Vapor Pressures, Heats of Vaporization, and Entropies of Some Alkali Halides

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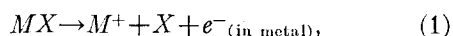*Department of Chemistry, Columbia University, New York, New York*

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Vapor pressures of crystalline KCl, KBr, KI, and NaCl have been measured in the pressure range of 10^{-1} to 10^{-7} mm by a surface ionization method. Heats and entropies of vaporization are calculated from the data. The heats of vaporization at $0°K$ and entropies at $298°K$ are also calculated. From the data, saturated KCl vapor is shown to be less than 2 percent associated at $800°K$ and the heat of dissociation of $(KCl)_2$ is shown to be less than 47 kcal.

INTRODUCTION

THE purpose of these experiments was to measure the vapor pressures of some alkali halides over their crystals, and to calculate heats of vaporization from the data. Previous experimenters,[1-6] with two exceptions,[7, 8] have only measured the vapor pressure of the molten salt. To measure accurately the extremely low pressures at the high temperatures involved, a combination of Knudsen's effusion method[9] with Langmuir's positive ion method[10] was employed.

Salt molecules escaping into a vacuum from a small hole in an oven at known temperature were allowed to fall on an incandescent tungsten filament whose surface was covered with a layer of adsorbed oxygen to increase the work function. Complete dissociation of the salt and ionization of the alkali metal took place at the surface of the filament, according to the equation

$$MX \rightarrow M^+ + X + e^-_{\text{(in metal)}}, \qquad (1)$$

and the escaping metal ions were then collected and their number measured electrically. Use of the well-known formula for the number of gas molecules striking a surface allowed calculation of the salt vapor pressure in the oven.

APPARATUS

The apparatus is shown in Fig. 1. Salt crystals placed in the oven A were heated by coils of Nichrome wire B wound on the quartz tube C. The whole was enclosed by a silver housing D. The oven A was a 4×1.5 cm polished silver tube and cover of 0.1-cm wall thickness. Salt vapor escaped from the oven through the hole E, of 0.165-cm diameter, which was finished with knife-sharp edges, and fell on the 0.02-cm tungsten filament F. Stray molecules were eliminated and the beam defined by apertures in the radiation shield G and collector ring H. The beam could be interrupted by a magnetically operated shutter at I. The ions leaving a known length (2.2 cm) of filament were collected by H; the remainder were collected by the guard rings J.

Current for heating the filament was supplied by storage batteries K. The voltage drop in the filament could be measured by means of potential leads soldered to its ends. The temperature of the filament was calculated from the tables of Langmuir and Jones.[11]

Current for heating the oven could be taken from a vacuum-tube voltage stabilizer[12] when desired. In this way the oven temperature could be held constant within 0.5°C for several hours.

The collector and guard rings were attached to

[1] H. von Wartenburg and Ph. Albrecht, Zeits. f. Electrochemie **27**, 162 (1921).
[2] H. von Wartenburg and H. Schultz, Zeits. f. Electrochemie **27**, 568 (1921).
[3] O. Ruff and S. Mugdan, Zeits. f. anorg. allgem. Chemie **117**, 161 (1921).
[4] E. F. Fiock and W. H. Rodebush, J. Am. Chem. Soc. **48**, 2522 (1926).
[5] S. Horiba and H. Baba, Bull. Chem. Soc. Japan **3**, 11 (1928).
[6] C. G. Maier, Tech. Paper 360, U. S. Bur. Mines, Washington (1925).
[7] V. Deitz, J. Chem. Phys. **4**, 575 (1936).
[8] J. E. Mayer and I. H. Wintner, J. Chem. Phys. **6**, 301 (1938).
[9] M. Knudsen, Ann. d. Physik **47**, 697 (1915).
[10] I. Langmuir and J. B. Taylor, Phys. Rev. **51**, 753 (1937).

[11] I. Langmuir and H. A. Jones, Gen. Elec. Rev., pp. 310–319 (June, 1927).
[12] H. K. Hughes and R. J. Hurka, Rev. Sci. Inst. **6**, 289 (1935).

the same potential source L, but the connection from the collector ring was through the galvanometer M (of 1.6×10^{-10} amp./div. sensitivity). The galvanometer was recalibrated after each run.

The temperature of the oven was measured with a silver-constantan thermocouple N. This thermocouple was frequently compared with a platinum-rhodium couple which had been standardized at the freezing points of Bureau of Standards samples of tin, zinc, and aluminum. No significant variation in the characteristics of the silver-constantan couple was found throughout its use. The hot junction of the couple was welded to a silver plug screwed into the end of the oven. The cold junction O was kept in a bath of crushed ice and water, and the e.m.f. was measured with a Leeds and Northrup type K potentiometer P. The leads were led through the wall of the apparatus by capillary tubes sealed with "Picein" cement.

All other leads were introduced by tungsten to glass seals. Metal parts other than those specifically described were made of nickel. Outgassing of the collector and guard rings was accomplished by heating a few coils of Nichrome wire (not shown in the figure) on the filament assemblage

FIG. 1.

to incandescence. Since the rings did not make contact with the glass envelope except through their leads, they could be readily heated by radiation.

The filament and oven assemblies were introduced into the glass envelope by means of ground glass joints and sealed with Apiezon "L" grease.

The system was evacuated by a single-stage mercury diffusion pump with mechanical backing. Residual gas pressure was measured by McLeod and improved ionization[13] gauges. Pumping speed was approximately 1.5 liters per second, and the limiting vacuum (after a few days' evacuation) with filament and oven hot was of the order of 5×10^{-7} mm. Mercury vapor was eliminated by means of cold traps. Liquid air could also be placed in the well at Q to remove condensible material from the filament chamber.

PROCEDURE

The procedure was as follows. C.P. salt was recrystallized twice and dried by heating to about 400°C in air. Meanwhile the apparatus was evacuated and outgassed. When the outgassing was complete, the apparatus was opened, about a gram of salt placed in the oven, and the apparatus evacuated again as quickly as possible. The oven temperature was raised to the desired point and kept there until the pressure of the residual gases dropped below 5×10^{-5} mm.

The electron emission and temperature of the filament were then measured to make sure that the work function of the surface was well above the ionization potential of the metal of the salt being investigated. If it was not, a small amount of air (approx. 10^{-4} mm) was introduced by means of a capillary and the filament heated to 1400°K to coat it with a layer of oxygen. Usually there was enough oxygen in the residual gases to keep the work function high.

Sufficient potential was put on the collector and guard rings to overcome space charge. The galvanometer was set at zero with the filament lit but with the shutter I closed in order to eliminate small stray currents. When the shutter was opened the resulting galvanometer deflection was assumed to be due entirely to alkali ions from the salt molecules.

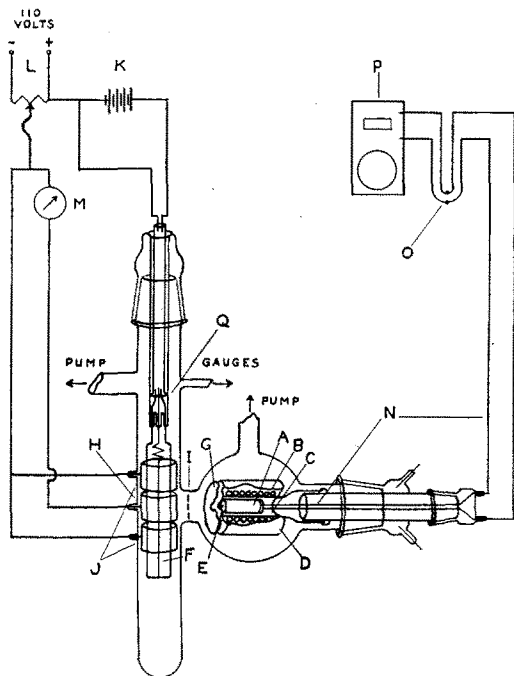[13] R. S. Morse and R. M. Bowie, Rev. Sci. Inst. 11, 91 (1940).

The vapor pressure was calculated from the equation

$$P = (N_0 \cdot R^2 (2\pi mkT)^{\frac{1}{2}}/r^2 \cdot A \cdot F)i, \quad (2)$$

where P is the pressure, N_0 Avogadro's number, R the distance from the filament to the oven, m the mass of the molecule, k Boltzmann's constant, T the absolute temperature of the oven, r the radius of the hole in the oven, A the area of the plane projection of the filament intercepting the molecules, F the Faraday, and i the measured ion current.

A correction for the scattering of the molecules in the beam by the residual gas was applied. This was determined by measuring the ion current at constant oven temperature while varying the residual gas pressure and extrapolating to zero pressure. The correction never amounted to more than 15 percent, and was reproducible within a few percent.

For measuring very low pressures a different procedure was employed. Salt vapor was allowed to condense on the cold filament for a measured length of time. The filament was then flashed, and the amount of salt evaporating measured by the ballistic kick of the galvanometer. By comparing the ballistic reading with the steady current reading at several temperatures at which the
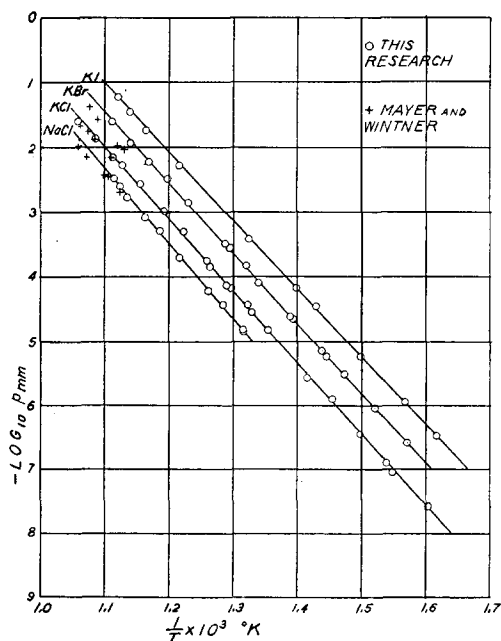

FIG. 2.

TABLE I. Experimental data.

KCl		KBr	
$-\log_{10} p_{mm}$	$\frac{1000}{T}$ (°K)	$-\log_{10} p_{mm}$	$\frac{1000}{T}$ (°K)
1.60	1.058	1.60	1.111
1.86	1.085	1.93	1.140
2.15	1.112	2.49	1.198
2.26	1.127	2.85	1.230
2.57	1.155	3.49	1.287
2.98	1.193	3.55	1.294
3.30	1.222	3.83	1.320
3.75	1.258	4.10	1.340
3.83	1.263	4.61	1.389
4.13	1.290	4.65	1.393
4.17	1.297	5.14	1.437
4.23	1.301	5.22	1.445
4.44	1.321	5.50	1.471
4.54	1.328	6.04	1.520
4.82	1.355	6.59	1.570
5.57	1.415		
5.88	1.454		
6.45	1.497		
6.90	1.538		
7.04	1.548		
7.57	1.603		

KI		NaCl	
$-\log_{10} p_{mm}$	$\frac{1000}{T}$ (°K)	$-\log_{10} p_{mm}$	$\frac{1000}{T}$ (°K)
		2.47	1.115
1.22	1.120	2.60	1.124
1.45	1.139	2.77	1.135
1.73	1.163	2.78	1.136
2.28	1.215	3.08	1.161
3.40	1.323	3.29	1.185
4.17	1.399	3.70	1.215
4.45	1.429	4.22	1.261
5.24	1.496	4.43	1.284
5.93	1.566	4.81	1.316
6.48	1.617	4.85	1.316

two methods could both be used, a calibration constant for converting ballistic throw into vapor pressure was obtained. This agreed within the experimental error with that calculated from the galvanometer constants, assuming complete ionization of the salt condensed on the filament, as long as the amount of salt on the surface corresponded to less than about 5 percent of a monomolecular layer.

EXPERIMENTAL RESULTS

The data are given in Table I and are plotted in Fig. 2. Data from an earlier paper[8] are also plotted, but were not used in the calculations.

We would expect the data to be described by equations of the form

$$\log_{10} p_{mm} = C - A(1000/T) + 2\log_{10}(1000/T) \quad (3)$$

where the 2 log $(1000/T)$ term arises from the

difference of heat capacities between gas and crystal. Examination of data compiled in the Landolt-Börnstein Tabellen and calculation of the heat capacity of the gas by standard methods[14] show that this difference is approximately $2R$ in the temperature range from 500°K to 1000°K. The exact value of $2R$ is not of much importance since it represents only a small correction term.

The experimental points are well fitted by equations of this form. The constants A and C were evaluated from the data by the method of least squares and are given in Table II. The curves in Fig. 2 are plots of Eq. (3) using these constants.

Heats of vaporization at 800°K were evaluated from Eq. (3) by means of the Clapeyron-Clausius relation

$$d \ln p/d(1/T) = -(\Delta H/R) \qquad (4)$$

and are tabulated in Table III.

DISCUSSION OF THE METHOD

For success, the positive ion method demands that the dissociation and ionization of the salt on the filament be practically complete. The ionization of the metal atom is the result of a competition between it and the filament surface for its valence electron. If the electron affinity of the surface, as measured by its "work function," is much higher than that of the atom, the atom is invariably ionized. High work functions are obtained by allowing a monomolecular layer of oxide to form on the surface, but this layer strips off when the temperature becomes too high.

On the other hand, if the temperature is too low, dissociation of the salt will not be complete. It is desirable, therefore, to make a quantitative analysis of the conditions under which the degree of dissociation α will be nearly unity and at the same time the ratio of metal ions to atoms, $r = p_M^+/p_M$ will be large (where p_M^+ and p_M are the pressures of the respective species). The size of α and r are controlled by two equilibrium constants which we will now discuss.

The first equilibrium constant is that of the reaction

$$M \to M^+ + e^-, \qquad (5)$$

$$K_I = (p_M^+ \cdot p_e)/p_M = \exp(-\Delta F^0/RT), \qquad (6)$$

$$\Delta F^0 = E_i - T(S_M^{+0} - S_M^0) + F_e^0, \qquad (7)$$

[14] J. E. Mayer and M. Goeppert-Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

where E_i is the energy of ionization of the metal atom, F_e^0 the standard free energy of the electrons, and S_M^{+0}, S_M^0, the standard entropies of the ions and atoms, respectively.

Now the supply of electrons from the filament is inexhaustible, so we may consider their pressure to be a constant (at constant temperature) and remove it from the equilibrium constant. When we do this we obtain the new constant

$$K_I' = r = \frac{p_M^+}{p_M} = \exp - \frac{(E_i + F_e^0 + RT \ln p_e)}{RT}$$

$$\cdot \exp \frac{(S_M^{+0} - S_M^0)}{R}. \qquad (8)$$

The quantity $F_e^0 + RT(\ln p_e)$ is the free energy of the electrons, which is approximately the negative of the quantity commonly called the "work function" of the filament surface,* and which is

TABLE II. Constants to be used in Eq. (3).

Salt	A	C
KCl	11.879	11.006
KBr	11.543	11.141
KI	11.263	11.277
NaCl	12.288	11.093

TABLE III. Heats of sublimation at 800°K and at 0°K.

Salt	ΔH_{800} (kcal.)	ΔH_0 (kcal.)
KCl	51.15±0.25	53.50±0.4
KBr	49.61±0.22	52.40±0.4
KI	48.33±0.27	51.41±0.5
NaCl	53.02±0.47	55.32±0.5

* Note: Some confusion exists in the literature concerning the exact meaning of the term "work function." The quantity here used, the negative of the free energy of the electrons, can be shown (reference 14) to be the numerator of the exponent of the expression

$$i = 120.1 T^2 \exp(-\epsilon \varphi/kT), \qquad (N-1)$$

where i is the electron emission in amperes per square centimeter. This equation is derived assuming only that the electrons are a perfect gas with a doubly degenerate internal quantum state (resulting from spin), and that the reflection coefficient of the surface for electrons is zero.

In most literature, however, the "work function" is defined as the numerator of the exponent of the empirical equation

$$i = A T^2 \exp(-\epsilon \varphi/kT), \qquad (N-2)$$

where the coefficient A has a value in general different from 120.1. For clean tungsten, for example, A has the value 60.2 (reference 11). The difference can be reconciled by making the φ of the first equation slightly temperature dependent.

For our purposes the difference is not important.

TABLE IV. Calculated dissociation constant of KCl as a function of temperature.

| T (°K)	$-\log_{10} K_{II}'$ (mm)
1400	6.1
1500	5.2
1600	4.4
1700	3.7

nearly independent of temperature. With $S_M^{+0} - S_M^0 = R \ln 2$, Eq. (8) now takes the final well-known form

$$r = 1/2 \exp (\epsilon\varphi - E_i)/RT, \qquad (9)$$

where φ is the work function of the filament surface.

In the first place, we see that the extent of ionization depends on the difference between the work function of the surface and the ionization potential of the alkali, as predicted. Calculation shows that for 99 percent ionization of potassium at 1500°K, the work function must be 5.01 volts or higher, for sodium 5.81 volts.

The second equilibrium constant which we must consider is that of the reaction

$$MX \rightarrow M^+ + X + e, \qquad (1)$$
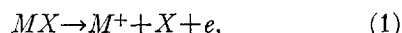
$$K_{II} = \frac{p_{M^+} \cdot p_X \cdot p_e}{p_{MX}} = K_{II}' \cdot p_e. \qquad (10)$$

With the same symbols and E_d, the energy of dissociation of the gas molecule, this can be shown to be

$$K_{II}' = \exp (S_X^0 + S_M^0 - S_{MX}^0 - R)/R$$
$$\cdot \exp (\epsilon\varphi - E_d - E_i)/RT. \qquad (11)$$

If α, the fraction dissociated, is nearly unity, the relation

$$\alpha = 1 - [(p_{MX \text{ initial}})/K_{II}'] \qquad (12)$$

holds approximately. K_{II}' may be calculated if the thermodynamic functions in Eq. (11) are evaluated by the statistical methods used elsewhere in this paper. This was done at several temperatures for potassium chloride using $\varphi = 5.20$ volts. The results are given in Table IV.

Taking the extreme case, it is seen that at the highest measured pressure of KCl (corresponding to log $p_{mm} = -5.4$ at the filament surface) $\alpha = 98$

percent at 1700°K. At lower pressures α is of course still nearer unity.

It was found possible to maintain work functions of 5 to 6 volts up to about 1800°K, so that there should be a region in the neighborhood of 1700° within which dissociation and ionization are complete. Experimentally, this region should appear as a flat maximum in the plot of ion current (at constant oven temperature) against filament temperature. Such a plot for KCl is shown in Fig. 3, and the expected maximum is found. This behavior is like that observed by other workers.[15] Similar maxima were observed for the other salts used, and the measurements were always made at filament temperatures lying within this region.*

In this and previous work of the kind it has been assumed that every halide molecule striking the surface sticks long enough to reach thermal and chemical equilibrium; i.e., the accommodation coefficient of the surface is assumed to be unity. Such as assumption has been shown to be correct for caesium on tungsten,[16] hydrogen on tungsten,[17] and probably true for chlorine[18] and bromine[19] on tungsten. On the other hand, it is
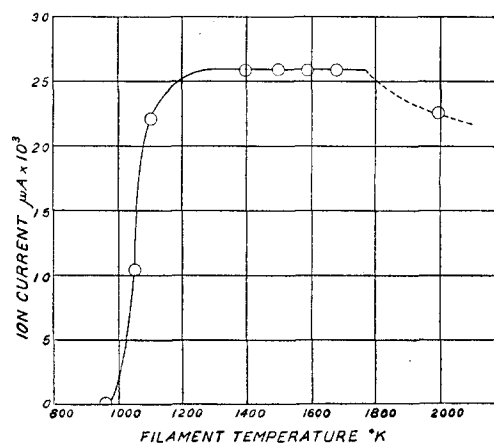

FIG. 3.

[15] T. E. Phipps, M. J. Copley, and J. O. Hendricks, J. Chem. Phys. 5, 868 (1937).
* Note: A direct experimental check of Eq. (11) was impossible because at the lower temperatures at which incomplete dissociation occurred the electron emission, from which the work function was determined, was too small to measure.
[16] I. Langmuir and J. B. Taylor, Phys. Rev. 44, 423 (1933).
[17] P. M. Doty, J. Chem. Phys. 11, 557 (1943).
[18] K. J. McCallum and J. E. Mayer, J. Chem. Phys. 11, 56 (1943).
[19] P. M. Doty, Thesis, Columbia University, 1944.

TABLE V. Entropies in cal./deg.

Salt	(S_{gas}^0/R) 800°K	$-\ln p_{mm}$ 800°K	S_{gas} 800°K	ΔS_{vap} 800°K	S_{cryst} 800°K	S_{cryst} 800°K $-S_{cryst}$ 298°K	S_{cryst} 298°K	S_{cryst} 298°K (from the literature)
KCl	39.92	8.41	95.98±0.14	63.94±0.38	32.04±0.40	12.69±0.2	19.35±0.5	19.75±0.06[a]
KBr	41.24	7.12	96.04± .14	62.01± .34	34.03± .37	13.16± .3	20.87± .5	22.6 ± .5[b]
KI	42.15	6.01	95.65± .14	60.41± .39	35.24± .41	13.01± .5	22.2 ± .7	24.1 ± .5[b]
NaCl	38.99	9.38	96.06± .14	66.28± .67	29.78± .67	12.77± .2	17.0 ± .8	17.3 ± .5[c]

[a] From heat capacity measurements. Cf. reference 21.
[b] From reststrahlen. K. K. Kelley, U. S. Bur. Mines Bull. 350 (1932).
[c] From reststrahlen supported by some heat capacity data. Kelley, reference b.

not true for methyl chloride[17] and hydrocarbons on tungsten and other metals. In general, accommodation coefficients of unity seem to be obtained for those gases and vapors which are chemi-adsorbed on the surface, whereas in cases in which only van der Waals forces are active very small accommodation coefficients are obtained. Since the image forces between a strong dipole such as an alkali halide molecule and the surface of a metal should be quite large, we might reasonably expect to find an accommodation coefficient close to unity. Also, the agreement between the values of the vapor pressure obtained by allowing the salt to fall on a cold (300°K) filament with subsequent flashing and the values obtained with the salt falling on a filament at 1700°K shows an independence of the accommodation coefficient of temperature that would be hard to explain if it were other than unity.

CRYSTAL ENTROPIES

The entropy of vaporization is related to the heat of vaporization by

$$\Delta H = T\Delta S. \tag{13}$$

The absolute entropy of the gas can be calculated accurately from spectroscopic data, and the heat capacity of the crystals above room temperature is known, so that sufficient information is available to calculate the entropy of the crystal at room temperature. The calculation of the gas entropy was performed using the usual statistical-mechanical equations[14] (including a small correction for rotational stretching and anharmonicity) and data from the compilation by Herzberg.[20] The heat capacities of the crystals above room temperature were taken from the

Landolt-Börnstein Tabellen. A short extrapolation was necessary for KBr and a long one for KI.

The calculations are summarized in Table V.

DIMERIZATION OF THE VAPOR

We have assumed that there is no dimerization in the saturated salt vapor. It is possible to show, at least for KCl, that this assumption is correct by comparing the crystal entropy as calculated above with the one calculated from very good heat capacity data (from 15°K to room temperature) by Southard and Nelson.[21] The two entropies agree within the experimental error, with ours, calculated assuming no association, being slightly lower. The presence of appreciable association would lower the calculated entropy of the gas and destroy the agreement of the two values. A detailed calculation (see Appendix) shows that for saturated KCl vapor at 800°K the fraction associated is certainly less than 2 percent and probably less than 0.3 percent. This is in agreement with the conclusion of Deitz,[7] who found saturated KCl vapor to be less than 10 percent associated.

The probable error introduced in the heat of vaporization by association can also be shown to be less than 0.1 kcal. (see Appendix). Because of their similar properties, it was assumed that the amount of association in the vapors of the other salts was likewise negligible. In view of the unreliability of the entropy values found in the literature for these salts no direct calculation of the degree of association was attempted.

HEAT OF VAPORIZATION AT ABSOLUTE ZERO

The heat content of the vapor was calculated statistically in the same manner as the entropy.

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[20] G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, Inc., New York, 1939).

[21] J. C. Southard and R. A. Nelson, J. Am. Chem. Soc. **55**, 4865 (1933).

The heat content of the crystal was obtained by integrating the available heat capacity data. The difference of these two quantities added to the heat of vaporization at 800°K gives the heat of vaporization at absolute zero. The results are tabulated in the last column of Table III.

ERRORS

The precision measure of the heats of vaporization is the square root of the sum of the squares of the following individual errors: the "probable error" in the least-squaring of the experimental points; a systematic error in temperature measurement of possibly 0.4 percent; a possible systematic error in the logarithm of the vapor pressure (resulting mainly from incompleteness of ionization) amounting to 0.2 percent for the potassium salts and 0.4 percent for NaCl.

The entropies of vaporization contain an additional possible 0.4 percent error from the temperature.

The precision measure of the entropies of the vapor is the square root of the sum of the squares of the errors resulting from probable errors in temperature, pressure, fundamental frequency (± 1 percent), and moment of inertia (± 3 percent).

APPENDIX

Calculation of the Extent of Association in KCl Vapor at 800°K

The outline of the method is this: We calculate the entropy of a gaseous mixture of monomer (KCl) and dimer $(KCl)_2$ and compare with the experimental entropy of the vapor. This allows us to set a maximum value for the extent of association. Using a thermodynamic equation connecting the extent of association, entropy, and heat content of the crystal and saturated vapor we then may calculate maximum and minimum values for the heat of association and the maximum error in the heat of vaporization of the monomer.

We shall use the following symbols to save space: S_2 and ΔH_2 for the entropy and heat of vaporization per mole of the dimer, S_1 and ΔH_1 for the same quantities per mole of monomer, and S_c the entropy of the crystal, all at 800°K.

Entropy of the Dimer

A rough calculation using only electrostatic terms shows that a square configuration with like atoms at opposite corners is energetically the most stable form of the mole-

cule. In view of the small difference between the interatomic distance in the monomer (2.79A) and in the crystal (3.14A), we shall assume that the interatomic distance in the dimer is the same as in the monomer.

Using this model, the entropy due to rotation is easily calculated.[14]

$$S_{2\ \text{rot}} = (\tfrac{3}{2})S_{1\ \text{rot}} - (\tfrac{3}{4})R \ln 2 + (\tfrac{1}{2})R \ln \pi. \quad \text{(A-1)}$$

The translational entropy at standard pressure (one millimeter) is

$$S^0_{2\ \text{trans}} = S^0_{1\ \text{trans}} + (\tfrac{3}{2})R \ln 2. \quad \text{(A-2)}$$

The vibrational entropy is less easily calculated since the frequencies are unknown. An inspection of the normal modes of vibration shows, however, that of the six, five should have approximately the same frequency as the monomer, while the sixth, the "bending" mode, should be lower by a factor of perhaps ten. The vibrational entropy is then

$$S_{2\ \text{vib}} = 6S_{1\ \text{vib}} + R \ln 10 (\pm 3R). \quad \text{(A-3)}$$

Inserting numerical values we obtain 114 ± 6 cal./deg. for the entropy per mole of the dimer at 1 mm pressure and 800°K.

Entropy of a Saturated Mixture of Monomer and Dimer

If x is the fraction of monomer associated, the entropy per mole of monomer in the saturated vapor will be (from Table V)

$$S_1 = 95.98 \pm 0.14 - R \ln (1-x). \quad \text{(A-4)}$$

The natural logarithm of the saturated vapor pressure is -8.41, so that the entropy of the dimer in the saturated vapor will be

$$S_2 = S_2^0 - R \ln p_2 = 131 - R \ln (x/2). \quad \text{(A-5)}$$

The entropy of the mixture will be

$$S = S_1(1-x) + S_2(x/2) = 95.98 \pm 0.14 - 30.5x$$
$$- R(1-x) \ln (1-x) - R(x/2) \ln (x/2). \quad \text{(A-6)}$$

The experimental entropy (from the values in Table V) is 96.38 ± 0.5.

It is seen that x must be small. Exactly how small to take it is a matter of taste; we prefer to set 0.02 as an upper limit with the probable value not greater than 0.003. We have assumed at this point that the presence of association does not appreciably affect the heat and hence the entropy of vaporization. This assumption will now be justified.

Error in the Heat of Vaporization due to Association

The quantity which was directly measured was the number of potassium atoms contained in the vapor molecules which hit a unit area. If we represent this number by Z_m, and the pressure calculated from it by p_m, we have

$$Z_m = \frac{p_m}{(2\pi m_1 kT)^{\frac{1}{2}}} = Z_1 + 2Z_2 = \frac{p_1}{(2\pi m_1 kT)^{\frac{1}{2}}} + \frac{2p_2}{(2\pi m_2 kT)^{\frac{1}{2}}}. \quad \text{(A-7)}$$

The fraction associated, x, is $2p_2/p_1$, and $m_2=2m_1$, so that

$$p_1=\frac{p_m}{1+(\sqrt{2}/2)x} \qquad (A-8)$$

$$\frac{\partial \ln p_1}{\partial (1/T)}=\frac{\partial \ln p_m}{\partial (1/T)}-\frac{\sqrt{2}}{2}\frac{\partial x}{\partial (1/T)} \quad \text{(if } x \text{ is small)} \quad (A-9)$$

$$\Delta H_1=\Delta H_m+R\frac{\sqrt{2}}{2}\frac{\partial x}{\partial (1/T)}. \qquad (A-10)$$

The fraction associated, x, can be shown to obey the equation

$$x=2p_2/p_1=2 \exp \{[(S_2{}^0-S_1{}^0-S_e{}^0)/R] -[(\Delta H_2-\Delta H_1)/RT]\} \qquad (A-11)$$

$$\frac{\partial x}{\partial (1/T)}=-x(\Delta H_2-\Delta H_1)/R. \qquad (A-12)$$

If we insert numerical values in Eqs. (A-10), (A-11), and (A-12), using $x=0.02$ and $S_2{}^0=114\pm6$, we find the error in ΔH_1 to be

$$0<\left[\frac{\sqrt{2}}{2}x(\Delta H_2-\Delta H_1)\right]<0.2 \text{ kcal.} \qquad (A-13)$$

If we use $x=0.003$, we find the error to be

$$0<\left[\frac{\sqrt{2}}{2}x(\Delta H_2-\Delta H_1)\right]<0.05 \text{ kcal.} \qquad (A-13a)$$

It is interesting to note that we are also able by Eq. (A-11) to set an upper limit on the heat of association (using $x=0.02$):

$$(KCl)_2\rightarrow2KCl, \quad \Delta H<47 \text{ kcal. (at } 800°K). \qquad (A-14)$$

The Reaction of Hydrogen Atoms with Acetylene*

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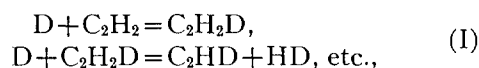(Received July 13, 1944)

An investigation has been made of the reaction between hydrogen atoms and acetylene. With the large hydrogen atom concentrations produced in the discharge tube, catalytic recombination of hydrogen atoms occurs but no hydrogenated products could be detected. With small hydrogen atom concentrations resulting from mercury photosensitization, ethane and butane are produced together with a partially hydrogenated polymer. The results are discussed from the point of view of the elementary reactions involved and it is concluded that ethyl and vinyl radicals play an important part in the reaction.
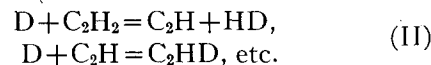
INTRODUCTION

IN a previous paper[1] on the mercury photo-sensitized polymerization of acetylene it was concluded that hydrogen atoms and C₂H radicals are probably produced in the initial step and that the polymerization is sensitized by these primary products. In an attempt to throw further light on the problem, the present paper is devoted to an investigation of the action of hydrogen atoms on acetylene.

This has already been done by a number of workers who produced hydrogen atoms either by a discharge tube[2-5] or by mercury photosensitization.[6] In the case of the discharge-tube method it was found that although acetylene catalyzed the recombination of hydrogen atoms, no products other than hydrogen and acetylene could be detected. However, if deuterium atoms were used[5] deuterization of acetylene took place with an activation energy of less than 5 kcal. In order to explain the rapid exchange as well as atom recombination, Geib and Steacie[5] suggested the alternative mechanisms

$$\begin{aligned}&D+C_2H_2=C_2H_2D,\\&D+C_2H_2D=C_2HD+HD, \text{ etc.,}\end{aligned} \qquad (I)$$

and

$$\begin{aligned}&D+C_2H_2=C_2H+HD,\\&D+C_2H=C_2HD, \text{ etc.}\end{aligned} \qquad (II)$$

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