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Measurements of Low Vapor Pressures of Alkali Halides

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The vapor pressures over the crystalline salts have been measured in the neighborhood of 900°K by Knudsen's method for the chlorides and bromides of sodium, potassium and rubidium. Heats of vaporization have been calculated from the data.

INTRODUCTION

KNUDSEN'S method of molecular effusion¹ is very suitable for the measurement of low vapor pressures at high temperatures. In the experiments to be described this method is applied to determine the small vapor pressures of alkali salts below their melting points. The salt vapors passing through a small opening of known area in a definite time interval, at constant temperature, are condensed on a cold surface and their amount measured. The vapor pressure, P , is calculated from the formula

$$P = (m/a \cdot t)(2\pi RT/M)^{1/2},$$

where a is the area of the opening, t the time, T the temperature, R the gas constant, M the molecular weight and m the amount of condensed salt. The area of the hole is supposed to be negligible when compared with the area of the walls of the vessel and with the exposed surface area of the salt crystals. Similarly, the diameter of the opening must be small compared to the mean free path of the gas molecules.

APPARATUS AND EXPERIMENTAL PROCEDURE

The apparatus is shown in Fig. 1. The cylindrical iron oven O containing the salt crystals

had an outside diameter of 5 cm and was drilled out on the inside to 2 cm. The six heating elements of "Global" (carborundum composition) were led through six holes in the oven wall parallel to the axis of the oven and fastened to an iron ring G above the oven. The Global rods were mounted in parallel and connected, at their lower ends, by small clamps and a copper wire. Small porcelain rings insulated the Global elements from the oven wall. When heated to 650°C, the oven had a resistance of about 4Ω and carried 5 amperes. In order to facilitate a good contact and a uniform heating both ends of the six rods had been dipped, when manufactured, into a metal solution. Untreated rods proved to be unsatisfactory.

The oven was open at its lower end. Correspondingly, the plate P carrying the salt crystals could be lifted and fit tightly into the interior of the oven. After thorough drying, the salt was sealed, under vacuum, into small bulbs L made of thinly blown Pyrex glass, and mounted somewhat higher than the lowered position of P . The bulb could be crushed by raising the plate against it with the help of a stopcock pulley and an attached string. When the salt was deposited on the plate, an electromagnet operating from the outside turned the empty bulb away and the plate was ready to be lifted into the oven.

¹ Knudsen, *Ann. d. Physik* **47**, 697 (1915).

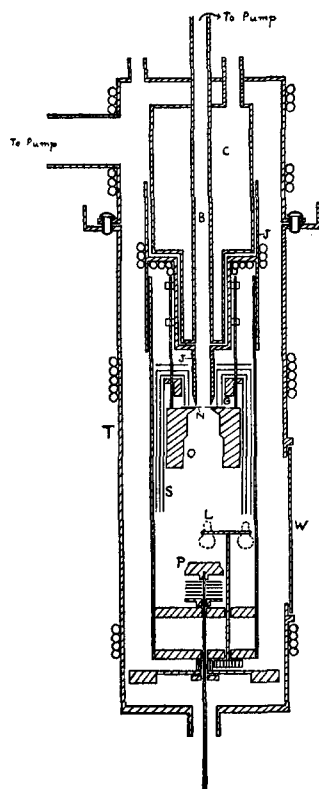


FIG. 1.

The nickel plate *N* screwed on top of the oven had in the center a small opening. Care was taken to have the opening drilled with a smooth and very thin edge. The salt vapors passing through the opening were condensed at the bottom of a copper stick (of about 20 cm in length) which could be lowered through the brass tube *B* into a position closely above the opening. The point of a steel needle welded to the end of the copper stick kept the proper distance of less than a millimeter from the nickel plate.

Particular precaution was necessary in order to keep the copper stick cold when the oven was heated. The brass tube *B* was led through a liquid-air container *C* carrying on its lower end (directly above the oven) a water-cooled brass jacket *J*. Little knobs with screws were soldered on *J*, holding the suspended oven on thin rods. The jacket was built in such a way as to form a prolongation of *B* and to reach almost as far as the nickel plate. It was important to have the copper stick fit as tightly as possible into the

tube *B* and at the same time not to prevent a smooth sliding. Three chromium plated iron shields *S* surrounding the sides and the top of the oven reduced the heat loss. In this manner the copper stick was kept cold in a very satisfactory manner. The rod carrying the plate *P* had also several radiation shields attached. Both the liquid-air container and the oven were enclosed in a wide brass tube *T* which led to a steel mercury diffusion pump. This brass tube as well as the Pyrex plate glass window *W* which was sealed into *T* with De Khotinsky cement were water-cooled. The detachable lower part of *T* was screwed on to the upper part, the joint being sealed with "Apiezon" sealing compound which has the advantage of requiring no heat to make the seal.

The oven temperature was measured with two C.P. platinum-platinum 10 percent rhodium thermocouples which were calibrated against the freezing points of several metals. A hole was drilled into the oven wall to receive one thermocouple, the other being attached to the removable plate *P*. In order to attain good contact the thermocouple junctions were welded into two small iron plugs, tightly fastened into their respective holes with a screw. The cold junctions were kept at 0°C. The two thermocouples agreed within one degree.

In order to keep the temperature constant for a longer period of time, it was necessary to construct a voltage regulator. The voltage across the oven was balanced against two storage batteries which operated a relay. The relay controlled the height of a column of mercury surrounding a Globar stick thus controlling the resistance in series with the oven. This arrangement kept the oven temperature constant within 1°C during the measurements.

A measurement was carried out the following way: When a good vacuum and the desired temperature had been attained, *P* was loaded with salt and raised into the oven. Constant temperature being reestablished the copper stick was lowered by means of an attached string and stopcock. The moment when the stick had the proper position above the orifice was read from a stopwatch by observing the moment when a knot in the string had reached a mark on the glass tubing. After a measured length of time

the copper stick with the salt condensed on it was raised. Passing through a wide stopcock the stick could be removed without breaking the vacuum in the part containing the oven.

The condensed salt was washed from the copper stick and the solution carefully condensed by evaporation so that, by titrating it with 1/50-normal silver nitrate solution, the change in color could be easily distinguished. A drop of a 10 percent solution of potassium chromate was used as indicator. A burette of 5 cc with gradings of 0.01 cc permitted titration of small amounts of salt solution. One cc could be titrated to within 1 percent.

The area of the opening was measured with a comparator, the measurement of the diameter being accurate to 0.3 percent. Two different sizes of holes (0.01574 cm², 0.02122 cm²) were used for the measurements. The results agreed within the limit of experimental errors.

A correction was made to take into account the extension of the opening caused by heating the oven and with it the nickel plate. The correction amounts to an increase of the area of about 1.7 percent in the range of the temperatures used.

EXPERIMENTAL RESULTS

Measurements were made on six salts, NaCl, NaBr, KCl, KBr, RbCl and RbBr. The vapor pressures at various absolute temperatures are recorded in Table I, and $\log_{10} P_{mm}$ is plotted against $1/T$ in Fig. 2. The solid lines of the figure represent the calculated vapor pressures from Eq. (3) with the values of the constants tabulated in Table IV.

CALCULATION OF THE HEAT OF VAPORIZATION

There are three, essentially independent methods available for the calculation of the heat

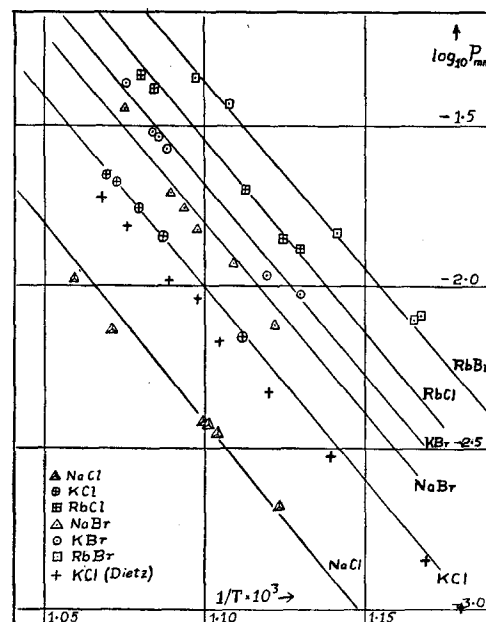


FIG. 2.

of sublimation, ΔH (vap.) from these and other known data.

The first method is that of plotting logarithm of pressure against reciprocal of temperature and using the well-known formula

$$d \ln P / d(1/T) = -\Delta H / R. \quad (1)$$

Owing to the rather small temperature and $\ln P$ interval for which these measurements are made the accuracy of this method is not very great. Small errors in the individual measurements result in rather large errors of slope. The results of this method, with the probable error, are recorded in column 2, Table II.

The second method involves the use of the measurements recorded in this article in conjunction with vapor pressure observations made by other workers over the liquid salt at much

TABLE I.

NaCl		NaBr		KCl		KBr		RbCl		RbBr	
T°K	$P_{mm} \times 10^3$	T°K	$P_{mm} \times 10^3$	T°K	$P_{mm} \times 10^3$	T°K	$P_{mm} \times 10^3$	T°K	$P_{mm} \times 10^3$	T°K	$P_{mm} \times 10^3$
890.2	2.11	891.2	7.65	899.4	6.98	884.9	9.48	885.0	13.1	856.4	7.99
905.7	3.55	901.5	11.8	920.1	14.3	893.1	10.8	889.4	14.1	857.7	7.90
907.9	3.74	910.8	15.1	926.5	17.8	918.9	26.8	898.5	19.9	876.2	14.5
909.5	3.82	914.1	17.5	932.3	21.2	921.1	29.1	922.2	40.8	902.7	36.8
933.6	7.32	917.4	19.5	935.3	22.0	922.5	30.2	925.6	45.0	911.4	44.4
944.1	10.5	930.1	35.6			929.4	43.0				

TABLE II.

SALT	$\Delta H(\text{VAP.}), 900^\circ\text{K. IN KCAL.}$				$\Delta H(\text{VAP.}, 0^\circ\text{K}) = \Delta E(\text{VAP.}, 0^\circ\text{K}) \text{ KCAL.}$
	FROM SLOPE OF THESE MEASUREMENTS	FROM $P(\text{VAP.})$ OVER LIQUID	FROM THEOR. ΔS CALCULATION	WEIGHTED AVERAGE	
NaCl	50.5 ± 2.5	53.6 ± 1.5	52.4 ± 1.7	52.4 ± 1.7	55.2 ± 2.0
NaBr	52.4 ± 3.0	49.6 ± 2.0	49.0 ± 1.7	50.0 ± 1.7	53.4 ± 2.0
KCl	53.2 ± 2.0	49.8 ± 1.5	49.8 ± 1.2	50.6 ± 1.2	53.8 ± 1.5
KBr	54.4 ± 3.0	48.3 ± 2.0	47.7 ± 1.4	49.6 ± 1.4	53.3 ± 1.7
RbCl	49.3 ± 2.0	46.6 ± 2.0	48.7 ± 1.7	48.1 ± 1.7	51.3 ± 2.0
RbBr	48.3 ± 2.0	46.7 ± 2.0	47.2 ± 2.0	47.4 ± 2.0	51.2 ± 2.3

higher pressures and temperatures. Essentially this method resolves itself into finding two consistent equations for the vapor pressure of one salt, over the liquid and crystal, respectively. The equations must agree with the experimental observations over the liquid, and those of this work, respectively. They must also lead to the same vapor pressure at the melting point, T_f . They must further lead to a reasonable value for the heat of fusion ΔH_f .

Measurements of the vapor pressure over the liquid salt for NaCl, NaBr, KCl and KBr have been made by Wartenberg and Albrecht,² and on RbCl and RbBr by Wartenberg and Schulz.³ All six salts have been measured Ruff and Mugdan.⁴ These measurements all cover about the same range from some 50 to 760 mm, or from 1320°K to 1720°K . The temperature scale of Wartenberg and co-workers was slightly in error, and this correction has been applied in our calculations. The values of these workers all agree moderately well. Fiock and Rodebush⁵ have measured NaCl, KCl and KBr from 5 to 50 mm (1180°K to 1430°K). Their measurements agree well with those of the previous workers. Horiba and Baba⁶ have reported measurements on NaCl and KCl which appear to be in error at low pressures, but which agree moderately well at higher pressures with the other workers. Finally Maier⁷ has recorded measurements on NaCl

² Wartenberg and Albrecht, *Zeits. f. Electrochem.* **27**, 162 (1921).

³ Wartenberg and Schulz, *Zeits. f. Electrochem.* **27**, 568 (1921).

⁴ Ruff and Mugdan, *Zeits. f. anorg. allgem. Chemie* **117**, 161 (1921).

⁵ Fiock and Rodebush, *J. Am. Chem. Soc.* **48**, 2522 (1926).

⁶ Horiba and Baba, *Bull. Chem. Soc., Japan* **3**, 11 (1928).

⁷ Maier, *Techn. Papers, Bureau of Mines, Washington* (1925).

which are not in agreement with those of the others.

By plotting all these recorded results on a moderately large scale one is able to draw fairly reliable vapor pressure curves for NaCl, KCl and KBr from about 1200°K to 1700°K , and for NaBr, RbCl and RbBr from 1350° to 1700°K . In order to correlate these values with ours over the crystalline salt at about 900°K it is necessary to make some assumption concerning the change of heat of vaporization, ΔH_v , with temperature, part of which is due to the heat of fusion, ΔH_f , and part of which is due to the difference in specific heats of the liquid, respectively crystal, and the gas, ΔC_p .

We have used values for the heat of fusion taken from *International Critical Tables* for NaCl, KCl and RbCl, and have guessed at values for the other three salts. These values are recorded in column 2, Table III. Of these, only that for NaCl is really reliable. The heat of fusion of KCl is given to within 0.9 kcal. by I.C.T. That of RbCl appears to be inordinately low, and the results of our calculations indicate this. Nevertheless the error in these values will scarcely exceed 1.5 kcal.

The further assumption is then made that the specific heat of the condensed phase, crystal or liquid, is uniformly higher than that of the gas by $3R$. The exact value $3R$ is not of great importance, but since the temperature range over which the measurements stretch is some 800° the total correction is not of negligible importance.

With these assumptions of the value of the heat of fusion and the difference in specific heats of gas and condensed phase, it is only necessary to use one value of the vapor pressure over the liquid at high temperatures and one average of our values to calculate ΔH_v . Due to the enormous pressure range considered, a range of about one hundred thousand-fold, comparatively little error is introduced by uncertainties in the vapor pressures themselves. The greatest single error is one of about 0.75 kcal. to 0.85 kcal. due to the uncertainty in the heat of fusion. The final results with the probable errors are tabulated in column 3, Table II.

The third method by which $\Delta H(\text{vap.})$ may be calculated is to evaluate the entropy change in

sublimation theoretically, and to use one measurement of pressure to determine ΔF . Using

$$-\Delta F_v = RT \ln P = -\Delta H_v + T\Delta S_v \quad (2)$$

ΔH_v can be immediately calculated.

The entropies of crystalline NaCl, KCl, NaBr and KBr are known at room temperature, the latter somewhat unsatisfactorily. The specific heat of KCl has been measured up to 600°K, and the curve is easily extrapolated to higher temperatures since it differs but little from the value $6R$. Using similar extrapolations for NaCl, NaBr and KBr give "experimental" entropies for these four crystalline salts at 900°K. Since the greater part of the entropy is present at room temperature this method appears to be fairly satisfactory.

The measurements of Barnes⁸ on the frequencies of the alkali halide crystals enable us to calculate the entropies of the salts by assuming six Debye degrees of freedom with the measured frequencies. The agreement in the case of NaCl, NaBr, KCl and KBr with the values obtained from specific heats gives us some confidence in the use of these values for the other two salts.

Sommermeier⁹ has measured the fundamental frequencies of several of the gaseous alkali halides, among them KBr and RbCl. The frequencies of the other molecules may be extrapolated without great error. Maxwell, Hendricks and Moseley¹⁰ have determined the interatomic distances in the molecules by electron diffraction. These data enable the calculation of the entropy of the gas to be made. A small correction for

anharmonicity and rotational stretching has been introduced.

The data and results of the calculations of entropy are given in Table III. From these values of $\Delta S(\text{vap.})$ and the values of $\ln P$ at 900°K the values of ΔH_v at 900°K have been calculated and are recorded in column 4, Table II.

The weighted average values of $\Delta H(\text{vap. } 900^\circ\text{K})$ are in column 5, and $\Delta H(\text{vap. } 0^\circ\text{K})$ in column 6 of Table II.

THE VAPOR PRESSURE CURVE

Finally, having arrived at a most probable value for $\Delta H(\text{vap. } 900^\circ\text{K})$ we may return to the second method used to determine ΔH , and, reversing the method calculate an equation for $\log_{10} P$. We use the form

$$\log_{10} P_{mm} = -A/T - 3 \log_{10} (T/1000) + C, \quad (3)$$

in which the unaccustomed $\log T$ term enters from the assumed $\Delta C_p = -3R$ previously discussed. At any temperature

$$\Delta H(\text{vap. } T) = 4.5738A - 3RT. \quad (4)$$

The constants A and C for liquid and crystal are tabulated in Table IV. We should have $4.57(A_{\text{cryst}} - A_{\text{liq}}) = \Delta H_f$, but since the integrated error in the assumption that $C_p(\text{gas}) - C_p(\text{condensed}) = -3R$ is empirically taken into this term we cannot attach any significance to its value.

The constants tabulated fit P , to within the experimental error, with the best average of the results of the various workers mentioned previously. Presumably they can be counted on to

TABLE III.

SALT	ΔH_f KCAL.	CRYSTAL				GAS			ΔS 900°K CAL./DEG.	$T\Delta S$ KCAL. 900°K
		FRE- QUENCIES (BARNES) ⁷ T	S (900°K) CAL./DEG.			FRE- QUENCIES (SOMMER- MEYER) ⁸ CM ⁻¹	INTERATOMIC DISTANCES (HENDRICK) ⁹ 10 ⁻⁸ CM	S 900°K CAL./DEG.		
			FROM ν	FROM C_p	PROBABLE VALUE					
NaCl	7.22	234.2	32.0	31.5	31.5±0.9	374	2.51	64.9±0.7	33.4	30.1±1.5
NaBr	(6.9)	191.7	34.3	35.1	35.1±1.1	330	2.64	67.5±0.5	32.4	29.2±1.5
KCl	5.52	202.4	33.7	34.3	34.3±0.6	348	2.79	66.7±0.5	32.4	29.2±1.0
KBr	(5.3)	162.6	36.3	37.8	37.8±1.0	283	2.94	69.4±0.3	31.6	28.4±1.2
RbCl	4.59	168.8	35.8		36.3±1.4	253	2.89	69.5±0.3	33.2	29.9±1.5
RbBr	(5.1)	125.6	39.4		39.9±1.4	198	3.06	72.2±0.5	32.3	29.1±1.8

⁸ R. B. Barnes, Zeits. f. Physik **75**, 723 (1932).

⁹ K. Sommermeier, Zeits. f. Physik **56**, 548 (1929).

¹⁰ L. R. Maxwell, S. B. Hendricks and V. M. Moseley, Phys. Rev. **52**, 968 (1937).

TABLE IV. For use in $\log_{10} P_{mm} = -A/T - 3 \log_{10} (T/1000) + C$.

SALT	NaCl	NaBr	KCl	KBr	RbCl	RbBr
$A(\text{cryst.})$	12629	12104	12229	12001	11674	11514
$C(\text{cryst.})$	11.345	11.391	11.341	11.391	11.157	11.156
$A(\text{liq.})$	11477	10480	10710	10490	10307	10224
$C(\text{liq.})$	10.275	9.811	9.909	9.883	9.772	9.805
M.P. °K	1077	1028	1045	1003	988	955

duplicate the true vapor pressures to within twenty or thirty percent over the whole temperature range from about 850°K to 1700°K.

The curves of Fig. 2 are those corresponding to the calculated constants of Table IV in the neighborhood of our measurements. The results of Dietz¹¹ have been plotted in Fig. 2 but neglected in making the calculations.

Dietz's measurements are uniformly about thirteen percent lower than ours which may be regarded as not unsatisfactory agreement. The difference in ΔF calculated from his measurements and ours is 0.5 kcal., and both methods of calculation if applied to his measurements instead of ours would result in a value of ΔH approximately 0.5 kcal. higher than that given here.

¹¹ Dietz, J. Chem. Phys. **4**, 575-580 (1936).

TABLE V. Energies in kilocalories of reactions at 0°K.

SALT	NaCl	NaBr	KCl	KBr	RbCl	RbBr
$M X_{\text{cryst}} \rightarrow M X_{\text{gas}}$	55.2	53.4	53.8	53.3	51.3	51.2
$M X_{\text{cryst}} \rightarrow M^+_{\text{gas}} + X^-_{\text{gas}}$	183.1	174.6	165.4	159.3	160.7	153.5
$M X_{\text{gas}} \rightarrow M^+_{\text{gas}} + X^-_{\text{gas}}$	127.9	121.2	111.6	106.0	109.4	102.3
$M X_{\text{cryst}} \rightarrow M_{\text{gas}} + X_{\text{gas}}$	152.6	139.1	152.6	140.5	152.8	141.6
$M X_{\text{gas}} \rightarrow M_{\text{gas}} + X_{\text{gas}}$	97.4	85.7	98.8	87.2	101.5	90.4

THE HEATS OF OTHER REACTIONS

The lattice energies of these salts give the energies of dissociation at absolute zero of the crystalline salt into gaseous ions. These have been calculated by Mayer and Helmholtz.¹² The difference between lattice energy and heat of sublimation at absolute zero gives the heat (or energy) of dissociation of the gaseous molecule at 0°K. Similarly from the data tabulated by Bichowsky and Rossini¹³ the energy differences (at 0°K) of crystalline salt and its component gaseous atoms can be calculated. The difference of these values and the heats of sublimation give the energy of dissociation of the gaseous molecule into atoms. The energies of these reactions at 0°K are tabulated in Table V.

¹² Mayer and Helmholtz, Zeits. f. Physik **75**, 19 (1932).

¹³ Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold, 1936).