Fusion:

$H_T - H_{298.16} = 0.448T - 0.32 \times 10^{-3}T^2 + 0.228 \times 10^5 T^{-1} + 19,745$

$S_T - S_{298.16} = 1.0309 \log T - 0.64 \times 10^{-3}T + 0.114 \times 10^5 T^{-2} + 13.46$

Glass (including heat of fusion):

$H_T - H_{298.16} = 46.923T + 3.527 \times 10^{-3}T^2 + 13.257 \times 10^5 T^{-1} + 1170$

$S_T - S_{298.16} = 108.045 \log T + 7.054 \times 10^{-3}T + 6.628 \times 10^5 T^{-2} - 260.96$

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Wilson Dam, Alabama

Pressure–Temperature Curves in Some Systems Containing Water and a Salt

By George W. Morey and W. T. Chen

A novel method for the determination of vapor pressures of saturated solutions has been applied to binary systems containing water and the salts LiF, NaF, KF, NaCl, KCl, RbCl, CsCl, PbCl$_2$, Li$_2$SO$_4$, Na$_2$SO$_4$, K$_2$SO$_4$, Tl$_2$SO$_4$, Na$_2$CO$_3$, K$_2$CO$_3$, Na$_2$O·4B$_2$O$_3$, Na$_4$P$_2$O$_7$, and K$_4$P$_2$O$_7$ at some or all of the temperatures 374, 400, 500, 600, and 700°

In this paper are presented a novel method for the determination of vapor pressures for the three-phase equilibrium gas + liquid + solid in binary systems containing water and a soluble salt, and numerous three-phase pressures so determined. In some of the solutions the solubility curve is continuous from ordinary temperatures to the melting point of the salt, and in some the solubility curve intersects the critical curve, giving rise to critical end-points. As can be seen from Fig. 1, with most of the salts studied the vapor pressure curves of the saturated solutions are continuous and pass through a point of maximum pressure. When at any temperature the pressure of steam is less than the three-phase pressure gas + liquid + solid, the salt is in a region in which only gas + solid is stable, and the salt will not be altered. But if the pressure is above the three-phase pressure, the salt will be in a region of gas + liquid, and it will deliquesce. In practice the salt is contained in a cylindrical crucible with a perforated bottom, so that the liquid formed will run out. Thus by varying the steam pressure at each temperature the vapor pressure of the saturated solution, the pressure above which the salt would deliquesce, could be located.

The apparatus is essentially that described by Morey and Hesselgesser.[1] Distilled water is pumped into a pressure line, which includes a pressure reservoir, a pressure gage and a pressure regulating apparatus, a bomb containing the charge and suitable valves. The purpose of the pressure reservoir, which has a volume of 2240 cc., is to increase the volume of the system so that each stroke of the pump does not have so much effect on the pressure. The pressure regulating device which controls the pump is a Baldwin fluid pressure cell, the sensitive elements of which are two Baldwin strain gages used in connection with a special Brown electronic indicating potentiometer. The apparatus was designed primarily for work at higher pressures and it was difficult to maintain pressures closer than ±25 p.s.i. Accordingly, most of the results are ±25 p.s.i., or 2 bars. Pressures were read on a 10-inch Bourdon type pressure gage which had been calibrated against a dead-weight gage. The temperature of the Nichrome-wound furnace was regulated by a Brown electronic indicating contact controller. The regulating thermocouple, either iron–constantan or chromel–alumel, was placed in a hole drilled in the cap of

the bomb to the level of the top of the chamber. An auxiliary winding, controlled by a separate Variac, was so adjusted that the bottom of the bomb was a degree warmer than the top. Temperatures were determined by a platinum–platinum 10% rhodium couple placed in a position similar to that of the control couple.

The bomb is connected with the pressure line by a hollow plunger. The stem is long enough so that the cone joint connection is about 3 cm. above the top of the furnace. A suitable system of valves enables the bomb to be connected with the pressure line or to blow off to the air. At the end of the run the valve connecting the bomb to the pressure line is closed.

The bombs or pressure vessels most used in this work were those described by Morey and Hesselgesser.[1] In some of the work the closure was a flat silver washer used with a flat plunger. For most of the work a modified Bridgman closure was used. This closure makes use of the internal pressure to maintain the seal. The head of the plunger fits inside the chamber of the bomb. A follower washer made with a slight taper, held in place by the cap, fits over the stem of the plunger, and the lower $1/4$ inch fits inside the chamber of the bomb. A washer $1/8$-inch thick fits over the stem of the plunger and is compressed between the head of the plunger and the follower. The washers usually are of silver, but copper and aluminum washers have been used. The initial closure is made by screwing down the nut bearing on the top of the cap; the final closure, by the action of the pressure in the interior of the bomb. The area of the head of the plunger is 0.60 square inch, that of the silver washer, 0.30 square inch, so that the pressure on the washer is twice the internal pressure. This closure has never leaked, even when subjected to wide changes in pressure and temperature. Most of the bombs were made of Inconel X, but in some cases stainless steel was used.

The experimental results are summarized in Table I and shown in Fig. 1. In the figure the pressure–temperature curve of water is shown, extended as a broken curve beyond the critical temperature of water by extrapolation by means of a linear equation of log p vs. $1/T$, and plotting the points so obtained.

Table Ia includes those salts in which the solubility curve does not intersect the critical curve. Runs were made at 374, 400, 500, 600 and 700°. The curves are of different shapes, resembling each other only in possessing a temperature of maximum pressure. The equation[2] of this P–T curve is

(1) G. W. Morey and J. M. Hesselgesser, *Am. J. Sci.*, Bowen Vol., 343 (1952).

(2) G. W. Morey, "Commentary on the Scientific Writings of J. Willard Gibbs," Vol. 1, Yale University Press, New Haven, Conn., p. 1936, p. 243.

TABLE I

THREE-PHASE PRESSURES, IN BARS, OF SOME WATER–SALT SOLUTIONS

Salt	M.p., °C.	Temperature, °C.					Max. pressure, °C.	
		374	400	500	600	700	Obsd.	Calcd.
a. Solubility curve is continuous								
KF	846	60		96	116		600	598
NaCl	800.4	136	173	330	406	395	640	604
KCl	770	112	129	209	218	198	580	582
RbCl	715		95	117	113		540	543
CsCl	638		64	64	29		450	492
PbCl$_2$	501	210	166					
Cs$_2$SO$_4$	1010		141	182	183	90	560	738
K$_4$P$_2$O$_7$	1105	20	60	150	167	230		803
K$_2$CO$_3$	895	31	76	158	203			627
Na$_2$O·4B$_2$O$_3$	816	47	85	136	150			612
b. Solubility curve intersects the critical curve								
LiF	844	>1000	>1000	>1000	>1000			598
NaF	990	>1000	>1000	>1000	>1000			691
Li$_2$SO$_4$	860	>1000	422	653	>1000			644
Na$_2$SO$_4$	884	> 250	850	>1000				662
K$_2$SO$_4$	1069	> 250	527	850				796
Na$_2$CO$_3$	851	> 250	>1000	>1000	>1000			598
Tl$_2$SO$_4$	632	> 275	230	272				521
Na$_4$P$_2$O$_7$	985	219	275	467				717

given by

$$\frac{dp}{dt} = \frac{(s^G - s^L) - \dfrac{x^G - x^L}{x^G - x^L}(s^S - s^L)}{(v^G - v^L)\dfrac{x^G - x^L}{x^G - x^L}(v^S - v^L)}$$

in which s, v and x represent specific entropies, volumes and weight fractions of the second component in the gaseous, G, liquid, L, and solid, S, phases. At the maximum the numerator becomes zero

$$\frac{x^G - x^L}{x^S - x^L} = \frac{s^G - s^L}{s^S - s^L}, \text{ or}$$

$$s^L = s^G\left(\frac{x^G - x^L}{x^G - x^S}\right) - s^G\left(\frac{x^S - s^L}{x^G - x^S}\right)$$

Beyond the point of maximum pressure the P–T curve has an increasingly negative slope.

The temperature of the maximum on the three-phase curve can be located approximately from the shape of the experimentally determined curve, and temperatures so located are given in Table I. Korvezee and Dingemans[3] derived an empirical equation between the melting temperature of the salt, T_s, and the temperature of the maximum on the three-phase curve

$$1/T_{max} = 1/T_s + 0.00021$$

in which temperatures are given on the Kelvin scale. Points so calculated are included in Table I. Considering the fact that the shape of the curve interpolated between the points and the position of the maximum are arbitrary, the agreement between the observed and calculated values is in many cases excellent.

There are few results in the literature which can be compared with those of this study. Benedict[4] devised an apparatus for determining the vapor pressure of saturated salt solutions and applied it to the system H_2O–KCl up to 600°. Keevil,[5] using the same apparatus, repeated Benedict's work with KCl and also made measurements on NaCl. Their results are shown as triangles in Fig. 1, to be compared with our results, shown as circles. There is a systematic difference, greater than that to be expected from the estimated precision of either group of experiments. For example, linear interpolation of Keevil's results gives for NaCl at 400°, 161.7 bars and at 500°, 308.9 bars; to be compared with the values of 173 and 330 bars in Table I. Benedict gave 123.2 and 200.9 bars for the vapor pressure of saturated KCl solution at 400 and 500°, respectively; to be compared with 128 and 209 bars in Table I. In the system H_2O–KCl the two sets of experimental results overlap in the region of maximum pressure, and in both H_2O–NaCl and H_2O–KCl the three-phase pressures found by Keevil at the highest temperatures are considerably lower than those found by us. Keevil also studied binary systems containing H_2O and NaBr, NaI and KBr. Dingemans and collaborators[6] studied binary systems containing H_2O with KCNS, $AgNO_3$, NH_4NO_3 and $Pb(NO_3)_2$; ternary systems containing the pairs $AgNO_3$ and NH_4NO_3, $PbNO_3$–NH_4NO_3, $AgNO_3$–$Pb(NO_3)$; and the quaternary system H_2O–NH_4NO_3–$AgNO_3$–$Pb(NO_3)_2$. These were not included in this study because of the small vapor pressures of the saturated solutions.

Table Ib includes those salts in which the solubility curve intersects the critical curve, giving rise to critical end-points. The experimental criterion is that at the critical temperature of water, 374°, the salt shall not be liquefied by a pressure of 250 bars, 29 bars above the critical pressure of water (221.06 bars). The salts LiF, NaF and Na_2CO_3 show the effect normally to be expected in the region above the first critical end-point and below the second critical end-point; namely, the salts were

(3) A. E. Korvezee and P. Dingemans, Rec. trav. chim., **64**, 194 (1945); THIS JOURNAL, **70**, 2818 (1948).

(4) M. Benedict, J. Geol., **47**, 252 (1930).

(5) N. B. Keevil, THIS JOURNAL, **64**, 841 (1942).

(6) P. Dingemans, Rec. trav. chim., **58**, 524 (1939); **60**, 317 (1941); P. Dingemans and K. Van Den Berg, ibid., **61**, 605 (1942); P. Dingemans, ibid., **62**, 85 (1943); **64**, 194, 199 (1945); P. Dingemans and L. L. Dijkgraaf, ibid., **65**, 477 (1946); **66**, 239 (1947).
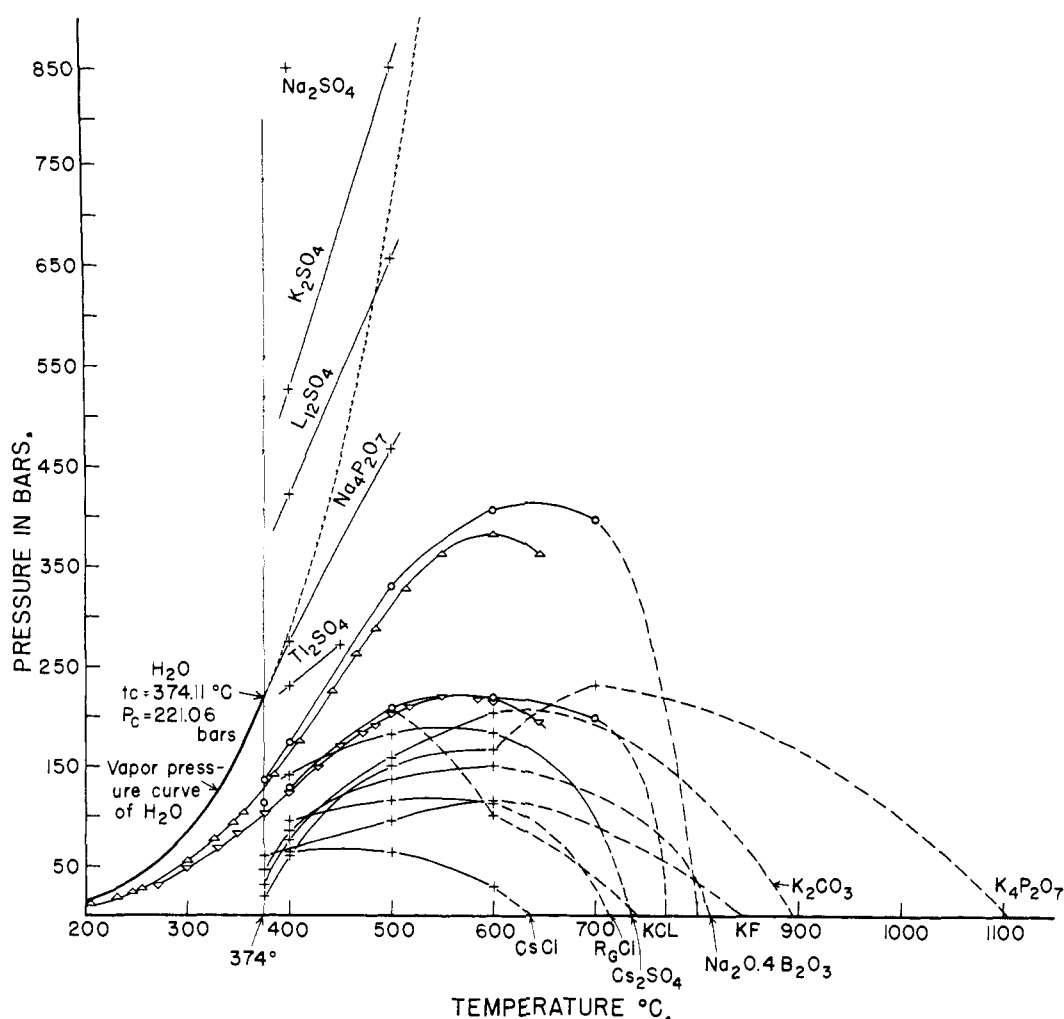
Fig. 1.—The experimental results. The vapor pressure of water is shown, ending at the critical point, and extrapolated along the dotted line.

not affected by water pressures up to 1000 bars at 374, 400, 500 or 600°. They were not even sintered. The sulfates Li_2SO_4, Na_2SO_4 and K_2SO_4 show an unexpected effect. There is no doubt that they both have retrograde solubility curves, with the first critical end-point near the critical point of water. This previously has been demonstrated for Na_2SO_4.[7] But in each case liquefaction took place at 400 and 500°, at a high pressure of steam. Li_2SO_4, for example, was not melted by 1000 bars at 374°, was melted by 422 bars at 400°, required 653 bars at 500°, and was not melted by 1000 bars at 600°. K_2SO_4 required 527 bars steam pressure to melt it at 400°, 860 bars at 500°. At first sight, it would seem that we mūst here be realizing the upper part of the three-phase curve water–salt, which would require that the upper critical end-point be between 374 and 400°. Morey and Hesselgesser[1] found such to be the case in the binary system H_2O–$Na_2Si_2O_5$, but in that case the P–T curve of the three-phase equilibrium was rising very rapidly with decreasing temperatures and it was possible to conceive of the gas and liquid phases becoming iden-

tical at some higher pressure, as is necessary at a critical end-point. That cannot be the case with these sulfates, because the three-phase pressure was found to be increasing with increasing temperature. It may be that we are here dealing with systems which form two liquid layers, possibly without a quadruple point being formed. The theory of such systems has been discussed by Büchner[8] and more exhaustively by Koers and Scheffer.[9] Decision as to details of the equilibrium must wait for further experimental work, but it should be noted that with K_2SO_4 at 500° and 1200 bars the gas phase contained 26% K_2SO_4, and at 600° and 1200 bars an uncertain measurement gave over 50%.

In the systems H_2O–$PbCl_2$ (not plotted) and H_2O–Tl_2SO_4 there is evident formation of two liquid layers, with the solubility in the water-rich layer becoming about zero at the critical temperature of water, since the P–T curve of H_2O–Tl_2SO_4 intersects the curve for pure water at the critical temperature. $Na_4P_2O_7$ is similar in that the pressure

(7) W. C. Schroeder, A. A. Berk, E. P. Partridge and A. Gabriel, THIS JOURNAL, **57**, 1539 (1935).

(8) "Die Heterogenen Gleichgewichte von H. W. Bakhuis Roozeboom," Vol. 2, part 2, Braunschweig, 1918.

(9) J. H. Koers and F. E. C. Scheffer, *Rec. trav. chim.*, **49**, 588, 915 (1930); **50**, 139 (1912); **53**, 279 (1934).

on the $P-T$ curve at $374°$ is the critical pressure of water. More work is needed on $Na_4P_2O_7$. The experimental results for $K_4P_2O_7$ do not fall on a single smooth curve, and the $P-T$ curve has arbitrarily been drawn as if there were a change in the solid phase in the neighborhood of $600°$. Morey, Boyd, England and Chen[10] did not observe an inversion in this region, but from analogy with

(10) G. W. Morey, F. R. Boyd, J. L. England and W. T. Chen, THIS JOURNAL, 77, 5003 (1955).

$Na_4P_2O_7$[11] polymorphic forms would be expected.

Experiments were made with $Na_2B_4O_7$, but the solutions obtained were so viscous they would not run out of the perforated crucible. On cooling the pasty hydrous glasses usually contained freshly crystallized $Na_2B_4O_7 \cdot 5H_2O$.

(11) E. P. Partridge, V. Hicks and G. W. Smith, ibid., 63, 454 (1941).

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Radiochlorine Exchange Reactions in Acid Chloride Solvents and in Liquid Sulfur Dioxide[1]

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Radiochlorine exchange reactions of both acid and basic chloride solutes have been studied in three non-aqueous solvents: thionyl chloride, selenium oxychloride and phosphorus oxychloride. Exchange appears to be reasonably rapid and complete in every case in support of self-ionization schemes which have been advanced for these solvents. The exchange between thionyl chloride and tetramethylammonium chloride dissolved together in liquid sulfur dioxide is also found to be very fast, rendering plausible the slight ionization of the former, in this solvent, to $SOCl^+$ and Cl^- ions.

Isotopic exchange experiments have shown that, despite its merits, the solvent systems interpretation of non-aqueous solvent phenomena cannot be uniformly applied with confidence. Thus neither liquid sulfur dioxide[3-5] nor liquid phosgene[6] show the anticipated ready exchangeability with the respective "acids" thionyl chloride (or bromide) and aluminum chloride. In contrast, nitrosyl chloride does exchange rapidly with chloride solutes[7] ("bases"), its assumed self-ionization to nitrosyl and chloride ions thus being apparently confirmed.

We have now examined the chloride exchange behavior toward solutes of three additional acid chloride solvents[8]: thionyl chloride, selenium oxychloride and phosphorus oxychloride, both acid and basic solutes being used. Self-ionizations which have been assumed for each solvent, yielding chloride ions (solvated or otherwise), e.g., equation 1 below, should lead to rapid isotopic exchanges in every case.

A problem related to its self-ionization is the nature of the ionic species (if any) which thionyl chloride may yield in liquid sulfur dioxide solution. The absence of isotopic exchange with the solvent[3-5] excludes the once assumed[9] thionyl ions, SO^{++}. On

(1) This research has been carried out under contract AT (45-1)-244 between the U. S. Atomic Energy Commission and Oregon State College.

(2) Taken from the Ph.D. thesis of B. J. Masters and the M.S theses of N. D. Potter and D. R. Asher, at Oregon State College, June, 1954.

(3) R. E. Johnson, T. H. Norris and J. L. Huston, THIS JOURNAL, 73, 3052 (1951).

(4) E. C. M. Grigg and I. Lauder, Trans. Faraday Soc., 46, 1039 (1950).

(5) R. Muxart, Compt. rend., 231, 1489 (1950).

(6) J. L. Huston, J. Inorg. and Nucl. Chem., 2, 128 (1956).

(7) J. Lewis and R. G. Wilkins, J. Chem. Soc., 56 (1955).

(8) For investigations of chemical phenomena in these solvents see, for example: H. Spandau and E. Brunneck, Z. anorg. allgem. Chem., 278, 197 (1955) (SOCl₂); G. B. L. Smith, Chem. Revs., 23, 165 (1938) (SeOCl₂); V. Gutmann, Z. anorg. allgem. Chem., 270, 179 (1952) (POCl₃).

(9) G. Jander, "Die Chemie in Wasserähnlichen Lösungsmitteln," Springer-Verlag, Berlin, 1949, p. 210.

the other hand, it would be plausible and consistent with their general chemical nature[10,11] for these feebly conducting[12] solutions to ionize slightly to the intrinsically more reasonable species[13] $SOCl^+$ (cf. equation 1). To test for this possibility we have studied the radiochlorine exchange between thionyl chloride and tetramethylammonium chloride, dissolved together in liquid sulfur dioxide. Such an ionization equilibrium would, naturally, lead to a rapid exchange.

Results and Discussion

Exchanges in Acid Chloride Solvents.—Given in Table I are percentage exchanges calculated generally from the measured final specific activities of separated solvent and solute (or solute-enriched solvent) fractions. Exchange is substantially complete in all but the ferric chloride–selenium oxychloride case. Here, however, the apparent incompleteness is probably illusory, resulting from inadequate removal of coprecipitated material from the solute-derived counting sample precipitates (see Experimental section). Such an effect, which naturally dwarfs the recorded counting uncertainties, is further indicated by the long-time run (5300 minutes), which fails to show exchange approaching completion, giving figures within the same range as three short-time runs. One concludes, therefore, that in every instance exchange is probably complete within the shortest recorded time.

The foregoing calculated percentages, together with the indicated uncertainty estimates, have been used to obtain the recorded approximate upper limits for exchange half-times. All are relatively

(10) Reference 9, pp. 209-307.

(11) B. J. Masters and T. H. Norris, THIS JOURNAL, 77, 1346 (1955).

(12) Reference 9, p. 237.

(13) L. C. Bateman, E. D. Hughes and C. K. Ingold, J. Chem. Soc., 243 (1944).