appeared in the solution of the oxidant. When electrolysis was taking place, on the other hand, appreciable quantities of metallic silver or of manganese dioxide were deposited and identified. Under these conditions it is scarcely conceivable that the reducing agent could be anything other than a lower valent beryllium species, which thus appears to be capable of at least transitory existence in aqueous solution.

Additional Observations.—The behavior of a beryllium anode in the presence of a number of other electrolytes was investigated, the conditions of electrolysis being similar to those described for sodium chloride. Results are tabulated below. No non-electrolytic attack on the anode was observed in any case.

Acknowledgment.—The authors are indebted to the Office of Ordnance Research, U. S. Army, and to the Cady Fund of the Department of Chemistry, University of Kansas, for financial aid in support of this investigation.

TABLE III

ELECTROLYSES WITH VARIOUS ELECTROLYTES

Electrolyte	V_i	Reduction product in anolyte	Remarks
$K_3Fe(CN)_6$	1.35	Prussian blue	
$KClO_4$	1.10	Cl^-	
$KClO_3$	0.83–0.90	Cl^-, ClO_2(?)	Some active intermediate capable of corroding Be must be formed
$NaClO_2$	1.05–1.27	Cl^-	Anolyte after electrolysis did not attack Be
$KMnO_4$	Passive		
$K_2Cr_2O_7$	Passive		
$NaNO_3$	Passive		Passivity destroyed by addition of small amount of chloride ion to anolyte

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICAL COMPANY, UNION CARBIDE AND CARBON CORPORATION]

Vapor Pressure and Critical Constants of D_2O[1]

BY GEORGE D. OLIVER[2] AND J. W. GRISARD

RECEIVED JULY 18, 1955

The temperature and vapor pressure relations of normal and heavy water have been determined by means of a high pressure ebulliometer. Experimental observations were summarized in table form and represented by the following equations from 208 to 300°: $\log_{10} P_{D_2O}/P_{H_2O} = -3.4273 \times 10^{-2} + 2.1988 \times 10^{-4} t - 2.9329 \times 10^{-7} t^2$; from 300 to 370.6°: $\log_{10} P_{D_2O}/P_{H_2O} = 0.21516 \times 10^{-2} - 0.22949 \times 10^{-4} t + 1.1143 \times 10^{-7} t^2$. The boiling points of the two compounds are equal at 220.7° and 340.9 p.s.i.a., and differ as much as 2° at the critical point of D_2O. The critical temperature of D_2O, measured by means of the quartz tube method and the vapor pressure method, was 370.9 ± 0.1°. A critical pressure of 3170 ± 5 p.s.i.a. for D_2O was estimated from a plot of the vapor pressure data.

Previous work on heavy water has been limited to the region below the point where the vapor pressure of D_2O and H_2O are identical. Miles and Menzies[3] and Riesenfeld and Chang[4] almost simultaneously published their measurements of the vapor pressure of D_2O from 20 to 230°. Their data include the crossover point which was estimated by these workers as 224 and 225°, respectively. Lewis and MacDonald[5] were probably the first workers to compare the vapor pressure of heavy and normal water from 20 to 110° and to report the boiling and freezing points of D_2O. Riesenfeld and Chang[6] measured the critical temperature of D_2O by the quartz tube method in which normal water was used as a reference. They also estimated the critical pressure from the vapor pressure of H_2O at the critical temperature. In the present work the critical temperature has been measured by both the quartz tube method and an ebulliometric method. The latter also was used to measure the vapor pressure of D_2O, and the pressure difference of D_2O and H_2O between the crossover point and the critical point.

Experimental

Material.—The D_2O used in this investigation was prepared at the Consolidated Mining and Smelting Company of Canada, Limited, Trail, British Columbia, and had the following properties when sealed in a glass bottle: conductivity, 2.7×10^{-6} mhos; *p*H 6.5; weight % D_2O, 99.87. Heavy water from Trail normally contains about 0.3% of the O^{18} isotope.

The normal water was distilled from a permanganate solution contained in a glass distillation apparatus which had not more than two theoretical plates. Distilled water from a Barnstead distillation apparatus was used to prepare the permanganate solution.

Apparatus and Procedure.—Detailed description and diagrams of the apparatus have been published by the authors[7] consequently only a brief resumė will be included. Two metal boiling point tubes were connected to a common pressure system which contained the necessary valves, gages and helium supply. Each tube was constructed of one inch heavy-walled monel tubing and was surrounded by three concentric shields with the outermost one forming a vacuum jacket. Two thermocouples were used for control purposes, while the temperature was measured with a platinum resistance thermohm through a Mueller G-2 bridge and galvanometer. The boiling temperature of the test liquid in one tube was compared directly with the boiling tempera-

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[1] This work was done at the Oak Ridge Gaseous Diffusion Plant operated for the government by Union Carbide and Carbon Corporation.

[2] Monsanto Chemical Co., Texas City, Texas.

[3] F. T. Miles and A. W. C. Menzies, THIS JOURNAL, **58**, 1067 (1936).

[4] E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B33**, 120 (1936).

[5] G. N. Lewis and R. T. MacDonald, THIS JOURNAL, **55**, 3057 (1933).

[6] E. H. Riesenfeld and T. L. Chang, *Z. physik. Chem.*, **B28**, 408 (1935).

[7] G. D. Oliver and J. W. Grisard, *Rev. Sci. Inst.*, **24**, 204 (1953).

ture of normal water, used as a reference, in the other. Pressure values were interpolated from steam tables.[8]

In order to verify the critical temperature of D_2O determined from the vapor pressure data, a simple apparatus was constructed to measure directly the critical temperature by the classical quartz tube experiment. This apparatus consisted chiefly of a quartz tube with a 2 mm. bore and 4 mm. wall, and a furnace made from an aluminum block, 3 inches o.d., by drilling holes for the quartz tube and thermocouple. Slits were cut in the side of the block for observation of the meniscus in the quartz tube. The temperature was measured with a calibrated iron–constantan thermocouple, placed adjacent to the quartz tube in the middle section of the block. The apparatus was further calibrated by measuring the critical temperature of H_2O. Stirring was accomplished by rocking the furnace and contents laterally through approximately a 30° angle. Considerable care was taken to remove H_2O from the quartz tube and to conditioning it with D_2O.

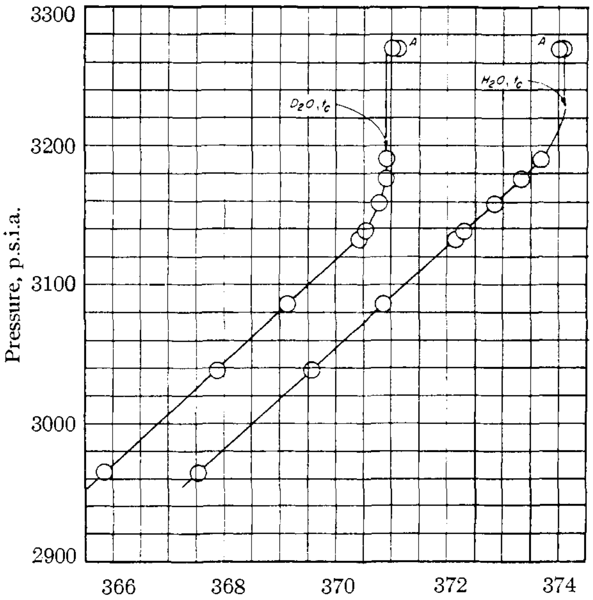

Fig. 1.—Boiling points of D_2O and H_2O near the critical point.

Results and Discussion

Vapor Pressure.—The present data cover the pressure and temperature range up to the critical point and overlap in the range 208 to 232° those measurements published by previous workers.[3,4] A comparison of the data in this range shows that the earlier data gave a lower vapor pressure for D_2O. Table I contains the experimental boiling point temperatures of D_2O at the respective pressures. Pressures listed were calculated from the steam tables of Osborne and Meyers.[8] Therefore, the accuracy of the measurements is consistent with that of the published steam tables since the temperature measurements were accurate to ±0.01°. The experimental data below 370.6° are represented by two equations over the temperature ranges

From 208 to 300°

$$\log_{10} \frac{P_{D_2O}}{P_{H_2O}} = -3.4273 \times 10^{-2} + 2.1988 \times 10^{-4}t - 2.9329 \times 10^{-7}t^2$$

From 300° to 370.6°

$$\log_{10} \frac{P_{D_2O}}{P_{H_2O}} = 0.21516 \times 10^{-2} - 0.22949 \times 10^{-4}t + 1.1143 \times 10^{-7}t^2$$

These equations were calculated by a method of least squares so that their first derivatives are equal at the 300° intersection. The calculated vapor pressure ratios deviate from the experimental values by less than 0.0003.

Table I

Vapor Pressure of D_2O and Boiling Point Difference between H_2O and D_2O

Pressure, p.s.i.a.	t_{obsd}, °C.	ΔT,[a] °C.	Pressure, p.s.i.a.	t_{obsd}, °C.	ΔT,[a] °C.
266.21	208.21	−0.141	1014.7	285.05	0.708
314.54	216.55	− .047	1204.5	296.77	.832
335.94	219.92	− .010	1370.4	305.89	.927
340.00	220.55	− .007	1435.0	309.23	.952
340.79	220.66	− .003	1594.9	316.96	1.063
340.92	220.68	.000	1792.3	325.74	1.150
342.27	220.89	.004	1799.5	326.04	1.162
345.29	221.34	.008	2022.6	335.04	1.268
350.71	222.15	.019	2215.6	342.24	1.343
354.91	222.78	.023	2492.3	351.67	1.468
360.18	223.55	.033	2737.0	359.30	1.575
364.53	224.19	.035	2964.5	365.85	1.68
371.00	225.11	.049	3037.9	367.87	1.70
376.46	225.90	.051	3086.2	369.12	1.75
385.03	227.09	.063	3132.3	370.41	1.72
386.03	227.22	.065	3138.4	370.51	1.78
410.00	230.45	.107	3158.5	370.75	2.08
415.04	231.12	.115	3176.5	370.9	2.39
610.89	253.05	.362	3190.6	370.9	2.71
810.15	270.39	.544	3270 ± 10	370.9	3.2

[a] Algebraically add ΔT values to b.p. of D_2O to obtain b.p. of H_2O.

Columns 3 and 6 of Table I give the difference in the boiling points measured up to the critical temperature. This difference increases gradually from zero at 220.7° to about 2° at the critical point of D_2O; then there is a sharp increase in the boiling point difference which reaches a maximum at the critical point of H_2O. This latter fact may be observed on the *p–t* plot of Fig. 1. The boiling point differences are not as accurate above 3000 p.s.i. since equilibrium in the boiling point tubes was more difficult to maintain as the critical region was approached.

Other measurements[3,4] of the temperature where the vapor pressure difference equals zero, *i.e.*, the crossover point, gave a value 4° higher than this research. Since those measurements were made in a mercury U-tube type apparatus, one can readily understand the difficulty of measuring precisely the pressure and temperature of the system and of knowing when the difference was zero. In the boiling point tubes, the pressure was changed in steps of 5 p.s.i. from 370 p.s.i.g. until the difference in the temperature in the tubes reversed in sign, then the pressure was varied by smaller increments until the difference in temperature was less than 0.001°, the limit of precise measurement of temperature difference. The temperature at which the boiling points of D_2O and H_2O differed by less than 0.001° was designated as the crossover tempera-

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[8] N. A. Osborne and C. H. Meyers, *J. Research Natl. Bur. Standards*, **13**, 1 (1934).

ture, 220.68 ± 0.1°. An examination of the boiling points and their differences above and below this temperature will show that the limit of 0.1° is justified. Calculation of the crossover point by means of the vapor pressure ratio equation yields a much less precise temperature of 221.04°. The pressure corresponding to the crossover temperature as calculated from the steam tables is 340.9 p.s.i.a.

Critical Constants.—Riesenfeld and Chang[6] reported a value of 371.5° for the critical temperature of D_2O which is 0.6° higher than the value 370.9 ± 0.1° determined in this work. In Fig. 1, there is a plot of vapor pressure data near the critical region for both D_2O and H_2O. It should be stated that the points marked A were measured with considerable difficulty, consequently their values are less precise. The curve representing the pressure and temperature relationship of H_2O is well defined by several points to show that the slope increases rapidly and approaches infinity at the accepted critical temperature[8] of 374.11 ± 0.1°. According to the phase relationship this should be true, since the liquid–vapor state no longer exists as such, the heat of evaporation has diminished toward zero, and any change in pressure does not cause a corresponding change in temperature. A similar curve was observed for D_2O in which dp/dt approaches infinity at 370.9°. The measurement of the critical temperature by the sealed quartz tube method yielded a value of 370.8 ± 0.1°; therefore it was concluded that the critical temperature of D_2O is 370.9 ± 0.1°. From an enlarged plot of Fig. 1, one may estimate the critical pressure of D_2O to be 3170 ± 5 p.s.i.a. This value is considerably less than the 3213 p.s.i.a. calculated by Reisenfeld and Chang from the pressure of H_2O and critical temperature of D_2O.

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TEXAS CITY, TEXAS

[CONTRIBUTION FROM THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Preparation of Some N-Disubstituted Hydrazines by Reaction of Chloramine with Secondary Amines

BY R. A. ROWE AND L. F. AUDRIETH

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The chloramine–amine reaction has been extended to include preparation of some typical N-dialkylhydrazines, R_2NNH_2 (where R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9). Use of an excess of ammonia in the preparation of chloramine from hypochlorite markedly improves dialkylhydrazine yields.

The reaction for the preparation of N-monosubstituted hydrazines from chloramine and the corresponding primary amines[1,2] has been extended to include some typical N-dialkylhydrazines, R_2NNH_2 (where R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9).

Chloramine solutions had previously been prepared by allowing hypochlorite and ammonia to react in equimolecular amounts. The analyzed chloramine content of such solutions usually varied between 50 to 60% of theory and this figure was employed in calculating yields of the alkyl hydrazines. It has been shown recently[3] that the available chloramine content of such solutions approaches that demanded theoretically when a 3/1 ammonia–hypochlorite mole ratio is employed. Since the amine–chloramine reactions take place much more rapidly than the ammonia–chloramine reaction, no difficulties were experienced in effecting the synthesis of the N-disubstituted hydrazines. Markedly greater yields of typical N-dialkyl hydrazines were obtained by employing an excess of ammonia in the preparation of chloramine.

Experimental

Analytical Methods.—Sodium hypochlorite solutions were prepared by the method of Coleman and Johnson.[4] The hypochlorite content was determined iodometrically. The excess sodium hydroxide in the hypochlorite solutions was determined by pH titration with standard hydrochloric acid to an equivalence point in the range of pH 10.2–10.4. An iodometric procedure was employed for chloramine.

The iodometric procedure[5] used for hydrazine proved to be adaptable to N-disubstituted hydrazines. Oxidation to the tetrazene occurs in solutions, maintained at a pH of 7–7.4, in accordance with the equation

$$2R_2NNH_2 + 2I_2 = R_2N{\cdot}N_2{\cdot}NR_2 + 4HI$$

Titration is carried out in a nitrogen atmosphere. The iodine solution is added rapidly to just about 1 ml. short of the approximate end-point at which time the starch solution is added. The drop which causes the solution to turn completely purple is considered to be the best end-point, even though the indicator fades rapidly thereafter.

Effect of the Ammonia/Hydrochlorite Ratio on the Yields of N,N-Disubstituted Hydrazines.—Chloramine solutions were prepared using 1:1, 2:1 and 3:1 mole ratios of ammonia to hypochlorite. Both reagents were first precooled to 0°. A 100-ml. quantity of the appropriate ammonia solution was then added to 50 ml. of 1 M sodium hypochlorite (0.44 M in sodium hydroxide). The resulting chloramine solutions were allowed to stand at 0° for 90 minutes and then treated with 50 ml. of a 4 M solution of the amine (diethylamine or piperidine).[6] After 30 minutes at 0°, the reaction mixtures were allowed to warm to room temperature before being analyzed iodometrically for dialkyl hydrazine content.

For mole ratios of ammonia to hypochlorite = 1, 2 and 3, the yields of diethylhydrazine were found to be 48, 57 and 63%, respectively. Percentage yields of N-aminopiperidine under similar conditions were found to be 28, 42 and

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[1] L. F. Audrieth and L. H. Diamond, THIS JOURNAL, **76**, 4869 (1954).

[2] L. H. Diamond and L. F. Audrieth, *ibid.*, **77**, 3131 (1955).

[3] L. F. Audrieth and R. A. Rowe, *ibid.*, **77**, 4726 (1955).

[4] G. H. Coleman and H. L. Johnson, *Inorg. Syntheses*, I, 60 (1939).

[5] R. A. Penneman and L. F. Audrieth, *Anal. Chem.*, **20**, 1058 (1948).

[6] Preliminary experiments had shown that the dialkyl hydrazine yields level off at an amine/NH_2Cl mole ratio of about 4:1.