[Contribution from the Oak Ridge National Laboratory, Chemistry Division]

Activity Coefficients of Uranyl Fluoride from Freezing Point Depressions: Undissociated Species and Dimerization[1]

By James S. Johnson and Kurt A. Kraus

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Freezing point depressions of aqueous uranyl fluoride solutions were obtained in the region 0.1–5 molal UO_2F_2 by a warming curve method. A thermistor was used as the temperature sensitive element in an automatically recording system. Activity coefficients of UO_2F_2 were calculated from these data. From these it can be concluded that uranyl fluoride in the concentration range studied is essentially undissociated and has a considerable tendency to associate. A dimerization constant K = 1.5 was evaluated for the reaction $2UO_2F_2 \rightarrow (UO_2F_2)_2$ on the assumption that the logarithm of the activity coefficients of the monomer and dimer vary linearly with molality of UO_2F_2.

In the course of the determination of the phase diagram of the system UO_2F_2–H_2O, Marshall, Gill and Secoy[2] found that the freezing point depressions θ were very small if interpreted on the assumption that uranyl fluoride dissociates into three ions (UO_2^{++} and $2F^-$). Thus it appeared that uranyl fluoride cannot be completely dissociated. A more detailed study of the freezing point depressions of uranyl fluoride solutions has now been carried out in an attempt to obtain accurate values of the activity coefficients. These have been interpreted in terms of the postulated species (undissociated) UO_2F_2 and its dimer $(UO_2F_2)_2$.

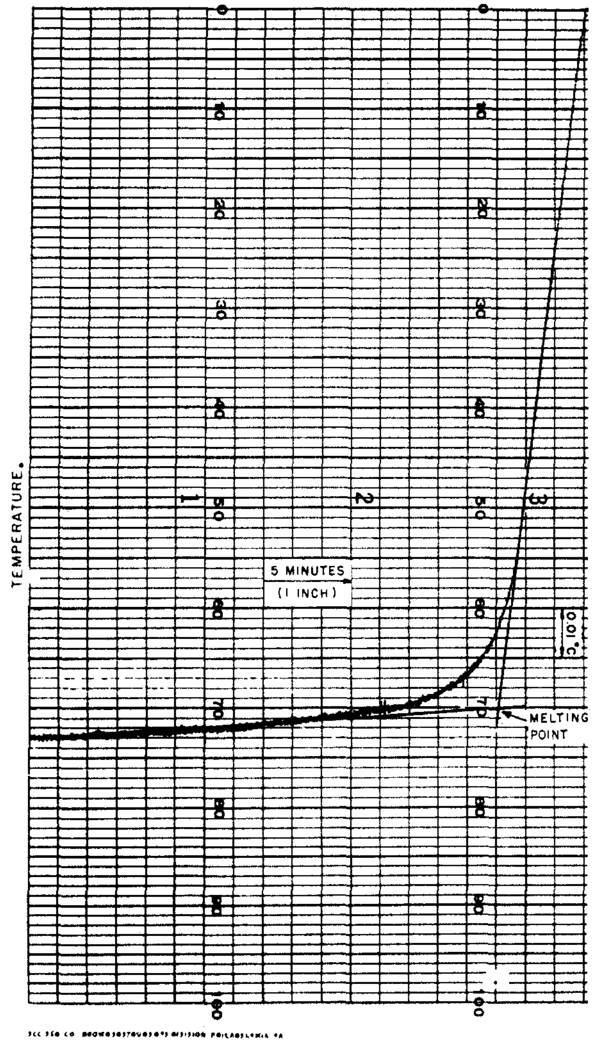

Fig. 1.—Warming curve 0.3 molal UO_2F_2.

Experimental

Procedure.—The freezing point depressions were determined by a warming curve method. The solutions were placed in a small unsilvered dewar flask which was fitted with an air-driven stirrer and supplied with inlet and outlet tubes to the jacket. The solutions were partially frozen by admission of a freezing mixture into the jacket. Using the jacket as a dead air space, a new ice-salt-bath was placed around the apparatus, the temperature of which was adjusted to give the desired warming rate.

A continuous temperature plot (voltage drop across a thermistor) was obtained on a Brown recorder as will be described below. The plot consisted (Fig. 1) of a slowly rising, practically linear branch in the presence of ice, followed by a linear, more rapidly rising branch after the ice had melted. The intersections of the extrapolated linear branches were assumed to give the freezing points of the solutions. These could be reproduced to better than ±0.006° in the concentration range 2.5–5 molal with heating rates differing often by a factor of two or more. The reproducibility for the more dilute solutions was usually better than ±0.002°.

Apparatus. Thermistor and Recorder.—The temperature sensitive element of the equipment was a Western Electric thermistor,[3] enclosed in a Pyrex jacket of approximately 2 mm. diameter, with resistance 365,000 ohms at 0°. It was mounted in a 0.6 cm. diameter, 4 cm. long, platinum thimble and held in place with a bismuth–lead–tin alloy of m.p. 150°. The thimble was sealed to a soft glass tube which served as a handle and accommodated the leads. The glass tube was filled with ceresin wax for insulation.

The thermistor was placed in series with a "standard" resistor of approximately 1,000,000 ohms and a 1.5 volt "telephone" battery. The voltage drop across the thermistor was measured with a vibrating reed electrometer.[4] The bucking potential was supplied with a Rubicon precision potentiometer in series with a Brown Electronik recorder which could be adjusted for 3 or 30 mv. full-scale sensitivity. Since the thermistor had a temperature coefficient of approximately 5% per °C., a distance of 2.5 mm. on the Brown recorder corresponded to less than 0.001° on the most sensitive scale. The time constant of the equipment was *ca.* 7 sec., which should not introduce an appreciable error in the results.

The "standard" resistor, with temperature coefficient 0.015% per °C., was mounted in a vessel thermostated at 25 ± 0.1°.

The thermistor was calibrated before and after the measurements (*ca.* 3-months period) against a Bureau of Standards calibrated platinum resistance thermometer (Mueller

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[1] This document is based on work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] (a) W. L. Marshall, J. S. Gill and C. H. Secoy, Abstracts 119th Meeting of the American Chemical Society, Cleveland (April, 1951); (b) C. H. Secoy, Report ORNL 795, (June, 1950).

[3] J. A. Becker, C. B. Green and G. L. Pearson, *Bell System Tech. J.*, **26**, 170 (1947).

[4] K. A. Kraus, R. W. Holmberg and C. J. Borkowski, *Anal. Chem.*, **22**, 341 (1950).

Bridge).[5] The two calibrations checked to within experimental accuracy. It was found that the equation proposed by Becker, Green and Pearson[3]

$$\log R = A + B \log T + C/T \qquad (1)$$

where R is the resistance of the thermistor, A, B and C are constants, and T the absolute temperature, was followed to ±0.001° in the temperature range of the measurement (0 to −10°). The constants determined for this thermistor were $A = 14.22484$, $B = -5.20968$ and $C = 1,101.04$.

To check the performance of the instrument, ice points were determined daily. To illustrate the reproducibility of the instrument, the ice points (of tap water ice washed in distilled water) determined over a 15-day period are shown in Table I. The standard deviation of these measurements is ±0.0011°, which is about that found by Richards and Campbell[6,7] ($\sigma = 0.0015°$).

TABLE I

ICE POINT DETERMINATIONS WITH THERMISTOR

Date	Thermistor resistance × 10^{-5}
12 Nov. A.M.	3.6520
12 Nov. P.M.	3.6519
12 Nov. P.M.	3.6524
13 Nov.	3.6522
15 Nov. A.M.	3.6524
15 Nov. P.M.	3.6523
19 Nov. A.M.	3.6521
19 Nov. A.M.	3.6523
19 Nov. P.M.	3.6519
20 Nov.	3.6520
23 Nov. A.M.	3.6523
23 Nov. P.M.	3.6524
24 Nov.	3.6524
27 Nov.	3.6522
Mean	3.65220

$\sigma = 19\ \Omega$ or $\pm 0.0011°$

Using this technique of warming curves, the freezing point depression of a 0.4120 molal HCl solution was determined to check the accuracy of the method. A freezing point depression $\theta = 1.487°$ was found which compares favorably with the interpolated values 1.485 of Randall and Young[8] and 1.488 of Chadwell.[9]

Materials.—Two preparations of uranyl fluoride were used, one prepared by Harshaw and one by the Chemical Department of the Oak Ridge Electromagnetic Plant (Y-12). Both samples were found to contain negligible impurities by spectrographic analysis and by activation analysis for sodium.[10] The fluoride to uranium ratios were found by the Y-12 Analytical Department to be 1.983 and 1.998, respectively, for the two samples, which showed no significant differences in the freezing point depressions.

Stock solutions were prepared from the two samples with distilled water. Dilutions were made on a weight basis. The stock solutions and a number of diluted solutions were analyzed for uranium (U_3O_8) through direct evaporation and ignition and through ignition after precipitation of ammonium uranate.[11] The methods agreed to within a few tenths of a per cent. and indicated that the solutions were not significantly contaminated. For the calculations averages of the two analyses were used.

Results and Discussion

The observed freezing point depressions θ and the values of θ/m, where m is the molality of UO_2F_2, are given in Table II. The freezing points were determined on four different solutions, which are identified in the table. The spreads indicated represent the average deviations of the freezing points determined on the same solution with different rates of warming. They do not represent the absolute accuracy of the data which is probably about ±0.5% of the value of θ/m above 0.5 molal and may be somewhat larger below this concentration.

TABLE II

FREEZING POINT DEPRESSIONS OF URANYL FLUORIDE

m	Solution[a]	θ, °C.[b]	θ/m
0.1005	4	0.176 ± 0.0005	1.75
.1972	2	.331 ± .001	1.678
.2974	2	.487 ± .001	1.638
.3005	3	.486 ± .0005	1.617
.4914	4	.768 ± .004	1.563
.4941	2	.772 ± .0005	1.562
.6943	4	1.058 ± .0000	1.526
.8875	2	1.334 ± .0005	1.503
.8936	1	1.344 ± .0005	1.504
1.077	1	1.610 ± .002	1.495
1.341	1	2.003 ± .001	1.494
1.348	3	2.004 ± .002	1.487
1.601	3	2.402 ± .001	1.500
2.077	2	3.189	1.535
2.086	4	3.203 ± .002	1.535
2.088	3	3.188 ± .005	1.527
2.554	3	4.033 ± .002	1.579
3.028	3	4.943 ± .004	1.632
3.427	3	5.812 ± .004	1.691
4.027	3	7.143 ± .005	1.774
4.558	3	8.406 ± .002	1.844
5.249	3	10.183 ± .006	1.940

[a] Solutions 1, 2, 3 prepared from Harshaw UO_2F_3; solution 4 prepared from Y-12 UO_2F_2. [b] Averages of measurements; ranges given indicate average deviations for separate measurements on the same solution. Actual uncertainty is considerably larger.

Activity coefficients γ can be calculated from the freezing point data by the use of the equation[12]

$$\ln \gamma = -j - \int_0^m j/m \, dm + \frac{c}{\nu}\int^m \theta/m \, d\theta \qquad (2)$$

where c is a constant (5.7×10^{-4}), $j = 1 - \theta/\nu\lambda m$, ν the number of moles of particles per mole of UO_2F_2 and $\lambda = 1.860$, the molal freezing point depression constant.

Since Dean[13] and Brown[14] found that the molar conductance of uranyl fluoride solutions is very small at 25° (less than 9 in 0.1 M UO_2F_2 and considerably smaller at higher concentrations), it is apparent that uranyl fluoride is not appreciably dissociated into ions in the concentration range studied. Hence in the evaluation $\nu = 1$ has been assumed.[15]

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[5] We are indebted to Mr. George Ritscher of the Oak Ridge National Laboratory Instrument Division for assistance with the calibration.

[6] L. A. Richards and R. B. Campbell, *Soil Sci.*, **65**, 429 (1948).

[7] Thermistors have been used for similar purposes by (a) B. M. Zeffert and S. Normats, *Anal. Chem.*, **21**, 1420 (1949); (b) J. R. Campbell, J. T. Pender and R. P. Puri, *J. Roy. Tech. Coll. (Glasgow)*, **5**, 89 (1950).

[8] M. Randall and L. E. Young, THIS JOURNAL, **50**, 989 (1928).

[9] H. M. Chadwell, *ibid.*, **49**, 2795 (1927).

[10] We are indebted to Mrs. M. Wittels, Mr. C. Feldman and Mr. G. W. Leddicotte of the ORNL Analytical Division for the analyses.

[11] We are indebted to Mrs. Helen Cutcher and Mr. Paul Thomason of the ORNL Analytical Division for the uranate analyses.

[12] G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., New York, N. Y., 1923, p. 347.

[13] G. R. Dean, Report CC-2092 (September 1944).

[14] R. D. Brown, private communication.

[15] Calculations for $\nu = 2$ and 3 have been carried out which yielded extremely small activity coefficients, clearly supporting the contention that ν is not larger than 1.

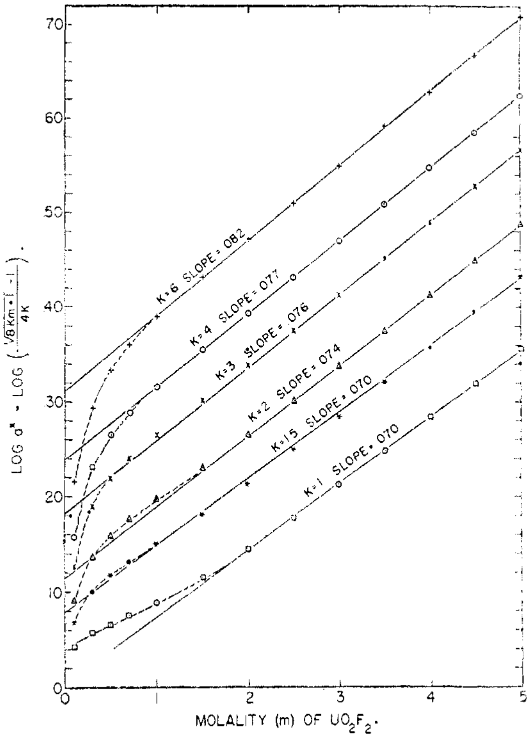

Fig. 2.—Evaluation of dimerization constant (plot of equation 11).

Dissociation of UO_2F_2 into ions, however, will occur at lower concentrations so that the integrals of equation 2 cannot be evaluated from $m = 0$ for $\nu = 1$. Hence formal activity coefficients γ^* were evaluated, setting

$$-\ln \gamma^* = j = 1 - \theta/\lambda\nu m \text{ at } m = 0.1 \quad (3)$$

γ^* is proportional to γ with a proportionality constant β as shown by the equation

$$\ln \gamma = \ln \gamma^* - \int_0^{0.1} \frac{j}{m}\, dm + \frac{c}{\nu}\int_0^{0.1} \frac{\theta}{m}\, d\theta = \ln \beta\gamma^* \quad (4)$$

The activity coefficients γ^* calculated from the smoothed values of θ are shown in Table III. It may be noticed that γ^* decreases to approximately 0.54 at $m = 2.5$ and then rises to approximately 0.62 at $m = 5$. An undissociated species would hardly be expected to give values of γ^* as low as these or to have such a minimum in γ^* as a function of m. Rather the activity coefficients might be expected to follow an equation of the type[16,17]

$$\log \gamma = bm \quad (5)$$

where b is a constant.

TABLE III

FORMAL ACTIVITY COEFFICIENTS OF URANYL FLUORIDE

m	j	$\int_{0.1}^{m} j/m\, dm$	$\int_{0.1}^{m} \frac{\theta}{m}\, d\theta$	γ^*
0.1	0.059	....	...	0.942
.3	.124	0.0980	0.53	.801
.5	.1603	.1707	0.99	.719
.7	.1796	.2280	1.44	.666
1.0	.1952	.2954	2.10	.613
1.5	.1958	.3755	3.21	.566
2.0	.1802	.4289	4.43	.545
2.5	.1544	.4671	5.80	.539
3.0	.1221	.4923	7.34	.543
3.5	.0872	.5085	9.08	.554
4.0	.0506	.5175	11.02	.570
4.5	.0135	.5211	13.17	.590
5.0	−.0247	.5205	15.55	.615

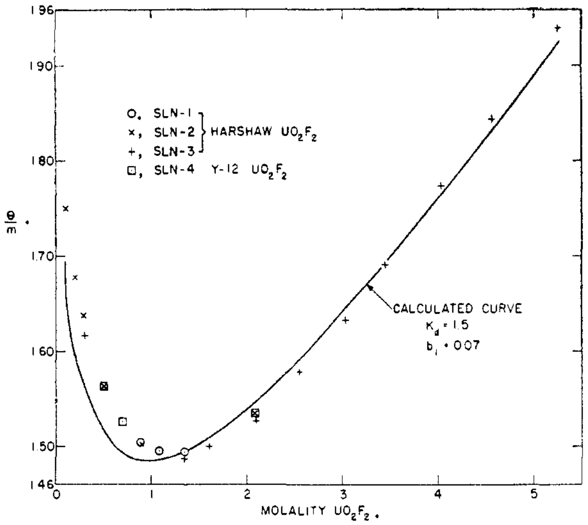

Fig. 3.—Freezing point depressions of UO_2F_2.

The decrease in the activity coefficients with molality at the lower concentrations suggests that UO_2F_2 tends to associate to a low molecular weight polymer. The rise of the activity coefficient curve beyond the minimum could then be explained on the assumption that the activity coefficients of the monomer and polymer increase with m. Calculations were carried out assuming that the polymer is a dimer with an association constant

$$K = a_2/a_1^2 \quad (6)$$

where a_1 and a_2 are the activities of the monomer and dimer, respectively. In addition, it was assumed that the activity coefficients of the monomer and dimer follow equation 5, *i.e.*

$$\log \gamma_1 = b_1 m \text{ and } \log \gamma_2 = b_2 m \quad (7)$$

where b_1 and b_2 are constants. On the basis of the non-electrostatic interaction terms of the equations developed by Scatchard and Epstein,[17] $b_2 = 2b_1$ appears reasonable. The monomer–dimer equilibrium constant K will then be

$$K = m_2\gamma_2/m_1^2\gamma_1^2 = m_2/m_1^2 \quad (8)$$

The activity of the monomer, $a_1 = m_1\gamma_1$, can be evaluated from the activity $a = m\gamma$ of the solute by the expression

$$a = a_1 = \gamma m = \beta m\gamma^* = \beta a^* \quad (9)$$

where m is the formal molality of solute, $a^* = m\gamma^*$, β a constant defined in equation 4, and γ^* the calculated formal activity coefficient of the solute (Table III). Since

$$m = m_1 + 2m_2 = m_1 + 2Km_1^2 \quad (10)$$

combination of equation 9 with equations 7 and 8 yields

$$\log a^* - \log (\sqrt{8Km + 1} - 1)/4K = b_1 m - \log \beta \quad (11)$$

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[16] **H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1950, Sec. Ed., p. 209.**

[17] G. Scatchard and L. F. Epstein, *Chem. Revs.*, **30**, 211 (1942).

Thus, there should be a value of K for which a plot of the left side of equation 11 *versus* m gives a straight line of slope b_1. Plots of this equation for several values of K are given in Fig. 2. In general, straight lines of slope 0.07 to 0.08 are obtained for large values of m. However, it may be noticed that large deviations from linearity are obtained at small values of m for $K > 3$. These deviations are opposite to those expected for dissociation of UO_2F_2 into ions, and hence the values of K for which such concavity downward occurs must be considered too large. Best linearity throughout the whole range of m is found for $K = 1.5$.

In Fig. 3 a comparison of the experimental values of θ/m with a theoretical curve calculated on the assumption $K = 1.5$ and $b_1 = 0.07$ is given. This theoretical curve was calculated by the use of the equation

$$\frac{\theta}{1.86m} = \frac{-55.5}{RT}\frac{\mu_s^e}{m} - = \frac{m_1 + Km_1{}^2}{m} + \frac{2.303\ b_1m}{2} \quad (12)$$

where μ_s^e is the excess of the chemical potential of the solvent over its standard chemical potential and is defined by the equation $\mu_s^e = \mu_s - \mu_s^0$. Equation 12 can be derived as follows: let μ_A^e be the analogous excess chemical potential for the solute, then

$$\mu_A^e/RT = \ln m_1 + 2.303\ b_1m \quad (13)$$

Use of the Gibbs–Duhem equation yields

$$\frac{1}{RT}\,\mathrm{d}\,\frac{\mu_A^e}{\mathrm{d}m} = \frac{\mathrm{d}m_1}{m_1\,\mathrm{d}m} + 2.303\ b_1 = \frac{-55.5}{mRT}\,\mathrm{d}\,\frac{\mu_s^e}{\mathrm{d}m} \quad (14)$$

Rearranging this equation, integrating, and substituting θ in terms of μ_s^e, with neglect of the higher terms in θ, yields equation 12.[18]

While the calculated curve clearly reproduces the general features of the experimental data, agreement is not obtained within experimental error and various attempts to fit it by different choices of the two parameters K and b_1 do not yield significantly better agreement. It is believed that the deviations are probably primarily due to partial dissociation of UO_2F_2 into ions at low m and changes of K, b_1 and b_2 with temperature. Nevertheless the agreement is sufficiently good to show that uranyl fluoride exists in solution primarily as neutral species, tends to dimerize with a constant K approximately equal to 1.5, that the logarithms of the activity coefficients of both the monomeric and dimeric species vary approximately linearly with m and that the corresponding proportionality constants are *ca.* 0.07 and 0.14.

Acknowledgment.—The authors are greatly indebted to Professor George Scatchard and to Dr. R. W. Stoughton for a number of very valuable discussions.

[18] See also ref. 16, p. 286.

OAK RIDGE, TENNESSEE

[CONTRIBUTION NO. 23 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

A Calorimetric Determination of the Vapor Heat Capacity and Gas Imperfection of Water

BY J. P. MCCULLOUGH, R. E. PENNINGTON AND GUY WADDINGTON

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Values of the heat capacity of water vapor were obtained at several pressures in the range $^1/_8$ to 1 atmosphere at each of five temperatures between 361 and 487°K. It was found that the vapor heat capacity is not a linear function of pressure. Experimental values of $(\partial C_p/\partial P)_T$ and the volume data of Osborne, Stimson and Ginnings were used to obtain empirical expressions for the second and third virial coefficients, B and C, of the equation of state, $PV = RT + BP + CP^2/RT$. By integrating the expression for $(\partial C_p/\partial P)_T$ in terms of this equation of state, an equation for the vapor heat capacity as a function of temperature and pressure was derived. In the range of temperature and pressure of the experiments, the equation represents the calorimetric data to within ±0.1% and values of C_p° computed from spectroscopic and molecular structure data within ±0.05%.

Although water has been the subject of intensive thermodynamic investigation, certain important properties of the vapor have not been determined experimentally. Accurate measurements have been made of the latent heat of vaporization,[1] enthalpy of the saturated liquid and vapor,[1] vapor pressure,[1,2] vapor heat capacity at high temperatures and pressures,[3] Joule–Thompson coefficient[4] and specific volume[5] of the vapor. These data have been correlated by means of a single equation of state.[2,6] The variation of the vapor heat capacity with pressure at pressures below atmospheric has not been studied previously. In addition, the indirect experimental determination of C_p° by Collins and Keyes[7] at and below 125° resulted in values 0.3% higher than those computed from spectroscopic and molecular structure data.[8] It was felt that further verification of this important property was desirable. For these reasons the heat capacity of water vapor was investigated at pressures from $^1/_8$ to 1 atmosphere at each of five temperatures between 361 and 487°K., using experi-

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[1] N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939) (original references cited there).

[2] F. G. Keyes, *J. Chem. Phys.*, **15**, 602 (1947) (original references cited there).

[3] (a) O. Knoblauch and W. Koch, *Mech. Eng.*, **51**, 147 (1929); (b) W. Koch, *Forsch. Gebiete Ingenieurw.*, **3A**, 1 (1932).

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[6] J. H. Keenan and F. G. Keyes, "Thermodynamic Properties of Steam," John Wiley and Sons, Inc., New York, N. Y., 1936.

[7] S. C. Collins and F. G. Keyes, *Proc. Am. Acad. Arts Sci.*, **72**, 283 (1938).

[8] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).