

[CONTRIBUTION FROM THE DEPARTMENT OF GEOLOGY, HARVARD UNIVERSITY]

Vapor Pressures of Aqueous Solutions at High Temperatures¹

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Water is known to play a dominant role in many geological processes and an important class of mineral deposits, usually containing hydrous minerals, formed at depths where higher than surface temperatures prevail, is known as hydrothermal. In spite of the importance of water in the genetic problems of economic geology, experimentation has not progressed far enough to be of decisive help in the interpretation of hydrothermal processes. Thus the theory of the origin of ore deposits is still a subject for surmise and debate. Graton has considered the question in some detail² drawing largely on geological evidence, and Morey and Ingerson have advanced somewhat different views on the basis of rather limited experimental data.³

As the last-named authors have shown, hundreds of papers on the hydrothermal reactions of minerals, chemical compounds and mixtures at elevated pressures and temperatures have been published, but relatively little systematic information has accrued. Most experimenters have been interested only in synthesizing particular minerals or in studying their decomposition. Often the details of composition, temperature and pressure were neglected and usually the information was of little or no use in providing fundamental equilibrium data.

The properties of water being well known, a comprehensive experimental study of hydrothermal reactions must begin with detailed investigations of two-component systems containing water. This involves accurate and complete specifications of composition, pressure, temperature and volume of each system under equilibrium conditions. This paper is concerned largely with the pressure of the vapor in equilibrium with saturated aqueous solutions of common salts.

While numerous vapor pressure measurements of aqueous solutions have been made during the past two decades, most of these have been limited to the range below the boiling point at atmospheric pressure. More interest has been shown in the effect on vapor pressures of concentration than

in the effect of temperature. Yet for our complete understanding of aqueous solutions, thermodynamic data over the entire range of concentration and temperature are needed.

The limited extent of experimental work at elevated temperatures is indicated by the temperature-concentration diagram (Fig. 1). Experimentation has been confined largely to the range indicated by the shaded portion. Solubilities of some of the salts investigated at high temperatures are indicated by the solid curves, assumed trends are indicated by the dashed curves. Except for boric oxide, the complete solubility range has not been covered for any salt melting above the critical temperature of water.

Vapor pressure measurements cover a still smaller range. Until the present program was initiated, few accurate vapor pressure measurements above 150° were available. Early experimental work in this field is reported in the "International Critical Tables,"⁴ and by Morey and co-workers,^{2,5} following the development of theory by Smits,⁶ and Roozeboom.⁷ By indirect methods some of the theoretical predictions have been verified for potassium nitrate solutions, whose vapor pressures have been determined over the complete temperature range for the system, from the triple point of water to the triple point of the salt, 334°,⁴ and for the system potassium silicate-water, in which a few approximate vapor pressures have been calculated from analyses of quenched charges⁵ within the temperature range 300 to 600°. Of less interest were measurements of vapor pressures of solutions of slightly soluble salts.⁸

The program of which the present work is a part represents the first systematic investigation of vapor pressures of a series of aqueous salt solutions determined by direct methods in the temperature range 150 to 650°. Data for potassium chloride were first obtained by Benedict,⁹ with the same apparatus.

(4) "International Critical Tables," Vol. III, 1928, p. 373.

(5) G. W. Morey and C. N. Fenner, *THIS JOURNAL*, **39**, 1173-1229 (1917).

(6) A. Smits, see ref. 3, pp. 612, 617.

(7) B. Roozeboom, "Die heterogenen Gleichgewichte vom Standpunkt der Phasenlehre," Vol. II, 1901.

(8) W. F. Waldeck, G. Lynn, and A. E. Hall, *THIS JOURNAL*, **54**, 928-933 (1932).(9) M. Benedict, *J. Geol.*, **47**, 252-276 (1939).

(1) Paper No. 74 published under the auspices of the Committee for Research in Experimental Geology and Geophysics and the Division of Geological Sciences at Harvard University.

(2) L. C. Graton, *Econ. Geol.*, **35**, Suppl. to No. 2, 197-358 (1940).(3) G. W. Morey and E. Ingerson, *ibid.*, **32**, 607-761 (1937); Morey and Ingerson, *ibid.*, **35**, 772-785 (1940).

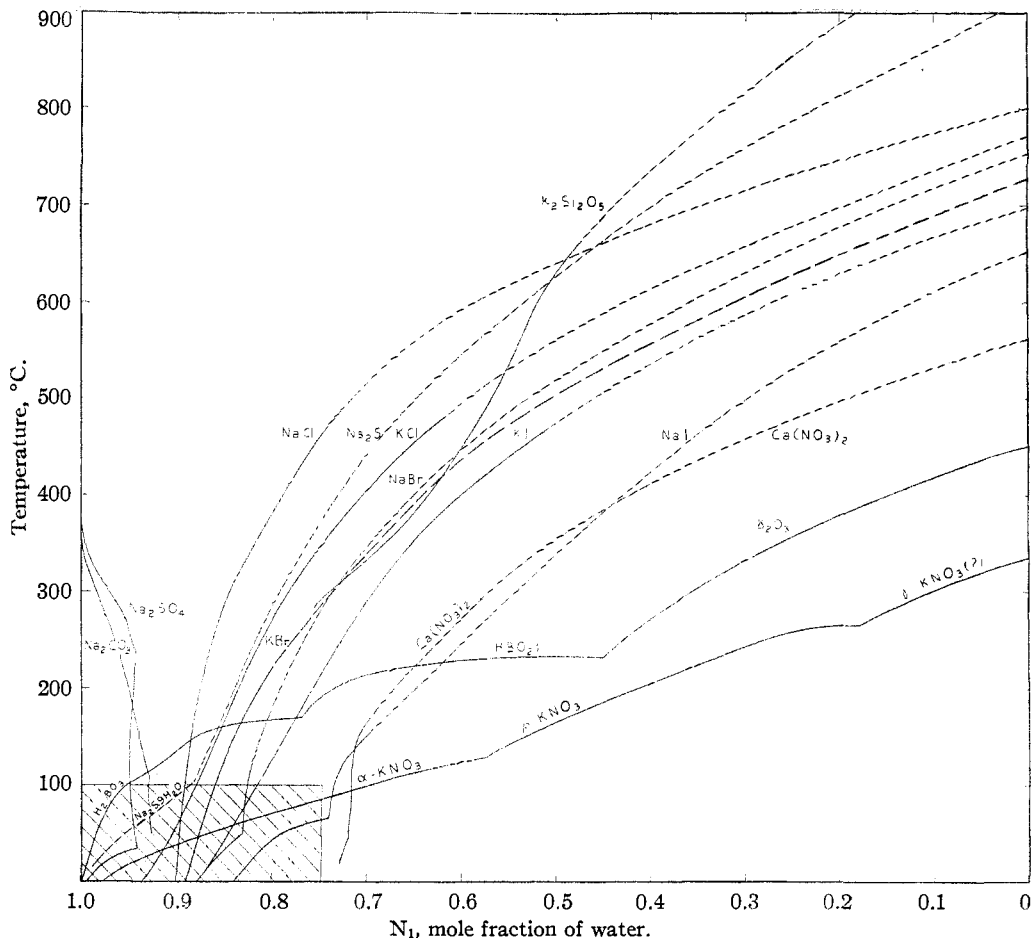


Fig. 1.—Extrapolated solubility curves of several inorganic salts in water.

Experimental Method

Salt and water were confined in a steel bomb of 16-cc. capacity by means of mercury, foreign gases having been removed previously by boiling and pumping. The bomb was made entirely of Allegheny 44 stainless steel, all valves being closed by forcing a 57° cone into a 60° seat. The experimental system was essentially as described by Benedict.^{9,10} Temperature was measured by means of a platinum to platinum-10% rhodium thermocouple sealed in Pyrex glass. The thermocouple was calibrated several times using boiling water, a mercury thermometer, and the boiling points of pure mercury and of sulfur.

Pressures were indicated roughly by a Bourdon gage, exact measurements being made with a dead-weight piston gage of the Bridgman type¹¹ standardized against the vapor pressure of carbon dioxide at 0° and 34.4009 atmospheres. Pressure balance was observed by means of a neon lamp in a circuit including an insulated needle within the fluid system. Vapor pressures of salt solutions were obtained by correcting observed pressures for the partial pressure of mercury calculated from data in the "International Critical Tables" and from Poynting's equation.

(10) M. Benedict, *Rev. Sci. Inst.*, **8**, 252-254 (1937).

(11) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **64**, 201-217 (1909).

The experimental procedure consisted in making a series of pressure-volume measurements at each of several temperatures for each salt. Usually the first series of measurements was made near 200°, followed by others at higher temperatures, *e. g.*, 300, 400, and sometimes over 600°. Other series of observations were then made at intermediate points, *e. g.*, at 550, 450, 350, and finally at 250°. In some cases a check on possible leakage or gas formation was obtained by making measurements at room temperature before and after the run. The volume of the salt-water system in the bomb was controlled by means of mercury and a screw compressor.

At the full expansion allowed by the bomb, gas and solid phases only were present in some cases. Under these conditions, decreasing the volume caused a marked change in the pressure required to balance the pressure of vapor. With further decrease in volume, liquid formed at the dew-point. Then with three phases and one degree of freedom, the pressure remained nearly constant as the volume was further reduced by injecting mercury into the bomb. When the vapor phase disappeared the pressure of the relatively incompressible bivalent system, salt-water, increased rapidly with further decrease in volume. In those cases where the solid phase disappeared before the boiling point was reached, a discontinuity in slope was ob-

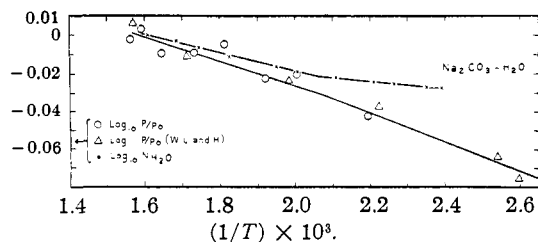


Fig. 3.—Curves of $\log N$ and $\log P/P_0$ vs. $1/T$ for sodium carbonate-water.

boiling and pumping was added to the bomb through a valve. Vapor pressure data are listed in Table II and Fig. 2, and the variations of $\log_{10} N_{H_2O}$ and $\log_{10} p/p_0$ with $1/T$ are shown in Fig. 4. If the solution were ideal all of the

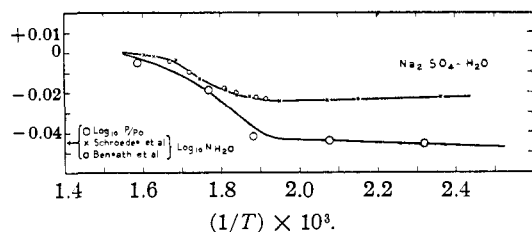


Fig. 4.—Curves of $\log N$ and $\log P/P_0$ vs. $1/T$ for sodium sulfate-water.

points would lie on a straight line. Pressure-volume data at a series of temperatures between 150 and 450° are given in Fig. 5. As with sodium carbonate solutions, the vapor pressures approach those for water as the critical temperature is approached. Solubility data indicate that the solubility falls off correspondingly, being zero at the critical temperature, within the limits of error.

TABLE II

VAPOR PRESSURE DATA FOR SODIUM SULFATE-WATER

Temp., °C.	Order of readings	Press. in bomb, atm.	Vapor press., atm.	Soly., mole fr. Na ₂ SO ₄	Log p/p_0
158.8	1 h	5.4	5.4	0.051	-0.0458
209.9	2 h	17.0	17.0	.054	- .0443
227.0	13 c	25.13	25.1	.055	
258.5	3 h	41.1	41.0	.050	- .0424
292.5	4 h	73.5	73.0	.029	- .0177
323	14 c	116.9	116.4	.011	
355.5	5 h	173.3	172.3	.002	- .0052
366.8	12 c ^a	202.5	201.0	.001	

^a Errors are larger after runs at high temperatures; highest temperature reached was 448.3°.

Results with Highly Soluble Salts.—Of the salts whose solubility curves are continuous to the melting point of the salt, sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium iodide, and calcium nitrate were studied. Some experiments were made also with a solution of boric acid and with a mixture of water, sodium bromide, and potassium chloride.

Sodium Chloride.—Sodium chloride of Mallinckrodt analytical reagent grade was dissolved in distilled water, and precipitated in part with washed dry hydrochloric acid gas prepared from pure sodium chloride and sulfuric acid. After filtering, the bulk of the water was removed by

pressing between filter paper and the crystals were dried for twenty-four hours in an oven at 450°.

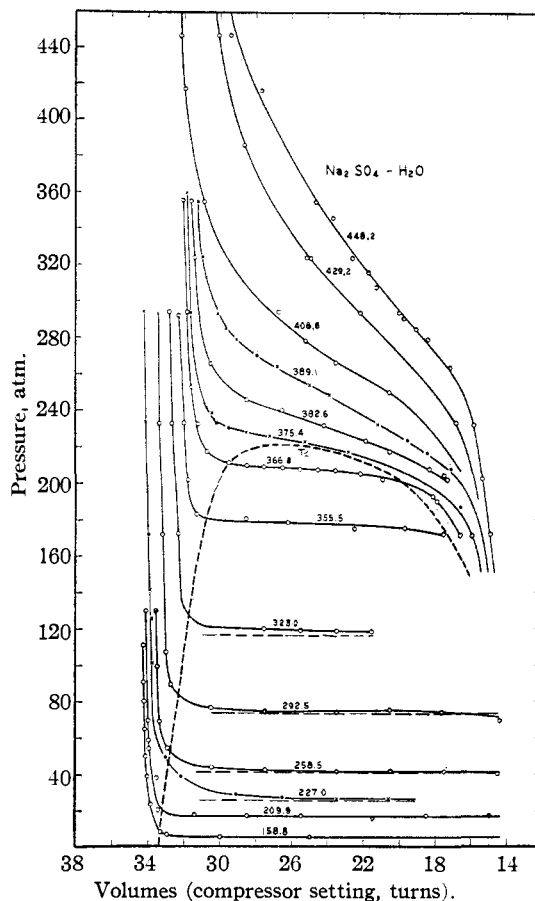


Fig. 5.—Pressure-volume curves for sodium sulfate-water at temperatures below and above the critical point.

The bomb was tested for pressure tightness before the run by submerging in kerosene for fifteen minutes with an internal pressure of nitrogen of 10,000 lb. per sq. in. 7.4749 grams of salt was introduced to the bomb and, after a blank run, 1.91 g. of gas-free distilled water was added through the special entry system. Twice during this series the capillary leading from the mercury supply and compressor to the bomb became plugged with salt but, in both cases, application of excess pressure freed the tube of salt, the release of pressure being quite noticeable in turning the compressor screw and in the vibration of the steel capillary. Normal readings were then obtained. A check on reproducibility was obtained by approaching the equilibrium from both sides, and staggering the temperatures, so that fairly uniform distributions of points were obtained with both increasing and decreasing temperatures. In Table III the notations in the second column indicate the succession of the readings. The agreement of the first reading (at 183°) with the last reading (at 205°), as shown in Fig. 6, shows that gas formation by reaction of the solution with the interior of the steel bomb introduced negligible error, as in the case of potassium chloride.⁹ Observed pressures and computed vapor pressures over the temperature range from 183 to 646° are given in Table III and in Fig. 6.

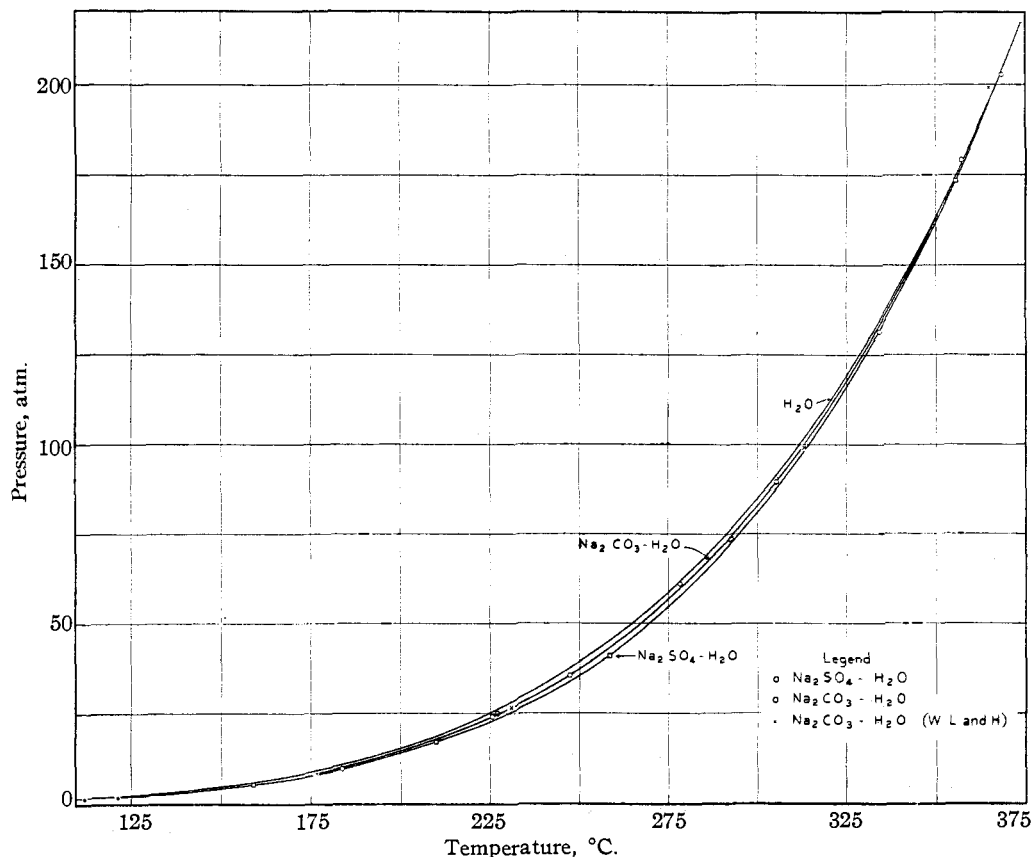


Fig. 2.— P - T curves for water and saturated aqueous solutions of sodium carbonate and sodium sulfate.

tained due to the additional degree of freedom (Fig. 7). This change at the disappearance of salt afforded an approximate measure of the solubility, useful in confirming the trends of the solubility curves at high temperatures (Fig. 1).

To obtain the three-phase vapor pressure, corrections were made where deviations from a straight line curve indicated the presence of foreign gas. These were made by plotting $1/(C - C_0)$ against W and obtaining W_0 by extrapolation to $1/(C - C_0) = 0$. C_0 is the compressor setting, C , at the lowest weight, W . W_0 is the true weight required on the pan of the dead-weight piston gage to balance the oil pressure at the boiling point (Fig. 7).

Results of Vapor Pressure Measurements

Slightly Soluble Salts.—Of the slightly soluble salts whose solubility curves intersect the critical curve (Class II),³ sodium carbonate and sodium sulfate were studied in saturated aqueous solutions.

Sodium Carbonate.—Pure sodium carbonate purified by several recrystallizations in Professor G. P. Baxter's laboratory was used for the experiments. To 9.7226 g. of anhydrous salt, 2.811 g. of water was added in a gas-free system. Vapor pressure data are listed in Table I, and in Fig. 2. Near the critical point for water the vapor pressures of the solution approach those for pure water, presumably as the solubility decreases toward zero. The relationships between pressure, composition, and tempera-

ture are shown in Fig. 3. Here deviations from ideality are indicated by deviations from a straight line of $\log N_{H_2O}$ and $\log p/p_0$ for water plotted against $1/T$, where N_{H_2O} is the mole fraction of water, p the vapor pressure of the solution, p_0 the vapor pressure of pure water, and $1/T$ the reciprocal of the absolute temperature.

TABLE I
VAPOR PRESSURE DATA FOR SODIUM CARBONATE-WATER

Temp., °C.	Order of runs	Press. in. bomb, atm.	Vapor press., atm.	Soly., mole fr. Na_2CO_3	Log p/p_0
112	W. L. and H. ^a		1.27	0.070	-0.07572
121	W. L. and H.		1.69	.067	- .06399
176.5	W. L. and H.		8.43	.055	- .03245
183.6	1 h ^a	9.72	9.72	.053	- .04252
225.8	2 h	24.37	24.37	.042	- .02053
231	W. L. and H.		26.6	.040	- .02365
247.3	10 c	35.63	35.57	.034	- .00229
278.2	3 h	61.2	61.0	.023	- .00460
305.5	9 c	90.0	89.4	.014	- .00923
313	W. L. and H.		99.0	.011	- .01100
334.4	4 h	132	131.2	.005	- .01048
357.0	5 h	180	179	.001	- .00341
365	W. L. and H.		199	.0004	- .00561
368.5	8 c	204	202.7	.0002	- .00235

^a In this and following tables h indicates bomb heated to temperature; c , that temperature was reached by cooling from a higher temperature.

Sodium Sulfate.—To 15.712 g. of sodium sulfate recrystallized eight times, 1.295 g. of water freed of gases by

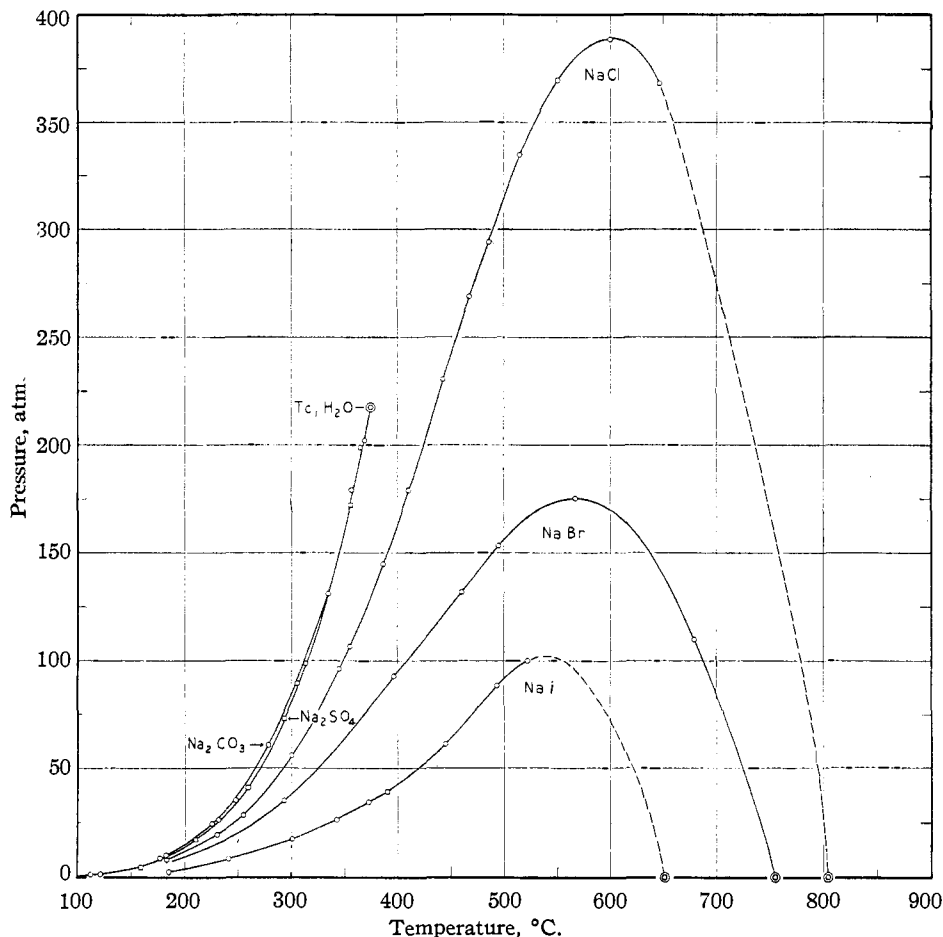


Fig. 6.—Vapor pressure curves of aqueous solutions of several sodium salts.

Sodium Bromide and Sodium Iodide.—For the experiments with sodium bromide and sodium iodide, the bomb

TABLE III
VAPOR PRESSURE DATA FOR SODIUM CHLORIDE-WATER

Temp., °C.	Order of measurements	Press. in bomb, atm.	Partial press. of Hg at P_b , atm.	Vapor press., atm.	Soly., mole fr. NaCl
183.0	1 h	7.28	0.01	7.27	0.120
205.1	18 c	11.78	.02	11.76	.124
230.2	2 h	19.34	.05	19.29	.130
246.7	17 c	25.16	.08	25.08	.135
254.6	3 h	27.61	.10	27.51	.138
299.3	4 h	56.59	.56	56.03	.155
327.3	16 c	79.24	.74	78.50	.169
344.4	5 h	97.20	.87	96.29	.178
354.3	15 c	107.4	1.0	106.4	.183
385.7	14 c	146.8	1.8	145.0	.205
410.0	6 h	181.5	2.6	178.9	.217
442.5	13 c	234.2	4.1	230.1	.238
467.5	7 h	274.9	5.9	269.0	.251
485.5	12 c	301.7	7.3	294.4	.270
514.2	8 h	345.4	10.3	335.1	.285
550.5	9 h	385.6	15.5	370.1	.335
600.0	10 h	413.7	25.0	388.7	.411
646.2	11 h	405.8	37.3	368.5	.505

TABLE IV
VAPOR PRESSURE DATA FOR SATURATED AQUEOUS SOLUTIONS OF SODIUM BROMIDE AND SODIUM IODIDE

Temp., °C.	Order of measurements	Press. in bomb, atm.	Vapor press., atm.	Soly., mole fr. of salt
Sodium Bromide				
293	6 c	35.4	35.4	0.249
396.0	1 h	94.54	92.56	.328
460.0	5 c	136.7	131.6	.390
493.8	2 h	161.1	153.3	.436
567.0	3 h	192.2	174.9	.555
678	4 h	155.0	109.7	.783
Sodium Iodide				
185.0	1 h	2.40	2.40	0.336
240.8	2 h	8.58	8.51	.390
300.2	3 h	18.15	17.58	.454
342	4 h	27.18	26.36	.502
372	5 h	35.97	34.63	.538
389.5	6 h	40.55	38.79	.559
444.0	7 h	65.3	61.2	.624
493.0	10 c	96.1	88.5	.690
521.4	8 h	110.73	100.04	.735
600.0	9 h	183.03	189.1 ^a	.888

^a Unsaturated.

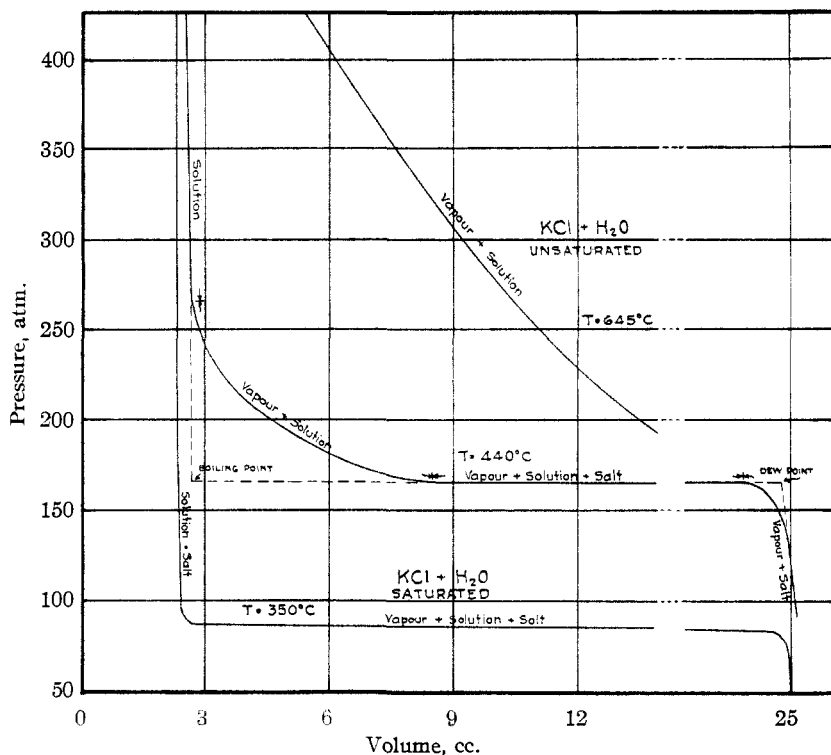


Fig. 7.— P - V curves for potassium chloride-water: (a) saturated solution; (b) solution saturated at high pressures, unsaturated at low pressures; (c) unsaturated solution.

was filled with loosely-packed salt of the Mallinckrodt analytical reagent variety previously air-dried in porcelain crucibles over gas flames, and about three-fourths of a gram of water added. The ratio of salt to water was estimated from extrapolated solubility curves to be in excess of that required for saturated solutions over the temperature ranges covered in these experiments. Some reaction of sodium iodide with the bomb occurred above 450° , as indicated by the change in slope of the curves. Uncertainties were thus introduced in the correction factors for large volumes of gas. At 600° the high pressures observed were probably due in part to unsaturation. At the completion of the run with the sodium bromide solution, the bomb became plugged.

The vapor pressure results for sodium bromide and iodide are summarized in Table IV, and compared with those of other sodium halides in Fig. 6.

Potassium Chloride.—The properties of aqueous solutions of potassium chloride were investigated in the same apparatus by Benedict. Three additional runs on potassium chloride were made, the results being in good agreement with those previously found⁹ (Table V, MB3 and MB5).

In addition, the effect of unsaturation was studied. In the first run, 3.922 g. of carefully purified potassium chloride was dissolved in 1.895 g. of boiled distilled water; in the second run, 2.012 g. of potassium chloride in 1.697 g. of water; and in the third run, 2.424 g. of potassium chloride in 1.05 g. of water.

At low temperatures, the conventional type of P - V

curve was obtained (Fig. 7a), but at higher temperatures, compression resulted in a change of slope before the disappearance of vapor was complete (Fig. 7b); this was due to the formation of unsaturated solution which added one degree of freedom. At temperatures above 450° in runs 2 and 3 no flat portions were found, indicating unsaturation in the P - V range covered at that temperature. The vapor pressures agreed with those found by Benedict; the data are in Table V and Fig. 8.

Potassium Iodide.—The bomb was filled with potassium iodide (analytical reagent quality), and a small amount of gas-free water added in quantity to provide saturated solutions over most of the range being investigated. Vapor pressures were measured up to 563° (Table VI), but at 602° no flat portion of the P - V curve was obtained. This was largely due to unsaturation, since reproducibility of vapor pressures after cooling from the high temperatures indicated negligible gas formation.

In Fig. 8 are given vapor pressure curves for all potassium salts studied up until the present time. Potassium nitrate solutions show the lowest pressures, but are less interesting than the other systems, which exhibit continuous curves to triple point temperatures which are above the critical point for water. The system K_2O - H_2O - SiO_2 was studied by Morey and Fenner,⁵ by an indirect method; while less accurate, the results were the first to indicate experimentally a maximum and continuous vapor pressure curve above the critical temperature of water.

Calcium Nitrate.—J. T. Baker c. p. analyzed crystals were dried and introduced to the bomb with a small quantity of water. Two vapor pressure readings were obtained before excessive reaction of the salt with the mercury, so the trend of the curve could be estimated. The data are in Table VII.

The maximum point of the vapor pressure curve is estimated to be at 35 atmospheres and 475° . Reaction of the calcium nitrate with the mercury progressed rapidly at 500° , red plate-like crystals of mercuric oxide ($d = 11.2 \pm 0.2$) plugging the capillary, and preventing even an approximate determination of the vapor pressure above this temperature.

Boric Oxide.—Mallinckrodt analytical reagent boric acid was recrystallized and dried over calcium chloride. To 8.0534 g., 1.166 g. of gas-free water was added by opening a valve to the evacuated bomb. This mixture contained 4.77 g. of boric oxide and 4.85 g. of water, the mole fraction of boric oxide being 0.203, less than the saturation concentration above 170° .¹² After first heating to 200° , a leak

(12) F. C. Kracek, G. W. Morey, and H. E. Merwin, *Am. J. Sci.*, **35A**, 143-171 (1938).

TABLE V

VAPOR PRESSURE DATA FOR POTASSIUM CHLORIDE-WATER

Temp., °C.	Number of run	Order of measurements	Press. in bomb, atm.	Vapor press., atm.	Soly., mole fr. KCl
190	1	1 h	8.58	8.58	0.160
213	2	1 h	14.6	14.5	.168
237.2	1	15 c	19.50	19.45	.180
237.6	3	1 h	19.86	19.81	.180
250	MB3	..	24.52	24.42	.185
269.2	1	2 h	32.47	32.33	.198
298	2	2 h	48.1	47.8	.216
298.1	1	14 c	48.56	48.26	.216
300	MB3	..	48.97	48.65	.217
330	1	3 h	69.03	68.40	.238
342.2	2	9 c	137	135 ^b	.247
349.4	3	2 h	83.74	82.80	.252
350	MB3	..	83.87	82.96	.252
350	MB5	..	83.98	83.07	.252
371	2	3 h	101.9	100.5	.270
372.5	1	4 h	103.17	101.8	.272
375	2	8 c	152	150 ^b	.274
375	3	3 h	103.73	102.2	.274
388	2	7 c	183	180 ^b	.287
397.3	1	5 h	123.9	121.8	.293
400	2	6 c	198	195 ^b	.295
400	MB5	..	127.74	125.59	.295
427.2	2	4 h	154	151	.322
428.6	1	13 c	154.1	150.7	.323
439.5	3	4 h	164.3	160.4	.335
450	MB5	..	173.32	168.84	.347
457.2	2	5 h	192	187	.354
472	1	6 h	191.1	185.0	.370
480.4	3	5 h	197.4	190.7	.377
485.8	1	12 c	201.2	194.0	.381
493.8	3	6 h	208.1	200.1	.393
497.2	1	11 c	210.2	202.0	.395
500	MB5	..	213.33	204.86	.398
516.1	1	9 c	224	214 ± 1	.416
526.4	1	10 c	230	218.5 ± 1	.427
529.7	1	7 h	229	217 ± 1	.432
538.9	3	7 h	231	218 ± 3	.444
548.7	1	8 h	232 ^a	218 ± 5 ^a	.458
550	MB5	..	238.51	223.74	.461
550	MB5a	..	238.52	223.75	.461
584.5	3	8 h	241	220 ± 5	.509
600	MB5a	..	244	220	.535
645	3	9 h	234	197 ± 5	.624

^a Minimum vapor pressure for unsaturated solution.

^b Unsaturated; minimum pressure of vapor considerably higher than vapor pressure for saturated solutions.

was suspected, but repeat measurements after cooling and tightening all valves showed no measurable loss of water. At a temperature of 484°, the bomb became plugged with solid boric oxide. A hard, solid, green glass of water and boric oxide was observed to fill most of the bomb after cooling to room temperature. Since, in the absence of the solid phase in the temperature range covered in this run, there are two degrees of freedom, equilibrium vapor pressures were not given by the isothermal P - V curves. However, average and minimum pressures of water vapor were obtained at several temperatures. These are considerably

TABLE VI

VAPOR PRESSURE DATA FOR POTASSIUM IODIDE-WATER

Temp., °C.	Order of readings	Press. in bomb, atm.	Vapor press., atm.	Soly., mole fr. of salt
306.3	8 c	40.30	39.91	0.301
388.0	7 c	75.63	73.85	.393
476.5	1 h	98.28	92.09	.520
506.5	2 h	98.90	90.01	.568
513.0	6 c	97.00	87.46	.579
538.0	3 h	94.56	82.03	.627
563.0	4 h	91.51	74.71	.674
602.0	5 h	100.7	76.8 ^a	.767

^a Unsaturated.

TABLE VII

VAPOR PRESSURE DATA FOR CALCIUM NITRATE

Temp., °C.	Press. in bomb, atm.	Press. of mercury vapor, atm.	Vapor press., atm.	Soly., mole fr. salt
329.4	19.6	0.75	18.87	0.431
451.3	38.40	4.5	34	0.655
500 ± 10	44	9	35 ± 15	0.761

higher than vapor pressures calculated for unsaturated solutions,¹² but they are considerably lower than pressures obtained for fluid water at these temperatures. While the P - V curve at 484° was distinctly more curved than that at 427°, it showed a region where the change of P with V was more gradual than in the case of water. P_{av} was taken from the intercepts of the tangents of the two arms of the curve, P_{min} , from the $W_0 - C_0$ treatment described above. The pressures at 484° were lower than those for water, (m. p. boric oxide = 450°) which may have been due to the presence of products other than boric oxide and water in the system.

TABLE VIII

VAPOR PRESSURE DATA FOR A BORIC OXIDE SOLUTION
 $N = 0.2$

Temp., °C.	Average pressure for solution-vapor		Minimum pressure for solution-vapor	
	Total press., atm.	Cor. for Hg atm.	Total press., atm.	Cor. for Hg. atm.
199	15	15	11.24	11.22
265.4	46.3	46.2	34.2	34.1
329.0	95	94	77.8	77.2
387.8	151	149	132.7	131
427.3	204	200	177	174
484.1 ^a	302	295	264	257

^a Above melting point of boric oxide.

TABLE IX

PRESSURES OF VAPOR OVER AN AQUEOUS SOLUTION OF POTASSIUM CHLORIDE AND SODIUM BROMIDE

Temp., °C.	Press. in bomb, atm.	Press. of vapor, (cor. for Hg)
439	79.9	76.2
480	109.8	103.3
490	112.9	105.6
540	94.6	81.6

Water-Potassium Chloride-Sodium Bromide.— P - V curves for a mixture of water, potassium chloride, and so-

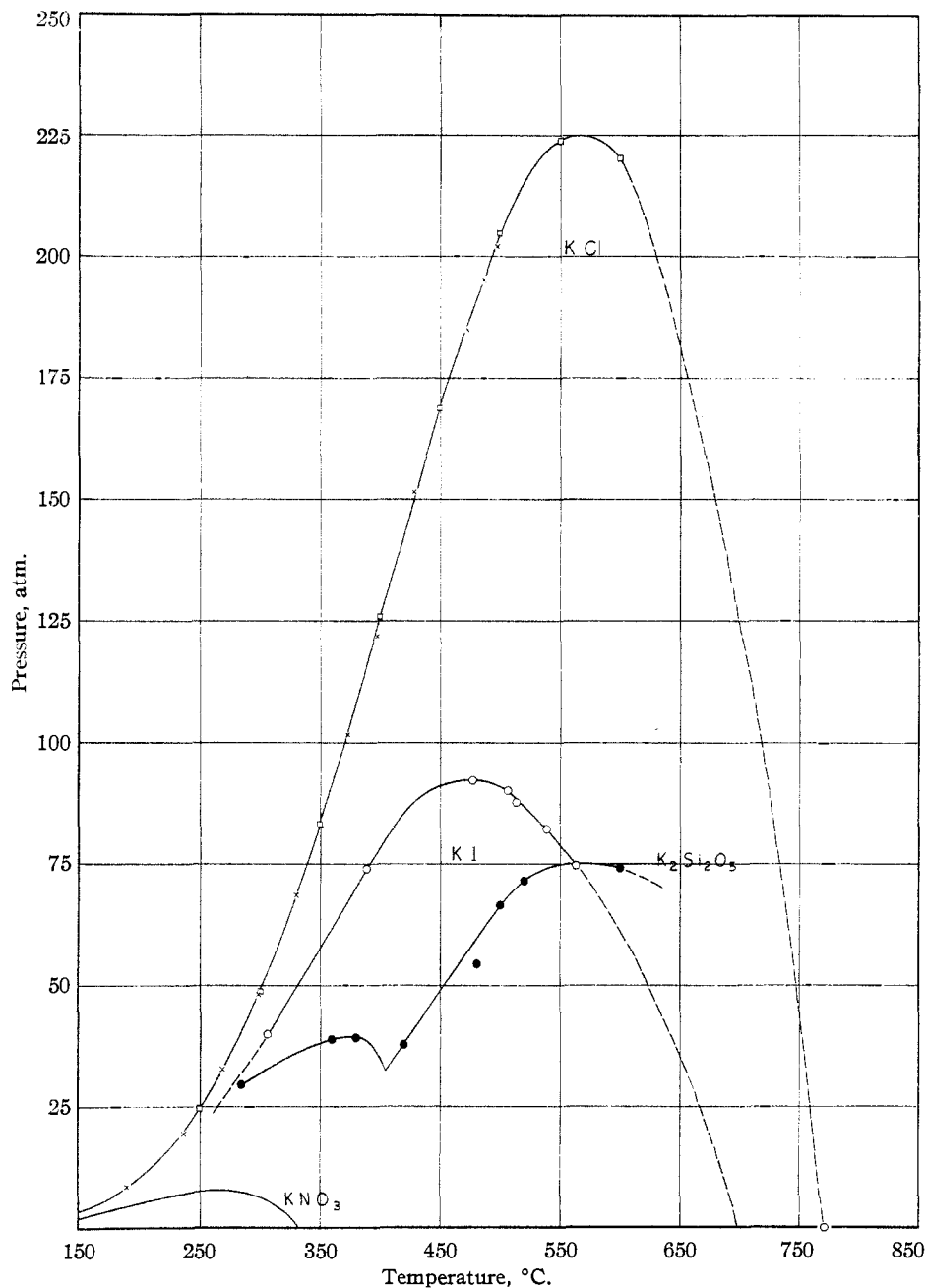


Fig. 8.—Vapor pressure curves of aqueous solutions of several potassium salts.

dium bromide were made at several temperatures. It was estimated that both salts were in excess of the quantities required for saturation, but at higher temperatures the shapes of the P - V curves indicated two degrees of freedom, so that average vapor pressures only could be obtained from the isothermals. Average vapor pressures of solutions saturated with respect to both components are given in Fig. 9. While the maximum may be somewhat high, the results are significant in that they show the pressures of vapor in this system to be considerably lower than the vapor pressures for solutions of either salt alone, a result of considerable geochemical interest.

Discussion of Results

The two types of vapor pressure curves found for dilute and concentrated solutions have been predicted theoretically, and both have been confirmed experimentally by earlier investigators in a few systems at moderate temperatures and pressures. The present results at higher pressures and temperatures have extended this work to include salts with higher melting points and with vapor pressures considerably in excess of the critical

pressure of water. The somewhat surprising results obtained for aqueous sodium chloride solutions show that the intermolecular forces may be

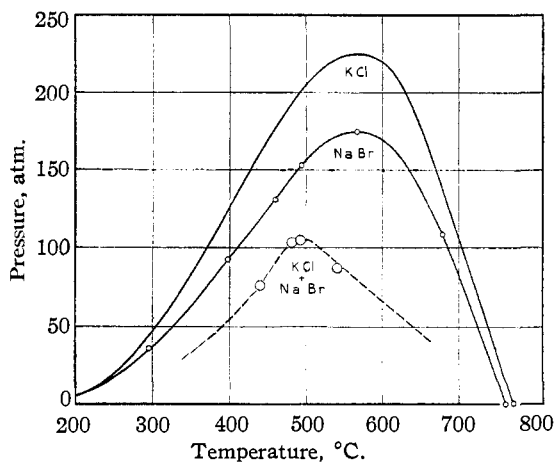


Fig. 9.—Pressures of vapor of aqueous solutions of potassium chloride and sodium bromide.

strong enough to prevent critical conditions even at temperatures as high as 800° and pressures of 400 atmospheres. In all cases of saturated solutions of highly soluble salts, the results indicate that continuous vapor pressure curves are obtained from the triple point of water to the triple point of salt. In saturated solutions of slightly soluble salts, the vapor pressure curve intersects the critical curve. In the cases of sodium carbonate and sodium sulfate, this occurs at or near the critical point of water, apparently coinciding with a decrease of solubility to zero at the critical temperature. Although no experimental data could be obtained with the apparatus described in this paper for dilute solutions of highly soluble salts, it is reasonable to assume that their vapor pressures would be higher than those for saturated systems, and that at sufficient dilution they would intersect the critical curve. It is an important problem of the future to determine the boundaries of the critical regions for dilute aqueous solutions, particularly of compounds of geochemical significance.

The data obtained for the nine systems studied in this research serve only to introduce us to the behavior of aqueous systems at high pressures and

temperatures. However, some interesting relationships have already been indicated. In Fig. 6 the sodium halides show decreasing maximum vapor pressures as the halide group changes from chloride to bromide to iodide; a similar relationship is indicated for the potassium halides (Fig. 8). In comparing these two series, it will be observed that lower maxima are found for potassium than for sodium halides. In all of these systems, lower vapor pressure maxima and lower vapor pressures on any corresponding parts of the curves are associated with larger ionic size and with greater solubility. The temperatures at which the maxima occur seem to be higher, the higher the triple point (or melting point) of the salt. These relationships of the position and magnitude of the maximum vapor pressure in the P - T section seem to hold in all the systems studied. A general rule seems to be that for any highly soluble salt whose solubility curve is continuous from the triple point of water to the triple point of the salt, a continuous vapor pressure curve is obtained

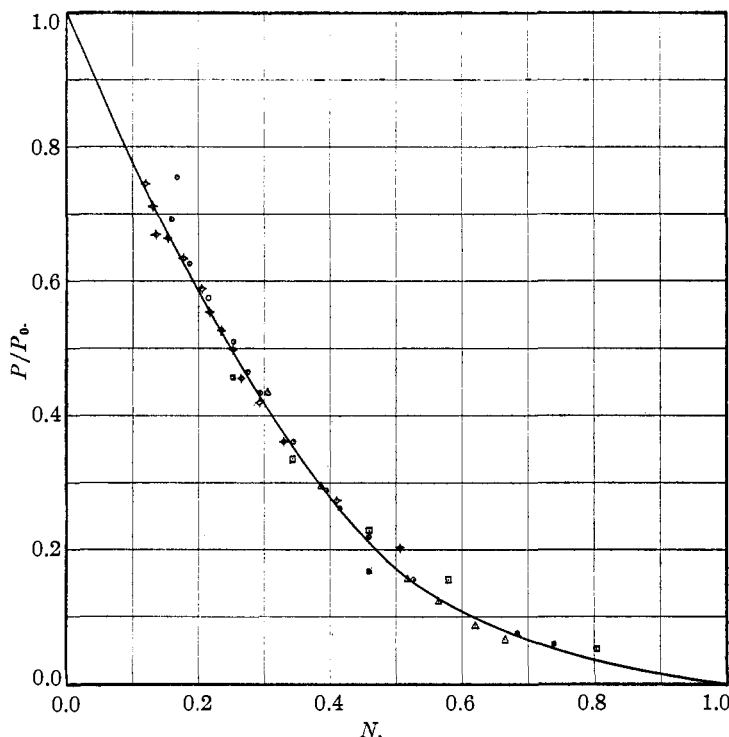


Fig. 10.—Curve showing large negative deviations of several inorganic salt solutions from Raoult's law: \circ , KCl; \square , NaBr; \bullet , $\text{Ca}(\text{NO}_3)_2$; \triangle , KI; \diamond , NaCl.

through the whole temperature range with no appearance of critical conditions; the end-point of the curve is determined by the triple point (so

that the melting point of the salt determines approximately the span of the curve), and the maximum vapor pressure is determined by the temperature coefficient of solubility, particularly in the first half of the temperature range. Thus for salts such as sodium iodide, where there is a marked increase in solubility with temperature in the region 100–300°, the maximum vapor pressure is low; for sodium chloride, when the rate of increase of solubility is relatively small, the maximum pressure is high; whereas for potassium chloride which exhibits an intermediate temperature coefficient, a moderate maximum vapor pressure is found.

The similarity in behavior of these inorganic systems is brought out by the curve showing similar negative deviation from Raoult's law (Fig. 10). Although the deviation from the straight line is appreciable in the plot of p/p_0 for water against the mole fraction, N , for salt most of the points fall on a smooth curve showing that changes in water vapor pressures at high temperatures are determined largely by mole fraction.

If melting point and solubility curves (Fig. 1) are examined approximations may be made of the positions of the curves for saturated solutions in the P - T system. Such a survey indicates several salts as unclassifiable. It, therefore, seems desir-

able that further work be done on such salts as magnesium sulfate and sodium fluoride to determine whether critical phenomena obtain (Class I) or the vapor pressure curves are continuous (Class II).

Summary

1. Vapor pressure data within the temperature range 150–650° are reported for saturated aqueous solutions of sodium chloride, sodium bromide, sodium iodide, potassium chloride, and potassium iodide, together with some data for sodium sulfate, sodium carbonate, calcium nitrate, boric oxide, and for a mixture of potassium chloride and sodium bromide.

2. Critical conditions near the critical point for water are confirmed for sodium carbonate, and for sodium sulfate.

3. Continuous curves are obtained for saturated solutions of highly soluble salts, showing maximum vapor pressures (up to 390 atmospheres for sodium chloride at 550°) at temperatures intermediate between the triple points of water and of salt, and no critical region.

4. The maximum vapor pressure appears to be less, the greater the initial temperature coefficient of solubility, and the lower the melting point of the salt.

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Radio Halogen Exchanges in the Phosphorus Halides

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Introduction

In several cases radio indicators have been used in a qualitative way for the determination of bond equivalence or non-equivalence. Using radiobromine, Roginsky and Gopstein¹ came to the conclusion that the two bromine atoms in solid cupric bromide are not equally reactive. Grinberg and Filinov² as a result of their exchange work concluded that probably the bromine bonds in K_2PtBr_4 and K_2PtBr_6 are equivalent, and Andersen³ proved that the sulfur atoms in thio-

sulfate ion are not equivalent. It is of considerable interest to investigate halogen exchanges in the phosphorus halides, especially the case of phosphorus pentachloride, since some investigations⁴ seem to indicate that the bonds are not all equivalent, at least not in the gas phase. It was decided to study these investigations in solution, and carbon tetrachloride was considered a convenient solvent to work in, since the amount of dissociation of the pentahalides in this solvent can be estimated from existing literature.⁵

Experimental

Materials.—Phosphorus tribromide was made by dropping bromine on phosphorus under carbon tetrachloride

* This work constitutes a portion of a thesis to be submitted by W. Koskoski in partial fulfillment of the requirement for the degree of Doctor of Philosophy in the Johns Hopkins University.

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