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J. R. Walton
L. K. Brice, Jr.

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MASS SPECTROMETRIC STUDY OF THE VAPOR STATE OF SILVER HALIDES

H. M. Rosenstock,[1] J. R. Walton, and L. K. Brice, Jr.[2]

Abstract

The mass spectra of AgCl, AgBr, and AgI vapor have been studied. All show evidence of trimeric vapor species. The heat of trimerization of AgCl was determined as 110 ± 20 kcal/mole. The ratios of heats of activation for vaporization were measured for various vapor species in LiBr, LiI, NaCl, KCl, and KI. The results for LiBr, LiI, and NaCl are in agreement with values determined by equilibrium thermochemical methods. The results for KI are in marked disagreement with measurements by effusion cell methods. Possible reasons for the discrepancy are discussed.

Introduction

A mass spectrometric study[3] of the vapor state of the cuprous halides showed evidence of extensive polymerization, in agreement with the results of thermochemical studies by Brewer and Lofgren.[4] The entropy of vaporization of the silver halides shows no anomalies such as those which led to the reinvestigation of the cuprous halides.[5] However, an early vapor density determination of silver chloride by Biltz and Meyer[6] indicated some association.

In the present study, mass spectra were obtained of the vapor state of silver chloride, silver bromide, and silver iodide. From observations of the intensities of $AgCl^+$ and $Ag_3Cl_3^+$ ions at various temperatures, the ratio of the heats of activation for vaporization of the monomer and trimer could be determined without an exact knowledge of the temperature. This ratio, when combined with other thermochemical data, yielded a value

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[1]W. H. Johnston Laboratories, Inc., Lafayette, Ind.

[2]ORINS Summer Participant, Virginia Polytechnic Institute, 1955.

[3]H. M. Rosenstock *et al.*, J. Chem. Phys. 23, 2442 (1955).

[4]L. Brewer and N. L. Lofgren, J. Am. Chem. Soc. 72, 3038 (1950).

[5]L. Brewer, Paper 7 in Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics, Div. IV, vol. 19B (L. L. Quill, ed.), McGraw-Hill, New York, 1950.

[6]H. Biltz and V. Meyer, Z. physik. Chem. (Leipzig) 4, 268 (1889).

for the heat of trimerization of silver chloride. The method was also applied to some alkali halides in order to determine its reliability.

Experimental

The mass spectra of the silver halides were obtained on an all-metal, 6-in.-radius, 60°-sector mass spectrometer (Fig. 1) with magnetic scanning. The ions were accelerated through a potential of 900 v, and the ion current was measured by a vibrating reed electrometer connected to a strip-chart recorder. A vacuum of better than 10^{-6} mm Hg was maintained during operation. The ions were obtained by bombardment of the vapor with 75-v electrons.

The silver halides were prepared from silver nitrate and the appropriate sodium halide by standard wet methods and then oven dried. The samples were placed on the central third of platinum filament ovens and heated until a sufficiently rapid rate of vaporization was attained. The temperature was estimated to be about 500°C. The filament ovens were constructed of 0.002 × 0.5 × 0.1 in. platinum strips. These were shaped into troughs and the ends flattened and spot-welded to 1/16-in.-dia tantalum posts held 1/2 in. apart on an insulated subassembly[7] (Fig. 2). The ovens were resistance-heated by means of a well-regulated a-c power supply. In some experiments the ends of the platinum troughs were spot-welded to 0.020-in.-dia platinum wire and the latter was spot-welded to the posts.

The ratios of the heats of activation for vaporization were determined in the following manner. The sample was placed on a filament and heated until a moderately intense ion current was obtained. The vapor was ionized with 30- to 40-v electrons. The various voltages on the slits of the Nier-type[8] ion source were adjusted to give maximum intensity on one mass peak. The intensity of a monomer peak was recorded, the magnetic field was varied until the polymer peak was received and measured, and then the monomer peak intensity was once again recorded. This procedure

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[7] J. R. Walton, High-Temperature Mass Spectrometer Oven, ORNL-1473 (Jan. 8, 1953).

[8] A. O. C. Nier, Rev. Sci. Instr. 18, 398 (1947).

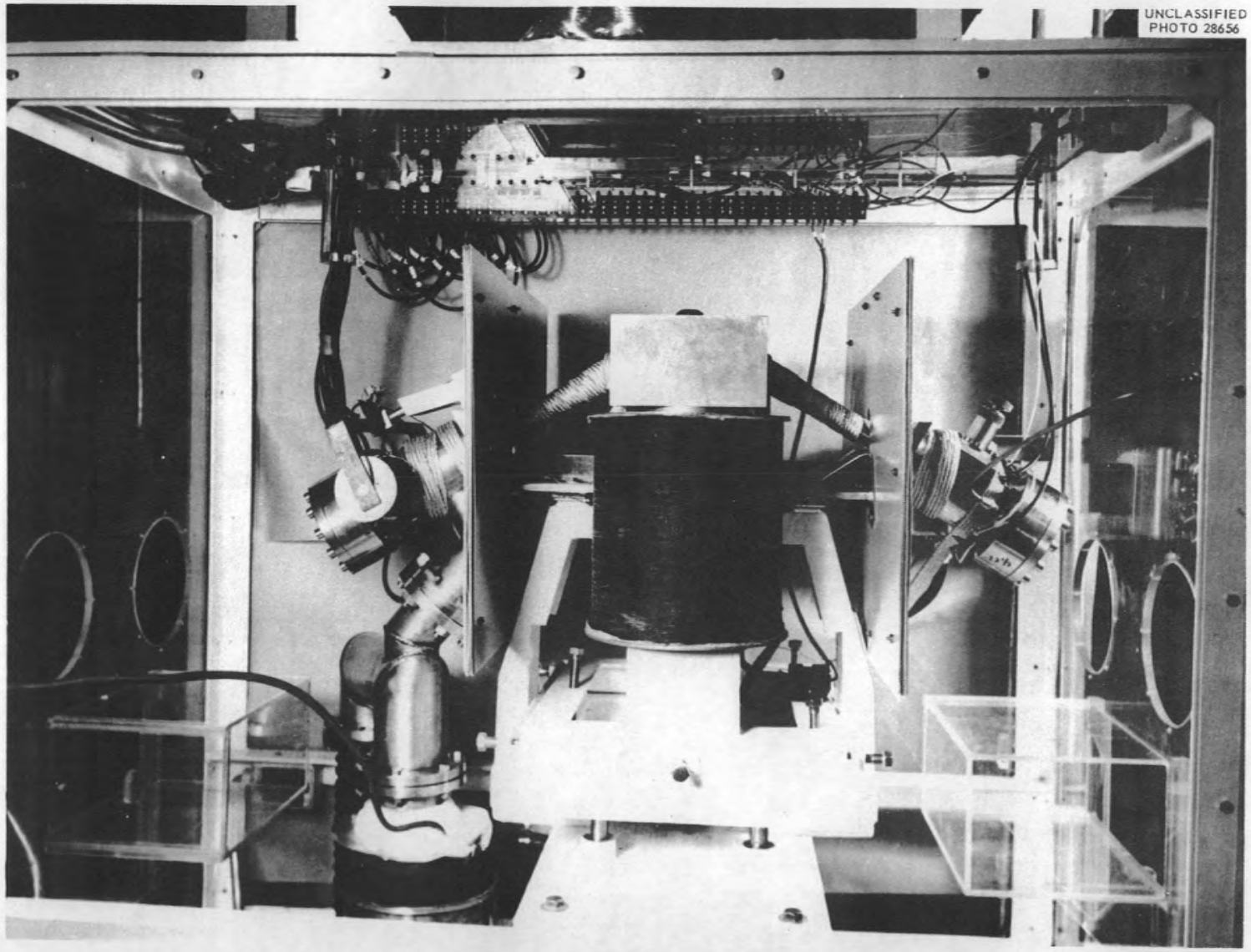

Fig. 1. All-Metal Mass Spectrometer.

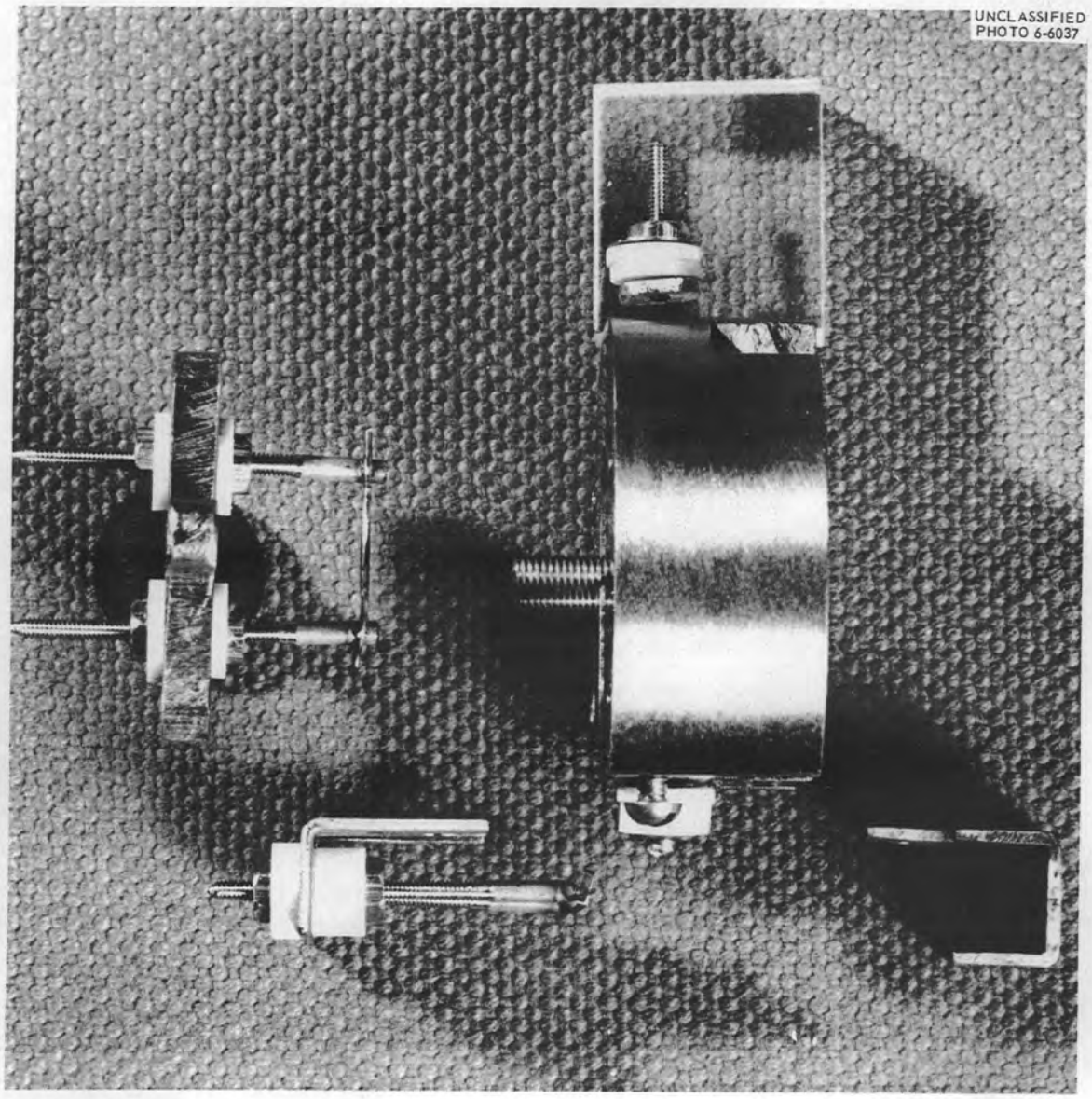

Fig. 2. High-Temperature Mass Spectrometer Oven.

was repeated until the respective intensities had attained constant values. Following this, the heater current was raised 50 to 100 ma and the procedure repeated. After each increase in current, several minutes elapsed before the intensity drift ceased. In all cases the most intense peak of an isotopic group was chosen for intensity measurement.

The possible interference of temperature gradients was examined by carrying out one ratio determination on KCl with a platinum oven identical in all respects except that it was notched at both ends near the weld to the tantalum posts in order to create high local resistance and to change the thermal losses. No significant variation was observed in the experimental results. In another experiment, again on KCl, each time that the oven temperature was raised the electrode voltages on the ion source were adjusted to give maximum ion intensity on the KCl^+ and K_2Cl^+ ions, respectively. The results were indistinguishable from those obtained at constant voltage. Only slight readjustment of the ion repeller voltage was required to maintain maximum ion intensity as the oven temperature was increased.

Results and Discussion

Mass Spectra of Silver Halides

The mass spectra of the three silver halide compounds are shown in Table 1.

Table 1

Mass Spectra of Silver Halides at 500°C

Ionic Species	Relative Intensity		
	AgCl	AgBr	AgI
Ag	100	20	100
AgX	90	30	95
Ag_2	25	10	25
Ag_2X	70	45	90
Ag_2X_2			
Ag_2X_3			
Ag_3	5	4	
Ag_3X	2	3	
Ag_3X_2	85	100	80
Ag_3X_3	40	40	60

The relative abundance of each species was based on the sum of the various isotopic peaks. Since the relative abundances are rather temperature-dependent, the results are to be regarded as semiquantitative and characteristic of a temperature of approximately 500°C. Halogen and hydrogen halide peaks were observed, but the results indicated that appreciable quantities of polymer exist in the vapor phase. The absence of dimer parent ions is striking and parallels Brewer's conclusion that dimeric species are not prominent in the cuprous halides.[4] This suggests that the Ag_2X^+ ions are formed by decomposition of trimer ions. The Ag_3X^+ and Ag_3^+ ions probably represent rearrangement peaks.[9] No tetramer ions were detected in the silver chloride mass spectrum, and the possibility of their presence in the bromide and iodide could not be studied because of instrument limitations.

Heat of Trimerization of AgCl

The similarity of the silver and cuprous halide mass spectra led to the suggestion that the trimers might have the same structure. There is some evidence that this might be a six-membered ring.[10] In order to obtain further information on this question, an attempt was made to determine the heat of trimerization of silver chloride.

As Honig has pointed out,[11] the energy quantities obtained from rate of vaporization studies are heats of activation for evaporation and not thermodynamic heats of vaporization. In the present study it was not convenient to measure temperature. However, useful information can still be gained by plotting the logarithm of the rate of vaporization of one species against that of another coming off the same surface. This should yield a straight line whose slope is equal to the ratio of the heats of activation for vaporization. The results on silver chloride (Fig. 3) yielded two straight lines which represent vaporization from a solid and liquid phase, respectively.

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[9]A. Langer, J. Phys. & Colloid Chem. 54, 618 (1950).

[10]C. Wong and V. H. Schomaker, American Crystallographic Association, Summer Meeting, Pasadena, June 27, 1955.

[11]R. E. Honig, J. Chem. Phys. 22, 126 (1954).

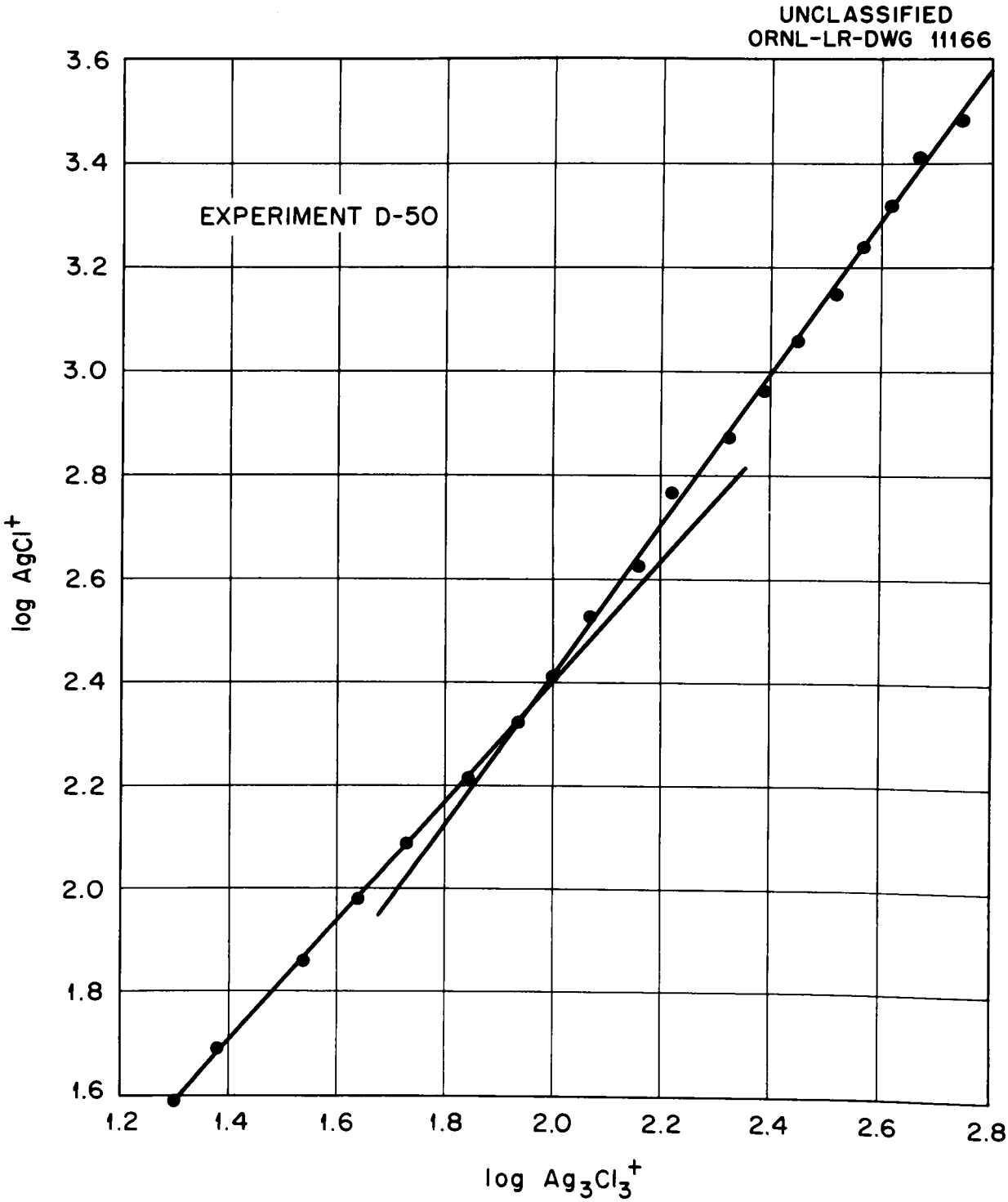

Fig. 3. Vaporization of Silver Chloride.

A number of experiments were also carried out on some alkali halides in order to provide a comparison between this method and other work done under equilibrium conditions with effusion cells. In these experiments data were obtained only on sublimation.

A summary of the results is given in Table 2. The errors given for

Table 2

Heat of Vaporization Ratios

Species	Condensed Phase	Number of Determinations	Ionic Species	Ratios	
				This Work	Other Work
$\frac{AgCl}{Ag_3Cl_3}$	Solid	5	$AgCl^+$, $Ag_3Cl_3^+$	1.21 ± 0.05	
$\frac{AgCl}{Ag_3Cl_3}$	Liquid	4	$AgCl^+$, $Ag_3Cl_3^+$	1.41 ± 0.05	
$\frac{Li_2I_2}{LiI}$	Solid	3	LiI^+, Li_2I^+	1.01 ± 0.05	1.03 ± 0.02*
$\frac{Na_2Cl_2}{NaCl}$	Solid	2	$NaCl^+$, Na_2Cl^+	1.13 ± 0.05	1.13**
$\frac{K_2Cl_2}{KCl}$	Solid	8	KCl^+, K_2Cl^+	1.17 ± 0.05	1.08**
$\frac{K_2I_2}{KI}$	Solid	2	KI^+, K_2I^+	1.22 ± 0.05	0.84**
$\frac{Li_3Br_3}{LiBr}$	Solid	2	$LiBr^+$, $Li_3Br_2^+$	1.2 ± 0.1	**
$\frac{Li_2Br_2}{LiBr}$	Solid	2	$LiBr^+$, Li_2Br^+	0.97 ± 0.05	**

*L. Friedman, J. Chem. Phys. 23, 477 (1955).

**R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).

the present work are estimates and are at least twice as large as the average deviation of the ratios determined in the set of experiments for each substance.

The results for LiI and NaCl are in agreement with the ratios determined by equilibrium methods. In the case of LiBr the comparison must be

made in a different manner. Miller and Kusch[12] give energies of dimerization and trimerization as follows: For

$$Li_2Br_2 \rightarrow 2LiBr, \qquad \Delta E_1 = 42.3 \pm 1.1;$$
$$Li_3Br_3 \rightarrow LiBr + Li_2Br_2, \quad \Delta E_2 = 36.5 \pm 0.5.$$

These energies are referred to a temperature of about 800°K. With the ratios determined in the present study and the energy of dimerization of Miller and Kusch, a value can be calculated for ΔE_2. The calculated value is within the limits of error of the data used. Thus for these three substances the two methods are in agreement.

The results for KCl and especially those for KI disagree with the results of Miller and Kusch. It is conceivable that this is due to an excess heat of activation of vaporization which, then, in the case of KI would be excessively great. However, it is noteworthy that in these two cases Miller and Kusch found that there is not very much dimer, indicating that the velocity analysis of their molecular beam may not give results of precision comparable to those for ions of appreciable polymerization.

The outstanding possibility of error in the present work is that the KCl^+ and K_2Cl^+ ions may not be satisfactory representatives of the monomer and dimer species. However, if neutral dimer molecules contribute to the KCl^+ ion current in appreciable amount, any such correction would further increase the disagreement. This possibility was the motivation for using the lowest electron energy consistent with a satisfactory ion intensity. The possibility of interference from thermal ionization was also considered. No polyatomic thermal ions were found in any of the alkali halides even when the rate of vaporization was sufficient to produce intense ion beams by electron bombardment.

The vapor pressure of silver chloride has been measured by Maier[13] in the range 1127 to 1429°K and by von Wartenberg and Bosse[14] in the range

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[12] R. C. Miller and P. Kusch, J. Chem. Phys. 25, 860 (1956).

[13] C. G. Maier, "Vapor Pressures of the Common Metallic Chlorides and a Static Method for High Temperatures," Technical Paper 360, Bureau of Mines, 1925.

[14] H. von Wartenberg and D. Bosse, Elektrochem. Z. 28, 384 (1922).

1528 to 1715°K. Kelley[15] has reported that both studies give the same value for the heat of vaporization, but the latter gives a more reasonable value for the entropy of vaporization. This discrepancy is understandable in terms of the polymerization found in the present study.

Some further calculations of interest can be carried out by assuming that the data of von Wartenberg give a reliable value for the heat of vaporization of the monomer. By use of the equation given by Kelley,[15] a value of 48 kcal is obtained for the heat of vaporization of the monomer just above the melting point. This quantity can be combined with the two ratios measured in this study to calculate a heat of fusion which is in agreement with the value of 3.15 kcal given by Brewer,[5] indicating that the measured ratios are self-consistent and closely approximate equilibrium heat of vaporization ratios. These then lead to a heat of polymerization of 110 kcal for the reaction $3AgCl \rightarrow Ag_3Cl_3$, for which we estimate a reliability of ±20 kcal. It is interesting to note that this value is of the same order of magnitude as the heat of polymerization of CuCl which was determined as 120 ± 15 kcal at 1300°K by Brewer and Lofgren.[4] The lower value for the heat of trimerization of AgCl is paralleled by a somewhat lower value for the dissociation energy of diatomic AgCl as compared with the dissociation energy of CuCl (ref 3).

The similarity in the mass spectra of the silver and copper halides, together with the magnitude of the heat of trimerization of silver chloride determined above, suggests that the molecular structures of both types of halides are similar.

Acknowledgment

We would like to acknowledge helpful discussions with A. E. Cameron, C. R. Baldock, W. R. Rathkamp, and H. W. Morgan of this Laboratory.

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[15] K. K. Kelley, U. S. Bur. Mines, Bull. 383, 95 (1935).

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