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## The Vapor Pressures of Some Alkali Halides\*

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The vapor pressures of six alkali halides, NaBr, NaI, KI, CsCl, CsBr, and CsI, have been measured in the range from about  $10^{-4}$ -mm to 0.1-mm pressure. The measurements were made by the diffusion method, using an oxygen-coated tungsten filament as detector.

### I. INTRODUCTION

VAPOR pressures of solid alkali halides have been measured by a number of investigators. Mayer and Wintner<sup>1</sup> used Knudsen's method of molecular effusion.<sup>2</sup> The amount of salt  $Q$  escaping into a vacuum from an oven at temperature  $T$  through a small hole of known area  $A$  in a definite time interval  $t$  is related to the pressure  $P$  in the oven by

$$P = (Q/At)(2\pi RT/M)^{1/2},$$

where  $M$  is the molecular weight of the salt and  $R$  is the gas constant. The effused salt was condensed on a cold surface and the amount determined by quantitative chemical analysis. Niwa<sup>3</sup> and Dietz<sup>4</sup> used the same method, but measured the loss of weight of the oven. Dietz also used an electromagnetic balance as an absolute manometer.

Zimm and Mayer<sup>5</sup> combined Knudsen's effusion method with the positive ion method of Langmuir.<sup>6</sup> The effusing salt beam was intercepted by a tungsten filament whose temperature and work function were sufficiently high to allow complete dissociation of the salt molecule and complete ionization of the metal atom, and the current due to the metal ions was measured. This method gives directly the rate of effusion and thus eliminates the measurement of the time

interval. It is not necessary to hold the oven temperature constant for long periods of time. The sensitivity of the detector allows the vapor pressure measurements to be extended to lower temperatures.

In this research, the method of Zimm and Mayer was used to measure the vapor pressures of sodium bromide, sodium iodide, potassium iodide, cesium chloride, cesium bromide, and cesium iodide. The heats and entropies of vaporization were calculated from these data. The entropies of the crystals at 800°K and the heats of vaporization at absolute zero were also calculated.

### II. PRINCIPLES OF THE METHOD

The number of salt molecules escaping per second into a vacuum from an oven at known temperature through a hole whose diameter is smaller than the mean free path of the molecules is given by Knudsen's formula

$$n = SP/(2\pi mkT)^{1/2}, \quad (1)$$

where  $S$ =area of hole,  $P$ =pressure inside oven,  $T$ =absolute temperature of oven,  $m$ =mass of molecules, and  $k$ =Boltzmann constant. The molecules leaving the oven are allowed to impinge upon a filament whose temperature and work function are sufficiently high so that every molecule hitting it is dissociated and every metal atom thus formed is ionized. If sufficient potential is put on the collector, the number of positive ions reaching it will equal the number of molecules hitting the filament. Consideration of the geometry of the apparatus allows the pressure in the oven to be expressed in terms of the positive ion current  $i_0$ .

$$P = [N_0 R^2 (2\pi mkT)^{1/2} / r^2 A F] i_0, \quad (2)$$

where  $r$ =radius of hole in oven,  $R$ =distance

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\*\* Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Columbia University.

<sup>1</sup> J. E. Mayer and I. H. Wintner, *J. Chem. Phys.* **6**, 301 (1938).

<sup>2</sup> M. Knudsen, *Ann. d. Physik* **47**, 697 (1915).

<sup>3</sup> K. Niwa, *J. Faculty Sci. Hokkaido Imp. Univ. Ser. III*, **2**, 201 (1938).

<sup>4</sup> V. Dietz, *J. Chem. Phys.* **4**, 575 (1936).

<sup>5</sup> B. H. Zimm and J. E. Mayer, *J. Chem. Phys.* **12**, 362 (1944).

<sup>6</sup> J. B. Taylor and I. Langmuir, *Phys. Rev.* **51**, 753 (1937).

between hole and filament,  $N_0$ =Avogadro's number,  $F$ =Faraday, and  $A$ =area of plane projection of filament.

The molecular effusion method allows the calculation of the vapor pressure from the effusion rate, provided the molecular weight of the gas is known. Zimm and Mayer showed it to be unlikely that the degree of association of KCl is greater than 0.3 percent at 800°K. Because the properties of the other alkali halide vapors are similar, it is assumed that the amount of dimerization is negligible in all cases. The extent of dissociation of the molecules into atoms may be estimated from the dissociation energy of the molecule. In the case of CsI, which has the lowest dissociation energy of the alkali halides, the dissociation would be about  $5 \times 10^{-5}$  percent at the vapor pressure of  $10^{-2}$  mm at 800°K.

The pressure of positive ions produced by the dissociation of the gas in the oven to ions is even less than the dissociation into atoms, and is consequently negligible. In the case of CsI, the extent of dissociation is about  $5 \times 10^{-3}$  percent and corresponds to a pressure of cesium ions of  $5 \times 10^{-12}$  mm at 800°K. Even considering

that the ions leaving the oven orifice carrying a current directly to the large collecting plate without requiring collision with the filament so that the geometric factor of  $R^2/A$  in Eq. (2) is much larger in this case, the low pressure negates any appreciable errors due to this cause.

### III. APPARATUS

A diagram of the apparatus is shown in Fig. 1. The oven  $A$  in which the salt was heated was a  $4 \times 1.5$ -cm polished silver cylinder whose wall thickness was 0.3 cm; the cover was 0.7 cm thick and screwed into the body of the oven to a depth of 0.4 cm. The hole  $E$  through which the molecules escaped was 0.1057 cm in diameter, finished with knife-sharp edges. Another oven, used for additional runs on cesium bromide, had a hole 0.0105 cm in diameter. The oven was heated by a Nichrome coil  $B$  wound around a quartz tube  $C$ ; both were enclosed by a silver housing  $D$ . Current for heating the coil was taken from a Solar regulating transformer. The silver-constantan thermocouple  $N$ , used to measure the temperature of the oven, was inserted into a hole bored in a silver plug which was then flattened to hold the couple securely; the plug screwed deep into the cover of the oven. The cold junction  $O$  was kept in a bath of crushed ice and water; the e.m.f. of the couple was measured with a Leeds and Northrup Type K potentiometer  $P$ . The couple was standardized at the freezing point of Bureau of Standards samples of tin, zinc, and aluminum; when it was later checked at a single point, it showed no appreciable deviation from the initial calibration. The beam of escaping salt molecules, defined by the aperture in the collector plate  $H$ , fell on a tungsten filament  $F$ , 0.02 cm in diameter, which had been previously aged for one hour at 2600°K. The filament (13.5–14 cm long) was suspended vertically, using a heavy tungsten spring to keep it taut when heated. The length of the filament exposed to the molecules was approximately 2 cm. Current for heating the filament was supplied by the d.c. line  $K$ . The voltage drop across the filament could be measured by means of platinum potential leads welded to its ends. The diameter of the filament was initially determined by weigh-

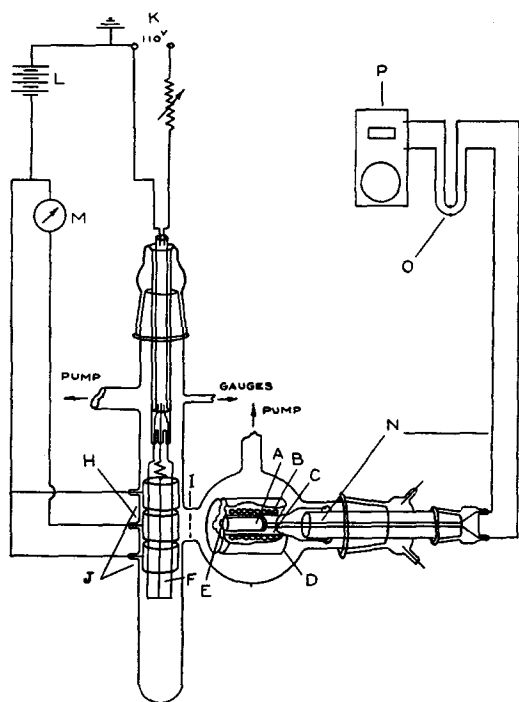


FIG. 1. Schematic diagram of the apparatus.

TABLE I. Values of  $(e\phi - I)$  for  $r = 99$ .

Temperature °K	$(e\phi - I)$ ev
1200	0.547
1400	0.638
1600	0.729
1800	0.820

TABLE II. Ionization potentials of the alkali metals.

Metal	Ionization potential ev
Sodium	5.138
Potassium	4.340
Cesium	3.893

ing a known length of aged wire. The diameter and temperature of the filament during the run were calculated from the tables of Jones and Langmuir.<sup>7</sup> The distance between the hole in the oven and the filament was approximately 10.50 cm. It was redetermined whenever changes were made in the tube elements. The ions leaving the filament were collected by the collector plate  $H$ ; stray ions were collected by the guard ring  $J$ . The plates were attached to the same potential source  $L$  but connection from the collector was through a Leeds and Northrup Type HS galvanometer  $M$  whose sensitivity was  $2.3 \times 10^{-10}$  amp./mm. The beam leaving the oven could be interrupted by a magnetically operated shutter  $I$ .

Thermocouple wires were introduced into the apparatus through capillary tubes sealed with Apiezon wax " $W$ ;" all other wires were introduced by means of tungsten to glass seals. The plates were made of hydrogen fired " $A$ " nickel. Two auxiliary filaments for outgassing were of tungsten. The filament and oven assemblies were introduced into the glass envelope by means of ground glass joints sealed with Apiezon " $W$ ." All stopcocks were greased with Apiezon " $N$ ."

The system was evacuated by two single-stage mercury diffusion pumps in parallel, with mechanical backing. Mercury vapor was eliminated by use of dry ice traps. Residual gas pressure was measured with a Distillation Products VG1A ionization gauge which had been calibrated against a McLeod gauge with liquid nitrogen traps.

<sup>7</sup> H. A. Jones and I. Langmuir, Gen. Elec. Rev. 310 (1937).

TABLE III. Dissociation energies of the alkali halide molecules.

Salt	Dissociation energy ev
NaBr	3.85
NaI	3.16
KI	3.33
CsCl	4.38
CsBr	3.99
CsI	3.32

TABLE IV. Experimental conditions and necessary values of work function to satisfy  $r = 99$ ,  $q = 99$ .

Salt	Filament temp. $T_f$ (°K)	$e\phi$ for $r=99$ at $T_f$ ( $e\phi$ ) <sub><math>r=99</math></sub> ev	Max. value $N_{MX}$ $N \times 10^{-14}$	Log $K$ for $q=99$ at $T_f$	$e\phi$ for $q=99$ at $T_f$ ( $e\phi$ ) <sub><math>q=99</math></sub> ev
NaBr	1400	5.78	0.447	-4.76	5.69
NaI	1250	5.71	4.61	-3.69	5.64
KI	1600	5.07	2.71	-3.78	4.29
CsCl	1800	4.71	2.92	-3.73	4.41
CsBr	1400	4.53	1.07	-4.10	4.83
CsBr	1800	4.71	1.07	-4.05	3.96
CsI	1400	4.53	4.92	-3.48	4.38

#### IV. OPERATING CONDITIONS

##### A. Scattering

The relationship

$$P = [N_0 R^2 \cdot (2\pi m k T)^{1/2} / r^2 A F] i_0 \quad (2)$$

has been derived assuming there is no scattering of the salt beam. If the molecules are moving a distance  $R$  with uniform velocity through a scattering gas, the number  $I$  of beam molecules received per second by a detector will be

$$I = I_0 e^{-R/L},$$

where  $I_0$  is the number of beam molecules received per second by the detector in the absence of scattering gas and  $L$  the mean free path. The calculation of  $L$  will be uncertain because the scattering cross sections are unknown. Therefore, the scattering correction  $I/I_0$  has been evaluated experimentally by measuring the positive ion current as a function of residual gas pressure (at constant oven and filament temperature) and extrapolating to zero pressure. The value of  $i_0$  used in Eq. (2) was calculated from the observed positive ion current  $i$  by applying the scattering correction  $I/I_0$ . The pressure of residual gas was usually kept low enough so that  $I/I_0$  was greater than 0.85. Within the working range, the curves of  $I/I_0$  versus pressure

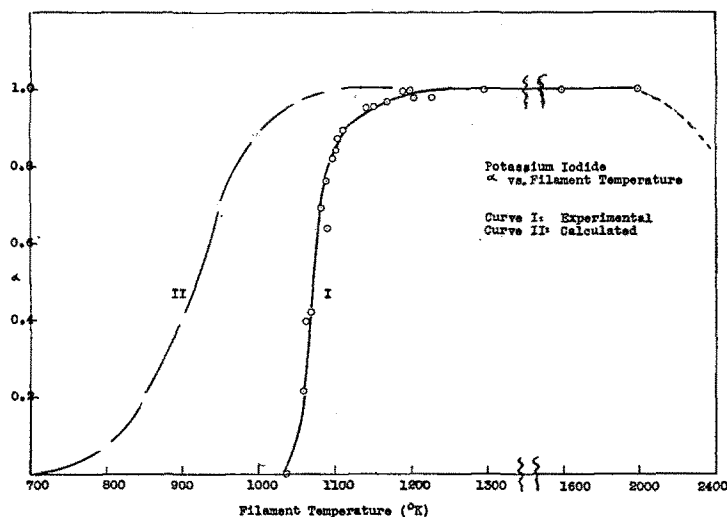
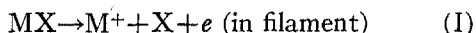


FIG. 2. Ion emission *versus* temperature.

for all the salts studied were within 5 percent of an average curve, and were reproducible within a few percent.

### B. Reaction on the Filament

We will now consider the reaction



which occurs on the surface of the filament to determine whether the assumption of complete conversion of MX molecules to  $\text{M}^+$  ions made in the derivation of Eq. (2) is valid.

#### 1. Equilibrium of Conversion Reaction

The M atoms of the incoming MX molecules may leave the filament as MX molecules, M atoms, and  $\text{M}^+$  ions only. The necessary conditions for complete conversion of MX to  $\text{M}^+$  are that the equilibrium ratios

$$n_{\text{M}^+}/n_{\text{M}} \text{ and } n_{\text{M}^+}/n_{\text{MX}}$$

are both extremely large. The two together are a sufficient condition, assuming no kinetic obstacle to the establishment of equilibrium. These ratios are given by

$$r = n_{\text{M}^+}/n_{\text{M}} = \frac{1}{2} \exp(e\phi - I)/RT, \quad (3)$$

where  $I$  = ionization potential of the atom and  $e\phi$  = work function of the filament surface. This is the Saha-Langmuir equation<sup>8</sup> assuming zero

<sup>8</sup> I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. 107A, 61 (1925).

reflection coefficients for both atoms and ions. From the equilibrium constant of reaction (I) and the principle of conservation of matter one obtains:

$$q = n_{\text{M}^+}/n_{\text{MX}} = [K/n_{\text{M}^+}] [r/(1+r)] \times [(1/2\pi\mu kT)^{1/2}], \quad (4')$$

where  $K$  = equilibrium constant for reaction (I),  $K = \exp[(e\phi - D - I)/RT + (S_{\text{M}^+}^\circ + S_{\text{X}}^\circ + S_{\text{MX}}^\circ)/R - \frac{1}{2}]$ , and  $\mu$  = reduced mass of MX. If the extent of reaction is so great that  $n_{\text{M}^+} \gg n_{\text{MX}}$ , then the number of  $\text{M}^+$  ions leaving a unit area of filament per second,  $n_{\text{M}^+}$ , approximately equals the number of MX molecules striking a unit area of filament per second,  $N_{\text{MX}}$ .

$$q \doteq [K/N_{\text{MX}}] [r/(1+r)] [(1/2\pi\mu kT)^{1/2}]. \quad (4)$$

A necessary and sufficient condition for 99 percent conversion of MX to  $\text{M}^+$  is that both  $r \geq 99$  and  $q \geq 99$ .

Table I lists the quantity  $(e\phi - I)$  which satisfies the relation  $r = 99$  at various temperatures. It can be seen that the work function necessary to ionize 99 percent of the metal atoms increases with increasing temperature.

At a given pressure of salt molecules at the filament, the ratio  $q$  depends on the equilibrium constant for the over-all reaction  $K$ , which is a function of the ionization potential of the metal atom  $I$ , dissociation energy of the salt molecule  $D$ , work function of the filament  $e\phi$ , temperature  $T$ , and the standard state entropy change  $\Delta S^\circ$ . For any molecule  $D$  and  $I$  are fixed and  $\Delta S^\circ$

TABLE V. Experimental data.

Sodium bromide -log $p_{mm}$ (1000/T) (°K)		Sodium iodide -log $p_{mm}$ (1000/T) (°K)	
1.77	1.098	0.49	1.108
1.91	1.114	1.11	1.160
2.05	1.129	1.20	1.169
2.32	1.153	1.49	1.190
2.62	1.179	1.83	1.221
2.67	1.182	2.03	1.244
2.82	1.197	2.13	1.253
2.87	1.201	2.17	1.255
3.15	1.228	2.67	1.300
3.73	1.278	2.75	1.311
3.98	1.301	3.27	1.358
4.20	1.319		

Potassium iodide -log $p_{mm}$ (1000/T) (°K)		Cesium chloride -log $p_{mm}$ (1000/T) (°K)	
0.90	1.114	0.89	1.122
1.24	1.144	1.12	1.141
1.37	1.152	1.16	1.146
1.39	1.153	1.58	1.184
1.46	1.162	1.60	1.185
1.63	1.177	1.73	1.200
1.67	1.179	1.85	1.209
1.69	1.179	2.03	1.223
1.95	1.207	2.37	1.256
1.98	1.209	2.40	1.263
2.00	1.204	2.61	1.281
2.00	1.209	2.71	1.290
2.02	1.205	2.78	1.298
2.29	1.237	2.80	1.305
2.43	1.251	3.01	1.321
2.51	1.260	3.05	1.325
2.56	1.263	3.17	1.336
2.63	1.262	3.33	1.354
2.63	1.264	3.43	1.363
2.93	1.301	3.55	1.379
2.94	1.297	3.58	1.381
2.94	1.302	3.76	1.397
2.95	1.297	3.85	1.406
3.09	1.315	3.88	1.409
3.44	1.344	3.88	1.413
3.51	1.356	4.02	1.421
3.55	1.363	4.14	1.435
3.81	1.383	4.25	1.449
3.84	1.386		

Cesium bromide -log $p_{mm}$ (1000/T) (°K)		Cesium iodide -log $p_{mm}$ (1000/T) (°K)	
0.92	1.111	1.92	1.202
1.00	1.120	1.95	1.210
1.02	1.121	1.95	1.210
1.21	1.141	1.97	1.215
1.21	1.141	2.00	1.209
1.22	1.145	2.00	1.218
1.23	1.145	2.04	1.220
1.24	1.144	2.13	1.230
1.24	1.146	2.23	1.236
1.26	1.144	2.25	1.237
1.26	1.148	2.25	1.239
1.27	1.153	2.37	1.243
1.31	1.150	2.38	1.254
1.38	1.158	2.39	1.255
1.39	1.161	2.42	1.266
1.40	1.159	2.48	1.255
1.40	1.159	2.50	1.261
1.44	1.162	2.55	1.271
1.44	1.165	2.66	1.277
1.47	1.164	2.69	1.277
1.49	1.166	2.69	1.281
1.49	1.168	2.70	1.281
1.49	1.170	2.84	1.291

TABLE V.—Continued.

Cesium iodide -log $p_{mm}$ (1000/T) (°K)		Cesium iodide -log $p_{mm}$ (1000/T) (°K)	
1.50	1.172	2.85	1.295
1.53	1.173	2.85	1.297
1.59	1.179	2.85	1.307
1.61	1.177	2.87	1.296
1.63	1.179	2.97	1.305
1.65	1.183	3.01	1.306
1.66	1.182	3.04	1.323
1.71	1.186	3.07	1.321
1.78	1.197	3.07	1.323
1.88	1.203	3.08	1.323
1.88	1.209	3.13	1.320
1.89	1.206	3.24	1.339
		3.41	1.353
0.59	1.118	2.07	1.253
0.62	1.120	2.07	1.254
0.70	1.128	2.27	1.265
0.71	1.127	2.32	1.273
0.96	1.147	2.58	1.305
0.99	1.151	2.63	1.310
1.32	1.182	2.73	1.315
1.35	1.179	2.85	1.327
1.50	1.198	3.12	1.353
1.53	1.195	3.26	1.371
1.70	1.214	3.54	1.398
1.85	1.234	3.68	1.418
2.07	1.245	3.85	1.437

varies slowly with temperature;  $K$  will therefore vary with  $T$  and  $e\phi$ . If it were possible to increase the work function of the surface without limit, the equilibrium constant at any temperature would be sufficiently large to satisfy the condition  $q=99$ . The actual existence of an upper limit to the work function means that there will be a minimum filament temperature below which the conversion of  $MX$  to  $M^+$  will be incomplete.

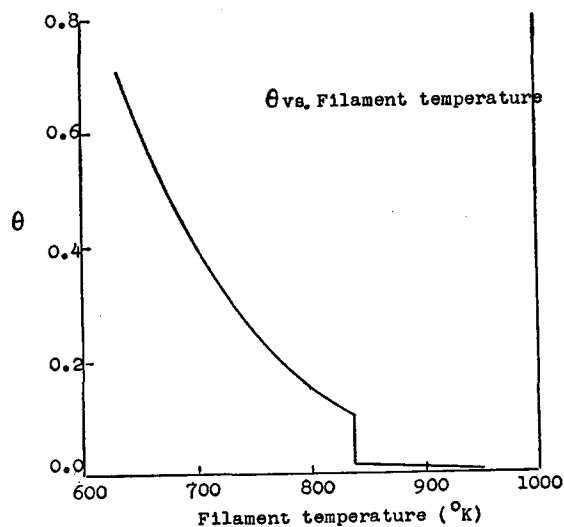


FIG. 3. Adsorption of cesium on tungsten (de Boer).

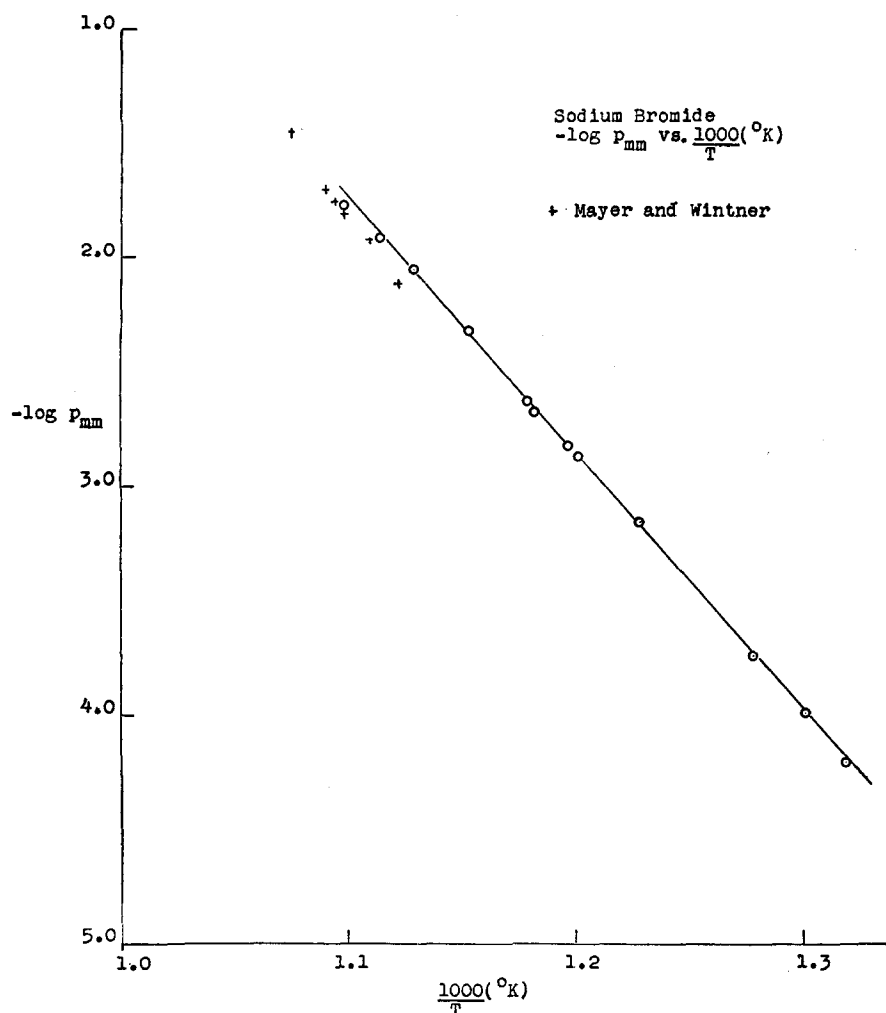


FIG. 4. Vapor pressure versus  $1000/T^{\circ}K$  (NaBr).

Ionization potentials listed in Table II are taken from Herzberg.<sup>9</sup> Dissociation energies tabulated in Table III are from Herzberg<sup>10</sup> or Mayer and Helmholtz.<sup>11</sup>

The experimental filament temperatures for each salt are given in Table IV. Column 3 of this table lists  $(e\phi)_{r=99}$ , the work function necessary for 99 percent ionization at  $T_f$ ; in column 6 are tabulated  $(e\phi)_{q=99}$ , the minimum work function satisfying the relation  $q=99$  at  $T_f$  and the highest pressure of incoming MX molecules. The larger of these two determines the lowest work function sufficient for 99 percent conversion.

Under experimental conditions it was possible to maintain a work function of about six volts, which is higher than any of the required work functions. Thus, equilibrium favors conversion of every molecule which hits the filament into the appropriate ion.

## 2. Kinetics of the Conversion Reaction

The following assumptions are made:

a. The rate of reaction is so fast that the reaction goes virtually to completion. There are three possibilities:

- (i) The rate is very slow; no conversion.
- (ii) There is partial conversion.
- (iii) The reaction is very rapid; complete conversion.

<sup>9</sup> G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944).

<sup>10</sup> G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

<sup>11</sup> J. E. Mayer and L. Helmholtz, *Zeits. f. Physik* **75**, 19 (1932).

The existence of a positive ion current eliminates the first possibility. If the conversion were incomplete, in all probability it would have a temperature coefficient. Only a reaction which had gone virtually to completion would not, since a change from 99.0 to 99.9 percent conversion is a tenfold change without change in result. A plot of the experimental ion current divided by the maximum ion current *versus* filament temperature for KI is shown in curve I of Fig. 2. The existence of a plateau indicates that the reaction is actually very fast in this temperature interval.

b. The rate of removal of products is rapid enough to prevent accumulation of metal ions on the surface, with consequent reduction of the work function. When the equilibrium requires

incomplete conversion, one may calculate the number of metal ions formed at any given temperature and work function (i.e., for any value of  $K$  and  $r$ ) for any value of the pressure of incoming molecules. One arrives at an expression for  $n_{M^+}$ :

$$(n_{M^+})^2 + [K/(2\pi\mu kT)^{1/2}]n_{M^+} - [KN_{MX}/(2\pi\mu kT)^{1/2}][r/(1+r)] = 0. \quad (5)$$

Thus  $\alpha = n_{M^+}/N_{MX}$ , the fraction of MX molecules which are converted to  $M^+$  ions under these conditions, may be calculated.  $\alpha$  for KI has been evaluated as a function of temperature, assuming a constant work function  $e\phi = 5.15$  volts, the work function required for  $r > 99$  at  $1800^\circ\text{K}$ . The oxygen coating strips at high temperatures, lowering the work function. Under the conditions of these experiments, stripping

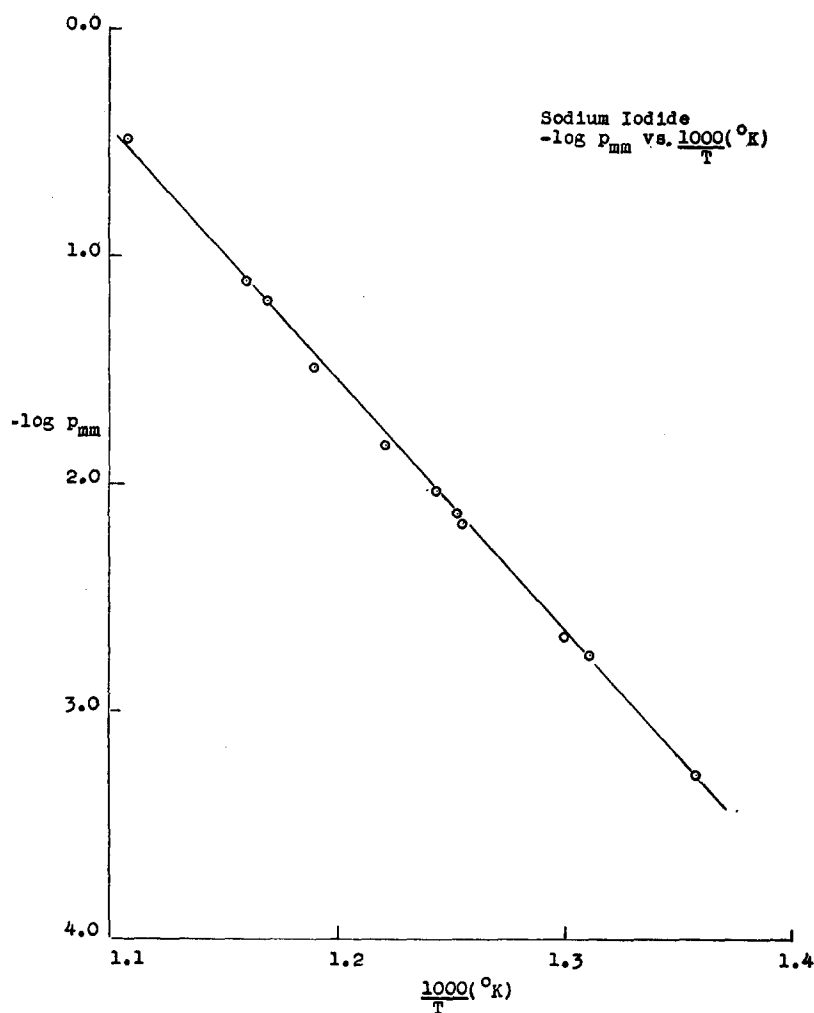


FIG. 5. Vapor pressure *versus*  $1000/T^{\circ}\text{K}$  (NaI).



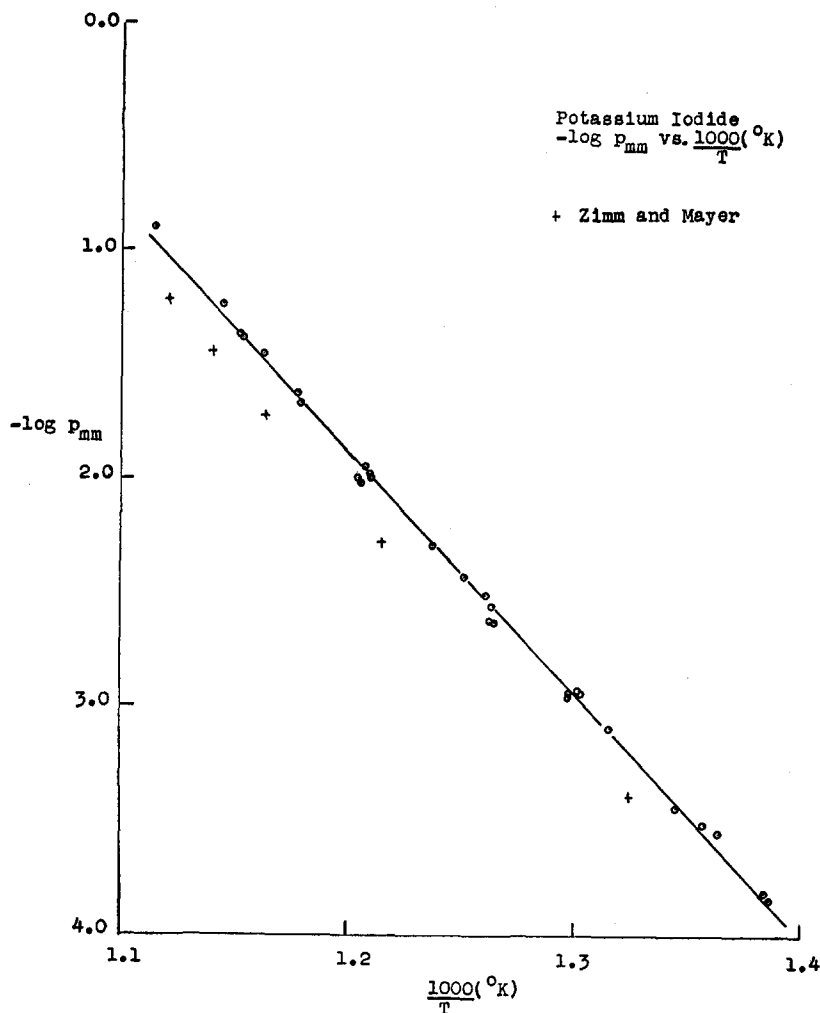


FIG. 6. Vapor pressure versus  $1000/T^{\circ}\text{K}$  (KI).

did not occur under  $2000^{\circ}\text{K}$ . The results of this calculation are plotted in curve II of Fig. 2.

A comparison of the experimental curve I and the theoretical curve II in Fig. 2 shows that in the case of KI the shift in the equilibrium does not account for the sharp drop in ion current at low filament temperatures. This phenomenon is probably due to the fact that desorption of metal ions is slow at low temperatures. Since the adsorption energy for metal ions on an oxidized tungsten filament is probably very large, the layer of metal ions will disappear in a very small temperature range above some critical temperature, and the work function of the filament will increase abruptly. This is illustrated by Fig. 3 taken from de Boer<sup>12</sup> which shows the

variation of  $\theta$ , the fraction of tungsten surface covered by adsorbed cesium, with increasing filament temperature, when the cesium is desorbed as ions. According to Taylor and Langmuir,<sup>6</sup> with a given pressure of cesium and with a sufficiently strong accelerating field for ions to overcome space charge there is a critical temperature  $T_c$ , above which every cesium atom that strikes the filament escapes as an ion; below  $T_c$ , ion emission is very small. The plateau in curve I of Fig. 2 implies a high enough work function and a rapid removal of metal ions in this temperature range.

Therefore it is possible to choose the experimental filament conditions so that the assumption of complete conversion of  $\text{MX}$  to  $\text{M}^+$  on the filament is valid. In these experiments, precautions were taken to have sufficient oxygen

<sup>12</sup> J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, Teddington, 1935).

present (using a capillary leak when necessary) to coat the filament and increase its work function. For each salt, the positive ion current at some constant oven temperature was measured as a function of filament temperature, and the vapor pressure measurements were made in the temperature range of the plateau.

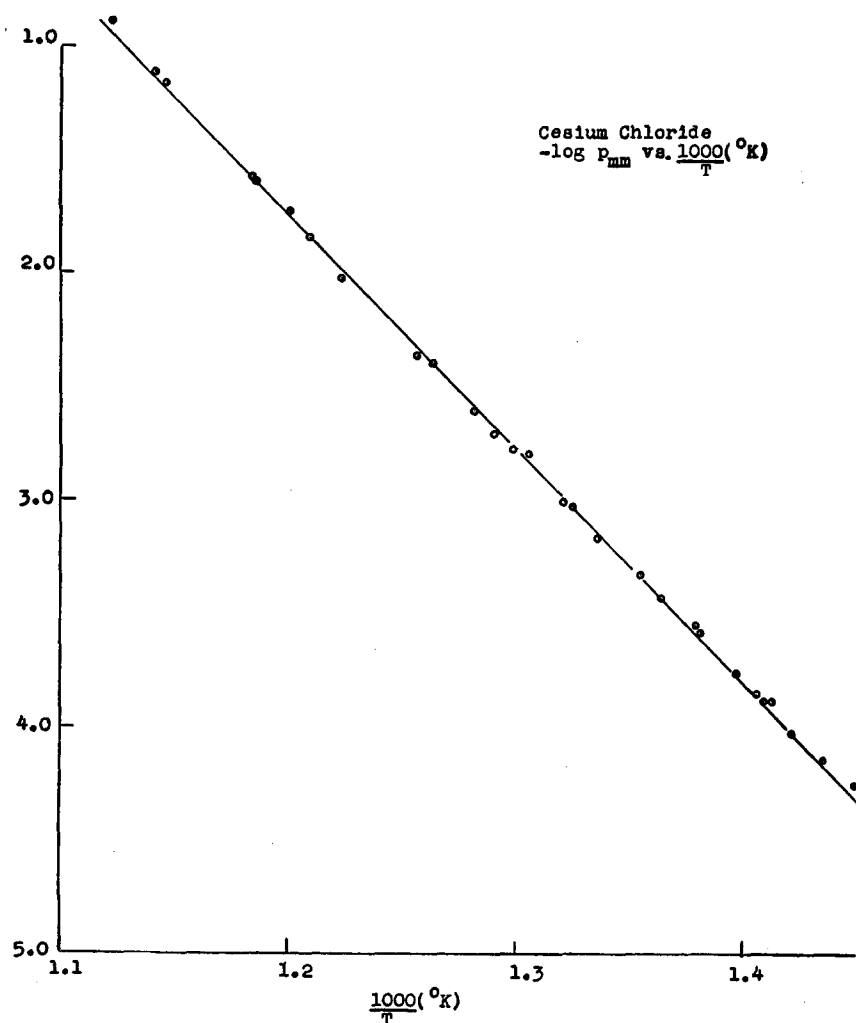
c. In order to measure the positive ion current, a potential of  $-45$  to  $-67.5$  volts was put on the plates to overcome ion space charge. To eliminate the effects of stray currents, the galvanometer deflection was first measured with the shutter closed, and the additional deflection when the shutter was opened was assumed to be due entirely to the positive ions. The deflections with closed shutter rarely exceeded ten percent of the ion deflection.

## V. MATERIALS

The sodium and potassium salts were prepared by recrystallizing C.P. grade salts from distilled water and drying them in a vacuum oven. The cesium salts were prepared by adding a small excess of the appropriate redistilled C.P. acid to C.P. cesium carbonate (Maywood Chemical Works) which had been recrystallized from absolute alcohol, precipitating the salt, and drying it in a vacuum oven.

The presence of a highly volatile impurity in the salt would give a very high apparent vapor pressure, but its concentration would change during the course of the run, and the resulting pressure would drift with time. The results of measurements on the same sample made on different days agreed with each other within the

FIG. 7. Vapor pressure *versus*  $1000/T^{\circ}\text{K}$  ( $\text{CsCl}$ ).



experimental error, and low temperature data could be repeated after keeping the sample at high temperatures for several hours.

#### VI. PRIMARY RESULTS

The experimental data are tabulated in Table V and plotted in Figs. 4 and 9. The data are well fitted by the equation:

$$\log p_{mm} = C - A(1000/T) + 5/2 \log(1000/T). \quad (6)$$

The term  $5/2 \log(1000/T)$  arises from an estimate of the difference of heat capacities between the gas and crystal. The exact value of the  $\Delta C_p$  term is unimportant, since it represents only a small correction term. An average value of  $\Delta C_p = -5/2R$  for the temperature range 500°K to 1000°K has been used.

The constants in Eq. (6) have been evaluated

by the method of least squares and are tabulated in Table VI. The curves in Figs. 4 to 9 have been drawn using the constants in Eq. (6).

#### VII. SOURCES OF ERROR

The sources of error in  $p$  are:

- A. Geometry:  $\pm 2.9$  percent; distance from hole to filament:  $R \pm 0.5$  percent; radius of hole:  $r \pm 1.1$  percent; length of filament:  $1 \pm 1.0$  percent; diameter of filament:  $d \pm 1.5$  percent.
- B. Ion current:  $\pm 2.8$  percent; measurement of galvanometer deflection:  $\pm 2$  percent; incomplete reaction:  $\pm 0.3$  percent; scattering correction:  $\pm 2$  percent.
- C. Temperature:  $\pm 0.2$  percent; maximum error:  $\pm 2$  percent; probable error:  $\pm 0.2$  percent.

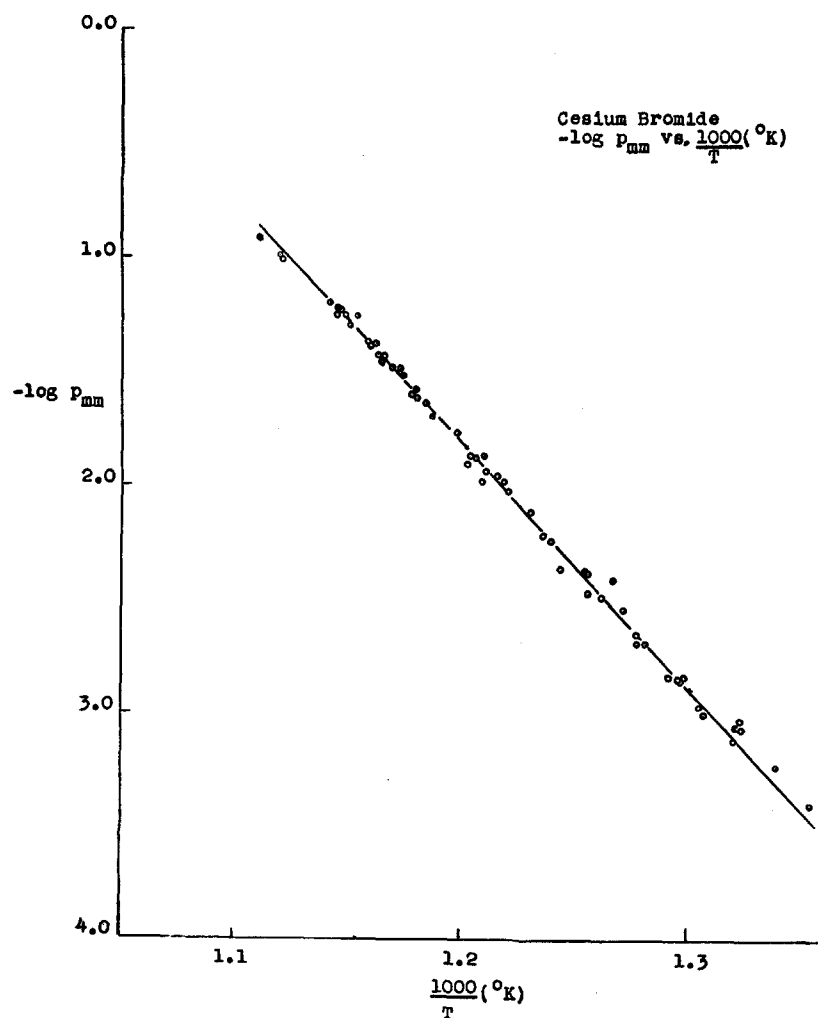


FIG. 8. Vapor pressure *versus*  $1000/T^{\circ}\text{K}$  (CsBr).

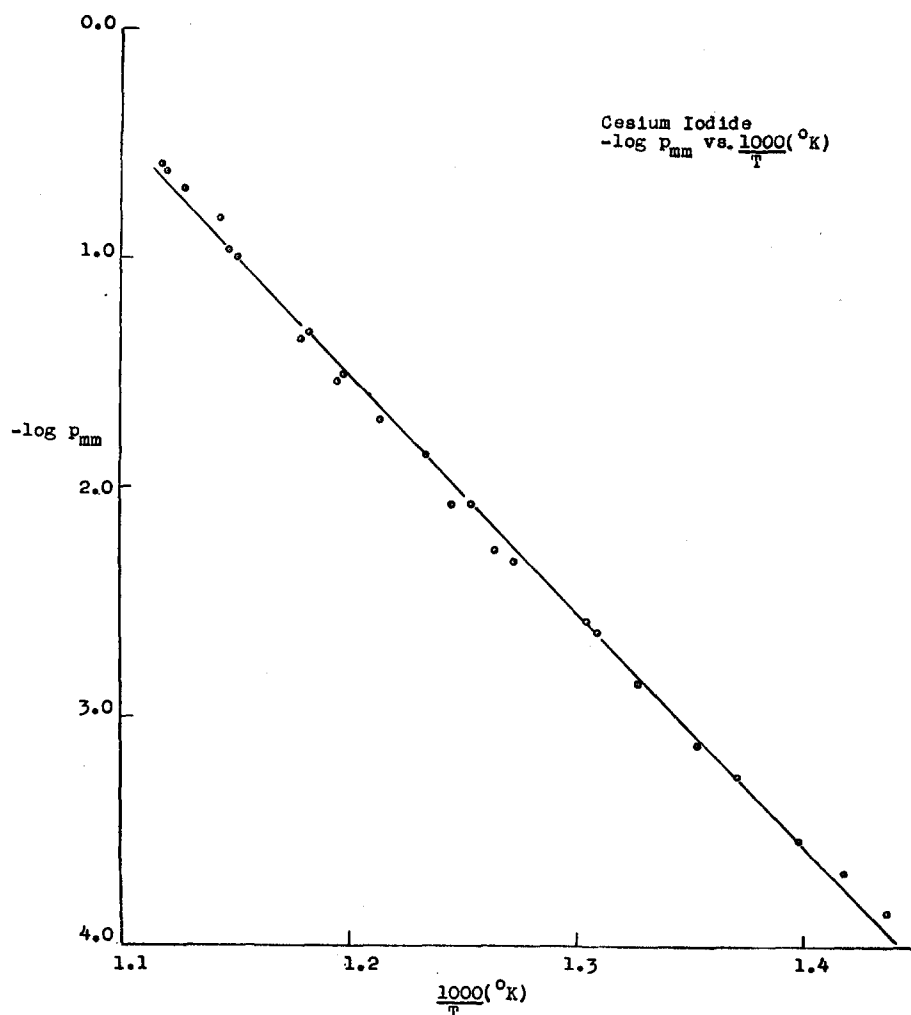


FIG. 9. Vapor pressure versus  $1000/T^{\circ}\text{K}$  (CsI).

The probable error in  $p$  is  $\pm 4.0$  percent. Therefore, the probable error in  $\ln p$  is  $\pm 0.040$ .

### VIII. DISCUSSION OF RESULTS

Cesium chloride exists in two crystalline modifications. The low temperature form is a body-centered lattice; at  $733^{\circ}\text{K}$  x-ray data<sup>13,14</sup> show a transition to a face-centered lattice. It is expected that the energy difference between these two cubic forms is small. From x-ray measurements, the heat of transition  $\Delta H_t$  is estimated as 1.8 kcal.<sup>13</sup> Thermal data give a  $\Delta H_t$  value of 1.34 kcal.<sup>15</sup> There is no observable break in the vapor pressure curve of cesium chloride (see Fig. 7).

<sup>13</sup> G. Wagner and L. Lippert, Zeits. f. physik. Chemie **B31**, 263 (1936).

<sup>14</sup> C. D. West, Zeits. f. Krist. **88**, 94 (1934).

<sup>15</sup> International Critical Tables 5, 207.

The probable error in the slope of the line including only those points below the transition temperature is 3.1 percent. The accuracy of these measurements would only be sufficient to say that the heat of transition probably does not exceed 3.1 percent of  $\Delta H_{\text{vap}}$  or 1.5 kcal.

Additional data on the vapor pressure of cesium bromide which have not been used in

TABLE VI. Constants to be used in Eq. (6).

Salt	A	Standard deviation of A	C
NaBr	12.003	0.083	11.347
NaI	11.895	0.14	12.525
KI	11.455	0.097	11.660
CsCl	11.076	0.062	11.346
CsBr	11.421	0.079	11.676
CsI	11.193	0.066	11.726

TABLE VII. Heat content in kcal./mole.

Salt	$\Delta H_{800}$	$H_{\text{gas}}$ $T=800$	$\omega^{\text{th}}$ wave no.	$H_{\text{crystal}}$ $T=800$	$\Delta H_0$
NaBr	$50.93 \pm 0.35$	6.79	133.9	9.38	53.52
NaI	$50.43 \pm 0.91$	6.83	117.0	9.65	53.25
KI	$48.42 \pm 0.46$	6.92	98.0	9.65	51.15
CsCl	$46.69 \pm 0.26$	6.90	98.0	9.76	49.55
CsBr	$48.26 \pm 0.33$	6.97	74.6	10.21	51.50
CsI	$47.23 \pm 0.28$	7.01	(61)*	9.82	50.04

\* Estimated.

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

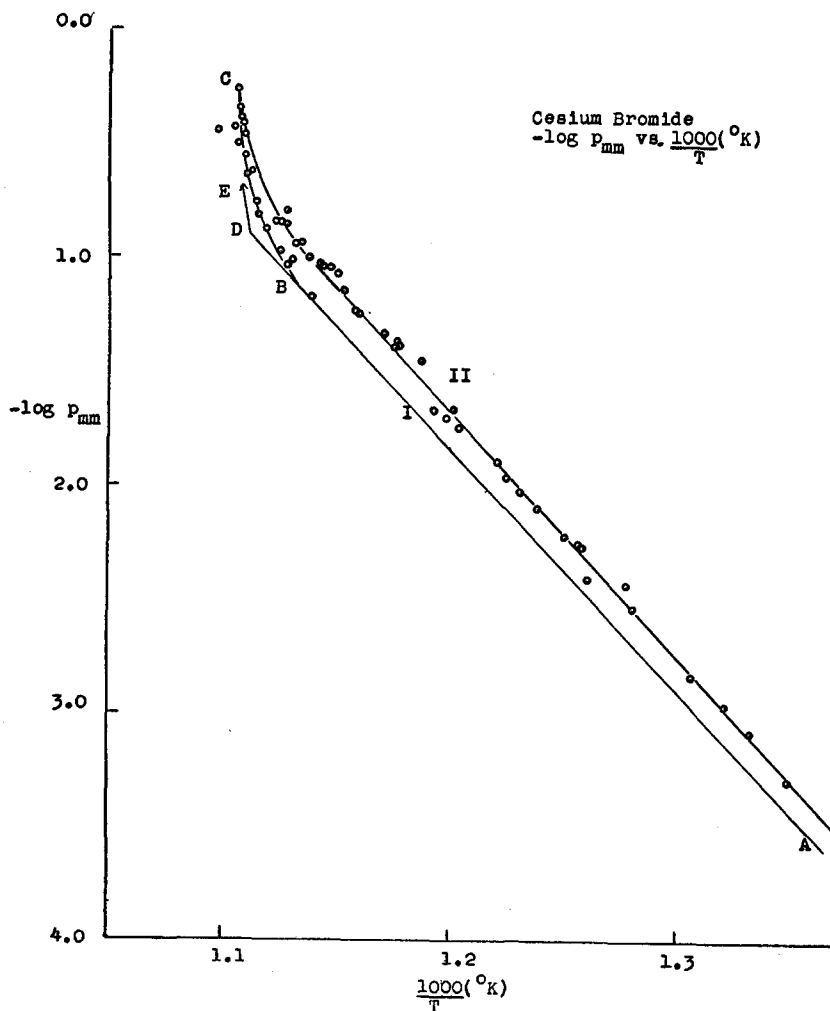
the evaluation of the constants in Eq. (6) are plotted in Fig. 10. These peculiar results are not explainable. Two ovens were used in these measurements (Oven I with a hole diameter of approximately 0.1 cm and Oven II with a hole diameter of approximately 0.01 cm) and the data were taken at two filament temperatures

TABLE VIII. Entropies in cal./degree.

Salt	$S_{\text{gas}}^0$ $T=800$	$-\ln p_{\text{mm}}$ $T=800$	$S_{\text{gas}}$ $T=800$	$\Delta S_{800}$	$S_{\text{crystal}}$ $T=800$
NaBr	79.60	7.86	95.21	63.66	31.55
NaI	81.33	4.84	90.94	63.04	27.90
KI	83.55	5.57	94.60	60.53	34.07
CsCl	83.17	5.20	93.50	58.36	35.14
CsBr	85.71	5.43	96.49	60.35	36.14
CsI	87.53	4.65	96.81	59.04	37.77

(1400°K and 1800°K) using many different samples of salt.

The portion of curve I labeled *AB* corresponds to Fig. 8 and was obtained in both ovens with fresh samples which had never been heated above  $T_c$  (approximately 875°K). The material looked powdered before and after heating. *BC* shows the rapid rise in vapor pressure when the

FIG. 10. Vapor pressure versus  $1000/T^{\circ}\text{K}$  (CsBr).

salt was heated above  $T_c$  in Oven I. The data then fall on curve II when the salt is cooled and remain on curve II throughout all subsequent heating and cooling. This material now appears sintered, but there is no indication that the sample had melted ( $T_{m.p.} = 909.2^\circ\text{K}$ ). No difference in structure was found from x-ray powder pictures of the original powdered salt, crushed sintered material, and small (but uncrushed) fragments of sintered material. Previous x-ray investigators had looked for a transition in cesium bromide but had never found one.<sup>13,14</sup> Microchemical analysis showed these materials to be the same within the error of the determination (original sample: 37.55 percent Br; sintered material: 37.98 percent Br). *BD* was obtained when fresh samples were heated above  $T_c$  in Oven II and is a continuation of *AB*. This material was still powdered after heating. *DE* shows the extremely rapid rise at  $900^\circ\text{K}$  (an increase in pressure from 0.1 to 7 mm in  $2.5^\circ$ ) when the sample was heated in Oven II. On cooling the data could be represented by curve II and the material was sintered. There is no evidence that the salt, which leaves the oven at a very great rate in the region of anomalous pressures, has condensed on the outer surface of the oven or radiation shields.

The data of Mayer and Wintner for sodium bromide are plotted in Fig. 4. In Fig. 6 the results of Mayer and Zimm for potassium iodide are given. Their entropy of vaporization agrees with ours to 0.5 percent, but the vapor pressures obtained in these measurements are 1.55 times those of Zimm and Mayer. Results of measurements on two samples of potassium iodide, one prepared in this laboratory and the other in the phosphor research laboratory at the Polytechnic Institute of Brooklyn, were the same within experimental error.

TABLE IX. Entropies in cal./degree.

Salt	$S_{\text{crystal}}(T=800)$ $-S_{\text{crystal}}(T=298)$	$S_{\text{crystal}}$ $T=298$	$S_{\text{gas}}^\circ$ $T=298$
NaBr	12.76	18.79	70.85
NaI	13.15	14.74	72.61
KI	12.92	21.15	74.80
CsCl	13.10	22.04	74.35
CsBr	13.73	22.41	76.87
CsI	12.80	24.97	78.72

## IX. DERIVED RESULTS

The measurements of this research permit the calculation of  $\Delta F_T^\circ$  for the vaporization of the salt (from the vapor pressure at any one temperature) and the  $\Delta H_T$  of vaporization from the relation:

$$d \ln p / d(1/T) = -\Delta H_T / R.$$

From these one may calculate the entropy difference between vapor and crystal. The heats of vaporization at  $800^\circ\text{K}$  are listed in Table VII; the entropies of vaporization at  $800^\circ\text{K}$  are given in Table VIII.

The entropies of the crystal and gas may be calculated from statistical equations<sup>16</sup> but with uncertain accuracy. The equilibrium internuclear distance in the gaseous molecule is known in all cases.<sup>17</sup> Since the frequencies of the gaseous molecule are known in some cases,<sup>6</sup> and a reasonably good estimate of the frequencies has been made in others,<sup>18</sup> the accuracy with which the vapor entropies may be obtained is good. The calculation of the crystal entropies, however, is more uncertain. In order to get good agreement between crystal entropies obtained from heat capacity data and those calculated using the Debye function, it is necessary to use the *reststrahlen* frequency to determine the parameter  $\theta_D$ . This is theoretically unsound. The use of this as an empirical relationship is limited because few of these reflection frequencies are known. The Nernst-Lindemann equation has a sounder theoretical basis, but does not give as good agreement with experiment. Therefore, the entropy of the crystal was obtained by using the experimental entropy difference between the gas and crystal and the calculated vapor entropy. The values of the entropies of the gas and crystal at  $800^\circ\text{K}$  are tabulated in Table VIII. Because heat capacity data are lacking above room temperature for most of these crystals, extrapolation of the crystal entropy from  $800^\circ\text{K}$  to  $298^\circ\text{K}$  has been made, using the heat capacity equations estimated by Kelley.<sup>19</sup> In the case of sodium bromide, a long extrapolation of the

<sup>16</sup> J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940).

<sup>17</sup> E. J. W. Verwey and J. H. Boer, *Rec. trav. chim.* **59**, 633 (1940).

<sup>18</sup> W. Gordy, *J. Chem. Phys.* **14**, 305 (1946).

<sup>19</sup> K. K. Kelley, *U. S. Bur. Mines Bull.*, 371 (1934).

TABLE A1. Quantities used in calculating gaseous entropies:  $I_e = \mu r_0^2$ ,  $B_e = h/8\pi^2 I_e c$ ,  $\omega^* = \omega_e - 2\omega_e x_e$ ,  $B_0 = B_e - (\alpha/2)$ ,  $\alpha/2 = 3(B_e^2/\omega_e)((\omega_e x_e/B_e)^{1/2} - 1)$ .

Salt	Reduced mass $\mu$ grams $\times 10^{23}$	Frequency $\omega_e$ $\text{cm}^{-1}$	Anharmonic correction $\omega_e x_e$	Inter-atomic <sup>a</sup> distance $r_{1800}$ $\text{cm} \times 10^8$	Equilibrium <sup>b</sup> distance $r_0$ $\text{cm} \times 10^8$	Moment of inertia $I_e$ $\times 10^{28}$	$B_e \times 10^2$	$uT = hc\omega^*/k$	$\sigma T = B_0 hc/k$	$\gamma = B_e/\omega_e$ $\gamma \times 10^4$
Sodium bromide	2.965	315 <sup>b</sup>	1.15 <sup>b</sup>	2.64	2.59	1.989	14.07	450.4	0.2019	4.47
Sodium iodide	3.232	286 <sup>b</sup>	0.75 <sup>b</sup>	2.90	2.84	2.607	10.74	409.4	0.1543	3.76
Potassium iodide	4.962	212 <sup>b</sup>	0.7 <sup>b</sup>	3.23	3.16	4.955	5.649	302.9	0.08110	2.66
Cesium chloride	4.643	226 <sup>c</sup>	(0.7)*	3.06	3.00	4.179	6.698	323.8	0.09620	2.96
Cesium bromide	8.278	168 <sup>c</sup>	(0.5)*	3.14	3.07	7.802	3.588	240.3	0.05154	2.13
Cesium iodide	10.77	137 <sup>c</sup>	(0.4)*	3.41	3.33	11.94	2.344	195.7	0.03367	1.71

\* Estimated.

<sup>a</sup> L. R. Maxwell, S. B. Hendricks, and V. M. Mosley, Phys. Rev. **52**, 968 (1937).

<sup>b</sup> See reference 10.

<sup>c</sup> See reference 18.

TABLE A2.  $S_k^\circ$  = translational entropy at 1 mm pressure,  $S_v^\circ$  = vibrational entropy,  $S_r^\circ$  = rotational entropy,  $S_c^\circ$  = correction to the entropy due to anharmonicity and stretching.

Salt	$T = 800^\circ\text{K}$				
	$S_k^\circ/R$	$S_v^\circ/R$	$S_r^\circ/R$	$S_c^\circ/R$	$S^\circ/R$
NaBr	29.144	1.588	9.286	0.058	40.076
NaI	29.698	1.681	9.556	0.019	40.954
KI	29.860	1.977	10.198	0.032	42.067
CsCl	29.881	1.912	10.028	0.060	41.881
CsBr	30.233	2.207	10.652	0.067	43.159
CsI	30.533	2.410	11.077	0.079	44.099

Salt	$T = 298^\circ\text{K}$				
	$S_k^\circ/R$	$S_v^\circ/R$	$S_r^\circ/R$	$S_c^\circ/R$	$S^\circ/R$
NaBr	26.673	0.688	8.298	0.015	35.674
NaI	27.234	0.757	8.568	0.003	36.562
KI	27.397	1.019	9.256	0.010	37.662
CsCl	27.403	0.964	9.040	0.029	37.436
CsBr	27.760	1.242	9.664	0.040	38.706
CsI	28.059	1.439	10.090	0.048	39.636

experimental heat capacity equation was necessary. The entropy of the crystal and the calculated entropy of the gas at 298°K are given in Table IX.

Because sufficient heat capacity data are unavailable, it was necessary to calculate the heat content of the crystal. The heat content of the crystal at  $T = 298$  was calculated in the following way:

$$H_T - H_0 = \int_0^T C_v dT + \frac{2}{5} a T^{5/2},$$

where the last term arises from the Lindemann-

Magnus approximation for  $C_p - C_v$ . The Nernst-Lindemann heat capacity equation was used to evaluate  $C_v$ :

$$C_v = (3nR/2)f_E(\theta_E/T) + (3nR/2)f_E(\theta_E/2T),$$

where  $f_E$  = Einstein function,  $\theta_E = h\nu_0/k$ ,  $\nu_0$  = optical absorption frequency, and  $n$  = number of atoms per molecule of crystal.  $\Delta H$  for the interval  $T = 298$  to  $T = 800$  was evaluated using the heat capacity equations of Kelley. The values of  $H_c = H_T - H_0$  are tabulated in Table VII. The difference between the heat content of the crystal and the gas at 800°K added to the experimental heat of vaporization at 800°K gives  $\Delta H_0$ , the heat of vaporization at absolute zero. These results are given in Table VII.

## X. ACKNOWLEDGMENT

The authors wish to thank Dr. Joseph E. Mayer for suggesting the problem and for many helpful discussions.

## APPENDIX

The entropy of the gaseous alkali halide molecules at 298°K and 800°K have been evaluated by the usual statistical mechanical equations.<sup>16</sup> The quantities used in these calculations are listed in Table A.1. In Table A.2 are given the various contributions to the entropy and the total standard state entropy (pressure 1mm).