

A Consistent Approach to Tabulation of Evaluated Solubility Data: Application to the Binary Systems $\text{RbCl-H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ ^{||}

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Many scientific disciplines require accurate solubility data. However, the proliferation of published values from research over the past century reveals a need for a consistent approach to tabulation and evaluation of these data, along with recommended methods based on theory for interpolation and extrapolation. The approach used in the IUPAC Solubility Data project is described, using as examples the binary systems $\text{RbCl-H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$. In this approach, all relevant solubility data are compiled and tabulated. The tabulated data are then evaluated using a systematic approach based upon thermodynamics. The results are tables of recommended values and fitting equations for solubilities and, in some cases, corresponding densities and vapor pressures.

INTRODUCTION

Solubility is defined as the analytical composition of a saturated solution, expressed as the proportion of the designated solute in a designated solvent.¹ "Saturated", for a solid solute, implies equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. For precise results, the equilibrium must be established for a carefully characterized crystalline solid phase under carefully controlled and accurately measured temperature and pressure.

Solubility data are fundamental to both basic and applied branches of almost all scientific disciplines. Accurate solubilities as a function of temperature and pressure are of importance in such diverse fields as agronomy, biology, chemical engineering, chemistry, environmental science, materials engineering, medicine, metallurgy, oceanography, pharmacology and physics. Accurate solubility data are of great value for practical applications such as manufacturing and reprocessing of nuclear fuels, mineral extraction, extraction of radionuclides from natural waters, manufacture of glasses and ceramics, the design of gas mixtures for life support systems, and the determination of drug dosages. Not infrequently, it is found that solubility data under specified conditions are not available from the published literature, and one must therefore address the problems of interpolation and extrapolation: i.e., how reliable are interpolated and extrapolated solubility data, and over what ranges are these data valid?

The interdisciplinary need for accurate solubility data has resulted in a proliferation of published data in numerous journals, internal industrial reports (often proprietary), pat-

ents, conference proceedings, textbooks, and handbooks. The number of primary sources (scientific journals) and of papers in these journals is so great that more and more reliance is placed upon secondary sources (e.g., review articles) and tertiary sources (e.g., handbooks or, more recently, electronic retrieval sources). The major problem with secondary and tertiary sources is that they are *selective*, and while tertiary sources may appear to be comprehensive, as a rule they are not *critical*.

The sheer volume of solubility data in the primary literature has overcome the ability of secondary and tertiary sources to respond to the needs of the practicing scientist or engineer, and to address this problem, the International Union of Pure and Applied Chemistry (IUPAC) created, in 1979, Commission V.8 on Solubility Data. The task of this Commission was, and remains, to produce comprehensive compilations and in-depth critical evaluations of published solubility data for gas-liquid, liquid-liquid, solid-liquid, and solid-solid systems. The Commission has formulated several innovative approaches which include detailed compilations of all primary data in a uniform format and comprehensive critical evaluations employing suitable statistical methods to produce, when possible, recommended values of solubility. These compilations and evaluations are being published in the ongoing *IUPAC Solubility Data Series* (SDS), and to date 58 volumes have been published. The systems covered are classified first as gases in liquids, liquids in liquids, and solids in liquids. Gases in liquids, to date, include the permanent gases, binary compounds containing hydrogen, oxides, some selected hydrocarbons, amines, and gases in molten salts. Liquids in liquids include hydrocarbons, alcohols, esters, and halogenated aromatics in water; more recently, alcohol-hydrocarbon systems have been added. Solids in liquids are divided into several groups: inorganic, organic and metal-organic salts, classified by type of anion; organics classified by structure; molten salts and alloys. Compilation of some of the more common salt systems has been slow because of the huge amount of data available. A complete list of self-descriptive titles can be

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found in the most recent volume of the Series. For a given solute–solvent system, the compilations contain all relevant data relating to source and purity of materials, experimental methods, experimental errors, and experimental solubility data given exactly as in the original publication.

By including all relevant details in the compilations, the users of the SDS need not face the sometimes daunting problem of acquiring copies of original publications (many of which are unavailable except in a few specialist libraries) in order to determine for themselves the quality of a given value of solubility. Since all published data are included in the compilations, users of the SDS may choose to carry out their own critical evaluations, or they may rely on the critical evaluations provided by the editors and contributors to specific volumes. The critical evaluations discuss the relative merits of individual studies, point out both exceptionally good and exceptionally poor data, and, with the aid of weighted averages, smoothing equations and graphical analyses provide either *recommended*, *tentative*, or *rejected* data.

As an example of the thoroughness of this approach, the following is a review of the treatment of the binary systems $\text{RbCl-H}_2\text{O}$ and $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$, taken in large part from, respectively, volumes 47 and 55 of the SDS.^{2,3}

It should be noted that, in many cases, values of solubilities published even in the first half of the 19th century often compare favorably with values measured recently and sometimes constitute the only source of data. Compilations based on these publications not only are, possible sources of reliable data but also are sources for the history of science and technology.

METHODOLOGY

1. Solubility of a Salt $\text{MX}_r\text{H}_2\text{O}$. In carrying out a critical evaluation, it is first necessary to compile all published data, while noting all relevant details on experimental methods and precision of the measurements and details about sources and purification of all materials.

When sufficient data are available, they can be analyzed using a convenient semiempirical relation which is based upon thermodynamics, as discussed in the introduction to SDS volumes in the solid–liquid subseries prior to vol. 53 (for example²) as well as in^{4–6} in a somewhat different way. This relation is derived by equating the chemical potential of the hydrated solid to the sum of the chemical potentials of its equilibrium dissociation products (salt and water) in the saturated solution and assuming that activity coefficients have the same form of dependence on temperature as the function Y defined in eq 1

$$Y = A/T + B \ln(T/T_f) + CT + D \quad (1)$$

where A , B , C , and D are adjustable coefficients. The quantity Y can be used in either of two forms. The first of these is based on ionic mole fractions

$$Y = \ln \left[\frac{x_1^2 (1 - x_1)^r (2 + r)^{2+r}}{r^r (1 + x_1)^{2+r}} \right] \quad (2)$$

where the solubilities, x_1 , are given as the mole fraction of the solute component 1, r is the hydrate number (amount water/amount anhydrous salt) in the solid phase, and T_f is a

reference temperature taken as the congruent melting point of the pure hydrated or anhydrous phase. "Congruent" implies that the composition of the solid and its equilibrium saturated solution are the same; ordinary melting points of pure anhydrous phases are always congruent. For a salt hydrate, the congruent melting point is often metastable relative to a peritectic temperature, which is an incongruent melting point. At the congruent melting point, $Y = 0$ and $x_1 = 1/(1 + r)$. For an anhydrous salt like RbCl , eq 2 simplifies to

$$Y = 2 \ln \left[\frac{2x_1}{1 + x_1} \right] \quad (3)$$

It is implicit in these equations that the reference state for the activity coefficients is the supercooled, liquid, completely-ionized salt at the given temperature and pressure. This choice (see, e.g., Pitzer⁷) is necessary in order to discuss solubilities which extend, as in the case of RbCl , over the whole composition range from pure water to pure anhydrous salt. The assumption of importance is that the activity coefficients along the solubility curve follow an equation of the same form as eq 1. The limitation of this assumption is that thermal quantities (e.g., enthalpies of solution) derived from eq 1 are apparent rather than true values.

The second form for the function Y is

$$Y = \ln(m/m_o) - (m/m_o - 1) \quad (4)$$

where m is the molality of component 1 in the saturated solution, and $m_o = 1/rM_2$ is the molality of the binary salt hydrate (with M_2 the molar mass of water), at which molality again $T = T_f$ and $Y = 0$. For this equation, the reference point for the activity coefficients is the infinitely-dilute solution. The two formulations, eqs 2 and 4, are equivalent. Equation 4 is clearly more useful for systems which are relatively dilute on the mole fraction scale ($x_1 < 0.5$, say). For example, in the system $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, the maximum solubility for the metastable dihydrate is $27.75 \text{ mol kg}^{-1}$, or mole fraction $x_1 = 0.3333$. Thus eq 4 is not useful when $r = 0$, and experimental values extend over the whole range of composition including pure anhydrous salt. The assumption concerning the functional dependence of the activity coefficients along the solubility curve remains the same.

Adjustment of the coefficients A , B , C , and D to fit the experimental liquidus curve is the basis of the critical evaluation. As an approximation, if the enthalpy of fusion, $\Delta_{\text{fus}}H$ (or fusion plus dissociation for a salt hydrate), the melting point T_f , and the heat capacity of fusion, $\Delta_{\text{fus}}C_p$, are known, the adjustable parameters in eq 1 are C and D since one can write, approximately

$$A = -(\Delta_{\text{fus}}H - T_f \Delta_{\text{fus}}C_p)/R \quad (5)$$

$$B = \Delta_{\text{fus}}C_p/R \quad (6)$$

$$C = -A/T_f - B \ln T_f \quad (7)$$

where R is the molar gas constant.

2. Solubility of Ice. For the solubility of ice, the quantities⁸ melting point $T_f \approx 273.15 \text{ K}$, $\Delta_{\text{fus}}H = 6.008 \text{ kJ mol}^{-1}$, and $\Delta_{\text{fus}}C_p = 38 \text{ J K}^{-1} \text{ mol}^{-1}$ can be used in eqs 5–7.

Two expressions for Y are used in the critical evaluations. For strongly solvated salts (e.g., LiCl , with large deviations

from ideality), a good fit to the data is often obtained using

$$Y = \ln \left[\frac{1 - (E + 1)x_1 - Fx_1^2}{1 - (E - 1)x_1 - Fx_1^2} \right] \quad (8)$$

In eq 8, E and F are adjustable parameters related to average hydration numbers. The second expression for Y takes into account the activity coefficient of water, f_2

$$Y = \ln f_2 + \ln \left[\frac{1 - x_1}{1 + x_1} \right] \quad (9)$$

The activity coefficient of water is expressed by the series

$$\ln f_2 = [x_1/(1 + x_1)]^{3/2}(E + Fz + Gz^2 + Hz^3)/T \quad (10)$$

with $z = \ln[x_1/(1 + x_1)]$; the coefficients E , F , G , and H are found by cubic regression of experimental values of the quantity

$$T[(1 + x_1)/x_1]^{3/2}\Psi = E + Fz + Gz^2 + Hz^3 \quad (11)$$

where

$$\Psi = \ln \left[\frac{1 + x_1}{1 - x_1} \right] + (\Delta_{\text{fus}}H - T\Delta_{\text{fus}}C_p)(1/T - 1/T_f)/R + (\Delta_{\text{fus}}C_p/R) \ln(T/T_f) \quad (12)$$

3. Vapor Pressure of Saturated Solutions. The vapor pressure p corresponding to the mole fraction solubility of component 1, x_1 (water is designated as component 2), is given by⁹

$$\ln \left(\frac{p}{p^\circ} \right) = \ln \left[\frac{1 - x_1}{1 + x_1} \right] + \ln \left(\frac{p_2}{p^\circ} \right) + \ln f_2 + \int_0^p \left(V_2 - \frac{RT}{p'} \right) dp'/RT \quad (13)$$

where p_2 and V_2 are the vapor pressure and molar volume of pure water vapor at temperature T , p° is the standard pressure (1 bar), f_2 is the activity coefficient of water in the saturated solution, and it is assumed that there is a negligible amount of component 1 in the vapor. The first term on the right side of eq 13 is negative and is the main contribution of the salt to the decrease in vapor pressure relative to that of pure water. The remaining contribution of the salt comes from the activity coefficient term, and the final term accounts for nonideality of the vapor. The term for the vapor pressure of pure water follows from an equation similar to eq 1, i.e.,

$$\ln(p_2/p^\circ) = a/T + b \ln(T/T_b) + cT + d \quad (14)$$

where T_b is the standard boiling point of water.

4. Pressure Effects on Solubility. From the Introduction of ref 2, the general equation for the dependence of solubility on both pressure and temperature using ionic mole fractions and the pure liquid reference state * is given by

$$Y + \ln[(f_1/f_1^*)^2(f_2/f_2^*)^2] = \int_{T_m}^T (\Delta_{\text{fus}}H/T)d(1/T) + \int_{T_m}^T \Delta_{\text{fus}}V dp/RT \quad (15)$$

Two cases arise. When the applied pressure is greater than

the vapor pressure of the saturated solution, the volume change on melting is generally negative for the hydrated or anhydrous salt, and the equation shows that the solubility decreases approximately linearly with increasing pressure at constant temperature. The second case arises when the total pressure is equal to the vapor pressure of the saturated solution. For the alkali metal chlorides, the volume change on melting (last term in eq 15) is of the order of⁹ $10^{-5} \text{ m}^3 \text{ mol}^{-1}$, and the maximum vapor pressure of about 200 bar occurs near $x_1 = 0.5$. The last term in eq 15 therefore constitutes about 3% of Y and can thus be assumed to be incorporated in an equation of the form of eq 1. The variation of the melting point of the pure salt (anhydrous at the maximum vapor pressure) is of the order of a few kelvins (9), and can also be accommodated within the adjusted coefficients of the fitting equation. Equation 1 is thus equally useful for describing the solubility at constant pressure or at the vapor pressure of the saturated solution.

5. Calculation of Adjustable Coefficients. The complete critical evaluation for the binary system $\text{RbCl-H}_2\text{O}$ is given in Chart 1, and an abridged critical evaluation for the binary system $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ is given in Chart 2. Details of the general treatment of the data and adjustment of the coefficients are now presented.

The first step is to eliminate obviously aberrant data points, and this can be done by tabulating and plotting all the data or by inspection (e.g., see Table 2 of the critical evaluation for $\text{RbCl-H}_2\text{O}$ and the obvious aberrant data points at 18, 25, and 50 °C). All the remaining data are then used to compute the first set of coefficients A_1 , B_1 , C_1 , and D_1 by the method of least squares. The experimental points with coordinates x_{1j} , T_j are then compared with the calculated points $x_1(T_j)$ and $T(x_{1j})$, and the relative ranges are calculated

$$\Delta x_1/x_1(T_j) = [x_{1j} - x_1(T_j)]/x_1(T_j) \quad (16)$$

$$\Delta T_j/T_j(x_{1j}) = [T_j - T(x_{1j})]/T(x_{1j}) \quad (17)$$

At this stage additional aberrant data points may be rejected, and the points retained are used for calculation of a new set of coefficients which satisfy one or other of the conditions

$$\Delta x_1/x_1(T_j) < \varrho \quad \text{and/or} \quad \Delta T_j/T_j(x_{1j}) < \tau \quad (18)$$

In eq 18, ϱ and τ are the maximum tolerated ranges which are chosen arbitrarily in such a way that the largest number of experimental points is retained. The choices for ϱ and τ are, however, guided by the analysis of the compilation sheets (e.g., purity of materials, experimental method, and errors). The calculations are repeated n times until a consistent set of adjusted parameters is obtained

$$A_n = A_{n-1}, \quad B_n = B_{n-1}, \quad C_n = C_{n-1}, \dots \quad (19)$$

A summary of this analysis is given in the flowchart of Figure 1.

6. Using the Fitting Equations. Calculation of solubility (given the temperature) or calculation of the equilibrium temperature (given the solubility) are, in general, not trivial exercises. The procedures for solubility of salts (expressed as mole fractions) are as follows. Procedures for calculations from fitting equations for ice and vapor pressure curves can be constructed in a similar way.

Chart 1

<p>COMPONENTS</p> <p>(1) Rubidium chloride; RbCl; [7791-11-9]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>R. Cohen-Adad,</p> <p>Université Claude Bernard (Lyon I), Laboratoire de Physico-chimie Minérale II, 69622 Villeurbanne, France.</p> <p>April, 1987</p>
<p>CRITICAL EVALUATION</p> <p>Solubility data for the system RbCl-H₂O have been presented in 29 publications. The solid phase in equilibrium with the liquid is either anhydrous RbCl or ice, depending on the particular region of concentration of interest.</p> <p>EXPERIMENTAL METHODS</p> <p>The solubility of RbCl in water has been measured using analytical methods where a sample of the saturated solution, prepared under isothermal conditions, has been taken and analyzed. In two cases, the solubility has been determined from isopiestic measurements (20a, 37), and in another from measurements of the vapor pressure as a function of concentration (14). The solubility of ice has been determined by cryoscopy (12,27).</p> <p>ANALYSIS OF SOLUTIONS</p> <p>The composition of the sample or of the saturated solution was determined, in most cases, by evaporation to dryness and weighing (2, 3, 8, 29, 33, 37), by interferometry (12, 27), by determination of chloride (2, 6, 14, 22, 24, 34-36), or by analysis for rubidium (33).</p> <p>PRODUCTS USED</p> <p>Most often RbCl was a pure reagent, sometimes recrystallized once, twice or three times. Belyaev (22) prepared RbCl from pure carbonate.</p> <p>MELTING POINT</p> <p>There are only a few rather disperse experimental values given in the literature: 710 (4, 21), 712-713 (5), 714 (9), 722 (20), 726°C (7). In their compilations, Perel'man (21) indicated 710 and 726°C, while Bahrin, Knacke and Kubaschewski (30) gave 988 K (= 715°C). We have adopted this latter value in the calculations.</p> <p>CRITICAL EVALUATION OF THE RESULTS</p> <p>1. <i>Fitting equations for the Solubility Curves</i></p> <p>All the data on the compilation sheets have been analyzed according to the procedure given in the Preface to this volume. The curves can be represented by equations of the form:</p> $Y(x_1) - Y(x_0) = A(1/T - 1/T_0) + B \ln(T/T_0) + C(T - T_0)$ <p>Solubility of RbCl:</p> $Y = 2 \ln[2x_1/(1 + x_1)]$ <p>Solubility of ice:</p> <p>A good representation of the experimental results was obtained from series expansion of the activity coefficient of water, according to an equation of the form:</p> $\ln f_2 = [x_1/(1 + x_1)]^{3/2} (E + Fz + Gz^2 + Hz^3)/T$ <p style="text-align: right;">(continued)</p>	

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

where

$$z = \ln[x_1/(1 + x_1)]$$

The coefficients *E*, *F*, *G* and *H* have been adjusted by cubic regression.

Table 1 - System RbCl-H₂O
Coefficients of fitting equations of solubility
Solid Phase

	RbCl	ice
<i>A</i>	-3243.86	
<i>B</i>	-11.7572	
<i>C</i>	1.3816x10 ⁻²	
<i>D</i>	70.7070	
<i>E</i>		730.96
<i>F</i>		613.93
<i>G</i>		201.73
<i>H</i>		15.79
Range/K	255-988	273-255

2. Critical Evaluation of the Data

2.1 Solubility of RbCl

The calculation of the solubility curve has been carried out using 41 numerical values over a range of temperature from 0°C (273.15 K) to 114.9°C (388.1 K). In addition, one supplementary condition has been imposed: the melting point ($x_o = 1$, $T_o = 988$ K) is a point on the solubility curve. The whole of the experimental results and calculations are given in Table 2. The data from the literature are very coherent among themselves and equally very coherent with the calculated values. With the exception of the results of Benrath (10), which show a deviation of almost 3 %, and those of Gehlen and Dieter (15), all the numerical values can be recommended, particularly those of the Earl of Berkeley (3, 8).

Table 2 - Solubility of RbCl in Aqueous Solutions

<i>T</i> /K - 273.15	mass % 100 w_1		mole fraction x_1		density		status		ref.
	exp.	calc.	exp.	calc.	exp.	calc.	a	b	
0	43.48	43.57	0.1028	0.1032			r		24
0.4	43.61	43.65	0.1033	0.1035			r		2
0.55	43.61	43.69	0.1033	0.1036	1.4409	1.4410	r r		3
1	43.30	43.78	0.1021	0.1040			t		1
7	45.32	45.03	0.1099	0.108			t		1
15.5	46.56	46.70	0.1149	0.1154			r		2
18	47.07	47.16	0.1170	0.1174			r		14
18	46.2	47.16	0.1134	0.1174			a		15
18.70	47.46	47.29	0.1186	0.1179	1.4865	1.4869	r r		3
20	47.7	47.53	0.1196	0.1189			r		23
22.9	48.45	48.05	0.1228	0.1211	1.4971	1.4959	t r		6
25.00	47.92	48.42	0.1206	0.1227			t		35
25	48.12	"	0.1214	"			t		17,19
25	48.21	"	0.1218	"			r		32
25	48.29	"	0.1221	"			r		26
25	48.47	"	0.1229	"			r		20a
25	48.48	"	0.1230	"			r		18
25	48.484	"	0.1230	"			r		37
25	48.50	"	0.1230	"	1.455	1.5000	r a		22

(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

Table 2 (continued)
Solubility of RbCl in Aqueous Solutions

T/K - 273.15	mass % 100 w ₁		mole fraction x ₁		density		status a b	ref.
	exp.	calc.	exp.	calc.	exp.	calc.		
25	48.50	48.42	0.1230	0.1227	1.487	1.5000	r	25
25.00	48.51	"	0.1231	"			r	34
25	48.54	"	0.1232	"			r	29
25	48.57	"	0.1233	"			r	11
25	48.58	"	0.1234	"			r	33
25	48.60	"	0.1235	"			r	24
25	48.67	"	0.1238	"			r	28
25	48.74	"	0.1242	"			t	36
25	49.71	"	0.1284	"			a	10
25	52	"	0.1394	"			a	1
31.5	49.65	49.41	0.1281	0.1275	1.5118	1.5125	r r	3
40	49.85	50.86	0.1290	0.1336			a	17
44.70	51.51	51.57	0.1366	0.1369	1.5348	1.5346	r r	3
50	51.2	52.33	0.1352	0.1405			a	31
50	52.2	"	0.1399	"			r	23
50	52.30	"	0.1404	"			r	24
50	52.5	"	0.1414	"			r	31
57.3	53.71	53.33	0.1474	0.1454			t	2
60.25	53.62	53.71	0.1469	0.1474	1.5558	1.5565	r r	3
75.15	55.46	55.53	0.1565	0.1569	1.5746	1.5745	r r	3
89.35	57.03	57.08	0.1651	0.1654	1.5905	1.5900	r r	3
113.710	59.62	59.41	0.1803	0.1790			r bp	8
114.0	59.46	59.44	0.1793	0.1792	1.6148	1.6150	r r bp	3
114.9	59.48	59.52	0.1794	0.1797			r	2

(a) status of solubility (b) status of density

 $e = |x_1(\text{obs}) - x_1(\text{calc})|/x_1(\text{calc})$ r = recommended value $e \leq 0.01$ t = tentative value $0.01 < e \leq 0.02$ a = aberrant value $e > 0.02$

bp = boiling point of saturated solution

2.2 Solubility of Ice

Calculations were made using 43 numerical values. The results of Dejak (16) reproduce the values of Karagunis (12), and have not been taken into account. The whole of the experimental data and calculations is given in Table 3. The concordance among the measurements and the calculations is excellent, and all values can be recommended.

2.3 Eutectic Point

No numerical value is given in the literature. The coordinates of the eutectic point have been determined by extrapolation of the solubility curves for ice and for salt, and are:

$x_1(\text{eutectic}) = 0.0896$; $T(\text{eutectic})/K - 273.15 = -16.4$. These results must be considered as tentative values.

2.4 Boiling Point at Atmospheric Pressure

Rimbach (2) indicated $x_1 = 0.1795$, $T/K - 273.15 = 114.9$. The Earl of Berkeley indicated $x_1 = 0.1793$, 114.0°C (3) and, subsequently, 113.71°C (8). This latter value is the most precise.

2.5 Influence of Pressure on the Solubility

This has been calculated at 18°C by Gehlen and Dieter (15), whose results must be considered as tentative values.

(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

Table 3
Solubility of Ice in Aqueous Solutions of RbCl

T/K - 273.15	mass % 100 w_1		mole fraction x_1		$\ln f_2$	status	ref.
	exp.	calc.	exp.	calc.			
-0.0473	0.155	0.155	0.000231	0.000232	0.00001	r	27
-0.06510	0.214	0.215	0.000321	0.000322	0.00001	r	12
-0.0771	0.259	0.256	0.000387	0.000383	0.00002	r	27
-0.0949	0.319	0.317	0.000477	0.000474	0.00003	r	27
-0.1423	0.488	0.481	0.000730	0.000721	0.00006	r	27
-0.15115	0.506	0.511	0.000758	0.000766	0.00007	r	12
-0.1935	0.663	0.660	0.000993	0.000989	0.00010	r	27
-0.2147	0.739	0.735	0.001108	0.001102	0.00012	r	27
-0.21900	0.746	0.749	0.001119	0.001124	0.00013	r	12
-0.2708	0.937	0.933	0.001407	0.001401	0.00018	r	27
-0.2774	0.932	0.955	0.001400	0.001436	0.00018	r	12
-0.2738	0.937	0.942	0.001407	0.001416	0.00018	r	12
-0.4152	1.451	1.446	0.002189	0.002182	0.00034	r	27
-0.4165	1.448	1.450	0.002184	0.002187	0.00034	r	12
-0.5352	1.876	1.873	0.002840	0.002837	0.00049	r	12
-0.5504	1.925	1.927	0.002916	0.002920	0.00051	r	27
-0.6296	2.215	2.210	0.003363	0.003357	0.00061	r	12
-0.6713	2.358	2.358	0.003585	0.003586	0.00067	r	27
-0.7872	2.784	2.770	0.004248	0.004228	0.00083	r	12
-0.8102	2.846	2.851	0.004345	0.004354	0.00086	r	27
-0.8211	2.898	2.891	0.004427	0.004417	0.00087	r	12
-1.0067	3.537	3.545	0.005433	0.005447	0.00114	r	27
-1.1690	4.102	4.113	0.006332	0.006351	0.00137	r	27
-1.194	4.208	4.202	0.006502	0.006492	0.00141	r	12
-1.4139	4.943	4.961	0.007687	0.007718	0.00173	r	27
-1.9758	6.851	6.860	0.010838	0.010857	0.00256	r	27
-1.988	6.927	6.901	0.010966	0.010924	0.00257	r	12
-2.7314	9.312	9.309	0.015067	0.015067	0.00364	r	27
-3.244	11.000	10.902	0.018080	0.017913	0.00434	r	12
-3.4660	11.591	11.576	0.019158	0.019142	0.00464	r	27
-3.789	12.660	12.540	0.021138	0.020927	0.00507	r	12
-4.0967	13.462	13.440	0.022650	0.022624	0.00547	r	27
-4.128	13.580	13.531	0.022875	0.022796	0.00551	r	12
-4.947	15.940	15.840	0.027474	0.027296	0.00654	r	12
-5.0217	16.079	16.045	0.027752	0.027706	0.00663	r	27
-5.606	17.660	17.618	0.030963	0.030902	0.00733	r	12
-6.2937	19.402	19.403	0.034621	0.034652	0.00813	r	27
-6.388	19.640	19.642	0.035131	0.035165	0.00824	r	12
-6.977	21.020	21.110	0.038138	0.038367	0.00891	r	12
-7.645	22.600	22.719	0.041687	0.041986	0.00965	r	12

(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

Table 3 (continued)
Solubility of Ice in Aqueous Solutions of RbCl (continued)

$T/K - 273.15$	mass % 100 w_1		mole fraction x_1		$\ln f_2$	status	ref.
	exp.	calc.	exp.	calc.			
-7.6634	22.676	22.763	0.041861	0.042086	0.00967	r	27
-8.672	25.090	24.087	0.047527	0.047544	0.01077	r	12
-10.4356	28.550	28.882	0.056184	0.057063	0.01266	r	27

$$e = |x_1(\text{obs}) - x_1(\text{calc})|/x_1(\text{calc}) \quad r = \text{recommended value} \quad e \leq 0.015$$

2.6 Densities of Saturated Solutions

These have been measured, between $T/K - 273.15 = 0.55$ to 114, by Berkeley (3). One adds to these results the values of Buchanan (6) and of Belyaev (22, 25) at a few other temperatures. The experimental values can be represented correctly by the formula:

$$d = a_1 + bx_1 + c_1x_1^2$$

a_1 , b_1 and c_1 , calculated by least squares, have the values:

$$a_1 = 0.9934 \quad b_1 = 5.5759 \quad c_1 = -11.8176$$

with a correlation coefficient equal to 1. The recommended values are those of Berkeley.

SOLUBILITY AND DENSITY FOR ROUNDED VALUES OF TEMPERATURE

Values of solubility and density are given in Table 4 and figures 1 and 2. The calculated values can be recommended between $T/K - 273.15 = 0$ and -12 for the solubility curve of ice, and between -10 and 130 for the solubility curve of the salt. In other regions, the results of the calculations must be considered as tentative.

Table 4
Solubility for Rounded Values of Temperature

$t/^\circ\text{C}$	mass % 100 w_1	mole fraction x_1	molality /mol kg^{-1}	density	$10^3 \ln f_2$	solid phase
0	0	0	0			ice
-1	3.52	0.00541	0.302		1.13	"
-2	6.94	0.01099	0.617		2.59	"
-3	10.15	0.01655	0.934		4.01	"
-4	13.16	0.02208	1.253		5.34	"
-5	15.99	0.02757	1.574		6.60	"
-6	18.65	0.03303	1.896		7.79	"
-7	21.17	0.03846	2.220		8.94	"
-8	23.55	0.04388	2.548		10.0	"
-9	25.82	0.04929	2.878		11.12	"
-10	27.97	0.05470	3.212		12.19	ice
-11	30.03	0.06010	3.550		13.26	"
-12	32.00	0.06551	3.891		14.32	"
-13	33.88	0.07092	4.237		15.41	"
-14	35.68	0.07634	4.588		16.51	"
-15	37.41	0.08178	4.944		17.63	"
-16	39.08	0.08723	5.305		18.79	"
-17	40.68	0.09269	5.671		19.98 m	"
-18	42.44	0.09817	6.043		21.21 m	"
-19	43.71	0.10368	6.421		22.49 m	"
-20	45.14	0.10920	6.805		23.82 m	"

(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

Table 4 (continued)

Solubility for Rounded Values of Temperature

$t/^{\circ}\text{C}$	mass % 100 w_1	mole fraction x_1	molality /mol kg^{-1}	density	$10^3 \ln f_2$	solid phase
-30	36.23	0.0780	4.699		m	RbCl
-25	37.58	0.0823	4.979		m	"
-20	38.88	0.0866	5.260	1.3715	m	"
-15	40.12	0.0908	5.542			"
-10	41.32	0.0949	5.823	1.4079		"
-5	42.47	0.0991	6.105			"
0	43.57	0.1032	6.385	1.4396		RbCl
2	44.00	0.1048	6.497	1.4396		"
4	44.42	0.1064	6.608			"
6	44.83	0.1080	6.720			"
8	45.24	0.1096	6.831			"
10	45.63	0.1112	6.942	1.4665		"
12	46.03	0.1127	7.052			"
14	46.41	0.1143	7.162			"
16	46.79	0.1158	7.272			"
18	47.16	0.1174	7.382			"
20	47.53	0.1189	7.491	1.4897		"
22	47.89	0.1204	7.600			RbCl
24	48.24	0.1219	7.708			"
26	48.59	0.1234	7.816			"
28	48.93	0.1249	7.924			"
30	49.27	0.1264	8.031	1.5097		"
32	49.60	0.1279	8.138			"
34	49.92	0.1293	8.244			"
36	50.24	0.1308	8.350			"
38	50.55	0.1322	8.455			"
40	50.86	0.1336	8.560	1.5271		"
42	51.17	0.1350	8.665			RbCl
44	51.46	0.1364	8.769			"
46	51.76	0.1378	8.872			"
48	52.05	0.1392	8.975			"
50	52.33	0.1406	9.078	1.5426		"
52	52.61	0.1419	9.180			"
54	52.88	0.1433	9.282			"
56	53.15	0.1446	9.383			"
58	53.42	0.1459	9.483			"
60	53.68	0.1472	9.584	1.5561		"
62	53.94	0.1485	9.683			RbCl
64	54.19	0.1498	9.783			"
66	54.44	0.1511	9.881			"
68	54.68	0.1524	9.980			"
70	54.93	0.1536	10.077	1.5686		"
72	55.16	0.1549	10.175			"
74	55.40	0.1561	10.272			"
76	55.63	0.1574	10.368			"
78	55.86	0.1586	10.464			"
80	56.08	0.1598	10.559	1.5800		"

(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

Table 4 (continued)

Solubility for Rounded Values of Temperature

$t/^{\circ}\text{C}$	mass % 100 w_1	mole fraction x_1	molality /mol kg ⁻¹	density	$10^3 \ln f_2$	solid phase
82	56.30	0.1610	10.654			RbCl
84	56.52	0.1622	10.749			"
86	56.73	0.1634	10.843			"
88	56.94	0.1646	10.937			"
90	57.15	0.1658	11.030	1.5907		"
92	57.36	0.1669	11.123			"
94	57.56	0.1681	11.215			"
96	57.76	0.1692	11.307			"
98	57.95	0.1704	11.399			"
100	58.15	0.1715	11.490	1.6010		"
102	58.34	0.1726	11.581			RbCl
104	58.53	0.1737	11.672			"
106	58.72	0.1748	11.762			"
108	58.90	0.1759	11.852			"
110	59.08	0.1770	11.941	1.6110		"
112	59.26	0.1781	12.030			"
114	59.44	0.1792	12.119			"
116	59.61	0.1803	12.207			"
118	59.79	0.1813	12.295			"
120	59.96	0.1824	12.383	1.6211		"
125	60.38	0.1850	12.602			RbCl
130	60.79	0.1876	12.819			"
135	61.18	0.1902	13.034			"
140	61.57	0.1927	13.248			"
145	61.94	0.1952	13.461			"
150	62.31	0.1976	13.673			"
200	65.62	0.2214	15.784	1.7159		RbCl
250	68.55	0.2451	18.023			"
300	71.37	0.2708	20.614			"
350	74.24	0.3004	23.837			"
400	77.26	0.3360	28.094			"
450	80.45	0.3801	34.039			"
500	83.84	0.4360	42.907			"
550	87.41	0.5084	57.399			"
600	91.12	0.6047	84.901			"
650	94.95	0.7370	155.545			"
700	98.84	0.9270	705.392			"
714.85	100	1.0000				"

m = metastable point

(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

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(continued)

Chart 1 (Continued)

CRITICAL EVALUATION (continued)

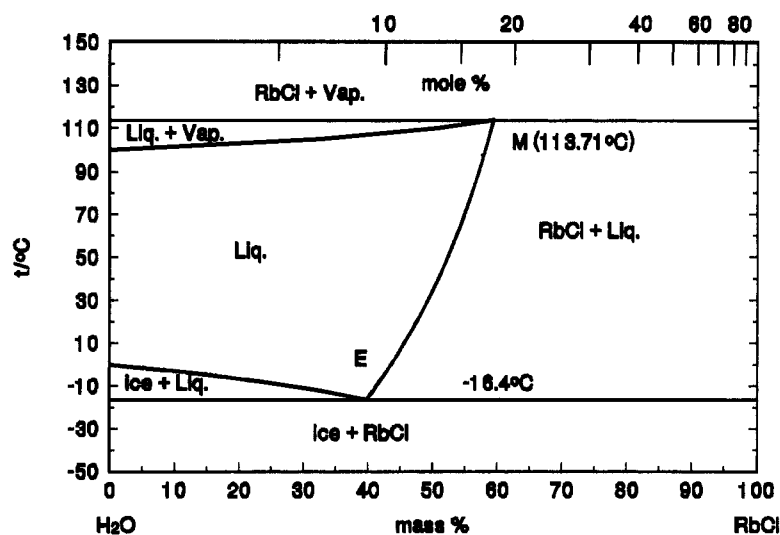
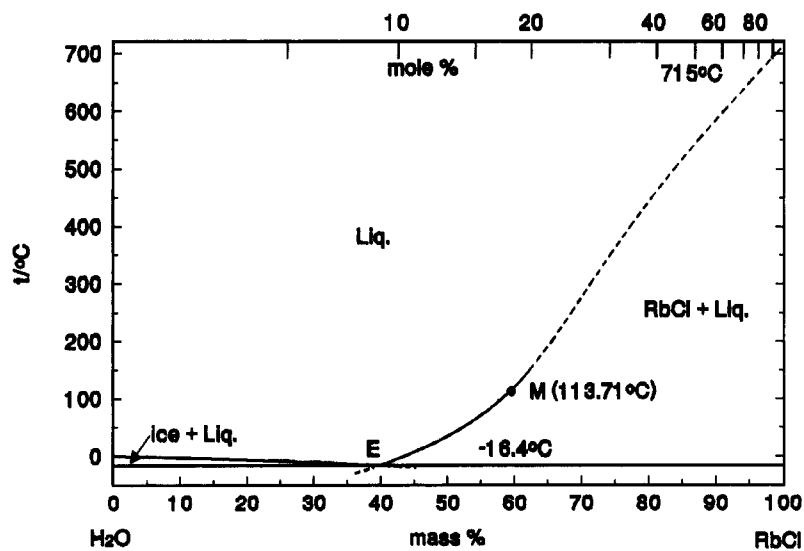
Fig. 1. Temperature-composition phase diagram for the system RbCl-H₂O at a pressure of 1 bar.Fig. 2. Temperature-composition phase diagram for the system RbCl-H₂O under the vapor pressure of the saturated solution.

Chart 1 (Continued)

COMPONENTS:		ORIGINAL MEASUREMENTS:	
(1) Rubidium chloride, RbCl [7791-11-9]		Kirchhoff, G.; Bunsen, R.	
(2) Water, H ₂ O [7732-18-5]		Ann. Phys. Chem. [4] 1861, 113, 337-81.	
VARIABLES:		PREPARED BY:	
T/K = 274, 280		J.W. Lorimer	
EXPERIMENTAL VALUES:			
t/°C	mass ratio RbCl/H ₂ O	mass % solid	phase
1	0.7638	43.30	RbCl
7	0.8289	45.32	RbCl
COMMENTS:			
These data are found on p. 352 of this paper, and were obtained in connection with the discovery and isolation of rubidium and caesium by the authors; the names of the elements are proposed in the paper, and the derivations of the names are also given. The preparation of RbCl appears to have been verely pure; the analytical data given (0.9740 g RbCl gave 1.1541 g AgCl on precipitation) correspond to $x = 1.0010$ in RbCl _x , or 29.31 % Cl (theory 29.32), when 1984 atomic weights are used (compiler).			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY OF MATERIALS:	
No details are given; presumably the isothermal saturation method was used.		RbCl was extracted from lepidolite from Saxony. A large sample was freed from lithia and "earths", leaving a residue of about 150 kg. Extraction made use of the lower solubility of RbPtCl ₂ , compared to the chloroplatinates of Na and K. The purity of the product was checked by the emission spectrum.	
		ERRORS:	
		REFERENCES	

Chart 1 (Continued)

COMPONENTS:			ORIGINAL MEASUREMENTS:		
(1) Rubidium chloride, RbCl [7791-11-9]			Berkeley, Earl of		
(2) Water, H ₂ O [7732-18-5]			Phil. Trans. R. Soc. London, Ser. A <u>1904</u> , 203, 189-214		
VARIABLES:			PREPARED BY:		
T/K = 274-387			M. Ferriol		
EXPERIMENTAL VALUES:					
t/°C	100 x mass ratio RbCl/H ₂ O	mass %	density	solid /g cm ⁻³	phase
0.55	77.34		43.61	1.4409	RbCl
18.70	90.32		47.46	1.4865	"
31.50	98.61		49.65	1.5118	"
44.70	106.24		51.51	1.5348	"
60.25	115.63		53.62	1.5558	"
75.15	124.52		55.46	1.5746	"
89.30	132.73		57.03	1.5905	"
114.0 ^a	146.65		59.46	1.6148	"
^a boiling point					
AUXILIARY INFORMATION					
METHOD/APPARATUS/PROCEDURE:			SOURCE AND PURITY OF MATERIALS:		
The salt-water mixture was stirred at the appropriate temperature and the density followed by pycnometric measurement until its value remained constant. The solubilities were determined by evaporation to dryness of the saturated solution in platinum crucibles, except at the boiling point, where Jena glass bulbs were used. According to the range, different temperature control systems were used. Temperatures were corrected to the hydrogen scale.			Purest product from Merck, checked by chloride titration. The RbCl was tested spectroscopically for the presence of potassium and caesium.		
			ERRORS:		
			Temperature: = ±0.01 K. Solubility: within ±0.16 mass %		
			REFERENCES:		

Chart 2

COMPONENTS:			EVALUATOR:		
(1) Uranyl nitrate; $\text{UO}_2(\text{NO}_3)_2$; [15905-86-9]			S. Siekierski Warsaw, Poland and S. L. Phillips Orinda, California U.S.A.		
(2) Water; H_2O ; [7732-18-5]					
CRITICAL EVALUATION:					
Table 1. Summary of the solubility of $\text{UO}_2(\text{NO}_3)_2$ in the binary system $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} - \text{H}_2\text{O}$ in the temperature range 253 K to 334 K, considered for fitting to Eq 1.					
T/K	Solubility mol/kg	Ref.	T/K	Solubility mol/kg	Ref.
253.15	2.105	12	*298.15	3.213	25
255.05	1.921	3	*298.15	3.217	8
261.05	2.119	3	*298.15	3.219	25
261.65	2.182	8	*298.15	3.22	21
*267.65	2.387	8	*298.15	3.22	30
268.95	2.099	8	*298.15	3.223	28,29,35
*270.95	2.414	3	298.15	3.04	18
273.15	5.756	9	*298.15	3.23	34
*273.15	2.482	3	*298.15	3.240	5,7
*273.15	2.49	28,29,30,34	*298.15	3.246	25
*273.15	2.52	21	*298.15	3.26	23
*273.15	2.477	25	298.15	3.3	20
*273.15	2.488	25	298.75	3.385	3
*278.15	2.67	21	305.05	3.728	24
*278.65	2.594	8	305.65	4.00	12
*278.85	2.671	12	*308.15	3.825	35
*280.75	2.702	8	*309.25	3.851	8
*283.15	2.75	21	*309.85	4.011	3
*285.45	2.846	3	*316.75	4.551	8
287	1.25	1	*318.35	4.734	3
287.15	2.94	24	*323.15	5.218	25
*288.15	2.839	8	*323.15	5.27	22
*288.15	2.84	21	*324.95 ^b	5.329	3
*288.15	2.85	30	*327.65	5.993	8
289.45	2.98	12	*329.25	6.510	8
*291.45	2.98	12	330.15	7.900	24
*293.15	2.98	19	*330.55	6.779	8
*293.15	2.990	16	*331.35	7.272	8
*293.15	3.028	8	*331.8	7.884	8
*293.15	3.028	9	332.15 ^c	8.50	24

Chart 2 (Continued)

CRITICAL EVALUATION: (continued)Table 1 (continued). Summary of the solubility of $\text{UO}_2(\text{NO}_3)_2$ in the binary system $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} - \text{H}_2\text{O}$ in the temperature range 253 K to 334 K, considered for fitting to Eq 1.

T/K	Solubility mol/kg	Ref.	T/K	Solubility mol/kg	Ref.
*293.15	3.03	21	333.15 ^c	9.27	24
*293.55 ^a	3.08	24	333.4 ^d	9.250	3
294.25	3.175	8	334.15 ^c	8.64	24
296.35	3.31	24			

^a Mean temperature.^b Temperature according to Ref. (8). There must be a typographical error in *Chem. Zentr.* 1910, 11, 1527.^c Metastable equilibrium.^d Temperature of the congruent melting point of the hexahydrate (3). The corresponding molality was calculated by the evaluators.

* Used in fitting to Eq 1.

Table 4. Values of the parameters and the standard deviations from the smoothing equation, Eq 1.

Parameter Value	Parameter	Standard Deviation
A	964.618 mol/kg	0.0149
B	-23711.09 mol/(kg K)	4.57
C	-172.094 mol/kg	0.00261
D	0.3187	0.0000489
m_0	9.25 mol/kg	0.0149 ^a

^aStandard error of the estimate.Table 5. Recommended and tentative solubilities in the system $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, obtained with Eq 1^a.

Solubility		Solubility	
T/K	mol/kg	T/K	mol/kg
258.15	2.17	298.15	3.21
263.15	2.28	303.15	3.44
268.15	2.39	308.15	3.71
273.15	2.49	313.1	4.07
278.15	2.61	318.15	4.53
283.15	2.73	323.15	5.17
288.15	2.87	328.15	6.17
293.15	3.03	332.15	9.25 ^b

^aThe equilibrated solid may be a hydrate with more than 6 waters in the temperature interval 258.15 - 268.15 K.^bCongruent melting point.

Chart 2 (Continued)

CRITICAL EVALUATION: (continued)

Table 13. Temperature for water freezing as a function of molality of uranyl nitrate. The solid phase is ice.

$t/^{\circ}\text{C}$	$\text{UO}_2(\text{NO}_3)_2$ mol/kg	Ref.
-0.2	0.0402	3
-0.3	0.217	8
-1	0.218	12 ^a
-1.0	0.22	21
-1.6	0.3082	3
-2.1	0.3536	3
-2.9	0.5264	3
-2.9	0.5320	8
-4.4	0.7800	3
-5	0.7780	12 ^a
-5.4	0.846	21
-5.4	0.8392	8
-6.0	0.9005	3
-7.3	1.067	8
-7.9	1.223	3
-11.2	1.505	3
-14.4	1.692	21
-18.0	1.918	8
-20	2.105	12 ^a

^aSolid phase is not specified in source publication, evaluator assumes ice is the solid phase.

Recommended values for water freezing as a function of molality of uranyl nitrate, based on fitting above data to Eq 1.

T/K	mol/kg ^b
253.15	2.436
258.15	1.436
263.15	1.511
266.15	1.221
268.15	0.8396
270.15	0.4556
272.65	0.1429

^bStandard deviation, 0.157

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Chart 2 (Continued)

CRITICAL EVALUATION: (Continued)

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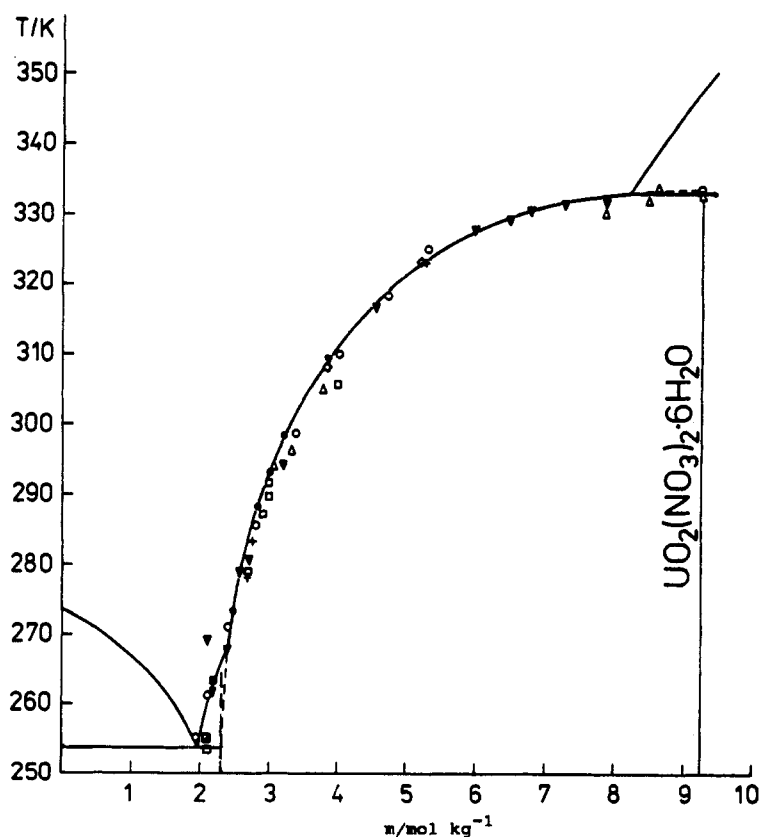


Figure 1.

Phase diagram for the $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ system. The solid line for the stable hexahydrate phase and the dashed line for the metastable hexahydrate phase were calculated from the smoothing equation. The solid line for solubility below 268 K and the solid line for the ice system were obtained by graphical smoothing. Experimental data: \circ , from Ref. 3; ∇ , from Ref. 8; \square , from Ref. 12; $+$, from Ref. 21 and Ref. 22; Δ , from Ref. 24; \diamond , from Ref. 25, 28 and 35; \blacksquare , from Ref. 32 and Ref. 39; \bullet , from mean solubility values in Table 2.

Chart 2 (Continued)

CRITICAL EVALUATION: (continued)

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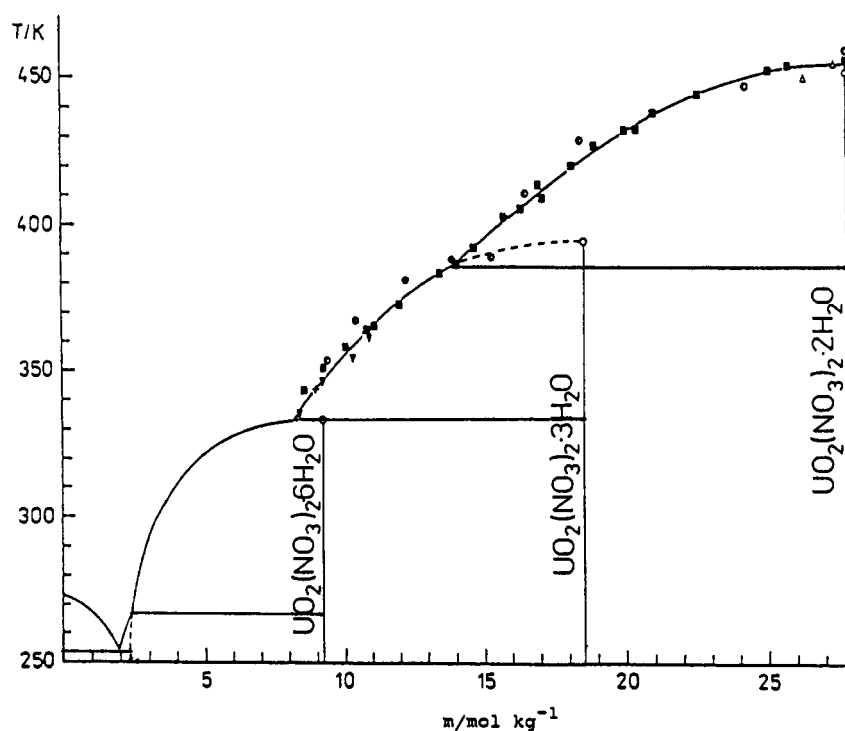


Figure 2. Phase diagram for the $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ system. The solid lines represent stable phases and the dashed lines are for metastable phases. These were calculated from the smoothing equation. Solid line for solubility below 268 K and the solid line for the ice system were obtained by graphical smoothing. Experimental data: ○, Ref. 3; ▼, Ref. 8; ●, Ref. 10; ■, Ref. 14, 17; +, Ref. 21, 22; Δ, Ref. 24.

COMMENTS: The molality corresponding to the congruent melting point of the 24-hydrate is 2.31 mol/kg, a value very close to the intersection point of the solubility curves at about 266 K. Therefore, if a 24-hydrate exists, its congruent melting point and the peritectic transition between the 24-hydrate and hexahydrate must almost coincide.

Chart 2 (Continued)

CRITICAL EVALUATION: (continued)

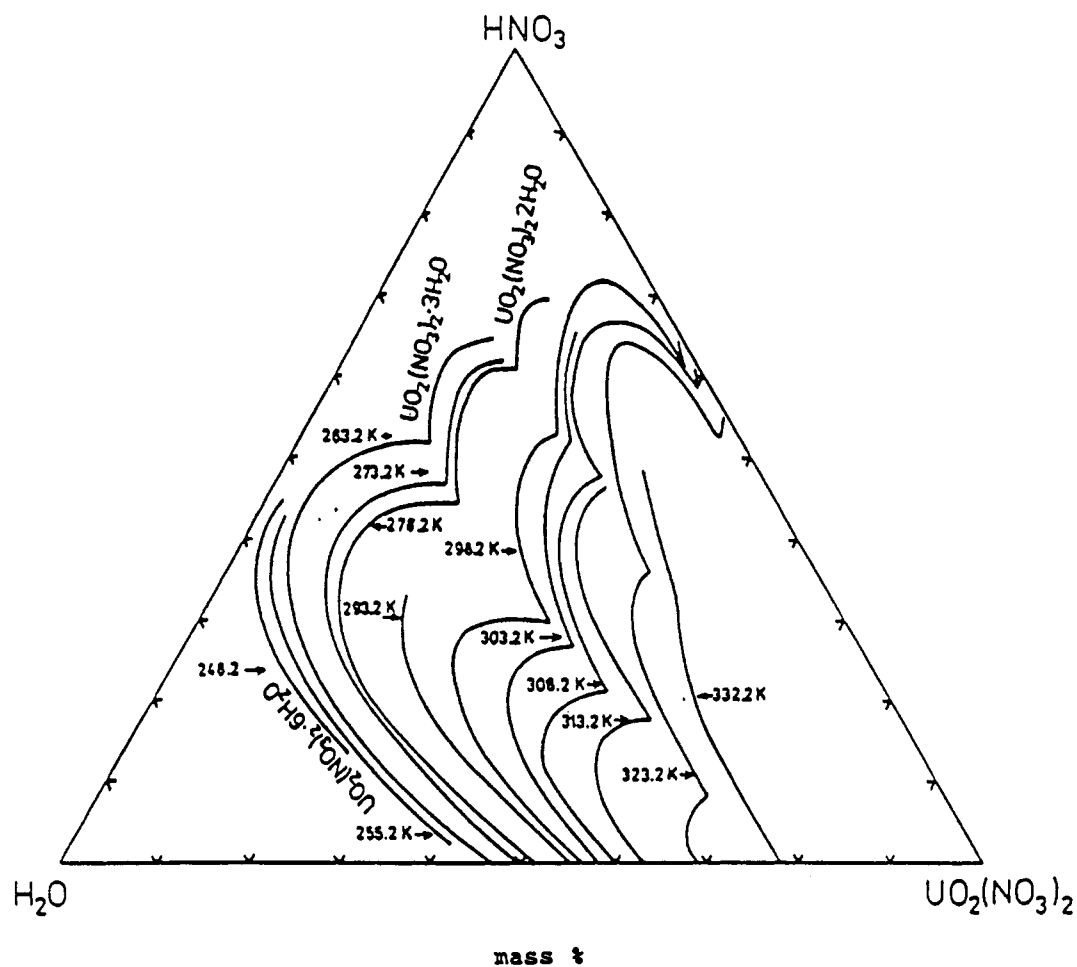


Figure 3. Phase diagram for the $\text{UO}_2(\text{NO}_3)_2$ - HNO_3 - H_2O system at various temperatures. The scales are 0-100 mass % along each axis.

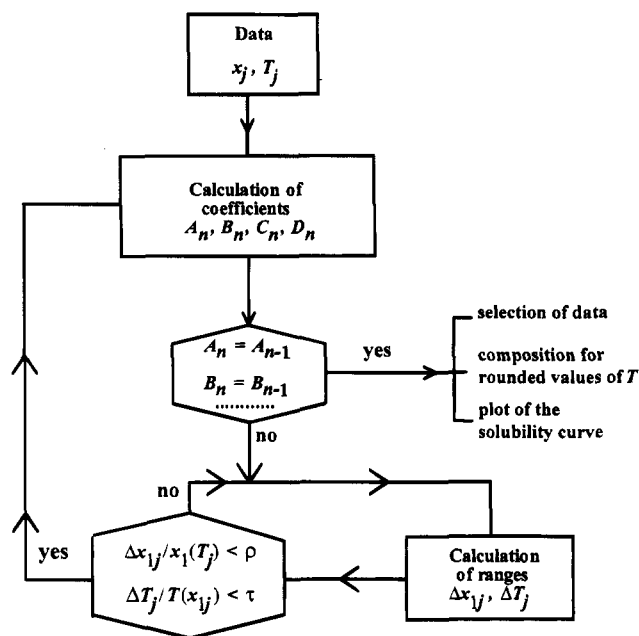


Figure 1. Flow chart for the critical analysis of solubility data.

(a) Calculation of solubility, given the temperature: The right-hand side of eq 1 gives the function Y . Define

$$z = e^Y / (2 + r)^2 (2/r + 1)^r \quad \text{for } r > 0$$

$$= e^Y / 4 \quad \text{for } r = 0 \quad (20)$$

(There is an error in the definition of $\exp(Y)$ in the original publication (ref 2).) Then, the mole fraction solubility x is a real root of the polynomial equation

$$0 = z(1 + x)^{2+r} - x^2(1 - x)^r =$$

$$z + (2 + r)zx + \sum_{n=0}^r \left(\frac{z(2 + r)!}{(n + 2)!} - \frac{(-1)^n r!}{n!} \right) \frac{x^{n+2}}{(r - n)!} \quad (21)$$

For anhydrous solids, the polynomial equation becomes linear, and the solution is straightforward

$$x_1 = 1/[2 \exp(-Y/2) - 1] \quad (22)$$

As the hydration number of the solid phase increases, the mole fraction solubility becomes smaller and, approximately, $x = 1/(2 + r)$, independent of z . Thus the solubilities of a hydrate, in its stable range, lie near this value of x , which becomes closer to the dystectic composition $1/(1 + r)$ (i.e., the composition of the hydrate) as r increases. The value $x = 1/(2 + r)$ is a satisfactory starting value for the solution of eq 22 by Newton's method.¹⁰ For the solubility as molality, eq 4 can be solved directly using Newton's method and $m = 1/2rM_2$ as a first approximation.

(b) Calculation of the equilibrium temperature, given the solubility: Equations 1, with one of 2, 3, 4, or 8–12 make possible, in the several cases, calculation of $Y(x_1)$ or $Y(m)$. Solution of these equations, as appropriate, by Newton's method, yields the equilibrium temperature.

Congruent melting of a hydrated solid is usually metastable with respect to a neighboring peritectic transformation; stable congruent melting points are observed only rarely. The congruent melting point (stable or metastable) can be estimated from the fitting equations by substitution of the appropriate mole fraction or molality of the hydrate and

solving for the temperature, as above. Calculation of the congruent melting point involves all coefficients of the fitting equation, and thus calculation of the corresponding estimated standard deviation involves all elements of the variance-covariance matrix. This matrix is produced routinely as part of the least-squares analysis.

RESULTS OF COMPILATIONS AND EVALUATIONS

For the binary system $\text{RbCl-H}_2\text{O}$, 29 publications were found, starting with the historically important paper of Kirchhoff and Bunsen published in 1861 and ending with the paper of Rard in 1984. The solid phases include both ice and RbCl . Two selected compilations from this system are reproduced in Chart 1. The Kirchhoff–Bunsen paper records the discovery and naming of rubidium and cesium, and how differential solubilities were used to prepare the first pure compounds of these elements. The paper of Berkeley (1904) has been chosen to illustrate that older papers often contain extensive and precise values of solubility. Application of eqs 1 and 3, and keeping only terms in A and D over a short range in temperature, permits an interpolated value 48.55 mass % at 25 °C to be calculated, which agrees well with the recent single value of Rard, 48.484 ± 0.044 mass %.

Volume 55 of the SDS is concerned with the solubility of actinide nitrates.³ It consists of critically-evaluated data obtained from a literature search covering the years from 1900 to 1992. The actinides for which data were found are uranium, neptunium, plutonium, americium, and thorium. The volume includes data for binary, tertiary, and quaternary systems with both aqueous and nonaqueous solvents. These are summarized in Table 1. While the larger work contains much more material than that in Table 1, only the binary aqueous system $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$ and a small part of the ternary system $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3\text{-H}_2\text{O}$ are described here.

For the binary system $\text{UO}_2(\text{NO}_3)_2\text{-H}_2\text{O}$, 26 publications have been found, with four solid phases $\text{UO}_2(\text{NO}_3)_2 \cdot r\text{H}_2\text{O}$, with hydrate numbers $r = 2, 3$, and 6, and ice. Selected examples of the evaluations are given in Chart 2. Data for the measurements of the solubility of $\text{UO}_2(\text{NO}_3)_2$ in water are mainly from systematic studies of the solubility of uranyl nitrate as a function of temperature. Some of these data were included in studies involving ternary systems such as uranyl nitrate, nitric acid, and water. Other data were obtained from investigations of mixed solvent systems, e.g., aqueous and organic solutions. Over 100 values of the solubility of uranyl nitrate in water cover a range of temperatures from the eutectic temperature with ice, about 254 K, to the congruent melting point of the salt dihydrate, about 456 K. The most commonly-used laboratory method for measuring these solubilities as a function of temperature has been the isothermal saturation method at several different temperatures. Most publications do not include the experimental errors.

The data used in the evaluation for the system $\text{UO}_2(\text{NO}_3)_2\text{-6H}_2\text{O}$ and resulting recommended values are given in Tables 1 and 5 of Chart 2. (Tables 2, 3, and 6–12 appear elsewhere in the Critical Evaluation and are not reproduced here.) Data in the range 253–334 K selected from Table 1 were fitted to the solubility eq 1. Values of the parameters A, B, C , and D which were obtained from least-squares fitting are given in Table 4, together with the standard deviations.

Table 1. Summary of Systems Containing Actinide Nitrates for which Solubility Data Exist in Both Aqueous and Nonaqueous Media^a

Uranium:	Thorium:
UO ₂ (NO ₃) ₂	Th(NO ₃) ₄
+ H ₂ O	+ H ₂ O
+ H ₂ O + HNO ₃	+ H ₂ O + HNO ₃
+ NH ₄ NO ₃	+ Al(NO ₃) ₃
+ LiNO ₃	+ HNO ₃
+ NaNO ₃	+ Cu(NO ₃) ₂
+ KNO ₃	+ Fe(NO ₃) ₃
+ RbNO ₃	+ UO ₂ (NO ₃) ₂
+ CsNO ₃	+ Al(NO ₃) ₃
+ Be(NO ₃) ₂	+ various organics
+ Mg(NO ₃) ₂	
+ Ca(NO ₃) ₂	Plutonium:
+ Sr(NO ₃) ₂	PuO ₂ (NO ₃) ₂
+ Ba(NO ₃) ₂	+ H ₂ O + NH ₄ NO ₃
	+ H ₂ O + HNO ₃ + organics
+ Zn(NO ₃) ₂	
+ Cd(NO ₃) ₂	Pu(NO ₃) ₄
+ Hg(NO ₃) ₂	+ H ₂ O + HNO ₃
	+ H ₂ O + HNO ₃ + KNO ₃
+ UO ₃	+ RbNO ₃
+ UO ₂ C ₂ O ₄	+ CsNO ₃
+ various organics	+ TiNO ₃
	+ various organics
+ H ₂ O + HNO ₃ + NH ₄ NO ₃	Neptunium:
+ CsNO ₃	NpO ₂ NO ₃ + H ₂ O + HNO ₃
+ Mg(NO ₃) ₂	NpO ₂ (NO ₃) ₂ + H ₂ O + HNO ₃
+ Ca(NO ₃) ₂	Np(NO ₃) ₄ + H ₂ O + HNO ₃
+ Sr(NO ₃) ₂	
+ Ba(NO ₃) ₂	Americium:
	Am(NO ₃) ₃ + H ₂ O + HNO ₃
+ Zn(NO ₃) ₂	Am(NO ₃) ₃ + H ₂ O + HNO ₃ + organics
+ Cu(NO ₃) ₂	
+ Al(NO ₃) ₃	
+ UO ₂ C ₂ O ₄	
+ UO ₃	
+ PuO ₂ (NO ₃) ₂	
+ Pu(NO ₃) ₄	

^a The organics include ethers, alcohols, esters, halides, ketones, and tributylphosphate.

The solubility equation, together with values of these parameters, was then used to interpolate solubilities at intervals of 5 K for the hexahydrate system. These recommended and tentative solubilities are given in Table 5.

The smoothed values from Table 5 are plotted as lines in Figure 1 of Chart 2. Experimental data used in the evaluation are also shown in Figure 1 of Chart 2. The portion of the plot from 0 to about 2 mol kg⁻¹ (about 250 to 273 K) reflects the composition of the solution as molality of UO₂(NO₃)₂, where the equilibrium solid phase is ice. This portion of the curve was obtained by graphical smoothing of the solubility data for the ice system in Table 13. The data in Table 13 were also fitted to the solubility equation, and resulting recommended values are given at the end of the table.

The solubilities in the binary systems UO₂(NO₃)₂·3H₂O–H₂O and UO₂(NO₃)₂–2H₂O–H₂O were analyzed in an analogous manner. The results are tabulated in,³ and the phase diagram is shown in Figure 2 of Chart 2. For completeness, both the ice and hexahydrate portions are also included in Figure 2 of Chart 2. The phase diagram for the ternary system UO₂(NO₃)₂–HNO₃–H₂O over the temperature range 248–332 K was constructed from the results of the evaluation of the binary system UO₂–(NO₃)₂–H₂O and from other extensive data on the effect of addition of nitric acid. This diagram is given in Figure 3 of Chart 2.

CONCLUSION

The methods described above are appropriate for evaluation of solubility data for salts in water and nonaqueous solutions. Other more complex methods involving, for example, equations for activity coefficients could be used. However, these methods draw on an area of current research, and the additional but necessary experimental evidence required to apply them is not available in a sufficient number of cases to be of wide general use for evaluations of data which cover large ranges of temperature and pressure.

One area which has been guided by current research on activity coefficients is the solubility of sparingly-soluble salts, and special methodologies are being developed for these cases.¹¹ Other areas, including solubilities of solid nonelectrolytes in liquids, mutual solubilities of liquids, and solubilities of gases in liquids, all require their own methodologies for evaluating data. Many of these methods have reached a mature stage of development in the Solubility Data Project, and their continuing refinement will be an ongoing feature of publications in the IUPAC Solubility Data Series.

ACKNOWLEDGMENT

Much of the introduction to this review was taken liberally from the works of the late A. S. Kertes (e.g., see refs 12 and 13), founder of the SDP, to whose memory this review is dedicated. The authors wish to thank IUPAC for permission to reproduce copyrighted materials from volumes 47 and 55 of the SDS in Charts 1 and 2.

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