O system at 15, 25, 35°C
Rivett, A.D.C., Neutralsalzwirkung auf die Gefrierpunkte von Mischungen in wässeriger Lösung, Z. Phys. Chem. (Leipzig), 80(1912)537-563	Freezing point depression of $CuSO_4$ solution
Bedford, T.G., The Depression of freezing point in very dilute aqueous solutions, Proc. Roy. Soc. London, A, 83(1910)454-461	Freezing point depression of $CuSO_4$ solution
Averina R.A., Shevchuk V.G., The CuSO4-MgSO4-(NH4)2SO4-H2O system at 25°C, Russ. J. Inorg. Chem., 13(1968)138-140(1)	SLE of $CuSO_4$ – H_2O at 25°C
Schreinemakers, F.A.H., Gleichgewichte im System: Kupfersulfat-Kupferchlorid-Ammoniumsulfat-Ammoniumchlorid und wasser, Z. Physik. Chem., 69(1909)557-568	SLE of $CuCl_2$ – $CuSO_4$ – H_2O at 30°C

Chambers V.J., Frazer J.C.W., On a minimum in the molecular lowering of the freezing point of water, produced by certain acids and salts, Am. Chem. J., 23(1900)512	Freezing point depression of $CuSO_4$ solution
Jones H.C., Pearce J.N., Dissociation as measured by freezing point lowering and by conductivity - bearing on the hydrate theory, Am. Chem. J., 38(1907)683-743	Freezing point depression of $CuCl_2$ solution
Hausrath H., Eine Differentialmethode zur bestimmung kleiner Gefrierpunktsdepressionen, Annalen der Physik, IV. Folge 9(1902)522	Freezing point depression of $CuSO_4$ solution
Albert Cherbury David Rivett, Frederick William Jeffrey Clendinnen, Mixed crystals and double salts: a comparison of systems containing water, ammonium chloride, and a chloride of manganese, iron, cobalt, nickel, or copper, J. Chem. Soc., Trans., 123(1923)1634-1640	SLE of $CuCl_2$-H_2O
Jones H.C., Getman F.H., On the nature of concentrated solutions of electrolytes. Hydrates in solution, American Chemical Journal, 31(1904)303-359	Freezing point depression of $CuSO_4$ and $CuCl_2$ solutions
Bruhn G., Gerlach J., Pawlek F., Untersuchungen über die Löslichkeiten von Salzen und Gasen in Wasser und wässrigen Lösungen bei Temperaturen ober 100°C, Z. anorg. allg. Chemie, 337(1965)68-79	SLE of $CuSO_4$ – H_2O
Schreinemakers, F. A. H., Over eenige dubbelzouten van het kopersulfaat, Chemisch Weekblad, 26(1908)465-472	SLE of $CuCl_2$ – $CuSO_4$ – H_2O at 30°C
Agde, G., Barkholt, H., Untersuchungen über die Trennung von Kupfervitriol und Eisenvitriol durch kristallisation, Z. Angew. Chem., 39(1926)851-855	SLE of $CuSO_4$ – H_2O
Benrath, A., Benrath, H., Über das heterogene Gleichgewicht bei 97 C in Systemen, die neben Wasser und Natriumsulfat Sulfate von Vitriol bilden, Z. Anorg. Chem., 179(1929)369-378	SLE of $CuSO_4$ – Na_2SO_4 - H_2O
Flöttmann, Fr., Über Löslichkeitsgleichgewichte, Z. Anal. Chem., 73(1928)1-39	SLE of $CuSO_4$ – H_2O
Crockford, H. D., The system: CuSO4-CoSO4-H2O, J. Phys. Chem., 36(1932)1594-6	SLE of $CuSO_4$ – H_2O
A. Massink, Doppelsalzbildung zwischen Nitraten und Sulfaten in wässerigen Lösung, Z.	SLE of Na_2SO_4-$CuSO_4$-H_2O system at 20°C

physikalische Chemie, 92(1918)351-380	
A. Chrétien, R. Weil, Le Système eau-chlorure de potassium-chlorure cuivrique, Bull. Soc. Chim., 2(1935)1577-1591	SLE of $CuCl_2$ - KCl – H2O at 0 to 120°C, 85 data points
Occleshaw VJ, The equilibrium in the system aluminium sulphate-copper sulphate-water and aluminium sulphate-ferrous sulphate-water at 25°, J. Chem. Soc., 127(1925)2598-2602	SLE of $CuCl_2$ – $AlCl_3$ – H_2O at 25°C
Caven RM, Mitchell TC, Studies of equilibrium in systems of the type Al2(SO4)3-M''SO4-H2O. Part I. Aluminium sulphate-copper sulphate-water and aluminium sulphate-manganous sulphate-water at 30°, J. Chem. Soc., 127(1925)527-31	SLE of $CuSO_4$ – $Al_2(SO_4)_3$ – H_2O at 30°C
Balarev, Kh., Spasov, D., Formation of double salts from chlorides of bivalent metals, Russ. J. Inorg. Chem., 25(1980)1551-1556	SLE of $CuCl_2$ – H_2O at 25°C
Huang, J. T., Pan, K., Osmotic and activity coefficients of copper(II) chloride and cadmium chloride from freezing point measurements, J. Chin. Chem. Soc., 13(1966)64-76	Freezing point depression of $CuCl_2$ solution
Isaachsen, D., Die Farbenanderung von Salzlösungen, Z. Phys. Chem., 8(1891)145	Freezing point depression of $CuCl_2$ solution
Ojkova, T., Georgiev, G., The CuCl2-MnCl2-H2O system at 25°C, Russ. J. Inorg. Chem., 22(1977)1714-6	SLE of $CuCl_2$ – H_2O at 25°C
Stortenbeker, W., Ueber Löslichkeit von hydratierten Mischkrystallen. II., Z. Phys. Chem., 22(1897)60-71	SLE of $CuSO_4$ – H_2O at 18°C
Averina R.A., Shevchuk V.G., The CuSO4-MgSO4-(NH4)2SO4-H2O system at 50°C, Russ. J. Inorg. Chem., 14(1969)692-4	SLE of $CuSO_4$ – H_2O at 50°C
Biltz, W., Zur Kenntnis der Lösungen anorganischer Salze in Wasser, Z. Phys. Chem., 40(1902)185-221	Freezing point depression of $CuCl_2$ solution
Crockford, H. D., Warrick, L. E., The system: CuSO4-H2SO4-H2O, J. Phys. Chem., 34(1930)1064-1070	SLE of $CuSO_4$-H_2SO_4-H_2O solutions, 55 data points at 0, 20, 40 and 55°C
Filippov, V. K., Udovenko, A. G., Nikitin, V. A., Charykova, M. V., Puchkov, L. V., Charykov, N. A., Phase equilibria in the Na+, Cu2+//Cl-, SO42--H2O system at 25°C, Russ. J. Inorg. Chem.,	SLE of $CuCl_2$ – $CuSO_4$ – H_2O at 25°C

43(1998)1961-5	
Skripkin M., Chernykh LV, Solubility in the systems CuCl2-MCl-H2O (M=Li, Na, K, Cs, NH4) at 25 and 50°C, Russ. J. Inorg. Chem., 39(1994)1671-1675	SLE of $CuCl_2$ – NaCl – H_2O at 50°C
Filippov, V. K., Charykov, N. A., Fedorov, Yu. A., Sodium chloride-nickel dichloride (copper dichloride)-water system at 25°C, Russ. J. Inorg. Chem., 31(1986)1071-4	SLE of $CuCl_2$ – NaCl – H_2O at 25°C
Novikov, G. I., Voropaev, L. E., Rud'ko, P. K., Zharskii, I. M., Copper(II)-hydrochloric acid-water system at 10, 25, 40 and 55°C, Russ. J. Inorg. Chem., 24(1979)451-2	SLE of $CuCl_2$ – HCl – H_2O at 10, 25, 40, and 55°C
Miles, F. T., Menzies, A. W. C., Solubilities of cupric sulfate and strontium chloride in deuterium water, J. Am. Chem. Soc., 59(1937)2392-	SLE of $CuSO_4$ – H_2O from 0 to 100°C
Benrath, A., Die Polythermen der ternären Systeme: CuCl2-(LiCl)2-H2O und NiCl2-(LiCl)2-H2O, Z. Anorg. Chem., 205(1932)417-424	SLE of $CuCl_2$ – H_2O from 0 to 100°C
Boye, E., Über die Löslichkeiten des Kupfer-2-chlorids in Wasser und die Umwandlungspunkte seiner Hydrate, Z. Anorg. Allgem. Chem., 215(1933)75-80	SLE of $CuCl_2$ – H_2O from -43 to 116°C, 63 data points
Foote, H. W., Equilibrium in the system, nickel chloride, cobalt chloride, cupric chloride-hydrochloric acid-water, J. Am. Chem. Soc., 45(1923)663-7	SLE of $CuCl_2$ – HCl – H_2O at 0 and 25°C
Schreinemakers FAH, Over het quaternaire stelsel: KCl-CuCl2-BaCl2-H2O, Akad. Amsterdam Versl., 23(1914)786-8	SLE of $CuCl_2$ – KCl – H_2O at 40 and 60°C
Filippov, V. K., Nokhrin, V. I., Solubility in the Na2SO4-CuSO4-H2O system at 25°C, Russ. J. Inorg. Chem., 30(1985)1688-9	SLE of Na_2SO_4-$CuSO_4$-H_2O system at 25°C
Druzhinin, I. G., Kosyakina, O. A., Solubility and solid phases in the CuCl2 + Na2SO4 = CuSO4 + Na2Cl2 aqueous reciprocal system at 25°C, Russ. J. Inorg. Chem., 6(1961)868-73	SLE of $CuCl_2$ - Na_2SO_4 - $CuSO_4$ – NaCl – H2O at 25°C
Caven, R. M., Mitchell, T. C., Equilibrium in the system cupric sulphate-potassium sulphate-water and cupric sulphate-ammonium sulphate-water at 25, 51, and 61°C, J. Chem. Soc.,	SLE of K_2SO_4 - $CuSO_4$ – H2O at 25, 51, and 61°C

125(1924)1428-31	
Bakeev, M. I., Shkodina, T. B., Zharmenov, A. A., Kalinskaya, N. N., The CuSO4-(NH4)2SO4-H2O at 25, 50, and 75°C, Russ. J. Inorg. Chem., 37(1992)986-9	SLE of $CuSO_4$ – H_2O at 25, 50 and 75°C
Nabiev, M. N., Tukhtaev, S., Kucharov, Kh., K2SO4-MgSO4-CuSO4-H2O system at 50°C, Russ. J. Inorg. Chem., 29(1984)1678-81	SLE of K_2SO_4 - $CuSO_4$ – H2O at 50°C
Tukhtaev, S., Kucharov Kh., Polytherm of Solubility in the System K2SO4 - CuSO4 - H2O, Uzb. Khim. Zh., (1977)28-31(1)	SLE of K_2SO_4 - $CuSO_4$ – H2O from -2 to 36°C
Akbaev, A., Solubility isotherm of a copper sulfate-sodium sulfate-water system and the solid phase at 60.deg, Izv. Akad. Nauk Kirg. SSR, (1970)43-5(5)	SLE of Na_2SO_4-$CuSO_4$-H_2O system at 60°C
Massol, Maldès, Sur la solubilité des mélanges de sulfate de cuivre et de sulfate de soude, Compt. Rend., 133(1901)287-9	SLE of Na_2SO_4-$CuSO_4$-H_2O system at 10 and 15°C
Caven, R. M., Johnston, W., Equilibrium in the systems MnSO4-K2SO4-H2O and MnSO4-(NH4)2SO4-H2O at 0°; also in the system CuSO4-Na2SO4-H2O at 0°, 25°, and 37.5°,J. Chem. Soc., (1927)2358-65	SLE of Na_2SO_4-$CuSO_4$-H_2O system at 0, 25, and 37.5°C
Laptev, V. M.; Akhmarov, F. I.; Dmitrevskii, B. A.; Kamalov, O. K., Solubility in the metal sulfate (MSO4)-sulfuric acid-water system where M = zinc, copper, cadmium, iron, and lead, Zhurnal Prikladnoi Khimii (Sankt-Peterburg, Russian Federation), 65(1992)2363-6(10)	SLE of $CuSO_4$-H_2SO_4-H_2O solutions at 20 to 73°C
J. M. Bell, W. C. Taber, The Three-Component System CuO, SO3, H2O at 25°, J. Phys. Chem., 12(1908)171-179	SLE of CuO – SO_3 – H_2O solutions at 25°C
H. W. Foote, A method of determining the hydrates formed by a salt, J. Am. Chem. Soc., 37(1915)288–292	SLE of $CuSO_4$-H_2SO_4-H_2O solutions at 25°C
G. Agde and H. Barkholt, Beiträge zur Kenntnis der Vitriolherstellung. II Untersuchungen über das System Kupfervitriol - Schwefelsäure – Wasser, Z. angew. Chemie, 40(1927)374-379	SLE of $CuSO_4$-H_2SO_4-H_2O solutions from 0 to 80°C, 80 data points
E. Posnjak and G. Tunell, The System, Cupric oxide-sulphur trioxide water, Am. J. Sci., 18(1929)1-34	SLE of CuO – SO_3 – H_2O solutions from 50 to 200°C

Leon A. McDowell, Herrick L. Johnston, The Solubility of Cupric Oxide in Alkali and the Second Dissociation Constant of Cupric Acid. The Analysis of Very Small Amounts of Copper, J. Am. Chem. Soc., 58(1936)2009-2014	SLE of $CuO – K_2O – H_2O$ solutions at 25°C
Cameron F.K. , Crockford H.D., The Aqueous Solution of Cupric and Ferrous Sulphates, J. Phys. Chem., 33(1929)709-716	SLE of $CuSO_4$-H_2SO_4-H_2O solutions at 30°C
Druzhinin, I. G.; Tusheva, L. A., Solubility of copper phosphate in systems of sodium phosphate and water at 25 and 50°, Izvestiya Vysshikh Uchebnykh Zavedenii, Khimiya i Khimicheskaya Tekhnologiya, 10(1967)1075-1078	SLE of $Cu_3(PO_4)_2$ - Na_3PO_4 – H_2O solutions at 25 and 50°C
Carter. R. H., Solubilities of some inorganic fluorides in water at 25°C, Ind. Eng. Chem., 20(1928)1195	SLE of CuF_2 – H_2O solutions
Kurtenacker, A., Finger, W., Hey, F., Zur Kenntnis der Fluoride zweiwertiger Metalle. I. Die normalen und sauren Fluoride, Z. Anorg. Chem., 211(1933)83-97	SLE of CuF_2 – HF - H_2O solutions
Nabiev, M. N., Usmanov, I. I., Tukhtaev, S., Adylova, M. R., The MSO4-H3PO4-H2O systems (M=Cu, Zn, or Co) at 30°C, Russ. J. Inorg. Chem., 24(1979)1232-5	SLE of $CuSO_4$ – H_3PO_4 – H_2O solutions at 30°C
Akbaev A, Copper(II) hydrogen phosphate-disodium hydrogen phosphate-water system at 30.deg, Russ. J. Inorg. Chem., 20(1975)303-305(2)	SLE of $CuHPO_4$ – Na_2HPO_4 – H_2O solutions at 30°C
Jaeger A. Über das Verhalten einiger Schwermetalfluoride in Lösung, Z. anorg. Chem., 27(1901)22-40	SLE of $Cu(OH)_2$ – HF – H_2O solutions at 25°C
Druzhinin, I. G.; Tusheva, L. A., System of phosphates, carbonates of copper, sodium, and water at 25 and 50°, Russ. J. Inorg. Chem., 11(1966)1273-1275 (10)	SLE of $Cu_3(PO_4)_2$ – H_2O at 25 and 50°C

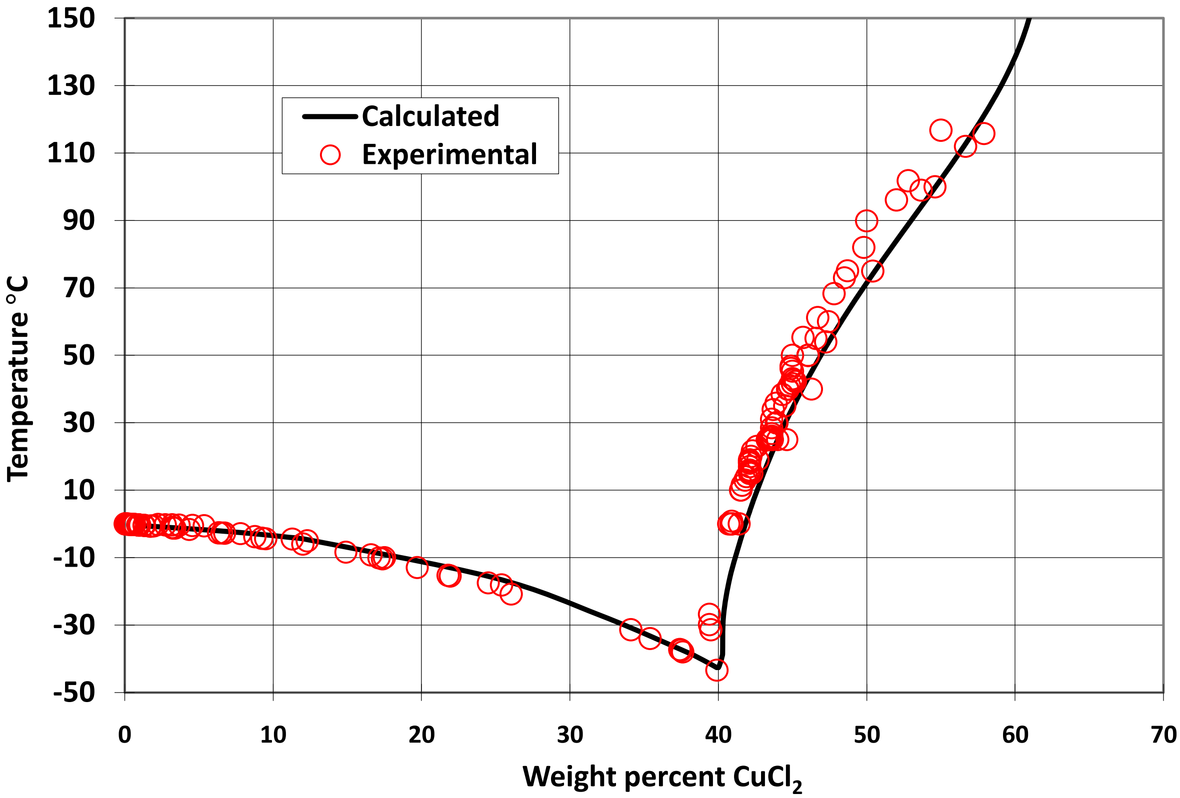

Figure 2: The solubility of $CuCl_2$. The diagram has two branches, the ice branch and the dihydrate branch for the solubility of $CuCl_2·2H_2O$. The experimental data from several sources (Table 2) are marked with circles. The model calculation is the solid line.

Systems with chloride

Copper chloride only forms one hydrate, the dihydrate, $CuCl_2·2H_2O$. This hydrate is stable from the eutectic point at about -43°C to 116.8°C, which is the highest temperature at which data were found. The binary solubility diagram for the $CuCl_2$-H_2O system is shown in Figure 2.

The system is a simple eutectic system in the temperature range considered here. The calculated solubility is in many cases 0.5 mass% higher than the experimental value. Especially the solubilities measured by Boye (1933), see Table 2, are slightly lower than the calculated values. The 63 measured data points from Boye are the cause of the apparent discrepancy between calculated and experimental data. These 63 points are all marked in Figure 2.

The two branches of the phase diagram in Figure 2 represent the equilibrium with ice and with $CuCl_2·2H_2O$ respectively. According to the above mentioned data from Boye (1933), four different hydrates of $CuCl_2$ appear between 0 and 100°C, namely tetrahydrate, trihydrate, dihydrate and

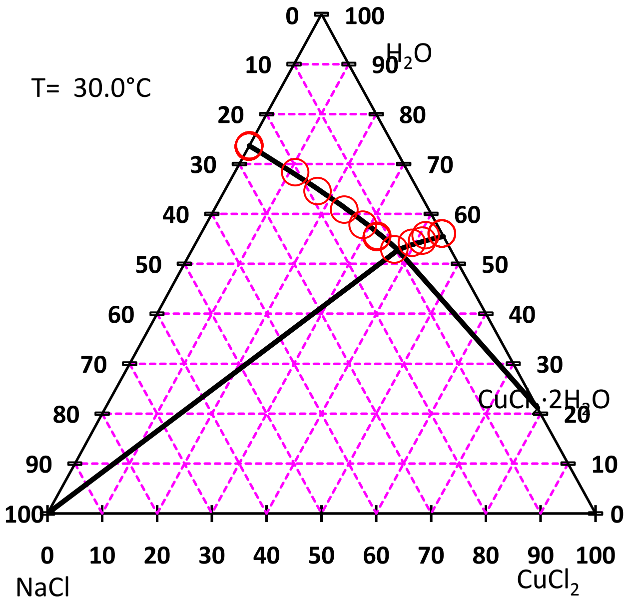

Figure 3: Calculated and experimental solubility data for the $CuCl_2$-NaCl-H_2O system at 30°C. The data are from Schreinemakers and de Baat, 1909

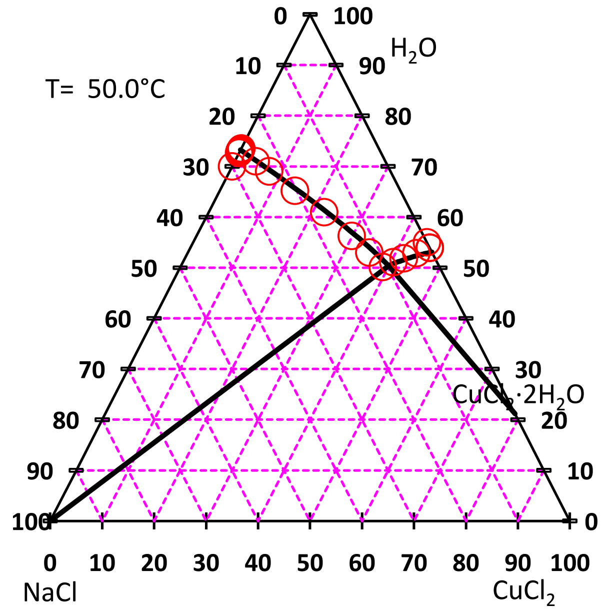

Figure 4: Calculated and experimental solubility data for the $CuCl_2$-NaCl-H_2O system at 50°C. The data are from Skripkin and Chernykh, 1994

monohydrate. According to Benrath[6] (1934), Boye's data are wrong because of insufficient stirring. Benrath rejects strongly the notion that there should be any other stable copper (II) hydrates than the dihydrate in this temperature range.

The $CuCl_2$-NaCl-H_2O system

Results for the $CuCl_2$-NaCl-H_2O system are shown in Figure 3 and Figure 4. The two figures show a good agreement between the model and the calculated values. Additional data for this ternary system were available at 15, 25 and 35°C. At these temperatures, the result is of similar quality. No double salts are forming in this system.

The $CuCl_2$-KCl-H_2O system

Results for the $CuCl_2$-KCl-H_2O system are shown in Figure 6, Figure 7, Figure 5, and Figure 8. In this system, three different double salts are formed. They are all very soluble. At temperatures from the ternary eutectic around -45 and up to 87°C the double salt $CuCl_2 \cdot 2KCl \cdot 2H_2O$ can form. The existence of this phase can be seen in Figure 6, Figure 7, and Figure 5. At temperatures from -30 to 50°C another double salt, $CuCl_2 \cdot KCl \cdot 2H_2O$, forms in solutions with low KCl content. This is shown in Figure 6 and Figure 5. At temperatures above 60°C, the anhydrous double salt $CuCl_2 \cdot KCl$ is formed. This is shown in Figure 5 and Figure 8.

The phase diagram in Figure 5 provides a map, marking the temperature ranges and composition ranges in which the different solid phases appear. A total of six different solid phases are able to

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[6] Benrath, H., Über die Löslichkeit des Kupfer-2-chlorids in Wasser und die Umwandlungspunkte seiner Hydrate, Z. Anorg. Allgem. Chem., 216(1934)207-8

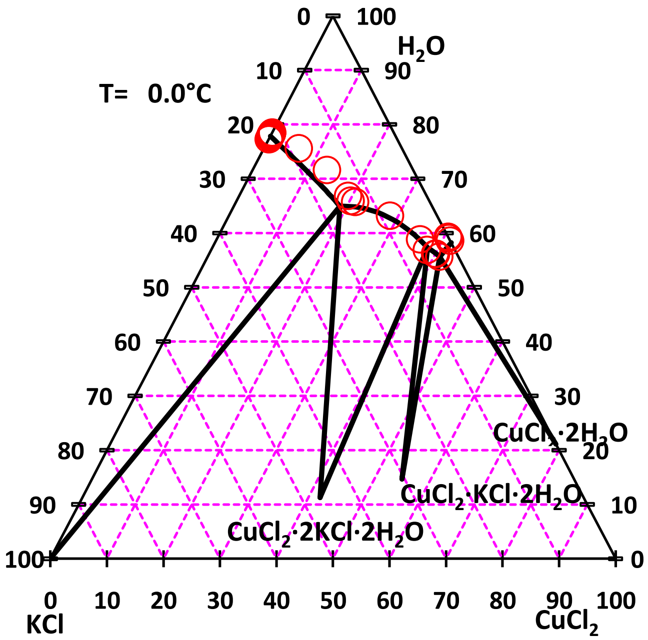


Figure 6: Solubility in the $CuCl_2 - KCl - H_2O$ system at 0°C, the experimental data are from Chrétien and Weil, 1935. Two double salts are formed, $CuCl_2{\cdot}2KCl{\cdot}2H_2O$ and $CuCl_2{\cdot}KCl{\cdot}2H_2O$.

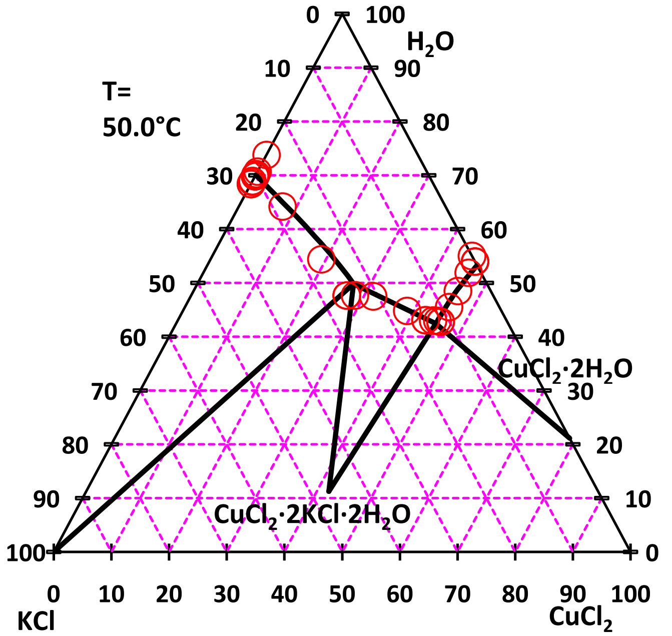


Figure 7: Solubility in the $CuCl_2 - KCl - H_2O$ system at 50°C, the experimental data are from Skripkin and Chernykh, 1994 and from Chrétien and Weil, 1935. The double salt $CuCl_2{\cdot}2KCl{\cdot}2H_2O$ is formed.

precipitate in the temperature range from -50 to 130°C.

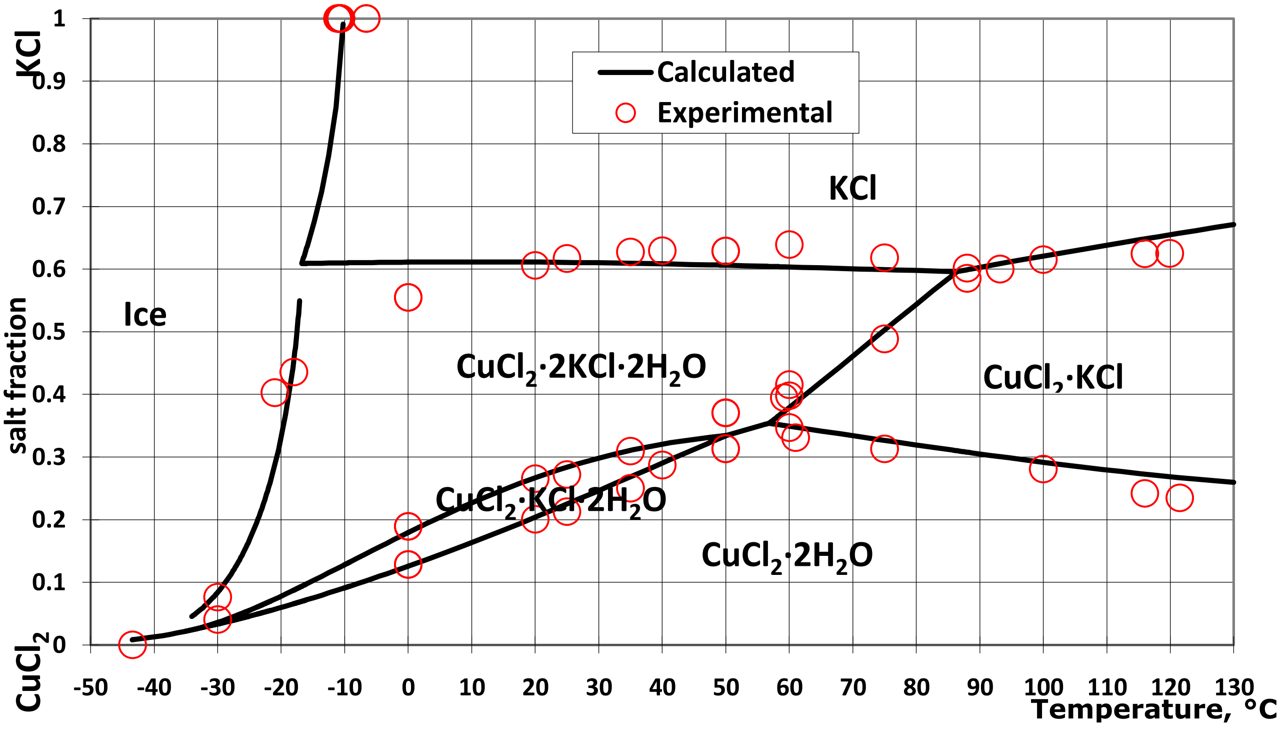


Figure 5: Phase diagram for the $CuCl_2 - KCl - H_2O$ system with the six solid phases that appear in the temperature range from -50 to 130°C. This phase diagram maps the temperature range and the composition range of the various solid phases

In Figure 5 it seems like there is a disagreement between the experimental data marking the border line between the KCl field and the $CuCl_2 \cdot 2KCl \cdot 2H_2O$ field, especially at low temperatures.It was impossible to reproduce the curvature of this border line. It is therefore assumed that the experimental data are at fault.

All the experimental data on this line are from Chrétien and Weil, 1935. If data from different sources were available, the validity of the experimental data could better be established.

The phase diagram in Figure 5 has temperature as abscissa and “salt fraction” on mol basis as ordinate. The water content of the solutions can not be seen in the diagram as the salt fraction is on dry basis. The isotherms depicted in Figure 6, Figure 7, and Figure 8 show all concentrations in the system, but are limited to a single temperature.

Chrétien and Weil, 1935 found solid solutions precipitating in this ternary system at temperatures between 55 and 60°C. Usually the solids precipitating from such solutions are pure salts. Solid solutions are mixtures of solids with variable composition and are more complicated to model than pure salts. No other researchers have verified the existence of solid solutions in this system. It is therefore assumed that the results of Chrétien and Weil are wrong, and no solid solution form in the $CuCl_2 - KCl - H_2O$ System.

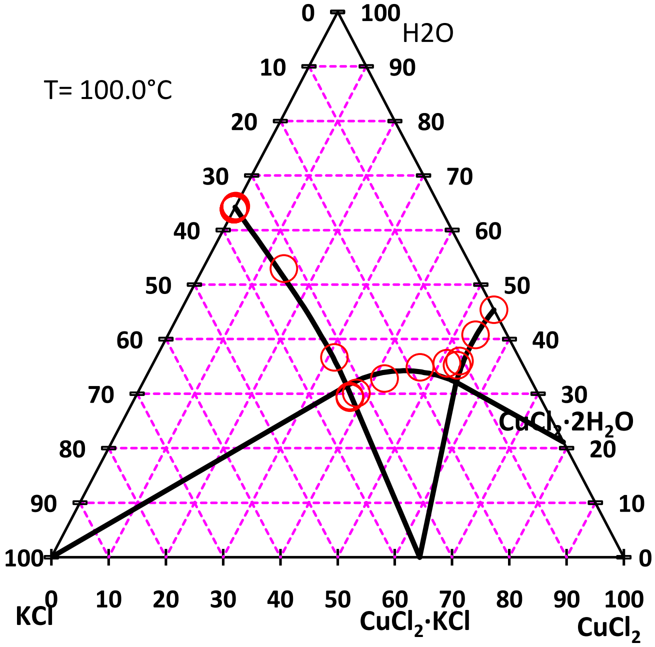


Figure 8: Solubility in the $CuCl_2 - KCl - H_2O$ system at 100°C, the experimental data are from Chrétien and Weil, 1935. The anhydrous double salt $CuCl_2 \cdot KCl$ is formed.

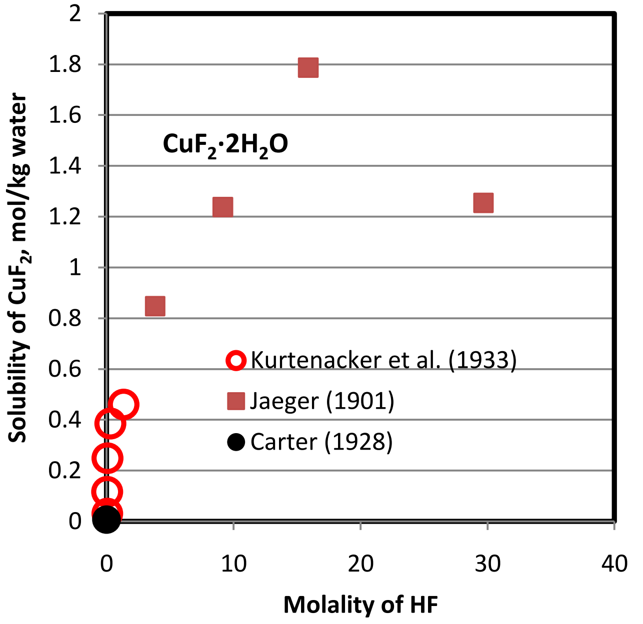


Figure 9: Experimental data for the solubility of CuF_2 in solutions with various amounts of HF. A strong salting in effect is observed.

Systems with fluoride

Only very few data points with CuF_2 are available. Data by Carter (1928), Jaeger (1901), and Kurtenacker *et al.* (1933) were used here. Data from the last two sources concern solutions that

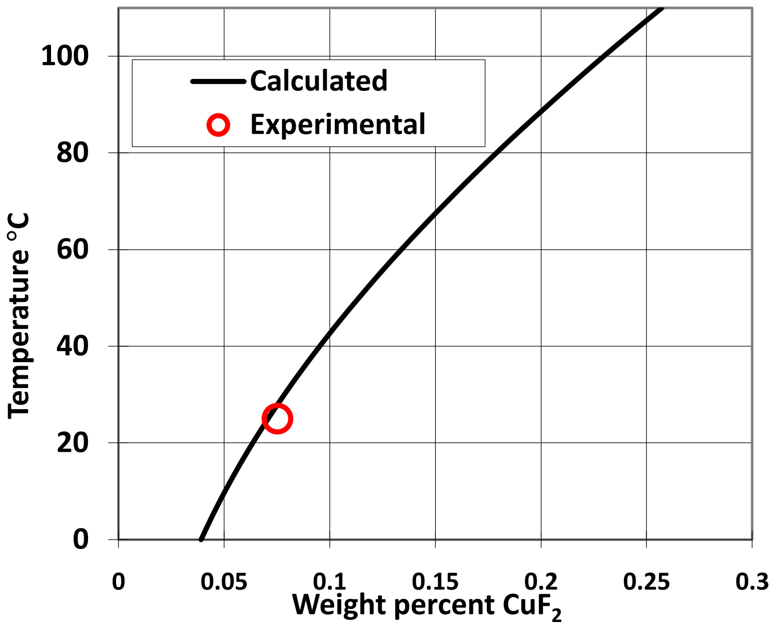


Figure 10: Solubility of CuF_2 in water. The only solid known to precipitate is $CuF_2·2H_2O$. The experimental data point is from Carter, 1928, See Table 2.

contain some amount of hydrofluoric acid, HF too. All the data are at 20 or 25°C, which is insufficient for proper modeling. Besides, the data containing HF show a very strong salting in tendency for CuF_2 in the presence of HF. It means that the solubility of CuF_2 increases rapidly by the presence of HF. The experimental data are shown in Figure 10.

The strong increase in CuF_2 solubility could be caused by the formation of fluoride complexes of the copper ion. The 10 experimental data points available at 20-25°C are insufficient for the modeling of the solubility of CuF_2 in the CuF_2 – HF- H_2O system.

It was therefore decided to only model the solubility of CuF_2 in pure water. The solubility of CuF2 in water is 0.075 wt% at 25°C. In order to model the solubility as a function of temperature, a typical increase in solubility was assumed and the result of model calculation is shown in Figure 10 together with the single experimental data point.

No data were found concerning the solubility of copper fluoride in ternary solutions with NaF, KF, or other relevant salts. The model will still be able to perform calculations for these ternary systems. But the calculations will only be predictions. The model will not be able to predict whether or not some double salt is formed between CuF_2 and another salt. The identities of possible solid phases need to be specified in the model beforehand.

Systems with sulfate.

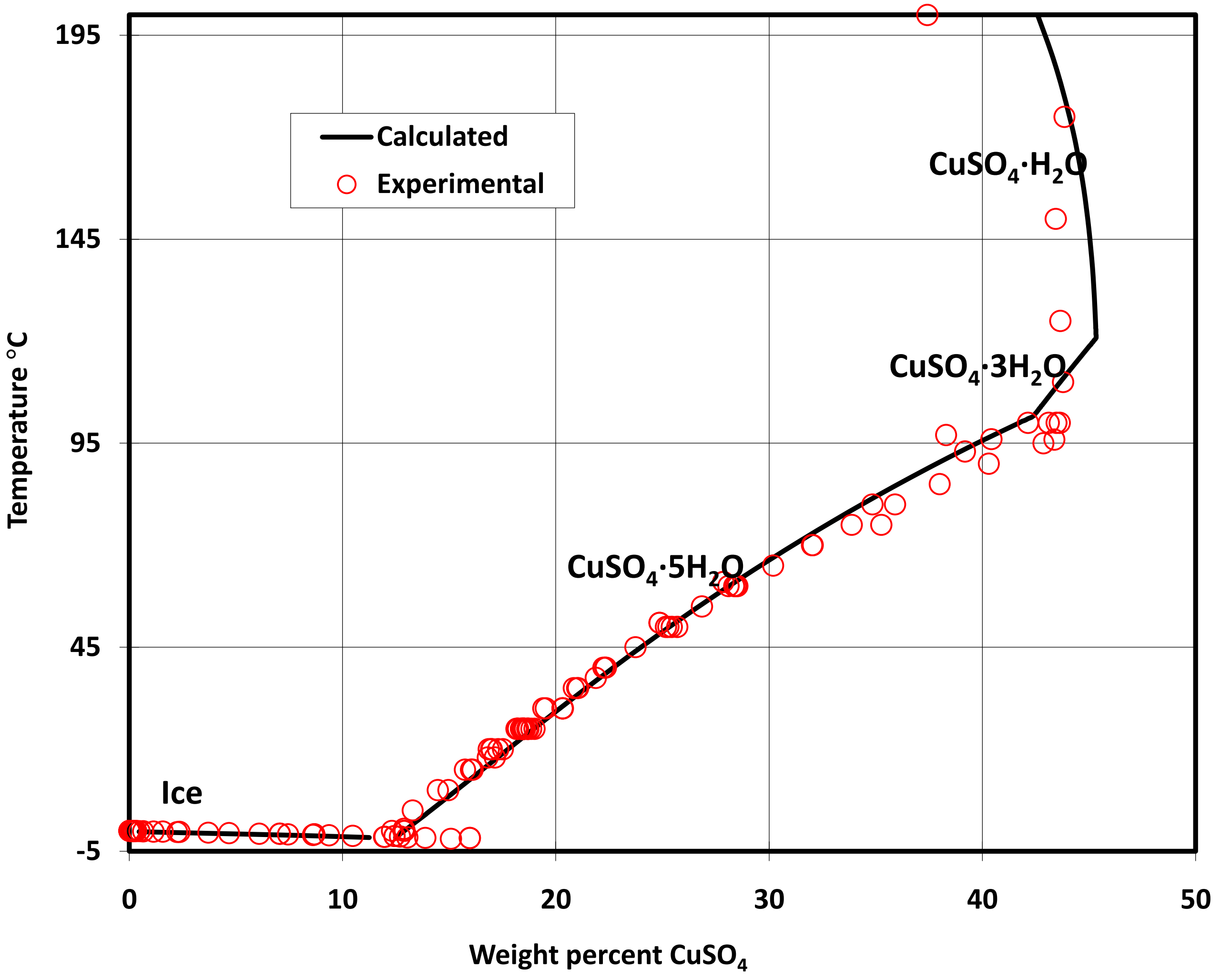


Figure 11: The solubility of $CuSO_4$ in water. In the considered temperature range, three different hydrates form.

Copper sulfate, $CuSO_4$ can precipitate in the anhydrous form or as a mono hydrate, $CuSO_4 \cdot H_2O$, a tri hydrate, $CuSO_4 \cdot 3H_2O$ or as a penta hydrate, $CuSO_4 \cdot 5H_2O$. There is some disagreement concerning the conditions required for precipitating copper sulfate in the anhydrous form. It is claimed to precipitate in concentrated sulfuric acid at temperatures as low as 25°C (Foote, 1915) and at high temperature. Bruhn *et al.* (1965) claim that anhydrous $CuSO_4$ is the stable solid phase from 200°C and up. The solubility of $CuSO_4$ is depicted in the phase diagram in Figure 11. At temperatures up to 100°C, there is a good agreement between experimental data and model calculation.

The $CuSO_4$ – $CuCl_2$ – H_2O system

Data for this ternary system are available at 15, 25, 30 and 35°C. The phase diagram calculated at 25°C is shown in Figure 12 together with experimental data. This is a simple eutonic system, no double salts are formed.

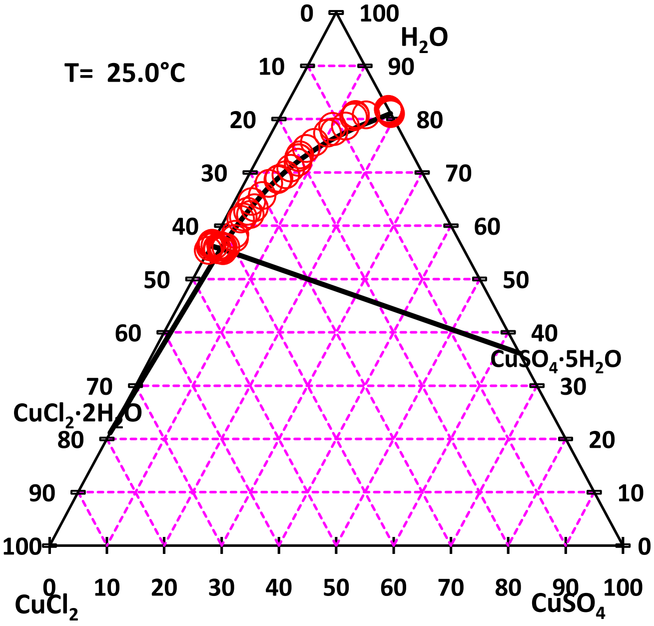


Figure 12: Solubility in the ternary $CuSO_4$ - $CuCl_2$ – H_2O system at 25°C. The experimental data are from several sources. There is a good agreement between calculated and experimental values.

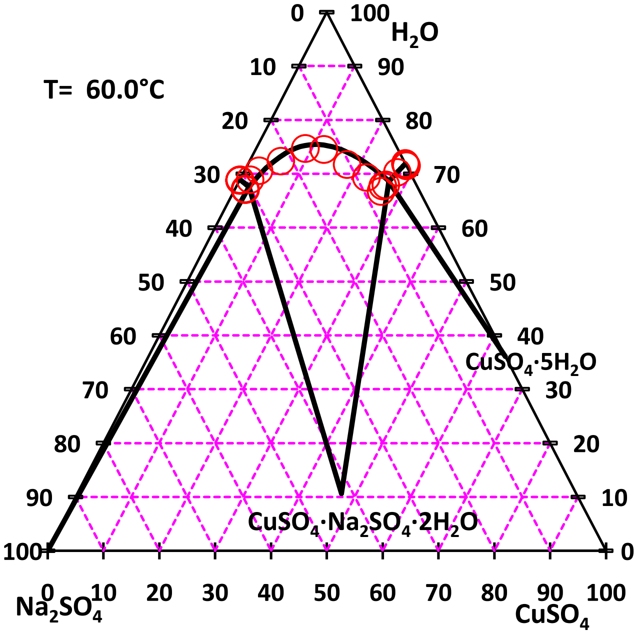


Figure 13: Solubility in the ternary $CuSO_4$ – Na_2SO_4 – H_2O system at 60°C. The double salt $CuSO_4·Na_2SO_4·2H_2O$ precipitates in a very large concentration range.

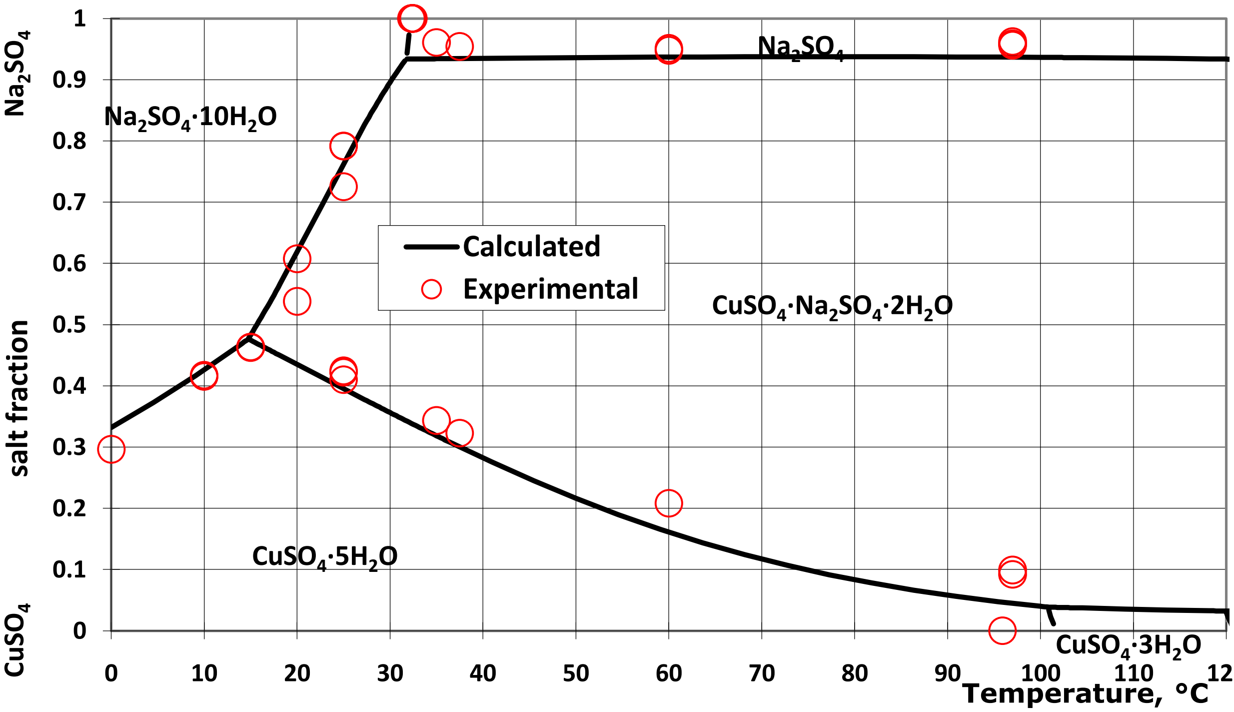


Figure 14: Phase diagram mapping the temperature and composition ranges of the various solids formed in this system. The double salt is taking up a significant part of the diagram. It is therefore difficult to avoid the double salt, especially at high temperatures.

The $CuSO_4$ - Na_2SO_4 – H_2O system

In the $CuSO_4$ - Na_2SO_4 – H2O system, the double salt $CuSO_4 \cdot Na_2SO_4 \cdot 2H_2O$ precipitates in a wide concentration range at temperatures above 15°C. The phase diagram at 60°C is shown in Figure 13. A phase diagram mapping the temperature and composition ranges of solid phases from the eutectic temperature to 120°C is shown in Figure 14. The double salt covers a wide concentration range and any separation in this system should take place at low temperature, where the double salt does not precipitate.

The $CuSO_4$ - K_2SO_4 – H_2O system

Also in the $CuSO_4$ - K_2SO_4 – H_2O system a double salt is forming. This double salt has the formula $CuSO_4 \cdot K_2SO_4 \cdot 2H_2O$. There are less data available for this system than for the corresponding sodium system. The double salt with potassium is less soluble than the double salt with sodium and it covers almost the whole temperature and concentration range from the freezing point of the solution to its boiling point.

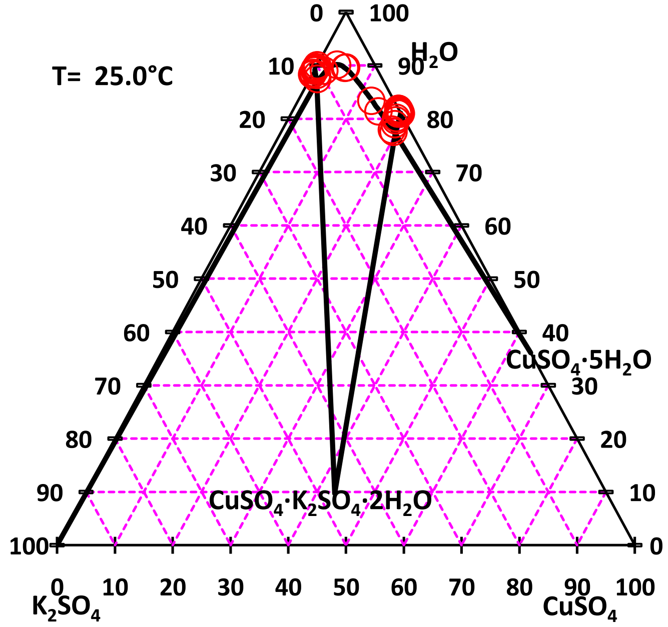


Figure 15: Solubility in the $CuSO_4$ - K_2SO_4 – H_2O system at 25°C. A double salt is precipitating at most concentrations in this system

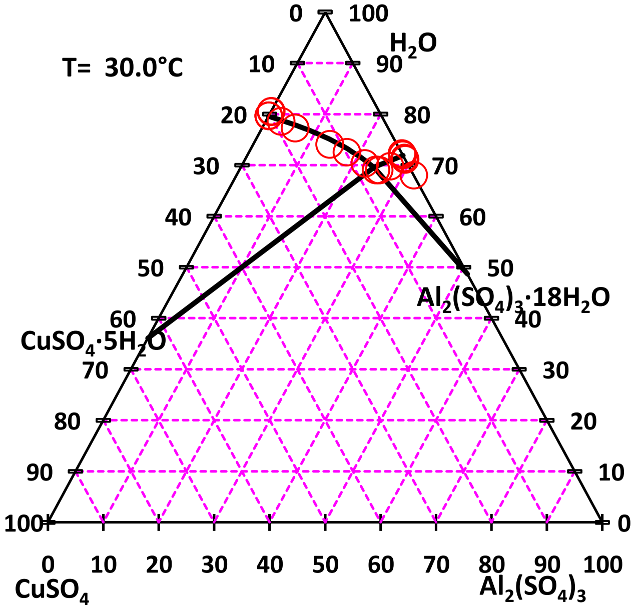


Figure 16: Solubility in the $CuSO_4$ – $Al_2(SO_4)_3$ – H_2O system at 30°C. No double salt is formed.

The $CuSO_4$ – $Al_2(SO_4)_3$ – H_2O system

Data for the ternary $CuSO_4$ – $Al_2(SO_4)_3$ – H_2O system were available at 25 (Occleshaw, 1925) and 30°C (Caven and Mitchell, 1925). The reason why two separate groups investigated this same system in 1925 was apparently of curiosity to see whether or not a double salt (alum) was forming in the aqueous copper (II) – aluminum – sulfate system. The corresponding iron (II) alum had just been identified in volcanic efflorescence in Iceland.

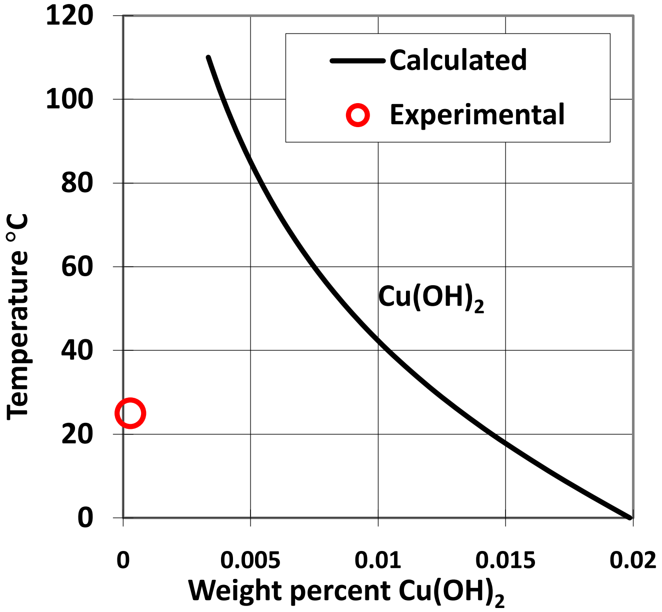


Figure 17: Calculated and experimental solubility of $Ca(OH)_2$. Only one experimental data point at 25°C is available.

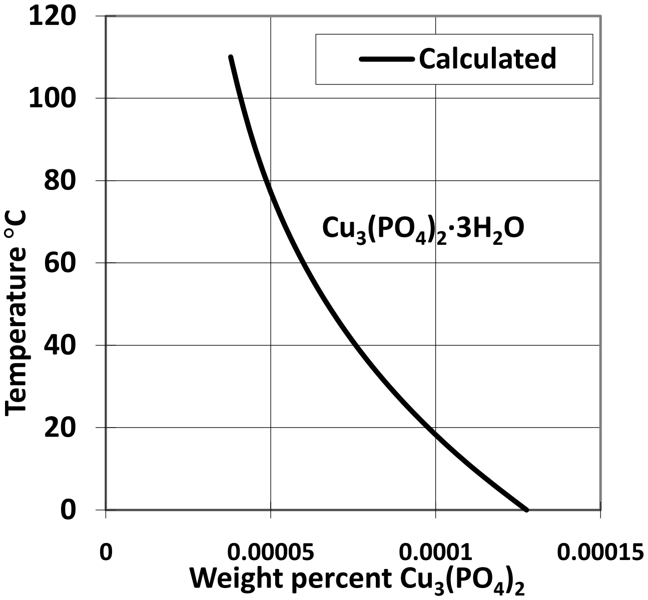


Figure 18: The solubility of tri copper phosphate tri hydrate.

Hydroxide systems

The solubility of $Cu(OH)_2$ is very low but increases slightly with increasing pH. Only data at 25°C were available and the tendency of increasing solubility could not be modeled due to lack of data. The calculated solubility diagram for $Cu(OH)_2$ is shown in Figure 17. The calculated solubility of $Cu(OH)_2$ is higher than the experimental value but reflects the larger solubility of $Cu(OH)_2$ at increased hydroxide concentration. If copper hydroxide is really as insoluble as this experimental point indicates, copper hydroxide should precipitate in all solutions of copper ions with pH higher than 8-9. This is not reported in the experimental data. According to the calculated solubility diagram, $Cu(OH)_2$ solubility decreases with increasing temperature. $Cu(OH)_2$ tends to decompose into CuO and H_2O according to McDowell and Johnston, 1936.

Carbonate systems

Copper forms two sparingly soluble carbonates: Azurite, $2CuCO_3 \cdot Cu(OH)_2$, and Malachite $CuCO_3 \cdot Cu(OH)_2$. These minerals are extremely sparingly soluble and the corresponding minerals are used as gemstones.

Phosphate systems

The solubility of copper phosphate is very low as shown in Figure 18. The only reported copper phosphate is the trihydrate, $Cu_3(PO_4)_2 \cdot 3H_2O$. There are only very few experimental data for the solubility of this salt. The very insoluble copper hydroxide, $Cu(OH)_2$ could be expected to precipitate from these solutions at the same time. But this is not reported in the experimental data. It is therefore concluded that copper hydroxide is more soluble than some sources claim.

There is also disagreement between different sources about the solubility of copper phosphate. The data for the solubility of $Cu_3(PO_4)_2$ in water reported by Druzhinin and Tusheva, 1966 indicate a much higher solubility than the one reported by Korf and Sugakevich, 1962.

Korf and Sugakevich studied the solubility isotherm of the CuO – P_2O_5 – H_2O system at 25°C in the concentration range from acidic solutions to more basic. The isotherm is shown in Figure 19 and Figure 20. The two figures are identical but in Figure 20 an enlargement of the acidic range of the phase diagram is shown. The experimental data in these figures are from Korf and Sugakevich except for the point marking the Cu(OH)2 solubility, which is from McDowell and Johnston, 1936.

Only a monohydrate of dicopper phosphate is reported, $CuHPO_4 \cdot H_2O$. Monocopper phosphate only precipitates as the anhydrous $Cu(H_2PO_4)_2$.

In systems with sodium ions, the double salt $Cu_3(PO_4)_2 \cdot Na_3PO_4$ and possibly others will form according to Druzhinin and Tusheva, 1966. The data they gave for the solubility of this salt do not match well with the solubility of the phosphates of copper used here. Therefore the phase diagram is not shown in this report.

There is clearly a need for new measurements of solubility in the cupric phosphate system. Only few data are available and half of them had to be discarded due to inconsistency with other data.

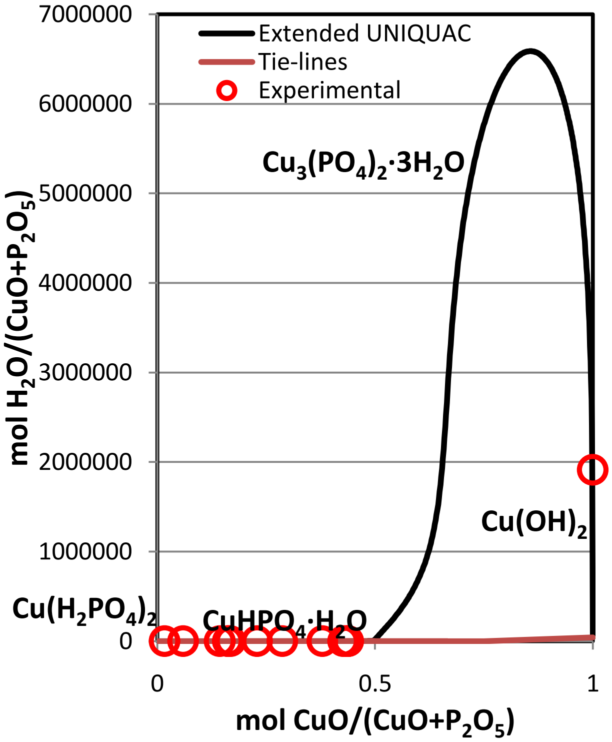


Figure 19: Solubility isotherm of the CuO – P_2O_5 – H_2O system at 25°C

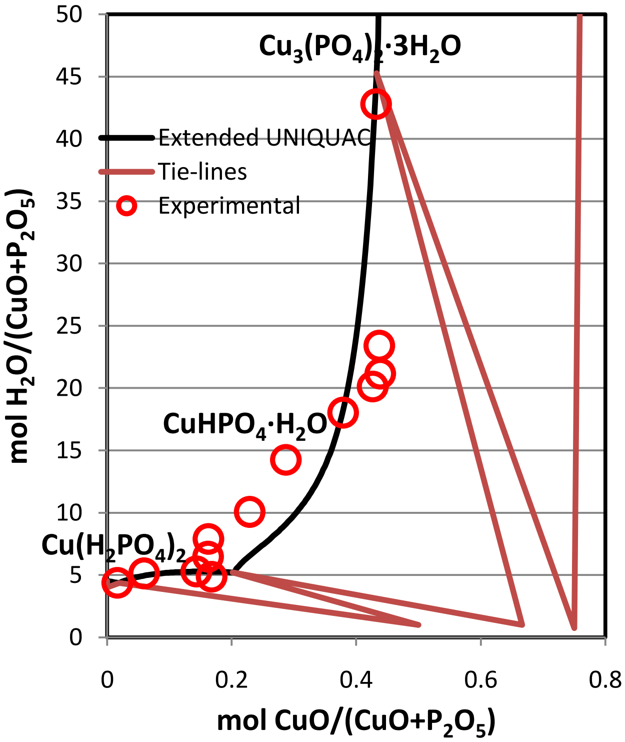


Figure 20: Solubility isotherm of the CuO – P_2O_5 – H_2O system at 25°C with focus on the monocopper and the dicopper phosphate concentrange range.

Modeling of systems with iron (III) ions (ferric ions)

Experimental data used for modeling iron (III) species

Table 3: Sources of experimental data used for determining model parameters for the Fe^{3+} ion.

Kangro, W. and Groeneveld, A., Konzentrierte wässrige Lösungen, I., Z. Phys. Chem. Neue Folge 32(1962)110-126	Osmotic coefficients of $FeCl_3$ at 20 and 25°C
Awakura, Y., Kawasaki, Y., Uno, A., Sato, K., Majima, H., Activities of water and hydrochloric acid in aqueous solution systems of hydrochloric acid-MCln including CuCl2, NiCl2 and FeCl3, Hydrometallurgy, 19(1987)137-57	Water activity for $FeCl_3 – HCl – H_2O$ mixtures
Blümcke, Ad., Ueber den Einfluss des Concentrationsgrades auf die specifische Wärme wässeriger und alkoholischer Lösungen von Metallchloriden, Annalen der Physik 23(1884)161-178	Specific heat of $FeCl_3$ solutions
Velázquez-Rivera, Mariano; Palmer, Donald A.; Kettler, Richard M., Isopiestic Measurement of the Osmotic Coefficients of Aqueous {xH2SO4 + (1- x) Fe2(SO4)3} Solutions at 298.15 and 323.15 K, Journal of Solution Chemistry, 35(2006)1699-1730(12)	Water activity of $Fe_2(SO_4)_3 – H_2SO_4$ solutions, 490 experimental data
Rumyantsev, Alexey V; Hagemann, Sven; Moog, Helge C, Isopiestic Investigation of the Systems Fe2(SO4)3-H2SO4-H2O, FeCl3-H2O, and Fe(III)(Na, K, Mg, Ca)Cl-H2O at 298.15K, Zeitschrift fur Physikalische Chemie, 218(2004)1089-1127 (9)	Osmotic coefficient for FeCl3 solutions, $FeCl_3 – NaCl$, $FeCl_3 – KCl$, $FeCl_3 – KCl$, $Fe_2(SO_4)_3 – H_2SO_4$ solutions. 450 experimental data.
Walther Kangro, Rudolf Flügge, Die Lösungswärmen von Eisen(III)chlorid in Wasser und in Salzsäurelösungen, Z. physikalische Chemie A, 175(1936)187-194	Specific heat and heat of dilution of $FeCl_3$ solutions
Malquori, G., I sistemi KCl-FeCl3-H2O e AlCl3-FeCl3-H2O fra 0° e 60°, Gazz. Chim. Ital., 58(1928)891-898	SLE data for the $KCl-FeCl_3-H_2O$ system and the $AlCl_3-FeCl_3-H_2O$ system from 0 to 60°C
Tananaev, I. V., Deichman, E. N., Physico-Chemical Analysis of systems of an analytical significance VI. Solubility at 25° in the system FeF3-HF-H2O, Zhur. Prikl. Khim., 19(1946)1018-28	SLE data for the $FeF_3 – HF –H_2O$ system at 25°C
Jones H.C., Getman F.H., Über das Vorhandensein von Hydraten in konzentrierten wässerigen Lösungen, Z. Phys. Chem., 49(1904)385-455	Freezing point depression of $FeCl_3$ solutions
Schäfer, H., Untersuchungen am System Fe2O3-FeCl3-H2O-HCl. IV. das Vierphasen-System FeOCl, FeCl3fest, (FeCl3 nH2O)flüss., Gas, Z. Anorg. Chem.,	Solubility of $FeCl_3$ in water

260(1949)127-140	
Roozeboom, H. W. B., Die Löslichkeitskurve für Salzpaare, welche sowohl Doppelsaltz als Mischkrystalle bilden, speziell für Salmiak mit Eisenchlorid, Z. Physik. Chem., 10(1892)145-164	Solubility of $FeCl_3$ in water
Cameron, F. K., Bell, J. M., The phosphates of magnesium and iron, J. Phys. Chem., 11(1907)363-368	Solubility in the $Fe_2O_3 – H_3PO_4 – H_2O$ system at 25°C
Carter, S. R., Hartshorne, N. H., The System ferric Oxide-Phosphoric acid-Water. A New Phosphate, J. Chem. Soc., 123(1923)2223-2233	Solubility in the $Fe_2O_3 – H_3PO_4 – H_2O$ system at 25 and 70°C
Applebey, M. P., Wilkes, S. H., The system Ferric Oxide-Sulphuric Acid-Water, J. Chem. Soc., 121(1922)337-348	Solubility in the $Fe_2O_3 – H_2SO_4 – H_2O$ system at 18 and 25°C
Wirth, F., Bakke, B., Über die gegenseitige Löslichkeitsbeeinflussung von Ferrisulfat und Aluminiumsulfat, Z. Anorg. Chem., 87(1914)47-51	Solubility in the $Fe_2(SO_4)_3 – Al_2(SO_4)_3 – H_2O$ system at 25°C
Cameron, F. K., Ferric sulfate in aqueous solutions of other sulfates, J. Phys. Chem., 40(1936)689-696	Solubility in the $Fe_2(SO_4)_3 – K_2SO_4 – H_2O$ system at 25°C
Roozeboom, H. W. B., Die Hydrate des Eisenchlorids, Z. physik. Chem., 10(1892)477-503	Solubility in the $FeCl_3 – H_2O$ system
N.S. Kurnakov, E.A. Nikitina, The Ice-Field in the Ssystem FeCl3 - HCl - H2O, Izv. Akad. Nauk SSSR, Ser. Khim., 2(1938)433-436	Freezing point depression in the $FeCl_3 – HCl - H_2O$ system
Linke, W. F., Ferric Chloride decahydrate; the systems FeCl3-H2O and FeCl3-HCl-H2O below 0C, J. Phys. Chem., 60(1956)91-96	Solubility in the $FeCl_3 – H_2O$ system
Malquori, G., Il sistema: AlCl3-FeCl3-KCl-H2O a 25°, Gazz. Chim. Ital., 59(1929)556-63	Solubility in the $AlCl_3$-$FeCl_3$-KCl-H_2O system at 25°C
Baskerville, W. H., Cameron, F. K., Ferric oxide and Aqueous sulfuric Acid at 25 C, J. Phys. Chem., 39(1935)769-779	Solubility in the $Fe_2O_3 – H_2SO_4 – H_2O$ system at 25°C
Belov, I. A., Rud'ko, P.K., Novikov, G. I., Solubility in the iron(III) chloride-hydrochloric acid-water system at 298.15 K, Khim. Khim. Tekhnol. (Minsk), 4(1990)3-6	Solubility in the $FeCl_3 – HCl - H_2O$ system at 25°C
Holldorf, H., Schwingeweitzen, G., Untersuchungen zum System FeCl3-HCl-H2O (Studies on the iron(III) chloride-hydrochloric acid-water system.), Freiberg Forschungsh. A, 671(1983)56-64	Solubility in the $FeCl_3 – HCl - H_2O$ system from 40 to 85°C
Holldorf, H., Rumler, E., Wahl, G., Isothermal aluminium chloride hexahydrate (AlCl3·6H2O) saturation lines of the aluminium chloride-iron(II) chloride, Freiberg. Forschungsh. A, 671(1983)65-83	Solubility in the $FeCl_3 – AlCl_3 - H_2O$ system from 40 to 85°C
Novikov, S. G., Rud'ko, P. K., Belov, I. A., Saskovets, V. V., Malyshev, A. A., Solubility of iron(II) and iron(III) sulfates in aqueous sulfuric acid solutions, Vesti Akad.	Solubility in the $Fe_2O_3 – H_2SO_4 – H_2O$ system at 60 and 75°C

Navuk BSSR, Ser. Khim. Navuk, (1989)43-6(5)	
Wirth, F., Die Löslichkeit des Aluminium- und Eisensulfats in Schwefelsäure, Z. Anorg. Chem., 79(1913)360-364	Solubility in the Fe_2O_3 – H_2SO_4 – H_2O system at 25°C
G.G. Babayan, R.C. Mnitaryan, G.C. Panosyan, A.A. Shahnazaryan, Phase Equilibria in the systems Fe2(SO4)3-CuSO4-H2O and Fe2(SO4)3-CuSO4-H2SO4-H2O (25°C), Arm. Khim. Zh., 26(1973)283-7	Solubility in the $Fe_2(SO_4)_3$ – $CuSO_4$ – H_2O system at 25°C
E.C.J. Mohr, Gleichgewichtsstudien über das System: Wasser, Salmiak, Eisenchlorid, Z. physik. Chemie, 27(1898)197	Solubility in the $FeCl_3$ – H_2O system
A. Atbir, S. Mancour-Billah, M. El Hadek, Solid-liquid equilibria in the quaternary system K+, Fe2+, Fe3+/Cl_-H2O at 288.15 K, Fluid Phase Equilibria, 215(2004)97-103	Solubility in the $FeCl_3$ – KCl – H_2O system at 25°C
Litvinenko, V. I.; Gorinskaya, V. S.; Isabekova, K. U., Solubility of aluminum and iron sulfates and phosphates in a mixture of acetic, phosphoric, and sulfuric acids, Trudy Instituta Khimicheskikh Nauk, Akademiya Nauk Kazakhskoi SSR, 38(1974)60-65	Solubility in the $FePO_4$ – H_2SO_4 – H_2O system at 20 and 80°C
Hinrichsen FW; Sachsel E, Über die Bildungs- und Löslickeitsverhältnisse der Doppelchloride des Eisens und der Alkalimetalle, Z. physikalische Chemie, 50(1905)81-99	Solubility in the $FeCl_3$ – NaCl – H_2O and the $FeCl_3$ – KCl – H_2O systems at 21°C
Atbir, A.; Boukbir, L.; El Hadek, M.; Cohen-Adad, R., Etude du Diagramme Polythermique du Système Ternaire NaCl-FeCl3-H2O de 5 à 50°C, Journal of Thermal Analysis and Calorimetry, 62(2000)203-209	Solubility in the $FeCl_3$ – NaCl – H_2O system at 5-50°C
F. K. Cameron, W. O. Robinson, Ferric Chlorides, The Journal of Physical Chemistry, 11(1907)690-694(9)	Solubility in the $FeCl_3$ – H_2O system
E. Posnjak, H. E. Merwin, The System, Fe2O3—SO3—H2O, J. Am. Chem. Soc., 44(1922)1965-1994	Solubility in the Fe_2O_3 – H_2SO_4 – H_2O system from 50 to 140°C
Jameson, R. F.; Salmon, J. E. Complexes involving trivalent iron and orthophosphoric acid. III. The system ferric oxide-phosphoric oxide-water at 25°C, J. Chem. Soc.(1954)28-34	Solubility in the Fe_2O_3 – H_3PO_4 – H_2O system 25°C
Alva W. Frazier, The phase system iron(III) oxide-ammonium oxide-phosphorus pentoxide-water at 75°C, Ind. Eng. Chem. Res., 31(1992)210-213 (1)	Solubility in the Fe_2O_3 – H_3PO_4 – H_2O system 75°C
Tananaev IV; Deichman EN, Physicochemical analysis of systems of analytical significance. V. The system FeF3-KF-H2O, Izvestiia Akademii nauk SSSR. Seriija khimicheskaia, (1946)373-380	Solubility in the FeF_3 – KF – H_2O system 25°C

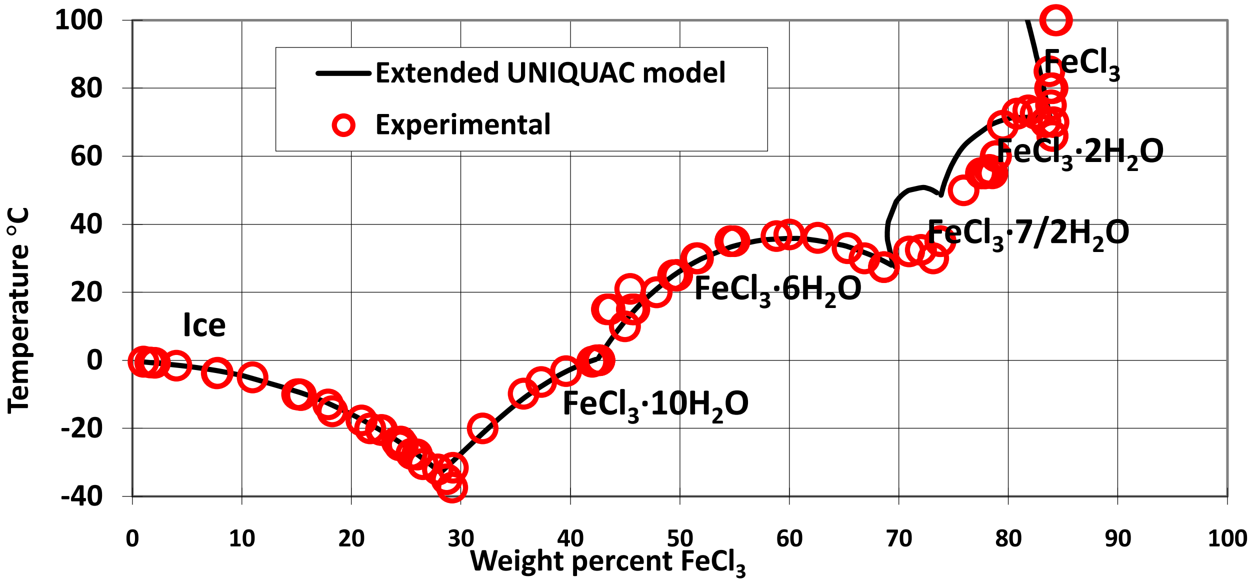


Figure 21: The solubility of $FeCl_3$ in water. At temperatures between 30 and 70°C, $FeCl_3$ can be saturated at three different concentrations at each temperature.

Results

Systems with chloride

The solubility of $FeCl_3$ is very high at all temperatures. At the same time, $FeCl_3$ has the special solubility behavior of having three different solubility values at each temperature at temperatures between 30 and 70°C. As mentioned in the introduction, it is claimed in the literature that iron (III) has a tendency to form several different complexes with chloride. Including these complex species did not improve the modeling of the system. It was therefore decided to not include these complexes. Calculated and experimental values of the solubility of $FeCl_3$ in water are seen in Figure 21. The hydrates formed are $FeCl_3\cdot10H_2O$, $FeCl_3\cdot6H_2O$, $FeCl_3\cdot7/2H_2O$, $FeCl_3\cdot5/2H_2O$ and $FeCl_3\cdot2H_2O$. At concentrations above 85 wt %, iron (III) chloride precipitates as anhydrous $FeCl_3$. The phase $FeCl_3\cdot5/2H_2O$ does unfortunately not appear in the calculated phase diagram, Figure 21. The modeling of this system was very difficult due to the many hydrates. Conflicts between experimental data from different sources make it impossible to reproduce all the data with the same set of parameters.

Calculated and experimental values of osmotic coefficients for $FeCl_3$ solutions are displayed in the parity diagram in Figure 22. Ideally, the data would be on the diagonal if there was total agreement between calculated and experimental values. The result is good even though there are some differences. The osmotic coefficient is a measure for the water activity of a solution. The corresponding diagram for water activities in $FeCl_3$ – HCl – H_2O solutions are shown in Figure 23. The agreement here is apparently better. In reality, the agreement between calculated water activities is identical in the two systems. The difference is that the osmotic coefficient is more sensitive to differences in water activity and therefore appears to be deviating more.

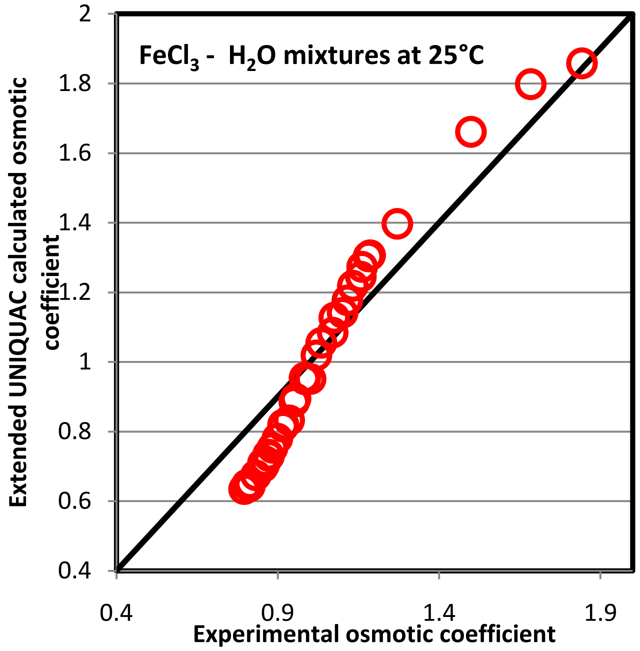


Figure 22: Experimental and calculated osmotic coefficient of FeCl$_3$ solutions at 25°C

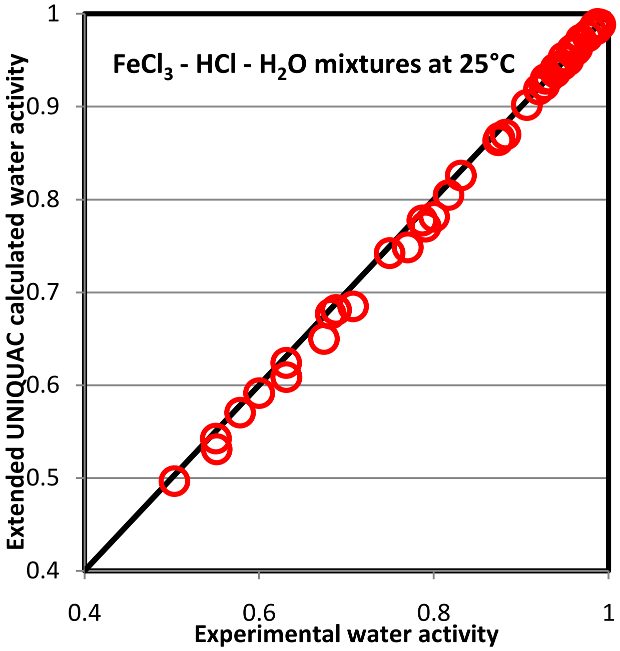


Figure 23: Experimental and calculated water activity in FeCl$_3$-HCl-H$_2$O solutions at 25°C

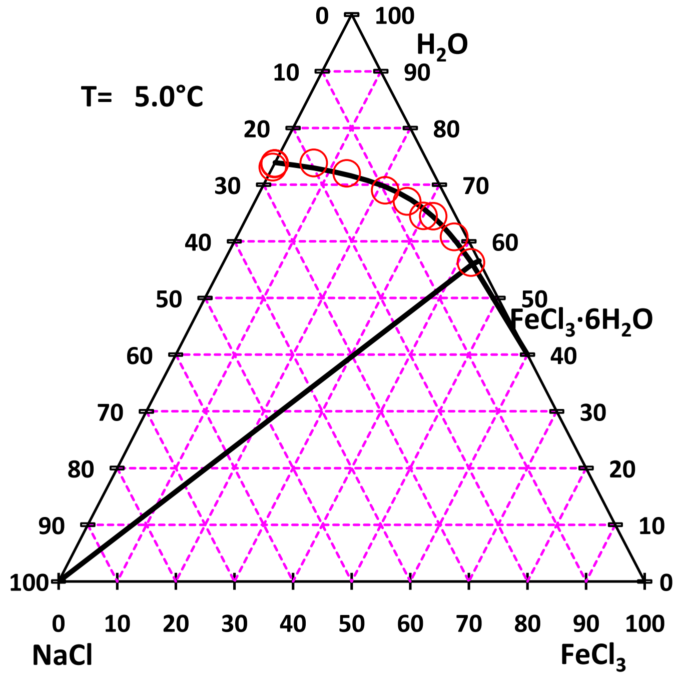


Figure 24: Solubility in the FeCl$_3$ – NaCl - H$_2$O system at 5°C

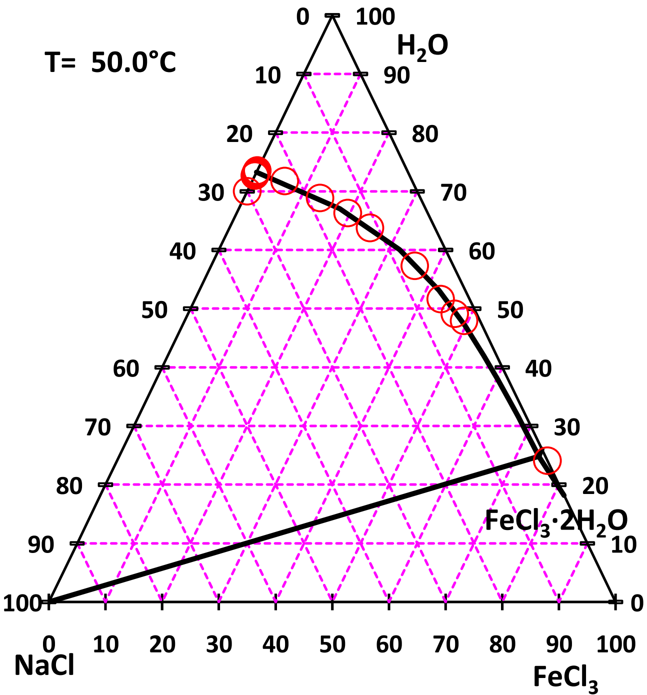


Figure 25: Solubility in the FeCl$_3$ – NaCl - H$_2$O system at 50°C

The FeCl$_3$ – NaCl – H$_2$O system

The FeCl$_3$ – NaCl – H$_2$O system was examined by Hinrichsen and Sachsel at 21°C in 1905 and by Atbir *et al.* at 5 to 50°C in 2000. While Hinrichsen and Sachsel determined that solid solutions were

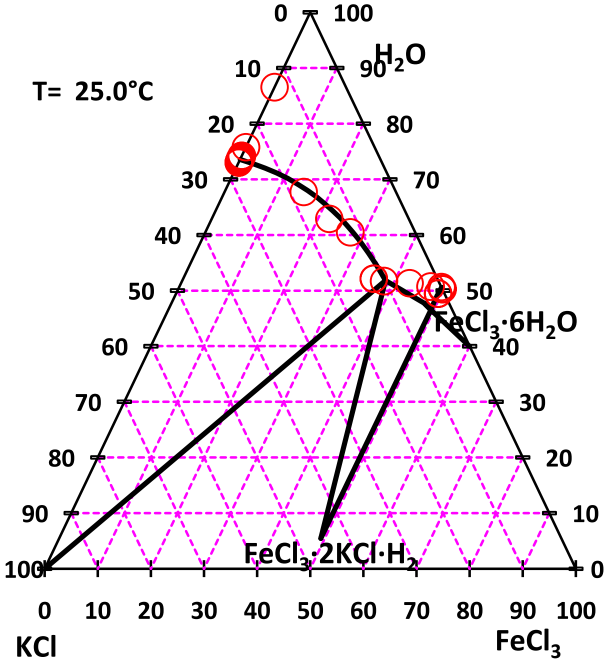


Figure 26: Solubility in the $FeCl_3$-KCl-H_2O system at 25°C. The double salt $FeCl_3·2KCl·H_2O$ is precipitating at all temperatures in which the system was investigated.

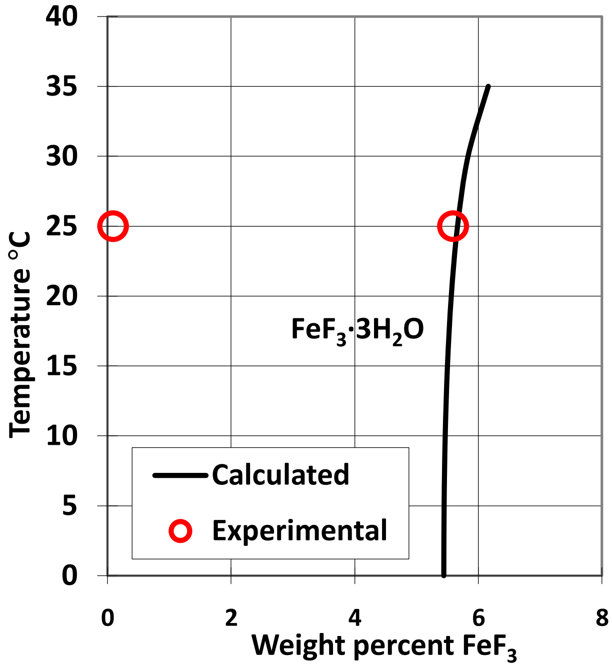


Figure 27: Solubility of FeF3. Only two points are available at 25°C and they have very different values.

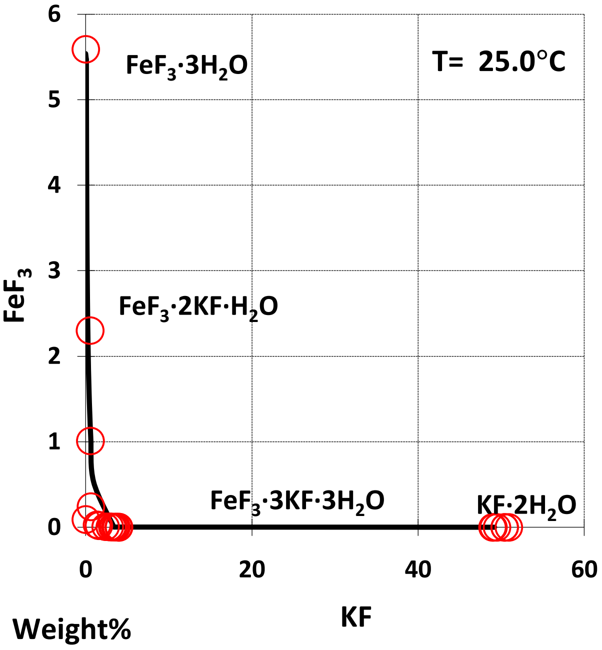
precipitating in the whole composition range, Atbir *et al.* found the system to be a simple eutonic system with two solubility branches. The phase diagram at 5°C is shown in Figure 24 and the diagram at 50°C is shown in Figure 25 together with experimental data. There seems to be no indication of a solid solution in this system.

The $FeCl_3$ – KCl – H_2O system

Hinrichsen and Sachsel also found solid solutions in the $FeCl_3$ – KCl – H_2O system in 1905. The system has later been investigated by Malquori in 1928 and 1929, by Cameron in 1936, and by Atbir *et al.* in 2004. None of these investigators found solid solutions, only pure, solid salt phases precipitate. The phase diagram for this system at 25°C is shown in Figure 26. The double salt $FeCl_3·2KCl·H_2O$ was found to precipitate in the temperature range from 0 to 60°C, in which the system was investigated.

The $FeCl_3$ – $AlCl_3$ – H_2O system

The $FeCl_3$ – $AlCl_3$ – H_2O system was examined at several different temperatures by different researchers. The system is a simple eutonic system. No double salt is forming. The solubility is high in this system, and the experimental data are reproduced well by the model.



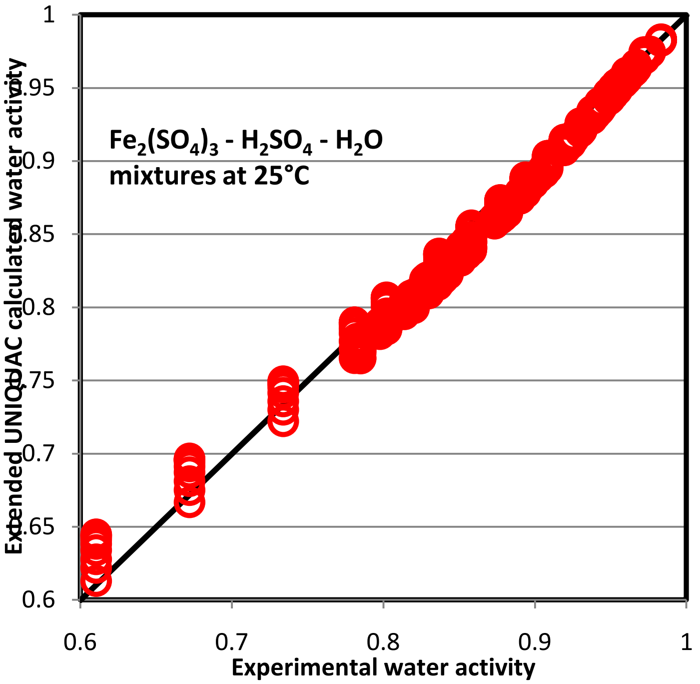


Figure 28: Solubility in the FeF_3 – KF – H_2O system at 25°C. Two sparingly soluble double salts are formed.

Figure 29: Measured water activity in $Fe_2(SO_4)_3$-H_2SO_4-H_2O mixtures at 25°C compared with calculated values. 750 experimental data are displayed in the figure.

Systems with fluoride

According to Carter[7](1928), the solubility of FeF_3 is 0.091 gram per 100 cm^3 water at 25°C. According to Tananaev and Deichman, 1946 (Table 3), the solubility of FeF3 is much higher, 5.59 wt% in pure water. It is the low solubility value given by Carter that apparently is accepted and believed by many. This value is for example used in MSDS (Materials Safety Data Sheets). But this number seems to be in conflict with all other experimental data available. The newest measurements were made by Österdahl and Rasmuson at KTH in Sweden[8]. They did not report their own solubility data, but seem to support the results of Tananaev and Deichman. The solubility of FeF_3 was only given at 25°C and it is not possible to predict the solubility at other temperatures. The model reproduces the solubility value of 5.59 wt % at 25°C. The solid phase precipitating at all temperatures is assumed to be the same as at 25°C, $FeF_3\cdot 3H_2O$. The phase diagram is shown in Figure 27.

The FeF_3 – KF – H_2O system

Two double salts with very low solubility form in the FeF_3 – KF –H_2O system, $2KF\cdot FeF_3\cdot H_2O$ and $3KF\cdot FeF_3\cdot 3H_2O$. Especially the second of these salts are very insoluble. Unfortunately, only data at 25°C are available for these double salts. It is therefore impossible to predict if the solubilities of these

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[7] Carter RH, Solubilities of some inorganic fluorides in water at 25°C, Ind. Eng. Chem., 20(1928)1195

[8] Österdahl, Kerstin M.; Rasmuson, Åke C., Solubility of ß-FeF3·3H2O in Mixtures of Nitric and Hydrofluoric Acid, Journal of Chemical & Engineering Data, 51(2006)223-229

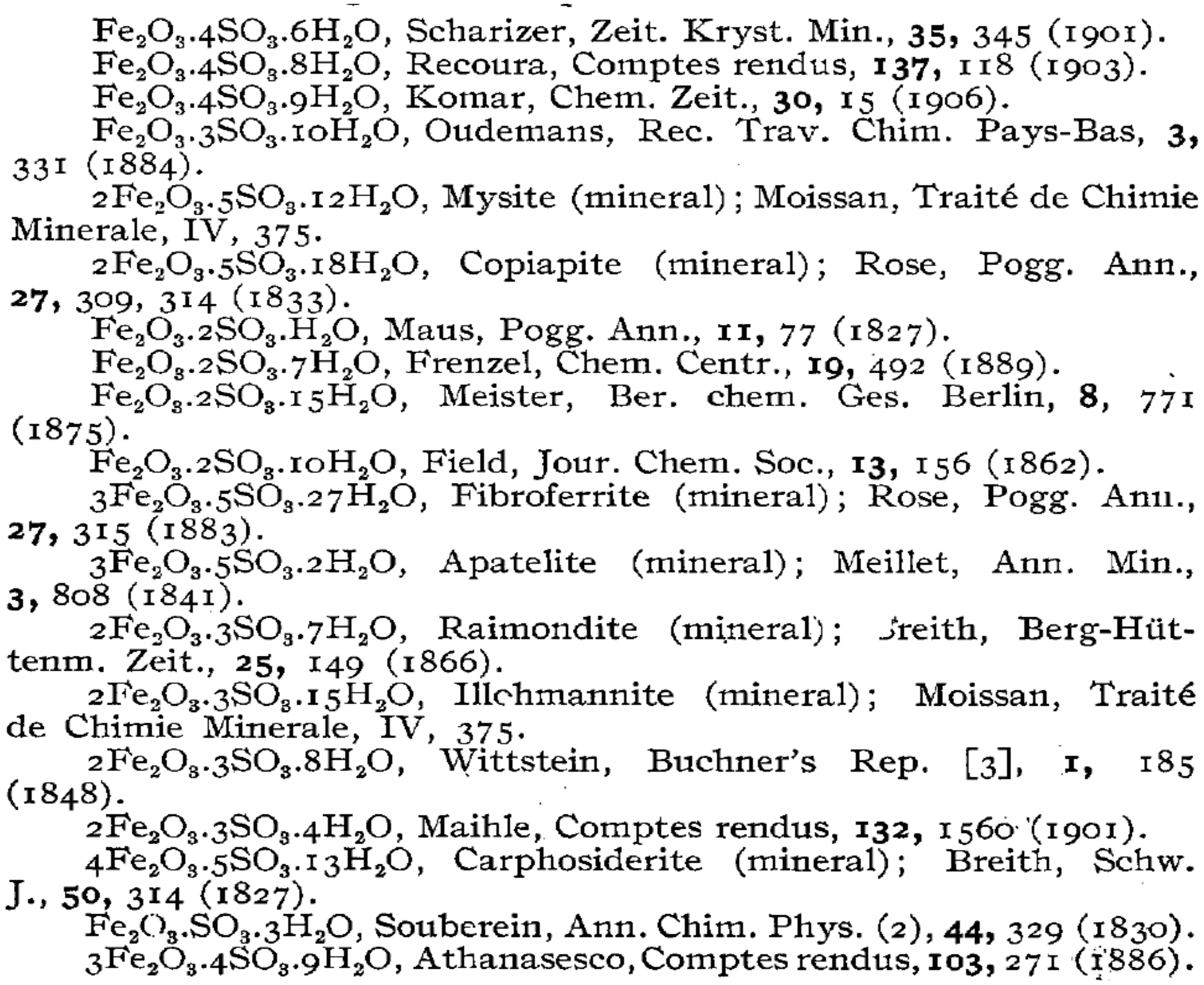
salts increase or decrease with temperature. The phase diagram for the FeF_3 – KF –H_2O system is shown in Figure 28.

The FeF_3 – HF – H_2O system

The double salt $FeF_3{\cdot}3HF{\cdot}3H_2O$ forms in solutions with very high concentration of HF. The double salt is very soluble.

Systems with sulfate

As mentioned in the introduction, Cameron and Robertson[5] mentioned 30 different ferric sulfates reported by previous investigators. The list is given in Figure 30 and Figure 31. Aqueous solutions of $Fe_2(SO_4)_3$ are obviously very difficult to analyze. One reason can be the formation of the very insoluble ferric hydroxide, $Fe(OH)_3$ or its anhydrous form, Fe_2O_3. Many solubility experiments were performed in sulfuric acid in order to avoid the formation of ferric hydroxide. The ferric sulfate salts formed in basic solutions must be characterized as solid solutions rather than pure salts.



$Fe_2O_3.4SO_3.6H_2O$, Scharizer, Zeit. Kryst. Min., **35**, 345 (1901).

$Fe_2O_3.4SO_3.8H_2O$, Recoura, Comptes rendus, **137**, 118 (1903).

$Fe_2O_3.4SO_3.9H_2O$, Komar, Chem. Zeit., **30**, 15 (1906).

$Fe_2O_3.3SO_3.10H_2O$, Oudemans, Rec. Trav. Chim. Pays-Bas, **3**, 331 (1884).

$2Fe_2O_3.5SO_3.12H_2O$, Mysite (mineral); Moissan, Traité de Chimie Minerale, IV, 375.

$2Fe_2O_3.5SO_3.18H_2O$, Copiapite (mineral); Rose, Pogg. Ann., **27**, 309, 314 (1833).

$Fe_2O_3.2SO_3.H_2O$, Maus, Pogg. Ann., **11**, 77 (1827).

$Fe_2O_3.2SO_3.7H_2O$, Frenzel, Chem. Centr., **19**, 492 (1889).

$Fe_2O_3.2SO_3.15H_2O$, Meister, Ber. chem. Ges. Berlin, **8**, 771 (1875).

$Fe_2O_3.2SO_3.10H_2O$, Field, Jour. Chem. Soc., **13**, 156 (1862).

$3Fe_2O_3.5SO_3.27H_2O$, Fibroferrite (mineral); Rose, Pogg. Ann., **27**, 315 (1883).

$3Fe_2O_3.5SO_3.2H_2O$, Apatelite (mineral); Meillet, Ann. Min., **3**, 808 (1841).

$2Fe_2O_3.3SO_3.7H_2O$, Raimondite (mineral); Breith, Berg-Hüttenm. Zeit., **25**, 149 (1866).

$2Fe_2O_3.3SO_3.15H_2O$, Illchmannite (mineral); Moissan, Traité de Chimie Minerale, IV, 375.

$2Fe_2O_3.3SO_3.8H_2O$, Wittstein, Buchner's Rep. [3], **1**, 185 (1848).

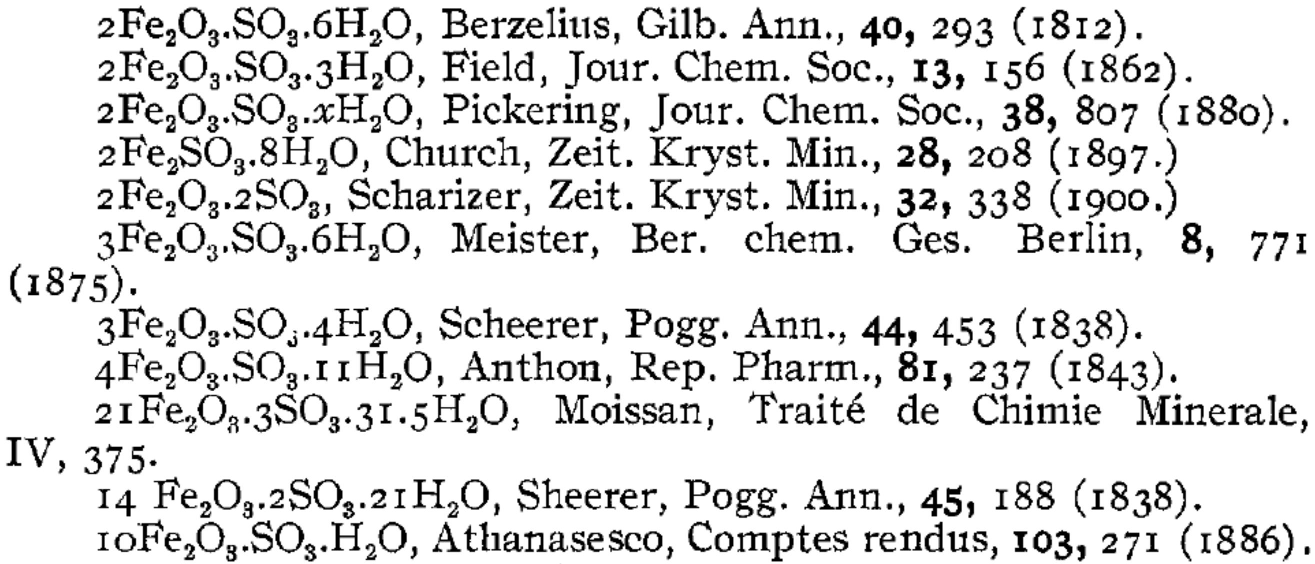
$2Fe_2O_3.3SO_3.4H_2O$, Maihle, Comptes rendus, **132**, 1560 (1901).

$4Fe_2O_3.5SO_3.13H_2O$, Carphosiderite (mineral); Breith, Schw. J., **50**, 314 (1827).

$Fe_2O_3.SO_3.3H_2O$, Souberein, Ann. Chim. Phys. (2), **44**, 329 (1830).

$3Fe_2O_3.4SO_3.9H_2O$, Athanasesco, Comptes rendus, **103**, 271 (1886).

Figure 30: List of ferric sulfates reported in literature. Continued on next page



$2Fe_2O_3.SO_3.6H_2O$, Berzelius, Gilb. Ann., **40,** 293 (1812).
$2Fe_2O_3.SO_3.3H_2O$, Field, Jour. Chem. Soc., **13,** 156 (1862).
$2Fe_2O_3.SO_3.xH_2O$, Pickering, Jour. Chem. Soc., **38,** 807 (1880).
$2Fe_2SO_3.8H_2O$, Church, Zeit. Kryst. Min., **28,** 208 (1897.)
$2Fe_2O_3.2SO_3$, Scharizer, Zeit. Kryst. Min., **32,** 338 (1900.)
$3Fe_2O_3.SO_3.6H_2O$, Meister, Ber. chem. Ges. Berlin, **8,** 771 (1875).
$3Fe_2O_3.SO_3.4H_2O$, Scheerer, Pogg. Ann., **44,** 453 (1838).
$4Fe_2O_3.SO_3.11H_2O$, Anthon, Rep. Pharm., **81,** 237 (1843).
$21Fe_2O_3.3SO_3.31.5H_2O$, Moissan, Traité de Chimie Minerale, IV, 375.
$14\ Fe_2O_3.2SO_3.21H_2O$, Sheerer, Pogg. Ann., **45,** 188 (1838).
$10Fe_2O_3.SO_3.H_2O$, Athanasesco, Comptes rendus, **103,** 271 (1886).

Figure 31: Continued list of ferric sulfates reported in literature.

When measuring water activity in solutions of ferric sulfate, ferric hydroxide also tends to precipitate. A large number of water activities for sulfuric acid – ferric sulfate – water solutions were available. The about 750 experimental data are plotted in a parity plot in Figure 29. The plot shows a very good agreement between experimental and calculated values of water activity.

Experimental data for solubility in the $Fe_2(SO_4)_3$ – H_2SO_4 – H_2O system at 60°C are plotted in Figure 32. A very good agreement between experimental and calculated values is observed. The

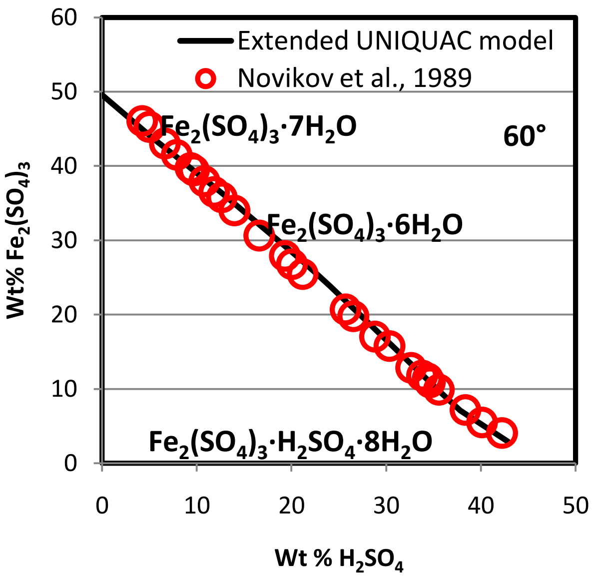


Figure 32: Solubility in the $Fe_2(SO_4)_3$ – H_2SO_4 – H_2O system at 60°C

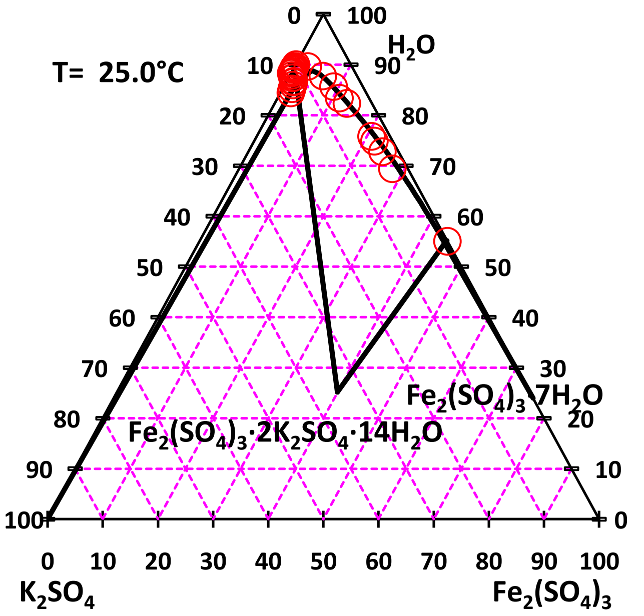


Figure 33: Solubility isotherm at 25°C in the $Fe_2(SO_4)_3$ – K_2SO_4 – H_2O system at 25°C. The double salt $Fe_2(SO_4)_3·2K_2SO_4·14H_2O$ forms.

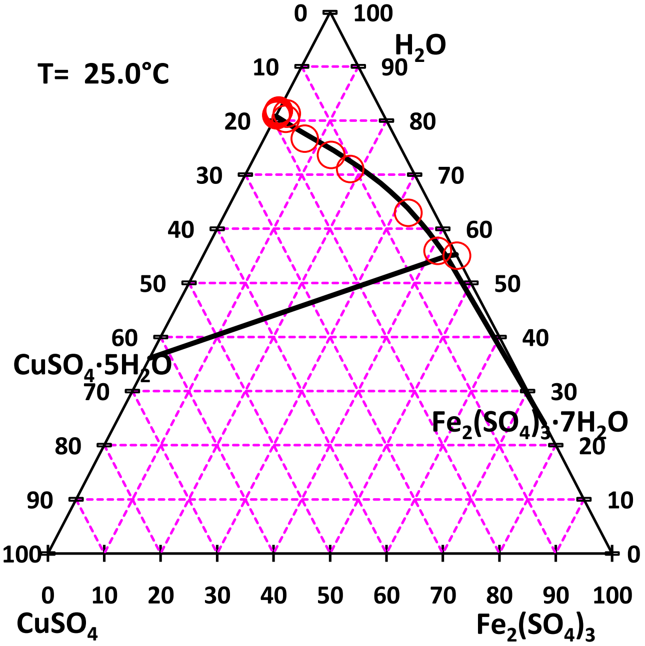


Figure 34: Solubility in the $Fe_2(SO_4)_3 – CuSO_4 – H_2O$ system at 25°C

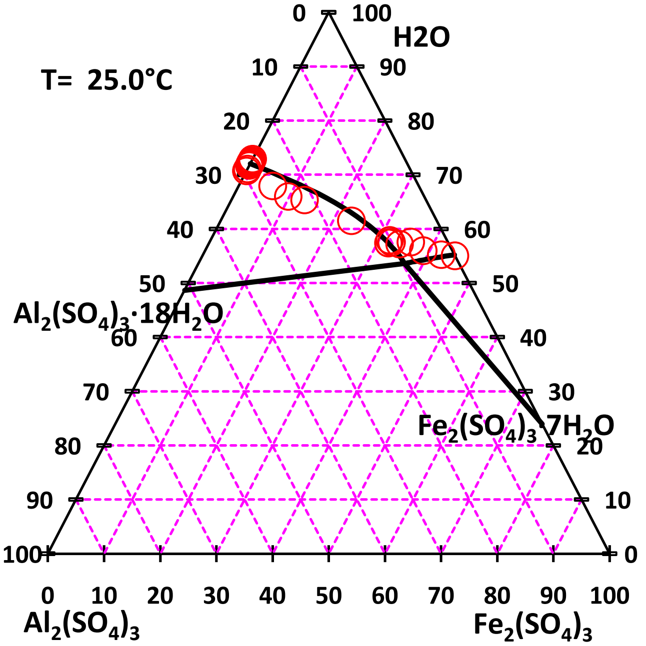


Figure 35: Solubility in the $Fe_2(SO_4)_3 – Al_2(SO_4)_3 – H_2O$ system at 25°C

heptahydrate of ferric sulfate is forming at sulfuric acid concentrations below 12.6%. The hexahydrate are formed at sulfuric acid concentrations up to 34.4%. At higher sulfuric acid concentrations, the double salt $Fe_2(SO_4)_3·H_2SO_4·8H_2O$ is forming.

The $Fe_2(SO_4)_3 – K_2SO_4 – H_2O$ system

Experimental data for one solubility isotherm in the $Fe_2(SO_4)_3 – K_2SO_4 – H_2O$ system was reported in literature. It is the 25°C isotherm. At this temperature, a double salt of relatively low solubility forms in this system. This is the salt $Fe_2(SO_4)_3·2K_2SO_4·14H_2O$. The phase diagram for this system is shown in Figure 33. If data were available at more temperatures, it would be possible to model the temperature dependency of the solubility of this salt. In order to determine a “reasonable” temperature dependency for the solubility of this salt, it was assumed that the salt has the same solubility at 55°C as it has at 25°C.

The $Fe_2(SO_4)_3 – CuSO_4 – H_2O$ system

The 25°C isotherm for the $Fe_2(SO_4)_3 – CuSO_4 – H_2O$ system was measured by Babayan *et al.* in 1973. At this temperature the system is a simple eutonic system as shown in Figure 34. The model reproduces the data well at this temperature. Experimental data were not available at other temperatures in this system.

The $Fe_2(SO_4)_3 – Al_2(SO_4)_3 – H_2O$ system

The 25°C isotherm for the $Fe_2(SO_4)_3 – Al_2(SO_4)_3 – H_2O$ system was measured by Wirth and Bakke in 1914. At this temperature the system is a simple eutonic system as shown in Figure 35. Also this system is well reproduced by the model. No data were found at other temperatures for this system.

Carbonate systems

There is no evidence in literature that Iron (III) carbonate, $Fe_2(CO_3)_3$ exists as a separate compound. This might be due to the very low solubility of ferric hydroxide, $Fe(OH)_3/Fe_2O_3$.

Phosphate systems

The solubility of $FePO_4$ is extremely low. The stable solid phase is FePO4·2½H2O. The solubility of this salt has been investigated by several researchers by bringing it in contact with phosphoric acid and measuring its solubility in phosphoric acid solutions of varying strength. Ferric phosphate has been found to precipitate as $Fe(H_2PO_4)_3$, $Fe(H_2PO_4)_3{\cdot}2H_2O$, $Fe_2(HPO_4)_3{\cdot}H_3PO_4{\cdot}5H_2O$, and as FePO4·2½H2O. The solubility of FePO4·2½H2O is so low that it will precipitate at pH values as low as 1.5. The phase diagram for the $Fe_2O_3 – P_2O_5 – H_2O$ system is shown in Figure 37. It can be seen that it is difficult to avoid the precipitation of FePO4·2½H2O, it precipitates in almost the whole pH range.

The solubility behavior in this system is very unusual because of the low solubility of FePO4·2½H2O. In Figure 37 experimental data can be seen in the lower left corner at high H_3PO_4 concentrations. This corner of the phase diagram is enlarged in Figure 38. From Figure 38 it can be seen that there are two solubility values at each $Fe_2O_3/(Fe_2O_3+P_2O_5)$ molar ratios. In the dilute region FePO4·2½H2O precipitates while the more acidic salts precipitate in the more concentrated region.

Figure 38 also indicates that the solubility of the acidic salts is not well reproduced by the model. This problem might be related to this very complicated solubility behavior. All the experimental points

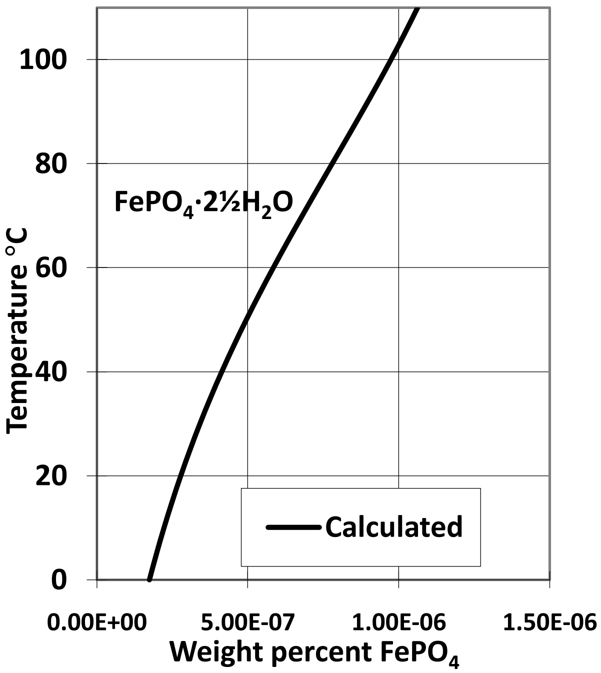


Figure 36: The solubility of $FePO_4$ is very low.

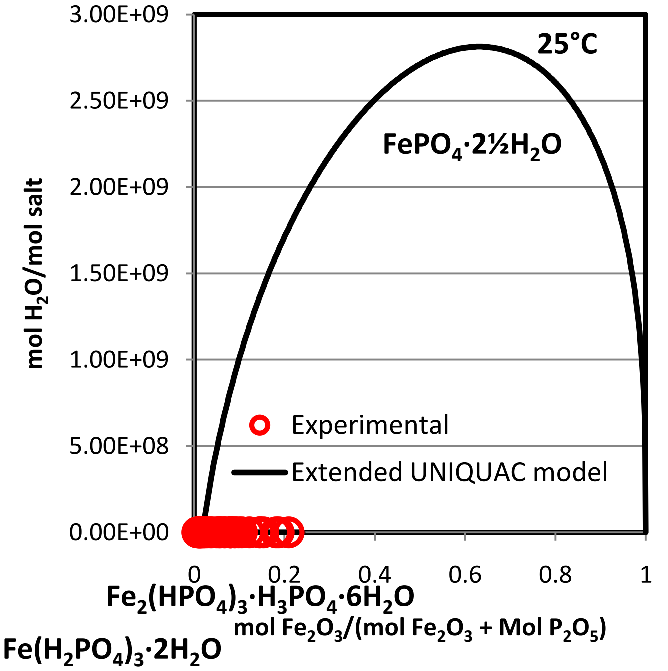


Figure 37: Solubility isotherm for the $Fe_2O_3 – P_2O_5 – H_2O$ system at 25°C. The very insoluble $FePO_4$·2½H2O covers most of the phase diagram.

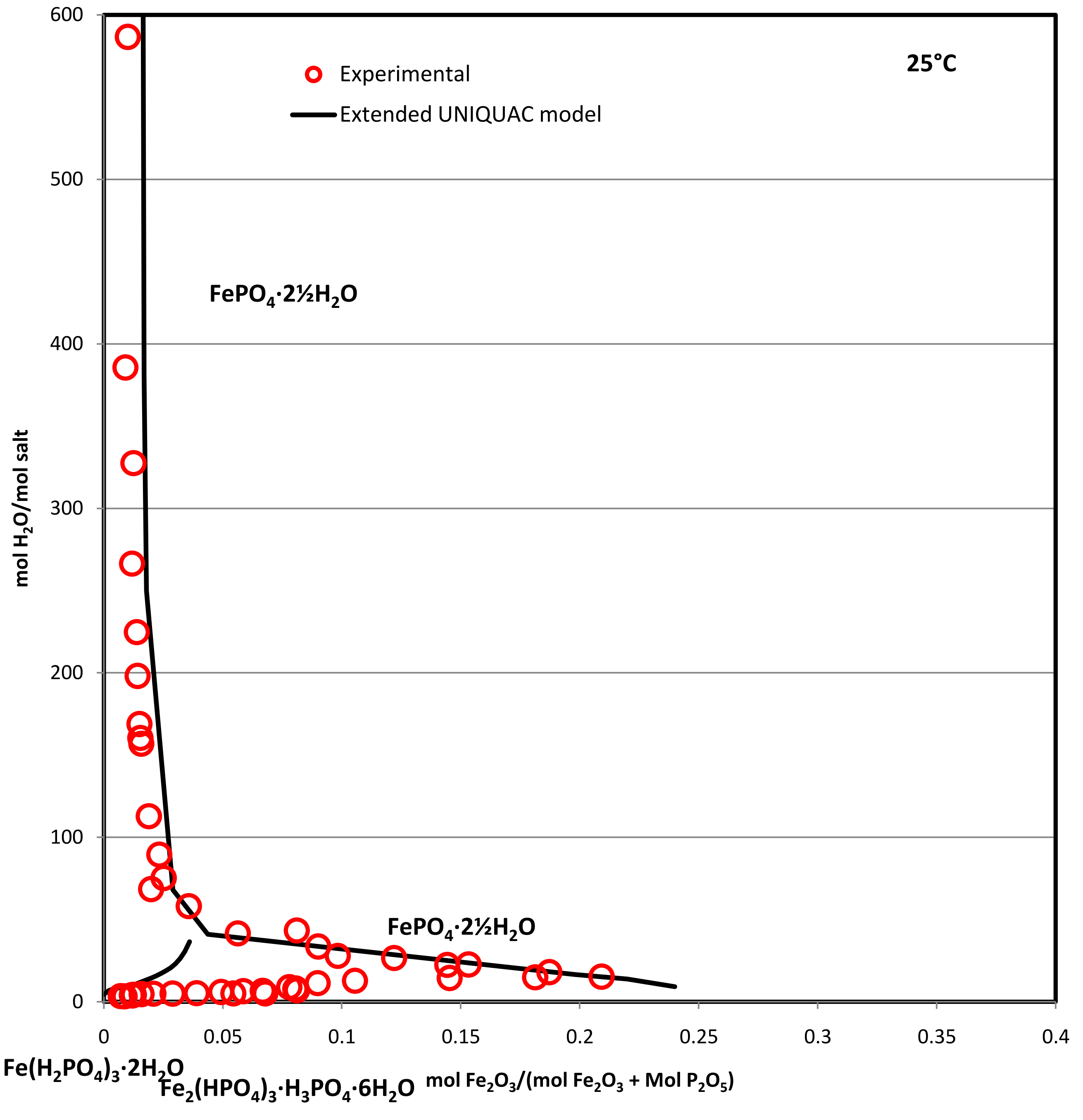


Figure 38: Enlarged corner of the solubility isotherm at 25°C for the $Fe_2O_3 – P_2O_5 – H_2O$ system at 25°C. It is seen that at each $Fe_2O_3/(Fe_2O_3+P_2O_5)$ molar ratio there are two different solubilities. The solubility of the more acidic salts is not well predicted by the model.

marked in Figure 38 were used for the parameter estimation and it was indicated that these experimental points had a saturation index very close to one, which means saturation. Yet these experimental points can not be reproduced very accurately by calculation. On the other hand, the model is obviously reproducing the solubility of the basic salt FePO4·2½H2O with good accuracy.

Conclusion

A correction term was introduced to make calculated pH values consistent with measured values. This goal was achieved by introducing an empirical term as a function of ionic strength. The correction term is only valid up to an ionic strength of 10 molal.

The cupric and the ferric ions were added to the model. In several cases the modeling result is impeded due to the lack of data or due to contradictions between data from different sources. In the case of ferric sulfate, modeling is made difficult due to the fact that ferric sulfate apparently does not precipitate as a pure substance, but as a solid solution of unpredictable composition. In several cases, some researchers found solid solutions to precipitate in systems from which other researchers found pure salts precipitating.

Due to the very low solubility of compounds like cupric and ferric phosphate, the solubility of these salts are very difficult to determine and the numbers given by different researchers inconsistent. In some cases, data were only available at 25°C. A temperature dependency of solubility can not be predicted from a single solubility. In these cases, a certain temperature dependency of solubility was assumed based on the known behavior of similar salts.

The model is now able to reproduce data in these systems with a reasonable accuracy considering the scarcity of the experimental data available.