

The Vapor Pressure of Potassium Chloride and Caesium Iodide Crystals

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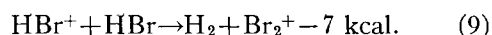
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calculated values. However, in Table III, experiments 7, 11, 12, 15 and 16 are the least satisfactory. In 7, 11, 15 and 16 we are dealing with a large pressure of hydrogen and an appreciable amount of hydrogen bromide. In the synthesis experiment 11 we calculate too large a yield of hydrogen bromide and in the decomposition experiments we calculate too much decomposition of hydrogen bromide. The reaction which is most plausible to explain these discrepancies is:



Experiment 12 is particularly interesting because it is the only experiment in which P_{H_2} is very small and that of Br_2 and HBr are large. For this condition it will be seen that $(1-B)$ has the very small value 0.059. Therefore, the values of A and of b are not important. And since P_{H_2} is so small that it likewise cannot play an important role, we must, therefore, look for a reaction which decomposes HBr without the intermediate formation of H atoms. The possibility of Br_2^+ or Br^+ reacting with HBr would be inadequate to explain the observed yield unless they too decomposed HBr without the formation of atoms. The only reaction of this type is



and this seems to be ruled out of consideration from energy considerations if the ionization potentials of HBr and of Br_2 are respectively 13.2 ev and 12.8 ev. However, the fact that Br_2^+

does not increase the yield of HBr in a hydrogen bromide mixture indicates that the reverse reaction to (9) is prevented either by endothermicity or a high energy of activation.

The preceding theory could be experimentally tested if (a) a procedure could be devised of carrying the ions to metal electrodes where they would combine without reacting and then measuring the residual reaction due to excited molecules; (b) measuring the relative rates of reaction of electrons with Br_2 and HBr to make $\text{Br} + \text{Br}^-$ and $\text{H} + \text{Br}^-$ respectively.

The discrepancies in Table III between the calculated and measured M/N yields could probably be accounted for by a consideration of reactions of the type of (8a) and (9) but we have preferred to await further investigation making more certain the reality of these discrepancies before carrying our analysis further. While clustering no doubt occurs we have regarded it as playing a very minor role. Thus the activation energy of certain reactions may be increased or lessened by a sheath of molecules in much the same way as this is accomplished for ions in solution. However, the course of reaction of the ions is governed chiefly by the same type of specific considerations important in any gas phase reactions.

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The Vapor Pressure of Potassium Chloride and Caesium Iodide Crystals

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THE measurements of Rodebush, Murray and Bixler¹ of the electric moments of the alkali halide molecules attribute a value of roughly ten Debye units to these molecules. Since this high value for the dipole moment has been calculated on the assumption of simple diatomic molecules,

it is of importance to consider the possibility of association into at least double molecules, $(\text{KCl})_2$. Such a molecule could conceivably have either a rhombic structure with a zero resultant moment or a linear structure with a corresponding large moment. If no association is present then the nearly 100 percent ionic nature of the alkali halide molecule is fairly well ascertained.

The vapor pressures were measured in a tem-

* National Research Fellow, 1935.

¹ Rodebush, Murray and Bixler, *J. Chem. Phys.* **4**, 372 (1936).

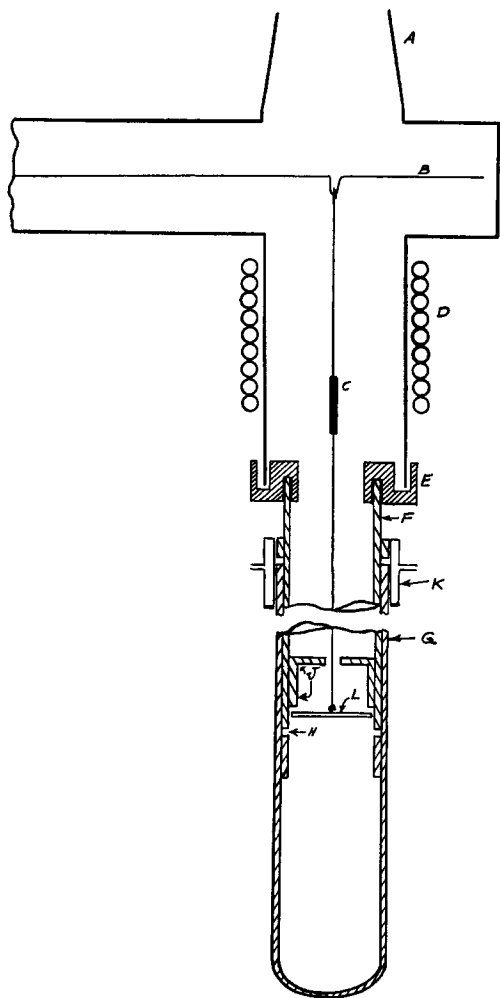


FIG. 1.

perature region comparable to that used in making the electric moment measurements cited above. The conditions in high temperatures (600–700°C) and low pressures (approximately 10^{-2} mm Hg) limit the number of methods available for making the measurements. The well-known molecular effusion method of Knudsen allows one to calculate the vapor pressure from the amount of vapor escaping through a hole in unit time, providing that the molecular weight is known. Since, in this investigation, the molecular weight is the unknown, it is necessary to measure the vapor pressure by an independent method.

The first attempt which was made to measure the absolute vapor pressure involved a molecular

beam experiment. A molecular beam of the salt vapor was completely intercepted by a very thin aluminum vane which, in turn, was centered on a quartz fiber of about two μ diameter. The axis of rotation in the fiber was about one centimeter from the center of the beam. The torsional deflection of the quartz fiber was observed by means of a light beam reflected from a tiny mirror fastened at the center of the vane. Consistent data were obtained only after taking special precautions to avoid electrostatic charges. Unfortunately, these data must be considered untrustworthy in view of the following considerations. A salt molecule on collision with the cold aluminum vane sticks to it, thus transferring a momentum equal to mv . In addition some adsorbed air molecules are kicked off due to the heat of condensation, thus contributing an additional momentum to the vane. Since the vacuum was about 10^{-6} mm Hg, the aluminum was in all probability instantly covered with adsorbed air molecules. Hence, the pressures as measured must be considered as too high to an extent which is at present unknown.

The second attempt to measure the vapor pressure was by means of an adaptation of the absolute manometer of Rodebush and Coons.² This method was carried out to a successful conclusion and it is described below. Some words might be pertinent as to the accuracy of the data necessary to establish the presence of association. If the vapor were 100 percent associated, the pressure would only be decreased by the factor $\sqrt{2}$ over that of an unassociated vapor. Thus, if one wants to establish association to within ten percent, it is necessary that the vapor pressure data be accurate to within four percent. Hence, it seems advisable to take all data in the same apparatus in order to assure a dependable temperature scale in putting the data together.

A. THE VAPOR PRESSURE MEASUREMENTS

The construction of the absolute manometer as used in this work is shown in Fig. 1.

Several attempts were made to make the apparatus of metal, but finally resort had made to an apparatus made of transparent vitreous

² Rodebush and Coons, J. Am. Chem. Soc. **49**, 1953 (1927).

quartz. *L* is a disk of fused quartz about 2.5 cm in diameter, the upper surface of which is ground to seat on the ground end of the quartz tube *J*. *C* is a small needle of soft iron, enclosed in glass, and *B* is a cantilever arm made from a quartz fiber by which the system is suspended. *B* is about ten inches long from the point of suspension to the point of support, which is a quartz to Pyrex seal to the rest of the apparatus. The arm *B* extends outwards for about two inches past the suspension support and is pulled out to a fine point, the extreme tip being about a millimeter from a plane window. A microscope was then used to measure the position of the arm and hence give the vertical position of the quartz disk. *D* is a coil through which a current is passed to bring an electromagnetic traction on *C*, thus pulling the disk upward to seat on *J*.

The ground seat, *J*, is sealed within a transparent quartz tube *F*, 12 mm bore, the top of which is sealed to the remainder of the apparatus by a De Khotinsky joint at *E* in the manner shown. Surrounding the quartz tube *F* is another transparent quartz tube, *G*, 14 inches long, which is closed at the bottom. A short length of quartz tube of the same diameter as *F* is sealed within *G*. The seal is made at the bottom, the top end having been previously ground to make a seat with the bottom of the inner tube *F* at *H*. The salt crystals are placed at the bottom of the outside tube *G*. This is then slipped into place and sealed at *K* by means of a water-cooled picein joint. The long suspension is lowered into place through the opening of the ground joint at *A*. The female part of the joint carries a test tube sealed concentrically within it which serves as a liquid air cooled surface.

The bottom of the outer quartz tube *G*, loaded with the salt, is placed snugly into a block of nickel into the top and bottom of which were drilled two holes to receive thermocouples. The junctions of the thermocouples extend through and touch the quartz tube.

A superheating coil was placed directly on *G* in the region around the quartz disk. This coil serves to keep the temperature of the disk several degrees above that of the salt in order to prevent condensation of the vapor on the quartz disk and seat. Finally, a pot furnace is raised into position to surround the entire assembly.

PROCEDURE

In operation no current is passed through the coil *D* and the system is evacuated to a pressure between 10^{-5} to 10^{-6} mm Hg. The salt is heated to within 50° of the point where the lowest pressure can be detected by the manometer. After 24 hours pumping the temperature is then raised and sufficient current is passed through the coil to seat the disk firmly on its seat. Time is allowed for pressure equilibrium to be established and then the current is decreased until the disk just drops from its seat on the end of the tube.

This "dropping current" is taken as the null-point and it was found to be reproducible. At the null-point the apparatus functions as an electromagnetic balance. The forces upwards consist of the tension in the quartz cantilever support, the magnetic pull of the solenoid, and the force due to the pressure of the vapor on the quartz lid, equal to the pressure times the area. The force downwards is the force of gravity. As the pressure increases, the pull necessary from the solenoid decreases. The data thus obtained for KCl and CsI at various temperatures are plotted in Figs. 2 and 3. At low temperatures one may observe

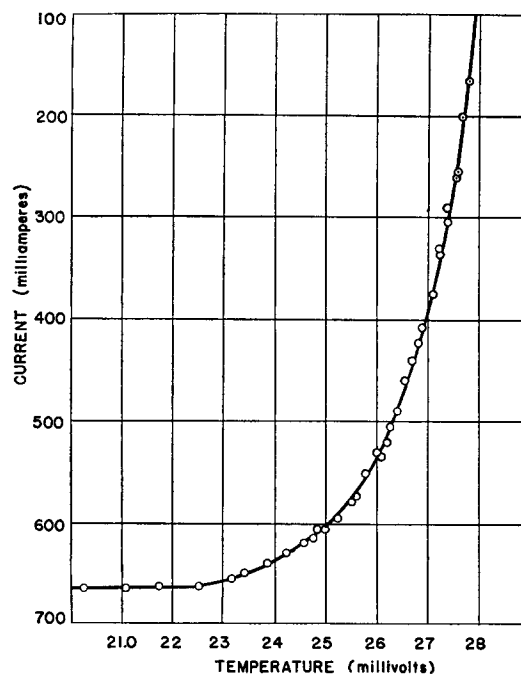


FIG. 2. KCl.

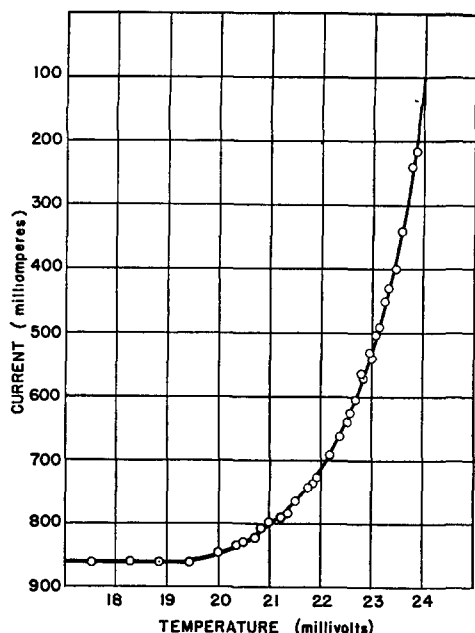


FIG. 3. CsI.

how the "dropping current" remains constant with temperature. Then as the temperature is raised, the curve pursues a typical vapor pressure plot. It was found that upon the first heating of the salts, the "dropping current" varied from ten to thirty percent higher than values obtained on subsequent heatings. This is attributed to adsorbed gases coming off of the salt crystals. The salt was fused preliminary to being placed in the apparatus and the fused mass broken up. It was then powdered in order to assure a sufficiently high rate of evaporation to maintain a saturated vapor. Because of this procedure the adsorbed gases mentioned above could not be avoided. All the remaining data are included in the graphs

of Figs. 2 and 3; these show the consistency of the data during subsequent heatings and coolings of the salt.

The vapor pressures were calculated from the above data with the following calibration. The quartz disk was replaced by an aluminum pan and sufficient weights added to make the total weight equal the weight of the quartz disk. The necessary current was then passed through the solenoid to bring the pointed end of the cantilever arm *B* to the null-point position, previously observed with the quartz disk seated in place. By removing weights from the pan and observing the corresponding decrease in the solenoid current, a calibration was obtained. The calibration curve was found to be linear and of a slope corresponding to a sensitivity of 0.280 milligram per milliampere. The "null-point" of the apparatus was found to be independent of temperature in the region in which the measurements were made. This is attributed to the fact that both the suspension and the quartz tube carrying the ground seat were made out of the same material, namely transparent vitreosil, and hence had the same coefficient of linear expansion. An additional calibration was made against a McLeod gauge by using air in the apparatus with the same results. The thermocouples were calibrated against the freezing point of a sample of aluminum obtained from the Bureau of Standards.

RESULTS

The results are given in Table I and Table II. In addition, an empirical equation has been fitted to each set of data, the equation being linear in $\log_{10} P$ and $1/T$, cf., Figs. 4 and 5.

The heats of sublimation of KCl and CsI as

TABLE I. Vapor pressure of KCl (crystal).

Temp. °K	Pressure (dynes)	
	Obs.	Calc.
847.2	1.35	1.33
855.6	1.89	1.80
879.4	3.95	4.08
892.1	6.22	6.08
903.8	8.86	9.07
910.0	11.10	11.04
918.0	13.8	14.1
929.1	20.3	19.9
936.2	24.9	24.6

$\Delta H_{\text{Sub}} = 51,800 \text{ cal./mole,}$
 $\log_{10} P_{\text{dynes}} = -11,300/T + 13.461.$

TABLE II. Vapor pressure of CsI (crystal).

Temp. °K	Pressure (dynes)	
	Obs.	Calc.
767.2	2.03	1.95
785.8	4.00	4.05
801.8	7.45	7.44
807.9	9.60	9.30
816.3	12.5	12.6
823.0	16.3	16.0
830.3	20.5	20.6
840.5	29.3	29.3
846.8	36.4	36.2

$\Delta H_{\text{Sub}} = 47,500 \text{ cal./mole,}$
 $\log_{10} P_{\text{dynes}} = -10,360/T + 13.793.$

given by Mayer and Helmholtz³ compare very favorably with the above data, namely, 51,600 and 47,300 calories as compared with the experimental values of 51,800 and 47,500 calories, respectively. The correction to 0° is almost negligible.

When the vapor pressure data for liquid KCl⁴ are extrapolated to the melting point, the plot is found to intersect the extrapolation of the above data for the solid at the temperature of 1095°K. This is less than five percent from the observed melting point of 1049°K, and is all that one can expect from an extrapolation over a temperature range of about 250°.

B. THE MOLECULAR EFFUSION MEASUREMENTS

The Knudsen formula for molecular effusion may be written as follows

$$p = (w/t)(2RT/M)^{1/2}(1/A + 3L/2\pi D^3),$$

where p is the pressure, w is the mass of vapor which passes in t seconds through an orifice of cross section A , of diameter D and of length L . M is the molecular weight and T the absolute temperature. By making a thin edged orifice in which L is between $D/5$ and $D/10$, one sees that the term $3L/2\pi D^3$ is only about five percent of $1/A$. The salts in these experiments were contained in small quartz capsules made in the following way.

A quartz tube with an inside diameter of two millimeters and a wall thickness of one millimeter was drawn down to a small constriction at one end. This constricted end was carefully heated;

and just before the hole collapsed, a bubble of about six millimeters diameter was blown. With sufficient luck there was sometimes formed a small thin edged circular hole, situated at the top of the bubble. The diameter of this orifice was accurately measured with a microscope. By carefully grinding the edge of the circular hole the thickness was reduced to a value between one-fifth and one-tenth the diameter of the hole.

These quartz capsules were suspended in the vapor pressure apparatus described above, from which the quartz disk had been removed. While the temperature was attaining a constant value, the quartz capsule was lowered into a region 50° cooler than that to be used. At a stipulated time the capsules were lowered and rested on the bottom of tube G of Fig. 1. At the conclusion of the run the capsules were pulled up out of the heated part and the external furnace which surrounded the apparatus was immediately lowered. As the duration of the runs was from five to eight hours, the time is considered known to an accuracy better than one percent. The loss of weight of the quartz capsules was obtained by weighings on a Kuhlmann Micro Chemical Balance by Mr. K. W. Eder, microanalyst of the Chemistry Department.

The results are assembled in Table III. The area of the orifice was varied by a factor of ten as a test for saturation. Samples of powdered fused KCl and of KCl fused directly in the quartz tube gave the same results. Blank runs assured no appreciable evaporation losses of the quartz itself and served as controls in the micro balance weighings.

The purity of the salts used was tested. They were shown to be free from appreciable amounts of impurities.

TABLE III.

	$T(^{\circ}\text{K})$	$t(\text{sec.})$	$w(\text{g})$	$1/A + 3L/2D^3$	$P(\text{single})$	$P(\text{double})$	$P(\text{obs.})$
No. 1. KCl (fused)	932.0	14,540	0.010610	356.	21.0	14.9	21.5
No. 2. KCl (fused)	932.0	22,560	.016423	356.	20.9	14.8	21.5
			.010010	615.	22.0	15.5	21.5
No. 3. KCl (powdered)	932.0	18,050	.006890	692.	21.2	15.0	21.5
			.004465	692.	11.5	8.14	
No. 4. KCl (powdered)	913.1	21,600	.003557	952.	12.5	8.85	12.1
			.005770	819.	10.6	7.50	
No. 5. CsI	813.3	18,120	.006937	682.	10.7	7.35	11.0
			.003097	819.	4.68	3.31	
No. 6. CsI	789.3	21,600	.003683	682.	4.64	3.27	4.65
			.004025	1970.	11.2	7.92	
No. 7. CsI	815.4	28,815	.002500	3500.	12.3	8.70	12.2

³ Mayer and Helmholtz, Zeits. f. physik. Chemie **75**, 27 (1932).

⁴ Rodebush and Fiock, J. Am. Chem. Soc. **48**, 2522 (1926).

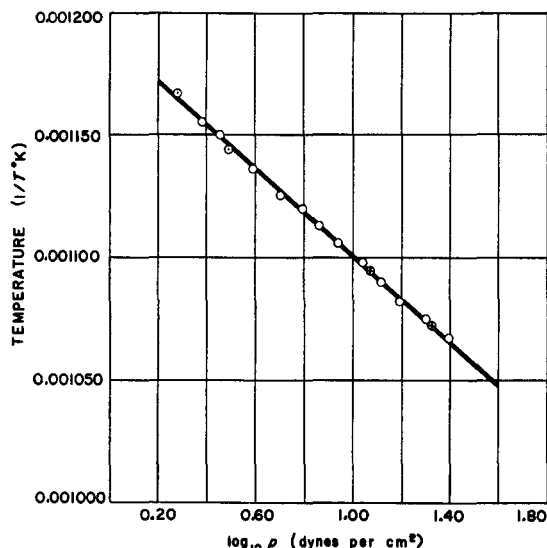


FIG. 4. KCl.

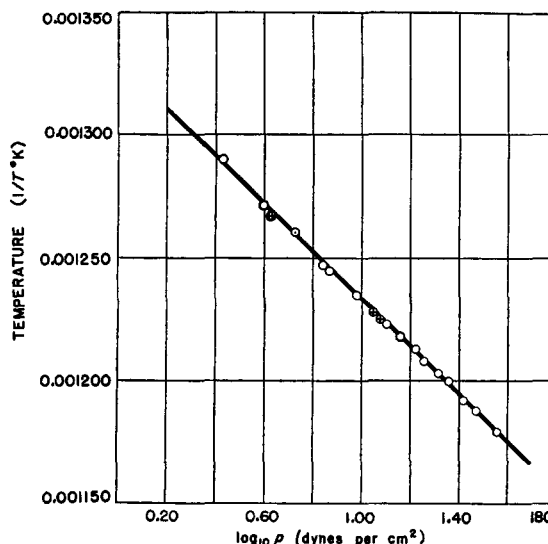


FIG. 5. CsI.

In columns 6 and 7 are the vapor pressures, calculated on the assumption of single and double molecules respectively. In column 8 are the corresponding pressures measured with the absolute manometer. Obviously single molecules are in the majority and one is able to say that to within an accuracy of ten percent the saturated vapor is not associated in the pressure region investigated. All the data are plotted in Figs. 4 and 5. The dots within circles are the absolute vapor pressure measurements and the crosses are the pressures calculated from the molecular effusion experiments.

DISCUSSION

The complete absence of association in the saturated vapor of molecules with such high dipole moments is somewhat surprising. If the heat of dissociation of the double molecule were small enough, the conditions of high temperature and low pressure would tend to prevent any association. Hence, one should further investigate the vapor for association at high pressures. But even at the higher saturated pressures it is doubtful whether the amount of association is ever very large. It can readily be shown that a large degree of association necessitates a large heat of dissociation of the double molecule into single molecules. A rough estimate is 75 kilocalories.

The heat of sublimation of KCl is in approx-

imate figures 50 kilocalories. If this is really the heat of sublimation to $(\text{KCl})_2$, then KCl gas would have 35 calories additional energy and would be 85 kilocalories above that of the crystal and, therefore, the heat of dissociation of KCl (g) into atoms must be only 65 instead of 101 kilocalories as calculated by Mayer and Helmholtz⁵ from Born cycle considerations.

Some preliminary theoretical calculations indicate that the heat of dissociation of the double molecules into single molecules might be as large as that estimated above. Using the newer values for the polarizability and the exponential repulsion potential of Born and Mayer⁵ one obtains by use of the old method of Born and Heisenberg,⁶ a value of 120 kilocalories for the heat of formation of KCl from ions. The calculated dipole moment is 8.23×10^{-18} e.s.u. This indicates that ionic forces predominate and by assuming Coulomb forces between two KCl molecules, a heat of dissociation of double molecules into single molecules of 75 kilocalories is obtained. The above calculation is being made the starting point of a perturbation calculation in anticipation of improving the agreement between theory and experiment.

The author wishes to express his appreciation to Professor W. H. Rodebush for his guidance in completing this research.

⁵ Born and Mayer, *Zeits. f. Physik* **75**, 1 (1932).

⁶ Born and Heisenberg, *Zeits. f. Physik* **23**, 404 (1924).