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MOLECULAR ASSOCIATION IN ALKALI HALIDE VAPORS

S. Datz

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ABSTRACT

Molecular association equilibria in alkali halide vapors were studied by measuring the temperature dependence of the molecular weights of gaseous sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium iodide, rubidium chloride, and cesium chloride. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. The pressure sensing element consisted of a fused silica U-tube manometer containing molten gold, and pressures were determined by measuring the argon pressure necessary to balance the gold manometer. The apparatus was used in the temperature range of 1175 to 1430°K. and pressures of from 10 to 40 mm. were measured with a precision of ± 0.05 mm.

The temperature dependence of the equilibrium constants for the reaction

$$(MX)_2 \rightleftharpoons 2MX$$

yielded dissociation energies (evaluated at 1300°K.) ranging from 48.0 kcal. mole^{-1} for sodium chloride to 34.7 for cesium chloride. The entropies of dissociation were found to fall within a small range, varying from 28.3 e.u. for sodium chloride to 25.0 for potassium iodide, and a statistical calculation of the entropy changes based on an ionic model was found to agree well with the experimental values. It is shown that these systems may be adequately described with an electrostatic model, although closer attention should be paid to the nature of polarization interactions.

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CHAPTER I

INTRODUCTION

A. A Summary of Previous Experimental Work

The earliest work recorded on the problem of the molecular weights of alkali halide vapors was that of Nernst[1] in 1904. In this work, which was primarily an attempt to demonstrate the applicability of the Victor-Meyer method to high temperature measurements, he found that at 2240°K. and one atmosphere pressure the molecular weights of sodium chloride and potassium chloride vapors could be represented, to within ten per cent, by the respective monomeric formula weights.

The problem was again taken up by Dietz[2] in 1936, who, in view of the high dipole moments observed for the alkali halides,[3] expected that some association might exist in the vapor phase. The method employed was to measure both the vapor pressure and the rate of effusion through a hole, from which the molecular weight could be calculated. The measurements (in the region 750°K. to 900°K.) indicated that, within ten per cent, no association existed in potassium chloride or cesium iodide vapors in equilibrium with the solid. Zimm and Mayer[4] in 1944 stated that the agreement between the value for the crystal entropy of potassium chloride as calculated from their effusion measurements of vapor pressure and that obtained from heat capacity data precluded the existence of appreciable amounts of dimer in the vapor and that, for saturated potassium chloride vapor at 800°K., the fraction associated was certainly less than 2 per cent and probably less than 0.3 per cent.

Indirect evidence for the existence of dimers was inferred by Honig, Mandel, Stitch and Townes.[5] Upon comparing their values of inter-nuclear distances for alkali halides, determined by microwave spectroscopy, with the values previously obtained from electron diffraction[6] (corrected for the average over vibrational states),[7] they found that the electron diffraction values were consistently higher. The discrepancy had its highest value at 4 per cent for the halides of smaller formula weights and decreased with increasing formula weight. The authors stated that a possible reason for this discrepancy was a small degree of dimerization in the vapors.* This would not affect the spectroscopic results,** but would make the electron diffraction values larger, since in a dimer the expected inter-nuclear distance would be larger than that for monomer.

The work of Ochs, Cote, and Kusch[8] in 1953, which prompted the large number of recent investigations in this field, was, oddly enough, not directly concerned with the problem of molecular weights, but was primarily a molecular beam experiment to measure the radiofrequency spectrum of sodium chloride. In this work, an additional absorption line was found

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*The authors of the electron diffraction paper had considered the possibility of dimer, and claimed that their experimental results served to confirm the absence of dimer in the vapor.

**Since the absorption in the microwave region is due to pure rotational transitions and requires the existence of a permanent dipole moment in the molecule, a dimer molecule, whose configuration is probably a planar ring, would not be expected to have a permanent dipole moment, and would therefore not absorb.

which could not be explained on the basis of a well-established theoretical treatment for diatomic molecules. Further investigation showed that the relative intensity of this line decreased upon increasing the source temperature at constant pressure. The authors therefore postulated that the beam must consist of more than one component, presumably monomer and dimer, and estimated that the diatomic molecules constituted 25 to 75 per cent of the total beam.

The discovery of this effect and the consideration of its impact on the results of the molecular beam radiofrequency spectroscopy of the alkali halides done at Columbia University and elsewhere[9,10] led to an extensive and ingenious investigation at Columbia into the problem of molecular association of alkali halide vapors. The technique developed by Miller and Kusch[11] was to analyse the velocity distribution of a molecular beam by means of a rotating screw time-of-flight velocity analyser. In this apparatus, only those beam molecules having a narrow range of velocities would be transmitted along the length of a rapidly rotating helical slot without colliding with either the leading or the trailing wall. The velocity distribution in the beam was determined by plotting transmission versus rotor speed. Once having established that the velocity distribution from an effusive orifice could truly be represented by a Maxwell-Boltzman distribution, they were able to use an analysis of the velocity distribution to determine the degree of association in beams of alkali halides.[12] This was accomplished by fitting the observed distribution with the calculated velocity distribution curve for an admixture of monomer, dimer and, in some cases, trimer. The mole fraction of dimer in the vapor in equilibrium with salt at a pressure of 10^{-2} mm. was found to decrease with increasing cation weight, ranging from a value of 0.87 for lithium chloride to essentially zero for cesium chloride. From the determination of the equilibrium constants and their variation with temperature, energies and entropies of association were calculated. Simultaneously with the work of Miller and Kusch, a mass spectrometric analysis was made by Friedman[13] on lithium iodide vapor admitted to the mass spectrometer from an effusion cell. Here also there was evidence for large amounts of dimer formation and for the presence of some trimer in the vapor of a lithium halide. However, observations of the infrared spectra in the region 430 to 630 cm.$^{-1}$ of alkali halides, made by Klemperer and Rice,[14,15] were found to be completely explicable on the basis of pure monomeric species. Moreover, the authors stated that a calculation of the vibrational frequencies expected for the dimer, from what was considered a reasonable model,[16] were such that they would be easily observable in the frequency region studied. These authors placed an upper limit on the possible amount of dimer present at 15 per cent. In a paper which followed,[17] the same authors stated that a consideration of the available thermodynamic and spectroscopic data precluded the existence of appreciable amounts of dimers.

The large discrepancies which existed between the findings of the infrared studies and those of the molecular beam velocity analysis were attributed by Klemperer and Rice[14] to the kinetics of vaporization, i.e., they postulated that in the case of beam studies the vapor from which the beam was formed was not the true equilibrium mixture, due to a relatively short residence time in the vapor source. This led to further investigation of the effect of mean residence time in the effusion source on the molecular composition[18] and to the counter proposal by Kusch that conditions favoring true equilibrium were better in the case of the effusion cell than those in the absorption cell used in the infrared spectrometer.[19] Further molecular beam work has since been done to improve the accuracy of previously reported results[18,20] and to measure the composition of beams formed by free evaporation from halide crystals.[21] The inconsistency with the infrared work has been partially resolved by the recent observation by Klemperer[22] of an absorption spectrum attributable to dimer.

Mass spectrometric analysis of vapor in equilibrium with solid alkali halides has recently been carried out by three separate groups,[23-27] but uncertainties in ionization cross section and mode of dissociation upon electron impact prevent quantitative measurements of the degree of association.

Information concerning vapor phase association may also be adduced from a comparison of results obtained from different methods of measuring vapor pressure, inasmuch as some methods, such as those which utilize direct momentum transfer, measure the total pressure regardless of the molecular species present while other methods involve mass transport and the validity of the pressures computed is a function of the molecular composition. Thus, Beusman[28] was led to conclude that the presence of dimer amounting to approximately 20 per cent in potassium chloride and 70 per cent in lithium chloride was possible by comparing the values of the vapor pressures he had obtained with a transpiration method and with the Fiock-Rodebush method.[29] A more extensive application of this approach was recently reported by Barton and Bloom,[30] who deduced the molecular weights of sodium chloride and potassium chloride vapors by comparing vapor pressures they had obtained by a transpiration method with those they had previously determined[31] by a boiling point method. The authors also calculated the energy of association from the temperature dependence of the molecular weight but the paucity of data reported detract from the dependability of this determination.

Noting the discrepancies which existed when an attempt was made to correlate the heats of sublimation measured by effusion,[4,32] the heats of vaporization measured by static methods,[29] and the calorimetric measurements of heat of fusion,[33] Datz and Minturn[34] extended the range of the effusion method to include measurements of the vapor pressure over both the solid and the liquid phases of sodium chloride and potassium chloride. The heats of sublimation obtained from the vapor pressures were in excellent agreement with published values, and, if the effect of association on the measurements was neglected, very good agreement was found between the heats of fusion obtained from the difference between the calculated heats of sublimation and vaporization, and the calorimetrically determined values. However, if the data were corrected for vapor phase association, as indicated by Miller and Kusch, the agreement was destroyed.

Peripheral experimental evidence for the existence of dimer has also been adduced for lithium halide vapors[35] from discrepancies found when crystal entropies calculated from heat capacity data and measured heats of sublimation were included in a Born-Haber cycle.

B. Theoretical Investigations

Several theoretical papers have recently been published in which a statistical mechanical treatment was used to predict the thermodynamic properties of gaseous alkali halide dimers. All of the investigators concluded that the dimer configuration was that of a rhombus. The first of these was a calculation of the configuration and energy of dimerization of sodium chloride vapor by O'Konski and Higuchi,[16] using a method developed by Rittner[7] in which the Van der Waals attraction and mutual polarization effects are considered, as well as the coulombic attractions and closed shell repulsions. A simplified model, in which only coulombic attraction and closed shell repulsion are considered, was developed by Pauling[36] for use in calculating the energies of monomeric alkali halide molecules and was used by Milne and Cubicciotti[37] for calculating the dimensions and heats of formation of eleven of the alkali halide dimers. Upon the comparison of seven of these with the experimentally determined values of Miller and Kusch,[12] they found discrepancies of from -6.2 to +8.5 kcal. mole^{-1}. These authors were also able to calculate the entropies of dimerization by estimating the vibrational frequencies of the dimer.

They assumed that of the six normal modes in the dimer the four stretching modes had the same frequency as the monomer and the two bending modes had frequencies equal to one-third of this value.

Bauer, Diner, and Porter[38] utilized what they called a "pseudo-electrostatic model" for the dimer. They assumed that the apex angle of the configuration and the increase in internuclear separation in the dimer found by O'Konski and Higuchi for sodium chloride was the same for all alkali halides. By assuming that two of the normal vibrational modes of the dimer had frequencies equal to the monomer and estimating the values for the other four, they were able to calculate the entropies of dimerization for eight alkali halides. These entropies were found to be in good agreement with the experimental entropies measured by Miller and Kusch for lithium chloride, sodium chloride, and sodium iodide, but in very poor agreement for sodium fluoride, potassium chloride, potassium iodide, and rubidium chloride. The authors concluded that the discrepancies were in the measurements of the energies of dimerization made by Miller and Kusch. They assumed that the measured degree of association was correct and, with their value of the calculated entropy, recalculated the energies of dimerization. The recalculated values were then shown to be consistent with a trend predicted by an electrostatic model.

A more rigorous calculation of the configurations of the dimers was made by Berkowitz[39] who also calculated the expected frequencies of two of the infrared active modes. Since the frequencies of the four remaining normal modes of the molecule were not computed, a calculation of the total vibrational entropy of the dimer is not possible from this work. However, an estimate of the other frequencies was made by the author for rubidium chloride which led to a total vibrational entropy for the dimer which was ca. 4 e.u. lower than that estimated by Bauer, Diner, and Porter.[38]

C. The Function, Method, and Scope of this Investigation

Since it is apparent from the foregoing discussion that many discrepancies exist between the reported thermodynamic values for the association equilibria in alkali halide vapors, the present work was undertaken with the object of measuring the characteristics of the equilibria by a more simple and direct method for a sufficient number of salts to reveal any systematic trends. Aside from the intrinsic value of the results themselves, they could also be used to assess the applicability of the various theoretical models that had been proposed to explain the behavior of these vapors.

In this work, the vapor phase association equilibrium of seven alkali halides was studied by the measurement of the molecular weights as a function of temperature. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal bulb of known volume. The choice of fused silica for use in fabrication of the bulb was dictated by the requirements of high temperature dimensional stability, non-reactivity with halide vapors, and the ability to be degassed and sealed off at high temperatures. The pressure measuring device must have its sensing element at a temperature higher than the condensation point of the gas and must be accurate to ±0.1 mm. The gauge used in the measurements reported here was a balanced manometer in which the manometric fluid was molten gold. The two arms of the manometer could be observed through a window in the furnace and the external pressure of argon required to balance the bulb pressure was read from an external mercury manometer. The choice of molten gold for the manometric fluid was made on the basis of the temperature range over which it is a liquid, its lack of chemical reactivity, and its low vapor pressure over the required temperature range.

The salts studied were sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium iodide, rubidium chloride, and cesium chloride. These were chosen to enable correlation of changes in thermodynamic functions with changes in cation and anion. A complete range of cation and anion variation was prevented by the reactivity of the lithium halides and the alkali fluorides with the silica container.

CHAPTER II

EXPERIMENTAL DETAILS

A. The Silica Apparatus

The bulb for containing the salt vapor was of double wall construction, and is pictured in Figure 1. In order to reduce the diffusion of ambient gas into the inner bulb at high temperatures, the space between the walls was evacuated. The outer bulb A was fabricated from 80 mm. i.d., 82 mm. o.d. clear silica tubing with end plates cut from 3.2 mm. thick silica plates made slightly convex to resist distortion at high temperatures. The inner bulb B was fabricated from silica tubing 77 mm. i.d., 79 mm. o.d. The bulb length was _ca_. 16 cm. providing a volume of _ca_. 800 ml. The pressure transmitting tube O, connecting the top of the bulb with the top of the manometer mounted vertically above it, was 8 mm. i.d. and 30 cm. in length. The manometer tube J was 10 mm. i.d. and contained 130 g. of gold (7.6 cc. when molten) giving a height of 3 cm. in each arm. Additional mechanical support of the bulb was provided by a 4 mm. silica rod M which bridged the manometer. The volume of the inner bulb was determined by measuring the amount of water required to fill it. The pressure balancing arm L was connected to a Pyrex pressure manifold through a graded seal located away from the high temperature region. Samples were introduced by opening the loading tube F. The system was evacuated through G and sealed at E.

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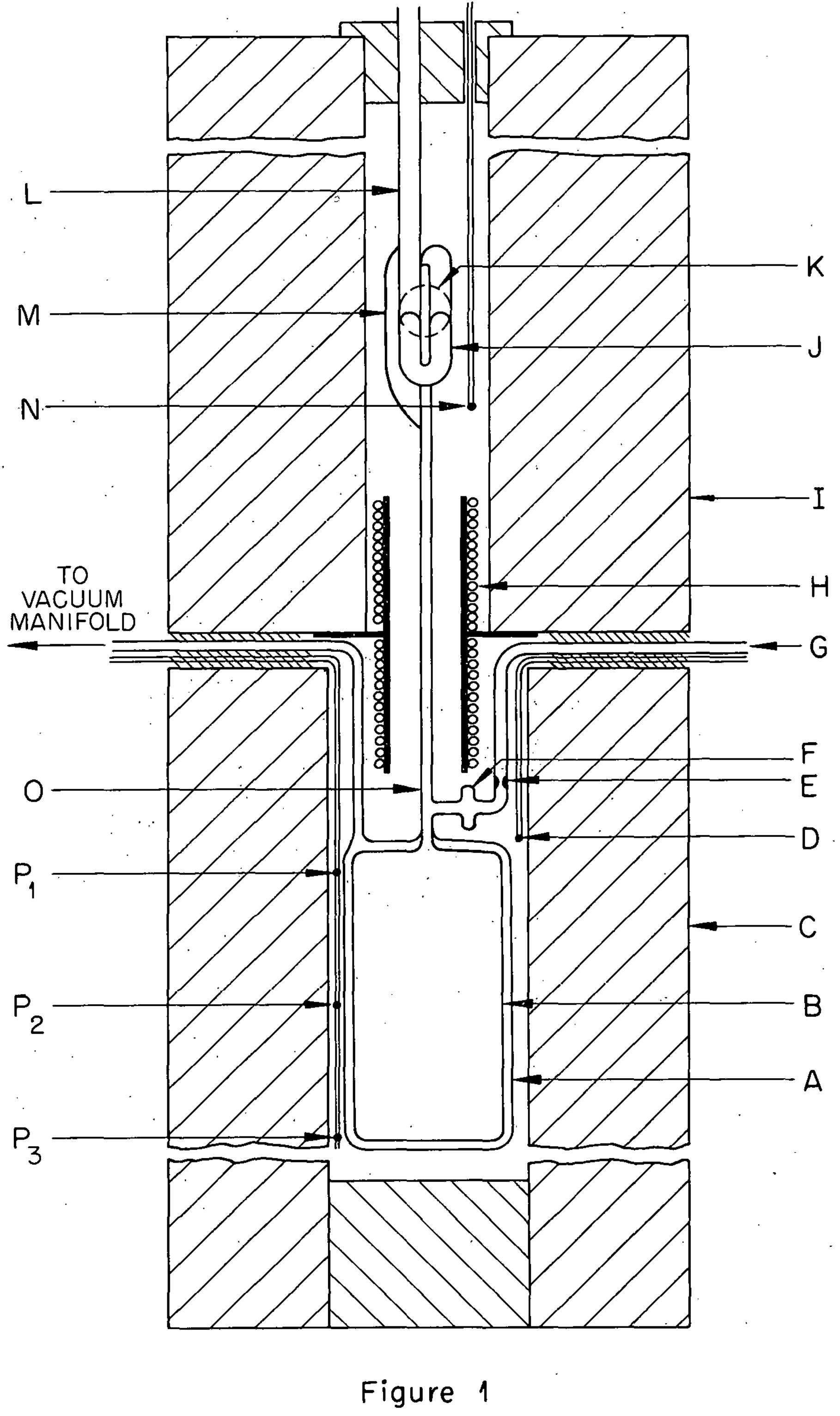

Figure 1
BULB AND GOLD MANOMETER APPARATUS

B. Furnaces

The heating system consisted of three electric tube furnaces. The bulb was heated in a Kanthal-wound tube furnace C, 16 in. long, with a 3.5 in. i.d.* Its temperature was controlled by a Speedomax recording potentiometer** with a 10 millivolt span, coupled with a Leeds and Northrup DAT controller,** using a chromel-alumel thermocouple D as the sensing element. Gradients over the length of the bulb were adjusted by shunting sections of the furnace winding. With this system, the temperature could be maintained constant to ±0.5° for several hours and the gradients over the length of the bulb ranged from 1° at the lowest operating temperature to 4° at the highest. To facilitate loading, pumping, and sealing, the furnace could be raised and lowered 4.5 in. by a pulley and counterweight system.

The manometer was heated by a Kanthal-wound furnace I, 16 in. long, and having a 2.5 in. bore.* This furnace was fitted with two 1 in. diameter windows K set at 180° to each other and centered 8 in. from the ends of the furnace. The temperature control of this furnace was accomplished with a Micromax potentiometer** coupled with a DAT controller,** using a chromel-alumel thermocouple. This furnace was mounted in a fixed position directly above the bulb furnace so as to leave a 0.5 in. gap between furnaces when the lower furnace was raised.

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*Marshall Furnace Company, Columbus, Ohio.

**Leeds and Northrup Company, Philadelphia, Pa.

In order to prevent condensation in the pressure transmitting tube, a third tube furnace H was mounted firmly to the bottom of the manometer furnace with 3 in. extending into the upper furnace tube and 2.5 in. into the lower furnace. The heating element consisted of a magnesium oxide swaged Kanthal heater wire in a 0.125 in. inconel sheath.[*] The furnace was made by wrapping the heating element, in the form of a bifilar helix, around a 2.5 in. i.d. inconel tube 6 in. long, and welding the element to the tube at both ends.

The upper end of furnace I and the lower end of furnace C were sealed with fire brick and fire brick dust and the gap between the two was lagged with Fiberfrax[**] packing.

C. Temperature Measurement

Temperatures were measured with three platinum vs. platinum-10-per cent rodium thermocouples (P_1, P_2, P_3) placed along the length of the bulb. The thermocouples were made of temperature standard quality wire[***] (0.020 in. dia.), which had been calibrated against a Bureau of Standards calibrated thermocouple. The differences were in all cases less than 1° at 1200°K. The thermocouple voltages, referred to a 0°C. ice-water cold junction, were measured with a precision potentiometer,[****]

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[*] Aeropak Heating Elements, Aero Research Instrument Co., Inc., Chicago, Illinois.

[**] The Carborundum Company, Perth Amboy, New Jersey.

[***] The American Platinum Works, Newark, N. J.

[****] Type B, Rubicon Co., Philadelphia, Pa.

using a Leeds and Northrup* galvanometer with a sensitivity of 0.42 microvolts per millimeter to indicate the balance point.

D. The Gold Manometer

The purest gold commercially available contains considerable amounts of dissolved gas and small amounts of other impurities which tend to collect at the liquid surface. For this reason, it was further purified as follows. Gold wire was first degreased and washed in hot nitric acid. It was then melted in a silica tube under vacuum and pumped for several hours. After cooling, the cast ingot was removed and cleaned again in boiling nitric acid.

Once the gold had been melted in the manometer, the manometer temperature was not allowed to drop below 600°C., since the silica would crack upon cooling to about 500°C. This effect may be due to a slight wetting of the silica by the gold, although the markedly convex appearance of the gold meniscus suggests that the silica is not wet. The temperature at which fracture occurs might be associated with the sharp decrease in coefficient of expansion of quartz occurring at 550°C., although no such transition is observed in vitreous silica.[40] According to a recent report, Moore and Thornton[41] have observed that gold will not stick to polished fused silica unless oxygen is present at ca. 0.1 atmospheres. However, since all melting in the present work was done under vacuum, the above findings did not seem to apply to this case.

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*Cat. No. 2430A, Leeds and Northrup Company, Philadelphia, Pa.

E. Sample Preparation and Purity

Those halides which were available in the form of pure single crystals from the Harshaw Chemical Company* were used without any further purification. In these cases, a large single crystal was cleaved and a single piece of this crystal, removed from the center, constituted a sample. Single crystals of sodium iodide, rubidium chloride, and cesium chloride were not readily available and were prepared by heating the reagent grade salt under vacuum to 500°C. and then melting it in an argon atmosphere.[42] Optically clear crystals were selected and single pieces cleaved from the center of a crystal constituted a sample.

Spectroscopic analysis** indicated that the rubidium chloride which had been purified by melting contained 0.6 per cent cesium, and 0.4 per cent potassium. However, the analyst found it necessary to use all of the remaining material to prepare his sample since only a few grams of rubidium chloride with even this degree of purity were available. Hence, the analysis does not reflect the degree of purification attained in the selected crystal pieces used in the experiment.

The remainder of the halides examined were found to contain less than 0.1 per cent of impurities.

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*Harshaw Chemical Co., Newark, N. J.

**The author would like to thank Mr. C. Feldman and his group for performing the analysis.

F. System Preparation

When a new silica-gold apparatus was installed, the entire system was heated to 1000°C. and evacuated ($p = 10^{-5}$ mm.) for at least 24 hours in an external atmosphere of argon. The function of this pretreatment was to remove dissolved gas from the silica and gold. The problem of dissolved gas in silica diffusing into an evacuated vessel had been noted in 1927 by Biltz and Müller,[43] who concluded that it was impossible to seal a silica bulb under vacuum and maintain the vacuum after heating. More recently, Machol and Westrum[44] have analyzed this gas and found it to be principally carbon monoxide, which presumably comes from the acetylene-oxygen flame used to melt the silica and which is dissolved in the silica during the manufacturing process. However, it was found by the above authors and verified by this author that this gas can be removed by prolonged heating and pumping.

After degassing for 24 hours, the gold was melted in the manometer and any remaining dissolved gas which formed bubbles in the gold was removed by vibrating the manometer while it was evacuated on both sides.

G. Procedure

Following the pretreatment, the gold was solidified and cooled to _ca_. 800°C. The bulb furnace was cooled and lowered, and argon was then admitted to the bulb. The system was then opened at F, the sample dropped in, and the system resealed at F. The bulb containing the sample was then evacuated and heated to 300°C. for several hours, after which the bulb was sealed under vacuum at E. The bulb furnace was then raised into place and the 0.5 in. gap between the upper and lower furnaces was packed with "Fiberfrax" insulation and the silica system surrounded by an argon atmosphere.

The gold in the manometer was then melted and the temperature of the bulb furnace increased. As the pressure in the bulb increased, the compensating pressure on the other side of the gold manometer was also increased by admitting argon to the manifold. Adjustment of the pressure in the manifold was accomplished by manipulation of two vacuum stopcocks, one connected to a vacuum system and the other to a bulb containing argon at a pressure slightly above the maximum anticipated pressure to be measured. Flow rates through the stopcocks were kept at a convenient level by plugging the bores entirely with paraffin and then piercing holes with a 0.004 in. tungsten wire.

When temperature equilibrium was reached, the pressure in the bulb was precisely balanced as indicated by a horizontal hairline in the telescope of a cathetometer. The cathetometer was then rotated to view a mercury manometer mounted adjacent to the furnace and the argon pressure was read. The temperature of the mercury manometer was kept between 25 and 27°C. by shielding it from the radiant furnace heat with a sheet of aluminum stapled to asbestos, and continually passing a stream of cool air (from the compressed air line) over it. Temperatures indicated by the three thermocouples placed along the length of the bulb were then recorded.

Since it had been observed that some gas apparently diffused into the bulb, especially at high temperatures, the temperature of the bulb was periodically dropped below the point where the salt vapor pressure was measurable and a determination of the residual gas pressure was made with the manometer.

To change samples, the vacuum was broken and the pumping tube reconnected. The old sample was then distilled out of the bulb to a cold portion of the pumping tube and a new sample introduced.

A diagram of the system is given in Figure 2.

H. Sources of Experimental Error

1. Reactivity of the Alkali Halides with Silica and Gold

In order to determine the reactivity of the halides investigated with the system that was to contain them, ampules made of 15 mm. i.d. silica tubing 10 inches long were loaded with some gold (ca. 0.5 cc.) and a weighed sample (100 mg.) of salt. The salts tested were sodium iodide, sodium chloride, and potassium chloride. The ampules were evacuated, sealed, and placed in a muffle furnace at 1100°C. for twenty-four hours, after which they were opened and the samples removed by dissolving them in water. The pH of the solutions was measured and it was found, in all cases, to be identical to that of the solvent, indicating that no alkali oxides had been formed. A quantitative analysis for the halide ion agreed with the original sample weight to within a ±0.1 per cent.

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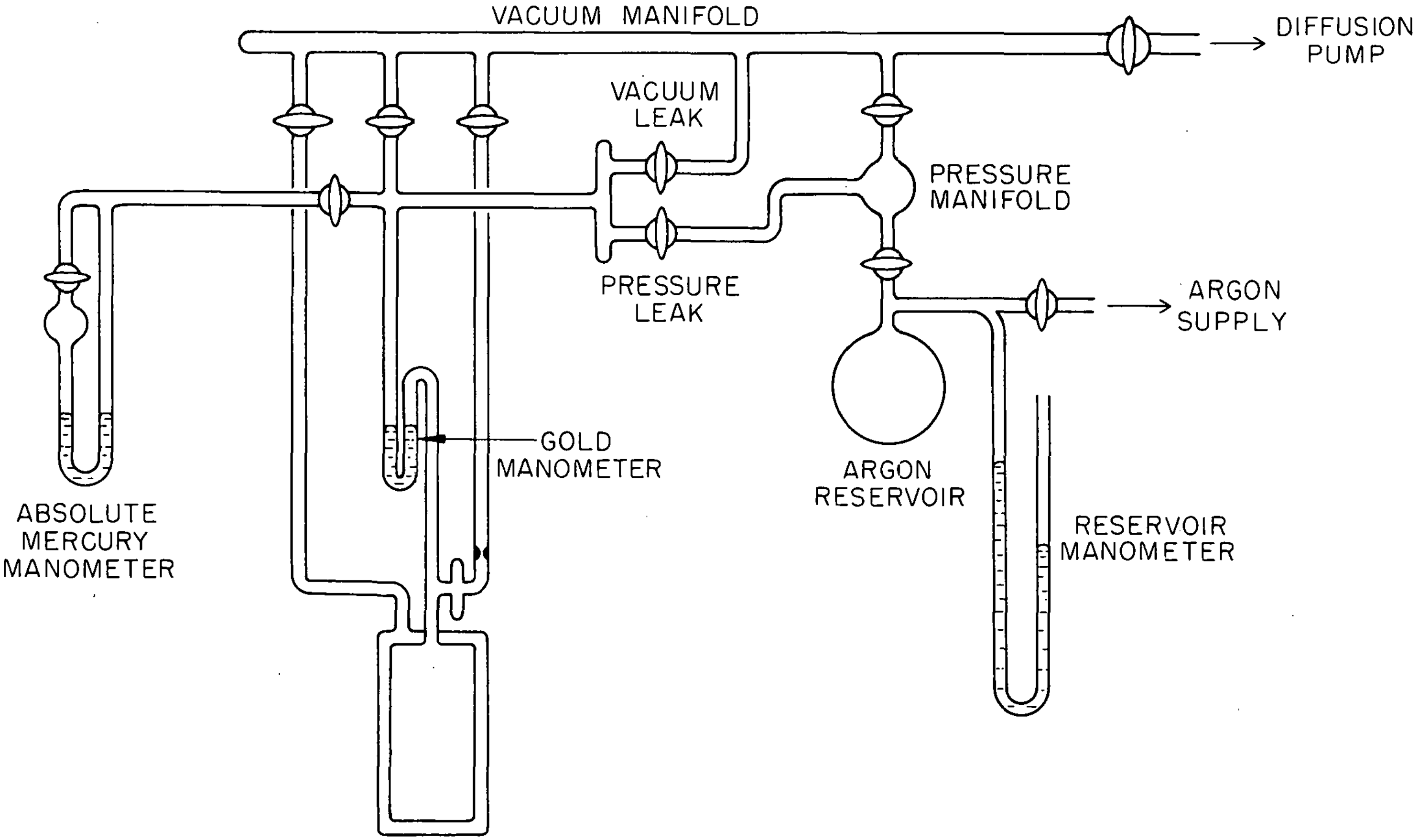

Figure 2
PRESSURE BALANCING SYSTEM

The only evidence for reaction, or diffusion of the halide into the silica, encountered during the course of the experiments was with a sample of potassium chloride which was heated to 1430°K. for a period of fifteen minutes. When the temperature was lowered to 1350°K., the pressure was 5 per cent less than the value that had been recorded previously at this temperature. A repetition of this experiment with another sample indicated that no loss occurred up to 1400°K., and that, while a loss was again observed upon raising the temperature to 1430°K., quantitative measurement of the rate was difficult due to the simultaneous diffusion of ambient gas into the system at these high temperatures.

2. Residual Gas Correction

Gases are known to diffuse through silica, especially at higher temperatures. Since oxygen would react with iodides and perhaps bromides at the experimental temperatures, the apparatus was surrounded with argon by maintaining a continuous flow of the gas through the furnace. Argon was chosen because of its inertness and its relatively low rate of diffusion through silica. The value quoted by Dushman[45] for the permability constant of silica to argon at 1173°K. is 0.58×10^{-9} cubic centimeters (S.T.P.) per second, per square centimeter of surface, per millimeter thickness, per centimeter pressure. For a bulb of the dimensions used in the experiment, a leak rate of only 0.03 mm. per hour would be expected and, as a result, only a single bulb was used for the measurements on sodium iodide and sodium chloride (the first two salts to be investigated). However, the necessity of operating at higher temperatures caused an increase in the rate of diffusion, and the observed leak rate (corrected to 0°C.) was found to vary from 0.4 mm. per hour at 1350°K. to essentially zero at 1200°K. Therefore, a correction was applied to the salt pressure measurements by measuring the residual pressure in the bulb at 500°K., correcting this to temperatures at which the salt pressure was measured, and subtracting from total observed pressure. The largest pressure correction required was 5 mm. in a total pressure of 30 mm. in a sodium iodide experiment. Confidence in the validity of this correction was gained when it was observed that subtraction of the temperature corrected residual gas pressure from total pressure measurements, made at five different temperatures below complete vaporization of the sample (i.e. vapor pressure), yielded values which were in good agreement with previously reported values of vapor pressure. Moreover, when a measurement was made on a separate sample heated rapidly to 1250°K. and then rapidly cooled to avoid any measurable leak up, the pressure measured was in good agreement with that obtained at the same temperature for the previous sample when the residual gas correction had been applied. In addition, the data were self-consistent and reproducible over the entire range of total pressure and pressure correction values.

If the source of permanent gas was either the argon diffusing through the silica or the release of carbon monoxide dissolved in silica,[44] the above correction was valid. There was, however, a bare possibility that the sodium iodide reacted with the silica to yield iodine which would be measured as a permanent gas. To determine this, a 41-mg. sample was kept at 1350°K. for eight hours, after which a total gas pressure of 2 mm. was observed at 400°K.

Visual comparison of the color of the gas in the bulb with a similar bulb containing iodine gas at known pressures indicated that, if any iodine gas was present, an upper limit could be placed at a value of 0.1 mm. A reaction of this sort would affect the value of the equilibrium constant in two ways. First, the effective sample weight would be diminished, and second, the residual gas correction extrapolated from a low temperature should be increased to take into account the dissociation of iodine at high temperature. These effects tend to cancel each other and the combined effect, when applied to the sodium iodide measurements, would alter the value of the equilibrium constant by only 2 per cent at most.

3. Determinate Errors in Measurement

Errors in the measurement of sample weight and volume (after correction for thermal expansion of the silica bulb) amounted to less than one per cent. Absolute temperature measurements were accurate to better than ±1° (0.1 per cent). Temperature gradients over the length of the bulb were, in most cases, kept to within 2° but in some cases the gradient was as much as 4°. Since a temperature difference of 4° will change the equilibrium constant by as much as 3 per cent in some cases, a weighted average temperature was always used in calculating the equilibrium constants. The larger temperature gradients existing along the pressure transmitting tube and the manometer itself did not significantly contribute to the error, since the volume involved was only 1.5 per cent of the total. Pressure measurements were found to be reproducible to within ±0.05 mm., which introduced a maximum error of less than one per cent in the measured pressure range (10 to

40 mm.). A precise knowledge of the density of the molten gold (ca. 17.0 g. cc.$^{-1}$) is not necessary since a null method was used.

I. Preliminary Investigations

Before arriving at the final method of measurement, which was described above, several other techniques were tried with only limited success. It may, therefore, be instructive to consider them briefly and to indicate the causes of their limitations.

1. A High Temperature Victor-Meyer Experiment

The apparatus used in this experiment is pictured in Figure 3. A weighed sample of the alkali halide contained in a small evacuated silica ampule was placed at the bottom of a stainless steel vessel having a volume of about one liter. The vessel contained stainless steel baffle plates to decrease the diffusion rate of the gases and was fitted with a plunger with which the capsule could be broken. A capillary tube connected this vessel to a gas measuring system. The volume of the system could be varied by means of a leveling bulb which controlled the height of a column of mercury in a gas burette.

The procedure followed was to evacuate the system, raise the temperature to the desired point, fill the system with argon gas to a pressure of about 30 mm., crush the ampule, and measure the increase in volume necessary to maintain constant pressure. The apparent molecular weight, M_o, could then be determined from

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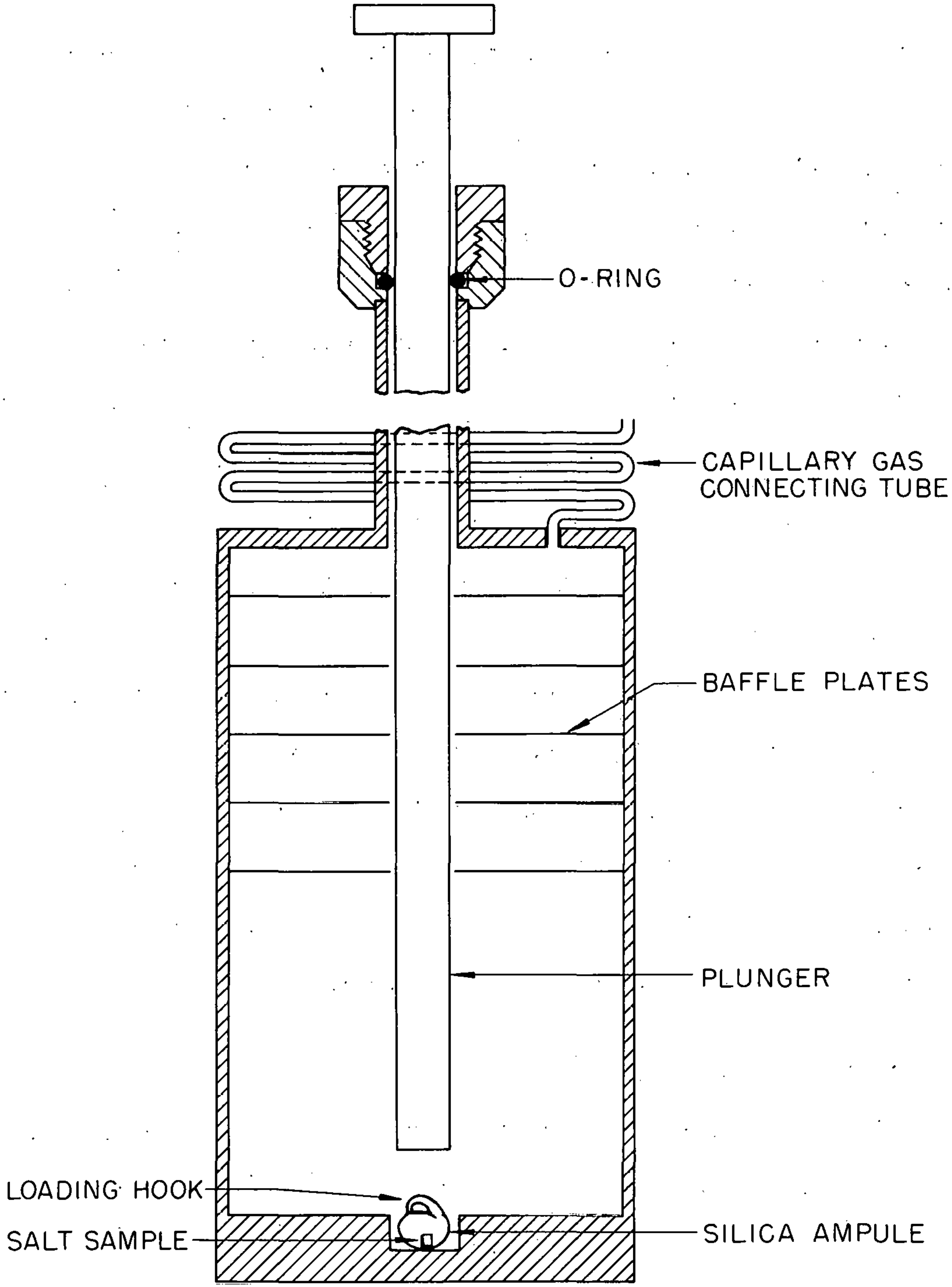

Figure 3
HIGH TEMPERATURE VICTOR-MEYER APPARATUS

$$M_o = \frac{g\ RT}{P\Delta V}$$

In practice, two principal difficulties were encountered. First, since the halide vapor diffused to regions of lower temperature and condensed, the value of ΔV decreased with time. This effect could be partially compensated by measuring ΔV as a function of time and extrapolating to zero time. Secondly, even though the stainless steel vessel had been continuously evacuated for several days at 1200°K. to remove dissolved gases from the metal, small pressure increases were still observable over the relatively short times necessary for an experiment, due either to further degassing of the metal or to the diffusion of ambient gas through it.

Aside from the experimental difficulties involved in this approach, there are two inherent faults in this method. First, a single sample yields only a single determination, and, second, the molecular weight observed is a function of the degree of mixing with the inert gas, since the degree of association is a function of concentration.

Several measurements were made by this technique on sodium chloride vapor, and, even though the data obtained were not sufficiently precise to report here, it can be stated that they were in qualitative agreement with those later obtained by more precise methods.

2. The Use of a Silica Bourdon Gauge

In this modification of the constant volume technique, the pressure sensing element was a silica Bourdon gauge,[46] which was made by collapsing one hemisphere of a thin walled silica bulb so as to give the configuration of a hollow spoon. A small pressure difference between the inside and outside of the spoon manifested itself in a lateral displacement of the end of the spoon. This displacement was magnified by a silica fiber 15 cm. in length, which was attached to the end of the spoon and extended outside the furnace which surrounded the apparatus. The gauge was contained in a silica tube and the external pressure of argon necessary to bring the pointer to the null position was a measure of the pressure inside the gauge. Gauges of this type were made which had a sensitivity of 0.2 mm. displacement for a 1.0 mm. pressure difference and, with the use of appropriate optical methods, the sensitivity of the gauge was approximately 0.1 mm. The primary difficulty with this method was that at temperatures above 1200°K. diffusion of the argon balancing gas through the thin silica membrane was appreciable, and an argon pressure build-up inside the bulb obfuscated the true salt pressure. This pressure measuring technique is usable at temperatures up to 800°C., as has recently been shown by Westrum and Machol.[47]

3. Electrical Capacitance Probe Measurement of the Gold Manometer Level

The first attempt to use the gold manometer utilized an electromechanical method for the determination of the manometer liquid level. Since it was then not necessary to see the manometer itself, the entire silica system could be shortened and contained in one tube furnace without a viewing port. An auxiliary furnace, similar in construction but smaller than the intermediate furnace used in the final apparatus, was built to surround the manometer and was itself contained within the larger furnace. The auxiliary furnace allowed the gold in the manometer to be melted, even if the measuring bulb temperature was below the melting point. Moreover, the manometer temperature could be maintained above 600°C., to prevent cracking the silica, while the sample was being changed in the bulb. The construction of the probe is shown in Figure 4. The probe was positioned by a stub micrometer through a vacuum tight O-ring seal, and rotation was eliminated by coupling through a thrust bearing and the use of a constraining pin. The combination of a platinum tube surrounding the silica tube containing the gold constituted an electrical capacitor, and contact of the probe tip with the surface of the gold was indicated by an imbalance in a capacitance bridge. This arrangement obviated the use of a second electrode in contact with the molten gold and was capable of high precision. However, the reproducibility of the zero point from day to day was not good, possibly due to removal of some material from the tungsten tip, to a variation in the thermal expansion of the probe assembly, and to a gas leak-up in the sealed bulb. Rather than attempting to assess the relative contributions of these errors, it was decided to change the arrangement to its final form so that both arms of the manometer could be viewed simultaneously.

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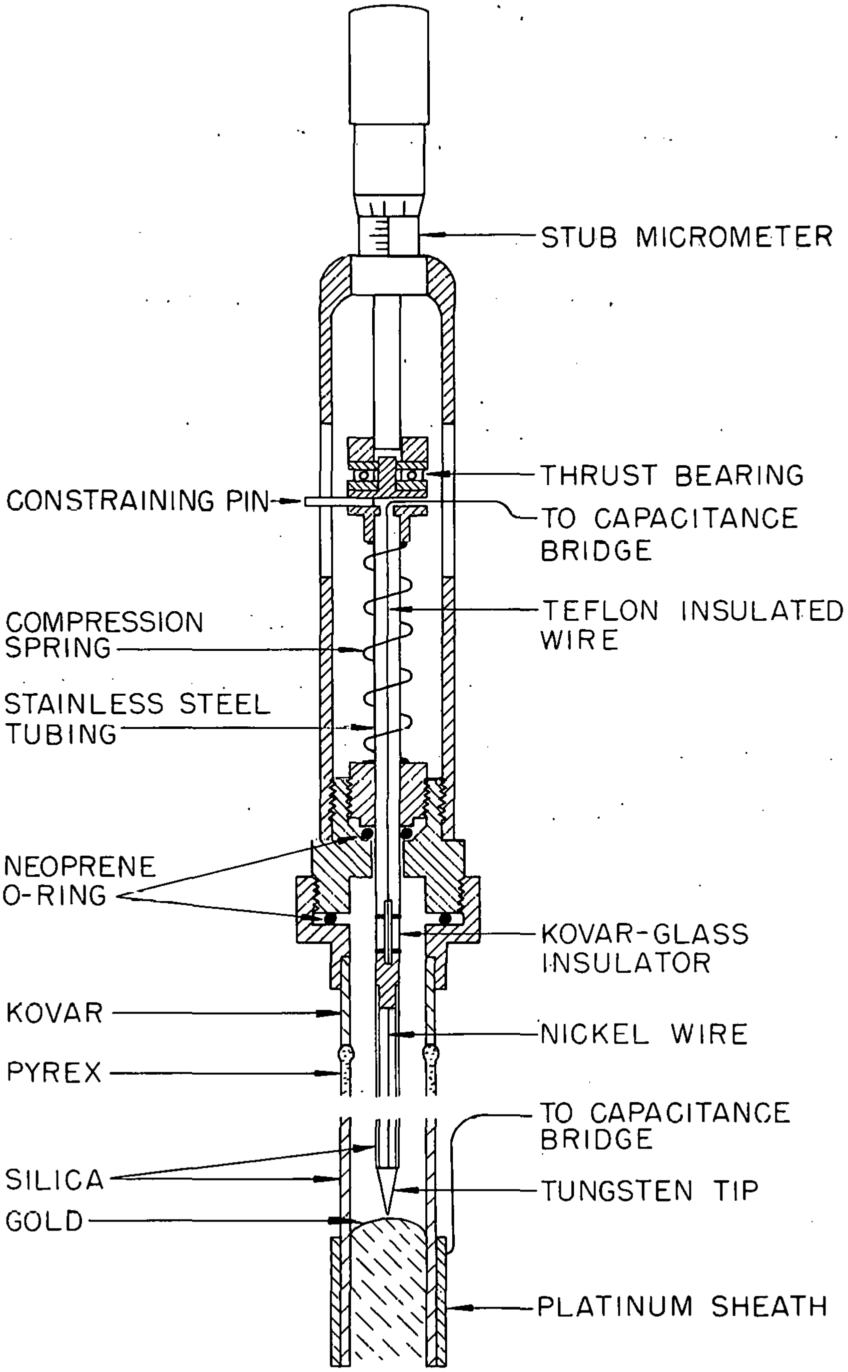

Figure 4

ELECTRICAL CAPACITANCE
PROBE ASSEMBLY

CHAPTER III

RESULTS

A. Calculation of Thermodynamic Quantities

If the assumption is made that the only two molecular species present in the gas are monomer and dimer,* the reaction is

$$(MX)_2 \rightleftharpoons 2\ MX,$$

and the equilibrium constant at constant volume is defined by

$$K_d = \frac{C_m^2}{C_d},$$

where C_m and C_d are the concentrations of monomer and dimer, respectively.

The experimentally measured pressure and temperature, when taken with the previously determined values of the volume and the sample weight, yield the average molecular weight of the gas by the ideal gas law,

$$M_o = \frac{gR'T}{PV},$$

The mole fraction of dimer is given by

$$N_d = (M_o/M_f) - 1,$$

where M_f is the formula weight of the alkali halide. The value of the equilibrium constant for a standard state of one mole per liter is then obtained from

$$K_d = \frac{C_m^2}{C_d} = \frac{P}{R'T}\frac{N_m^2}{N_d}$$

---

*The validity of the assumptions, concerning the molecular species present and the applicability of the ideal gas law, is discussed in Chapter IV.

where P is in atmospheres and R' is the gas constant in l. atm. mole^{-1} deg.^{-1}

The change in internal energy (ΔE^{o} in cal. mole^{-1}) accompanying dissociation of the dimer is obtained from the slope of the log K_d vs. 1/T line by the method of least squares since*

$$d \ln K_d / d\,(1/T) = \Delta E^{o}/R,$$

where R is the gas constant in cal. mole^{-1} deg.^{-1} The standard change in entropy for a standard state of one mole per liter, ΔS_c^{o}, was obtained from the zero intercept of this line since

$$-\log K_d = (\Delta E^{o}/2.303R)\,(1/T) - \Delta S_c^{o}$$

The more commonly used entropy change for a standard state of one atmosphere ΔS^{o} was then obtained from

$$\Delta S^{o} = \Delta S_c^{o} + R\,(1 + \ln R'T).$$

B. The Experimental Data and Derived Quantities

The data obtained, and the thermodynamic quantities derived therefrom, are set forth in tabular and graphical form in Tables I-VII and Figures 5-11. For each of the seven alkali halides investigated, a table lists the measured temperature and pressure for the given sample weight and bulb volume. Following these are listed the average molecular weight, the mole

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*The correction to ΔE^{o} for the difference in heat capacity of the reactants and products (ΔC_v) was not included in this calculation since the precision of the data over the measured temperature range was not sufficient to warrant this correction (Chapter IV).

fraction of dimer, the logarithm of the equilibrium constant, and the deviations of log K_d from the smoothed value, log K_d'. In an additional column, labeled "Chron.", is listed the chronological order in which the measurements were made.

Together with each table is a graph of the equilibrium constant versus the reciprocal of the absolute temperature. The equation for the straight line obtained by the method of least squares is also presented on the figure.

The values of the equilibrium constants at 1300°K. and a summary of the standard energy and entropy changes for dissociation, together with the standard errors in these quantities obtained from the least squares treatment, are presented in Table VIII. An additional column lists the standard error of fit σ_f which for a linear fit is defined by

$$\sigma_f = \left[\frac{\sum_{i=1}^{n} r_i^2}{n - 2}\right]^{1/2}$$

where $\sum r_i^2$ is the sum of the squares of the residuals and n is the number of observations. Considering the limited range of the measurements in the log K_d <u>vs</u>. 1/T coordinate system, the value of σ_f may be interpreted as approximating the average deviation in log K_d.

TABLE I

DATA AND EQUILIBRIUM CONSTANTS FOR Na_2Cl_2 DISSOCIATION

	P(mm.)	T(°K.)	M_o	N_d	$-\log K_d$	$\log \frac{K'_d}{K_d}$	Chron.
	8.80	1277	93.61	.601	4.532	-.006	4
	9.15	1289	90.93	.555	4.392	.057	5
	9.35	1304	90.13	.542	4.352	.001	3
Sample No. 1	9.90	1331	87.21	.491	4.202	-.014	2
8.24 mg.	10.35	1355	84.64	.447	4.077	-.023	8
V = 795 cc.	10.40	1357	84.41	.444	4.068	-.030	1
	10.65	1367	83.11	.422	4.005	-.023	9
	11.05	1381	80.63	.379	3.884	.022	7
	11.75	1406	77.40	.324	3.724	.044	6
Sample No. 2	7.65	1296	89.57	.533	4.413	-.022	2
6.74 mg.	8.00	1315	87.04	.489	4.288	-.011	1
V = 795 cc.	8.75	1357	82.00	.403	4.050	-.014	3

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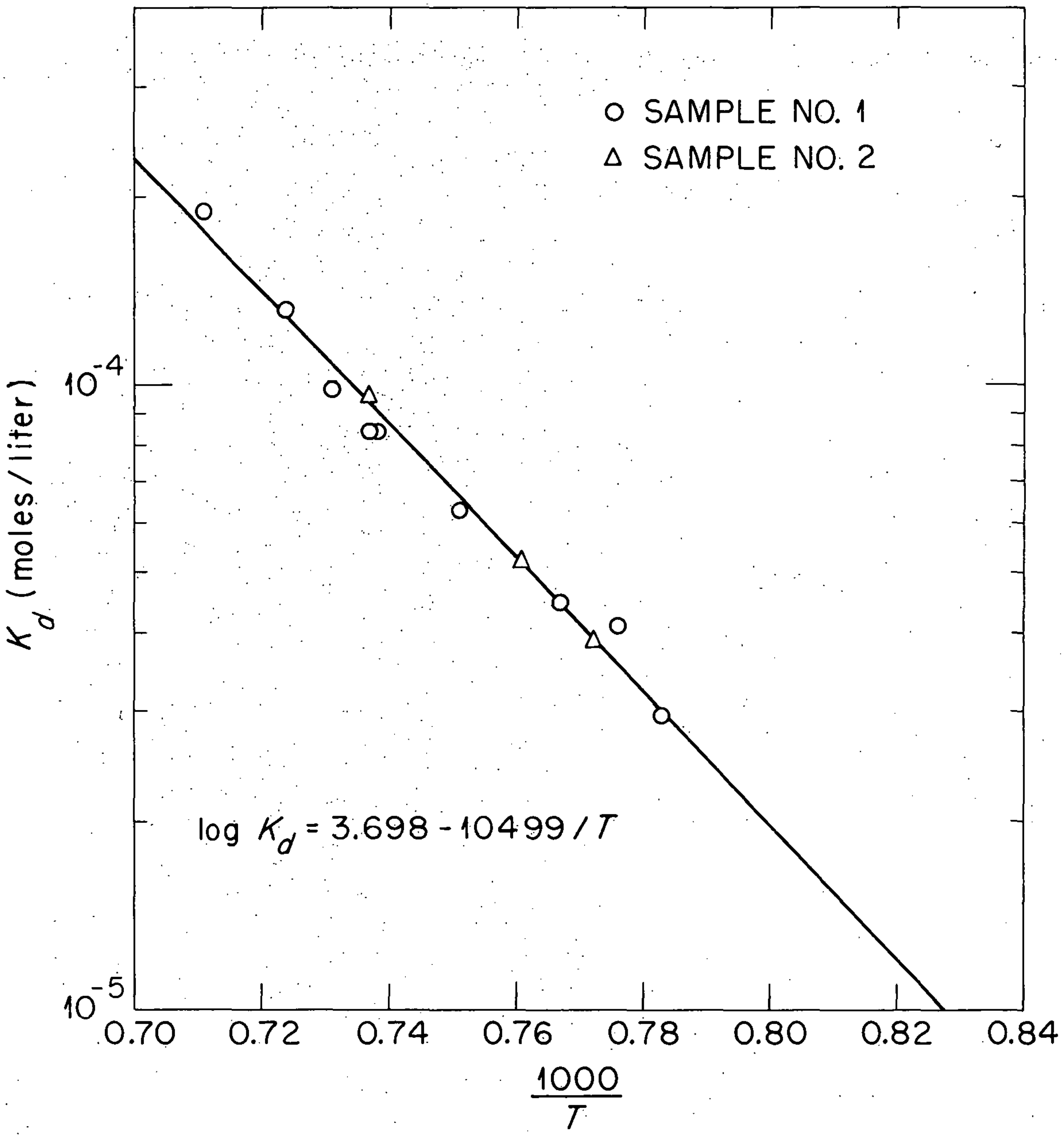

Figure 5
DISSOCIATION CONSTANT OF SODIUM CHLORIDE DIMER
vs RECIPROCAL TEMPERATURE

TABLE II

DATA AND EQUILIBRIUM CONSTANTS FOR Na_2Br_2 DISSOCIATION

	P(mm.)	T(°K.)	M_o	N_d	$-\log K_d$	$\log \frac{K'_d}{K_d}$	Chron.
	26.00	1293	139.9	.360	3.435	.006	9
	27.45	1316	134.9	.311	3.292	.023	8
	29.05	1343	130.1	.264	3.148	.023	7
Sample No. 1	29.40	1351	129.3	.257	3.124	.007	1
60.2 mg.	30.20	1368	127.5	.238	3.066	-.022	6
V = 685 cc.	31.15	1384	125.0	.215	2.985	-.021	2
	32.15	1398	122.3	.189	2.892	.005	3
	32.40	1408	122.3	.188	2.889	-.040	4
	33.20	1421	120.4	.171	2.820	-.032	5
	34.40	1317	140.5	.366	3.336	-.027	9
	35.35	1330	138.1	.342	3.268	-.028	8
	36.55	1341	134.6	.309	3.169	.013	7
Sample No. 2	37.85	1361	132.1	.284	3.094	-.015	6
40.3 mg.	39.10	1375	129.0	.254	3.001	.008	1
V = 685 cc.	39.70	1382	127.7	.242	2.960	.015	2
	41.15	1398	124.7	.212	2.858	.039	3
	42.25	1413	122.7	.193	2.788	.037	4
	43.75	1434	120.3	.175	2.720	.009	5

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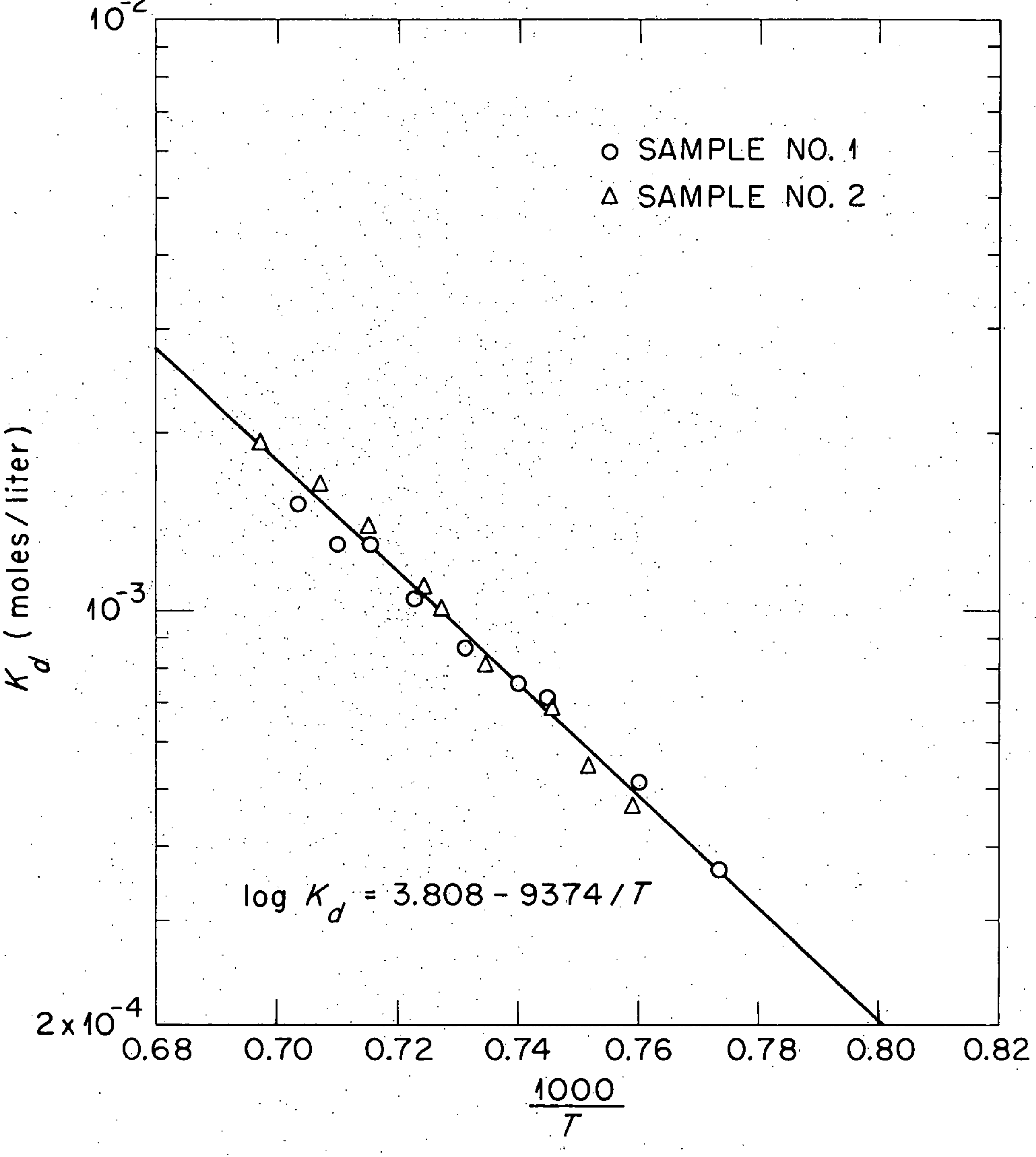

Figure 6
DISSOCIATION CONSTANT OF SODIUM BROMIDE DIMER
vs RECIPROCAL TEMPERATURE

TABLE III

DATA AND EQUILIBRIUM CONSTANTS FOR Na_2I_2 DISSOCIATION

	P(mm.)	T(°K.)	M_o	N_d	$-\log K_d$	$\log \frac{K'_d}{K_d}$	Chron.
	17.60	1212	223.0	.488	3.902	-.062	6
	19.80	1256	205.1	.368	3.561	.025	7
Sample No. 1	20.00	1262	204.1	.361	3.542	.011	4
42.0 mg.	21.25	1295	197.1	.315	3.407	-.032	2
V = 796 cc.	21.35	1297	196.1	.308	3.386	-.022	5
	21.75	1301	193.2	.288	3.327	-.016	3
	23.95	1344	181.2	.208	3.066	.062	8
	24.05	1353	181.5	.210	3.074	.010	1
	8.25	1179	210.8	.406	4.009	.034	1
	8.80	1207	203.2	.356	3.866	.004	2
Sample No. 2	9.35	1233	195.0	.301	3.704	.012	3
20.0 mg.	9.85	1260	188.9	.260	3.578	-.003	4
Vol. 836 cc.	10.40	1286	182.3	.216	3.431	.013	5
	10.90	1314	177.5	.184	3.315	-.022	6
	11.35	1337	174.0	.161	3.224	-.047	7

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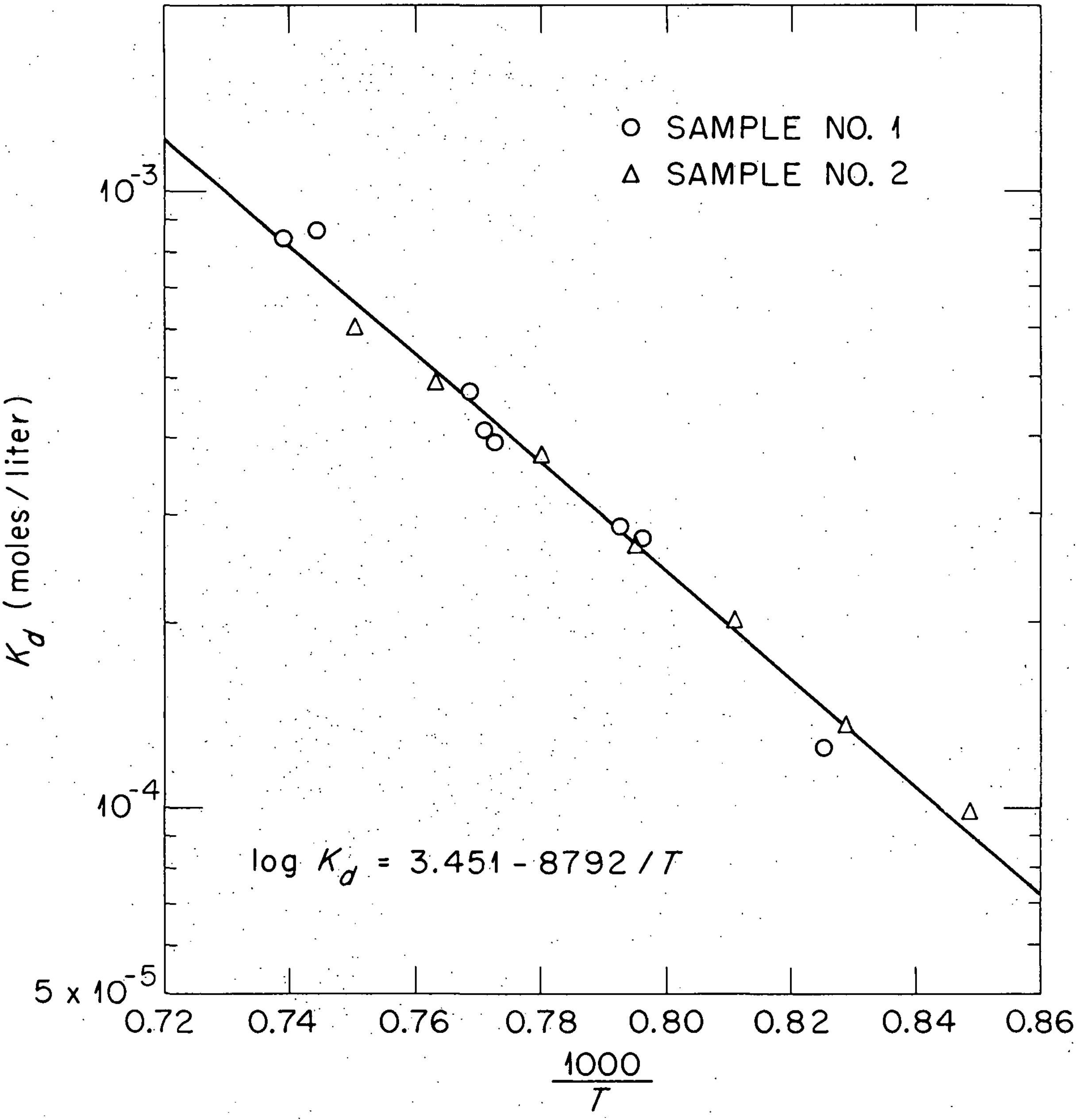

Figure 7
DISSOCIATION CONSTANT OF SODIUM IODIDE DIMER
vs RECIPROCAL TEMPERATURE

TABLE IV

DATA AND EQUILIBRIUM CONSTANTS FOR K_2Cl_2 DISSOCIATION

	P(mm.)	T(°K.)	M_o	N_d	$-\log K_d$	$\log \frac{K'_d}{K_d}$	Chron.
Sample No. 1 29.0 mg. V = 685 cc.	36.75	1364	98.01	.315	3.190	-.016	1
	38.05	1377	95.56	.282	3.091	.021	2
	38.30	1385	95.49	.281	3.088	-.014	3
	39.10	1389	93.81	.258	3.017	.039	4
	39.60	1404	93.62	.256	3.009	-.023	5
Sample No. 2 15.8 mg. V = 685 cc.	19.20	1310	98.16	.317	3.460	-.013	1
	20.30	1330	94.26	.264	3.300	.042	2
	20.50	1343	94.25	.264	3.300	-.022	9
	20.80	1346	93.10	.249	3.250	.013	3
	21.00	1353	92.69	.243	3.232	-.004	8
	21.20	1360	92.29	.238	3.214	-.021	4
	21.65	1371	91.11	.222	3.161	-.020	5
	22.40	1383	88.83	.191	3.052	.032	6
	22.55	1388	88.55	.189	3.099	-.040	10
	22.90	1397	87.77	.176	2.993	.025	7

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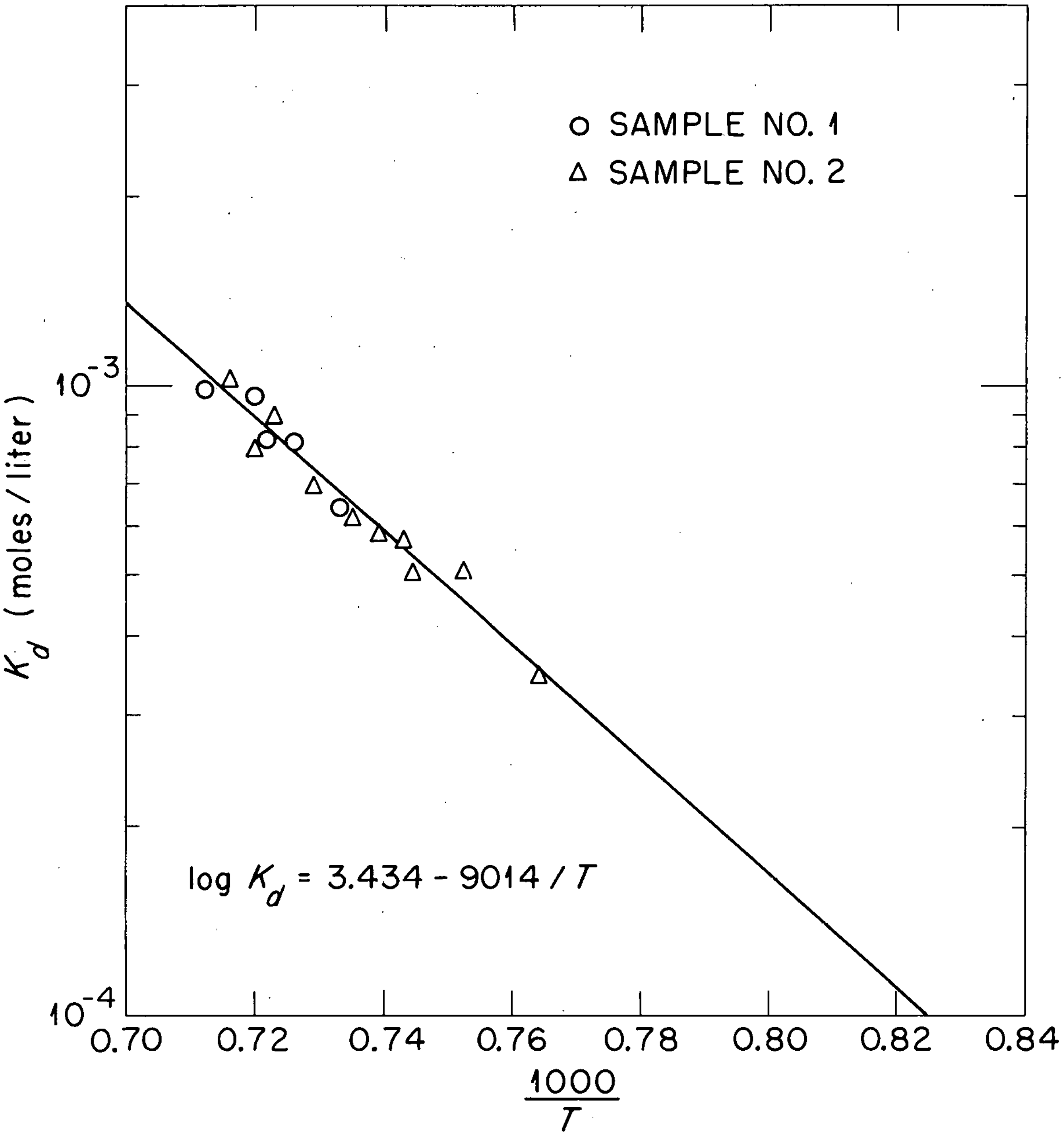

Figure 8
DISSOCIATION CONSTANT OF POTASSIUM CHLORIDE DIMER
vs RECIPROCAL TEMPERATURE

TABLE V

DATA AND EQUILIBRIUM CONSTANTS FOR K_2I_2 DISSOCIATION

	P(mm.)	T(°K.)	M_o	N_d	$-\log K_d$	$\log \frac{K'_d}{K_d}$	Chron.
Sample No. 1 37.8 mg. V = 675 cc.	20.85	1226	205.4	.237	3.175	.023	10
	21.20	1240	204.3	.231	3.152	-.025	9
	21.85	1253	200.3	.207	3.070	-.005	8
	22.35	1262	197.2	.188	3.002	.019	7
	22.80	1275	195.3	.177	2.954	.006	6
	23.80	1300	190.8	.149	2.847	-.001	5
	24.50	1314	187.3	.128	2.752	.031	4
	25.50	1341	183.7	.106	2.640	.027	3
	26.25	1364	181.5	.093	2.565	.007	1
	27.05	1385	178.8	.077	2.462	.025	2
Sample No. 2 61.45 mg. V = 675 cc.	35.90	1292	203.7	.227	2.931	-.049	1
	38.10	1324	196.7	.185	2.780	-.040	2
	40.55	1355	189.2	.139	2.593	.016	3
	42.00	1380	186.0	.120	2.503	.004	4
	42.70	1395	184.9	.114	2.471	-.022	5
	43.50	1408	183.2	.104	2.416	-.017	6

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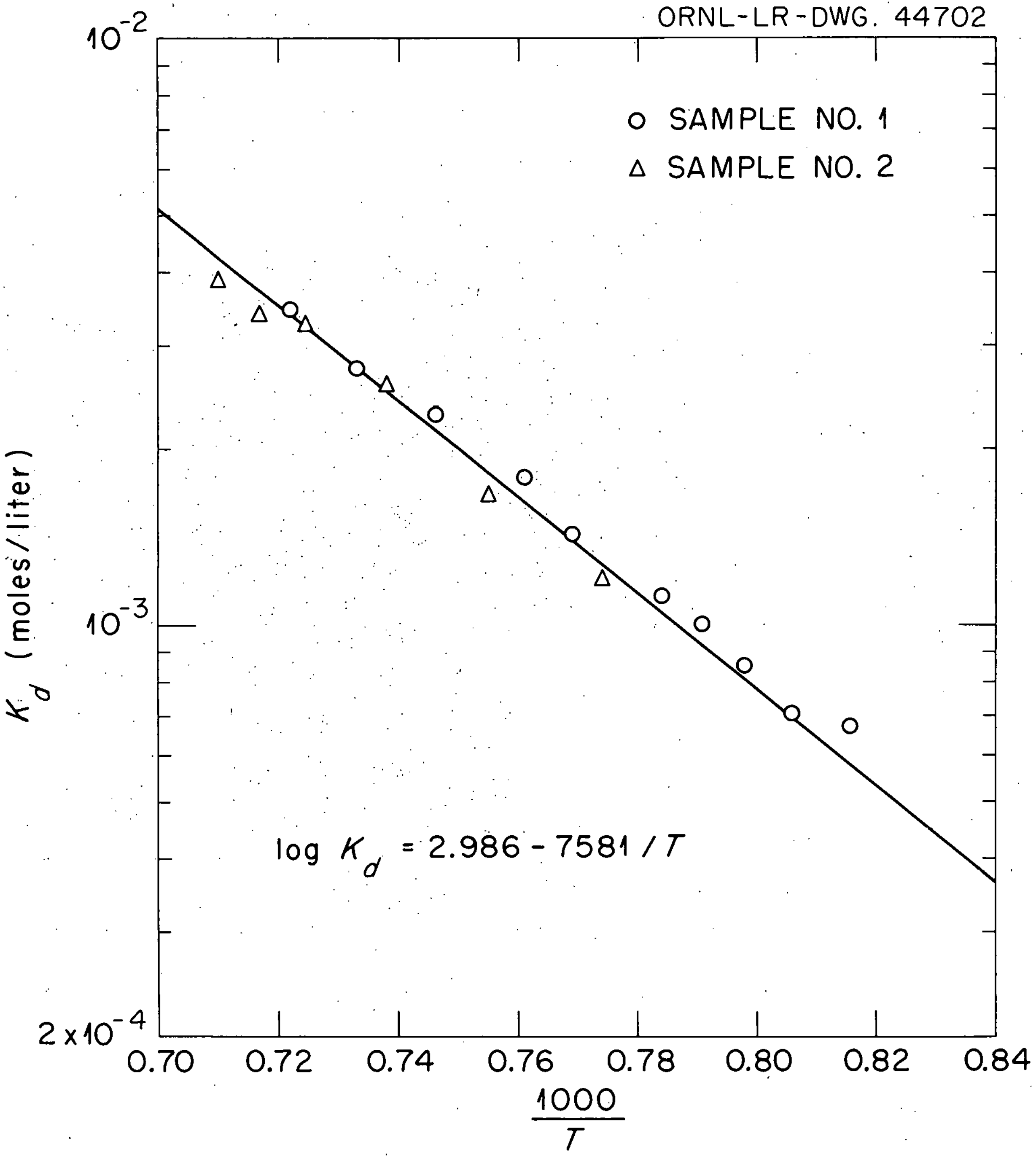

Figure 9
DISSOCIATION CONSTANT OF POTASSIUM IODIDE DIMER vs RECIPROCAL TEMPERATURE

TABLE VI

DATA AND EQUILIBRIUM CONSTANTS FOR Rb_2Cl_2 DISSOCIATION

	P(mm.)	T(^{o}K.)	M_o	N_d	-log K_d	log $\frac{K'_d}{K_d}$	Chron.
	17.50	1302	145.8	.205	3.178	-.057	1
	18.00	1312	142.8	.181	3.087	-.017	9
	18.60	1325	139.6	.154	2.980	.026	8
Sample No. 1	18.75	1335	139.5	.153	2.977	-.020	7
21.2 mg.	19.35	1348	136.5	.128	2.865	.030	6
V = 675 cc.	19.45	1353	136.3	.127	2.858	.014	2
	19.65	1362	135.8	.123	2.838	-.008	5
	20.20	1379	133.7	.106	2.750	.001	3
	20.25	1380	133.5	.104	2.740	.007	4
	28.30	1350	141.1	.166	2.852	.033	1
	29.00	1362	138.9	.148	2.777	.052	7
Sample No. 2	29.35	1372	138.2	.143	2.753	.030	2
32.0 mg.	29.20	1372	138.9	.149	2.779	.004	6
V = 675 cc.	29.70	1386	138.0	.141	2.745	-.025	5
	30.20	1400	137.1	.133	2.711	-.052	3
	31.10	1414	134.4	.112	2.603	-.006	4
	31.10	1415	134.5	.112	2.607	-.014	8

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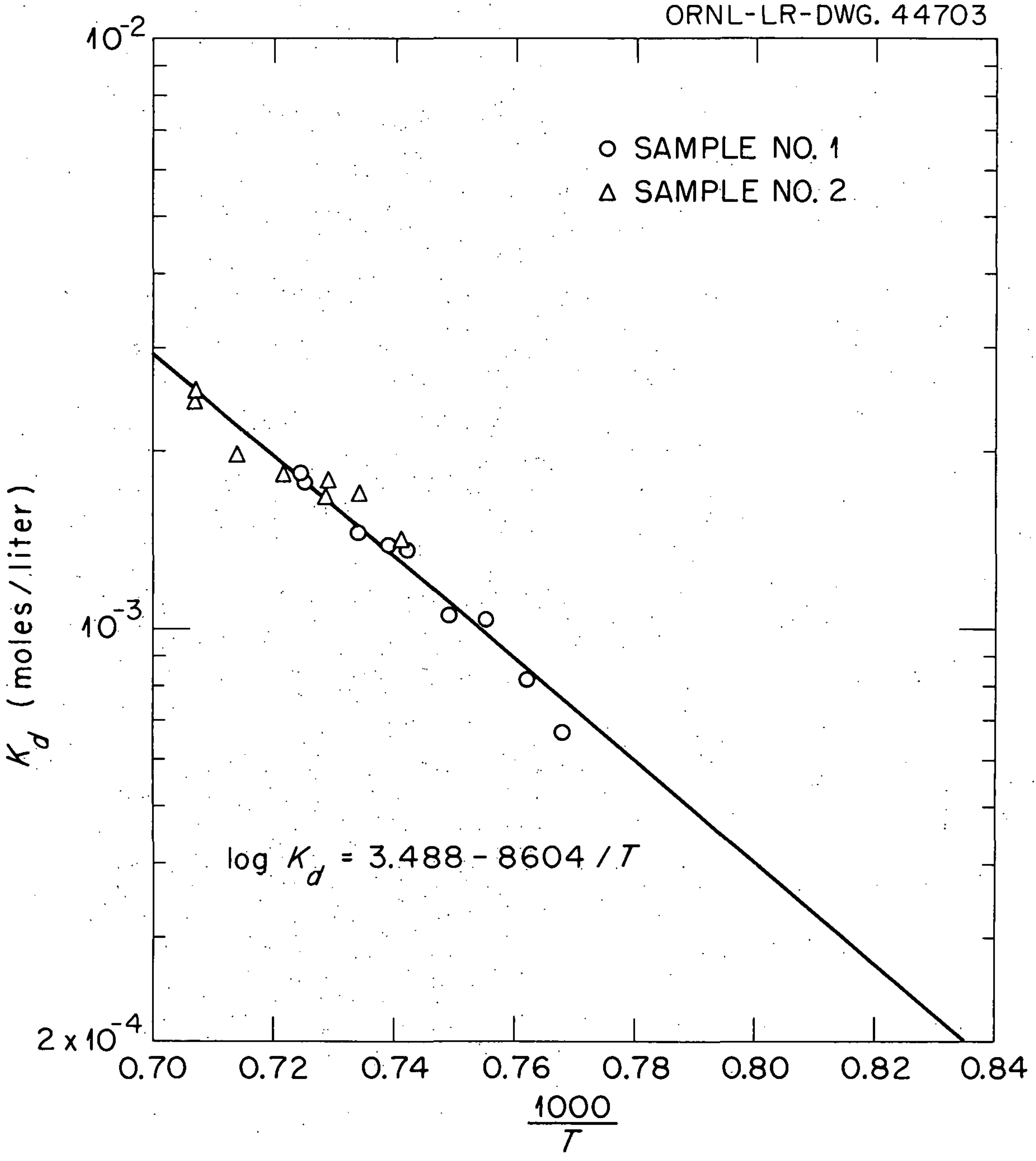

Figure 10
DISSOCIATION CONSTANT OF RUBIDIUM CHLORIDE DIMER
vs RECIPROCAL TEMPERATURE

TABLE VII

DATA AND EQUILIBRIUM CONSTANTS FOR Cs_2Cl_2 DISSOCIATION

	P(mm.)	T(°K.)	M_o	N_d	$-\log K_d$	$\log \frac{K'_d}{K_d}$	Chron.
	19.50	1224	208.6	.239	3.209	-.055	11
	19.85	1227	205.5	.220	3.145	-.007	10
	20.30	1231	201.6	.197	3.063	.055	9
	20.55	1246	201.5	.197	3.063	-.018	8
Sample No. 1	21.30	1257	196.2	.165	2.940	.051	7
40.5 mg.	21.55	1269	195.7	.163	2.930	.004	6
V = 760 cc.	22.20	1280	191.7	.138	2.826	.056	5
	22.45	1298	192.2	.141	2.840	-.040	4
	22.50	1298	191.8	.139	2.828	-.028	12
	23.20	1313	188.1	.117	2.725	.008	1
	24.05	1342	185.5	.102	2.641	-.033	2
	24.85	1371	183.4	.089	2.568	-.079	3
	35.50	1291	200.7	.192	2.824	.008	8
	36.40	1307	198.2	.177	2.767	-.007	9
	37.60	1326	194.6	.156	2.680	-.003	7
	39.20	1351	190.2	.130	2.566	-.005	6
Sample No. 2	39.80	1359	188.5	.119	2.515	.023	5
67.2 mg.	40.55	1376	187.3	.112	2.479	-.010	4
V = 760 cc.	41.80	1396	184.3	.095	2.382	-.008	3
	42.45	1408	183.1	.087	2.336	.010	2
	43.25	1418	181.0	.075	2.251	.052	1

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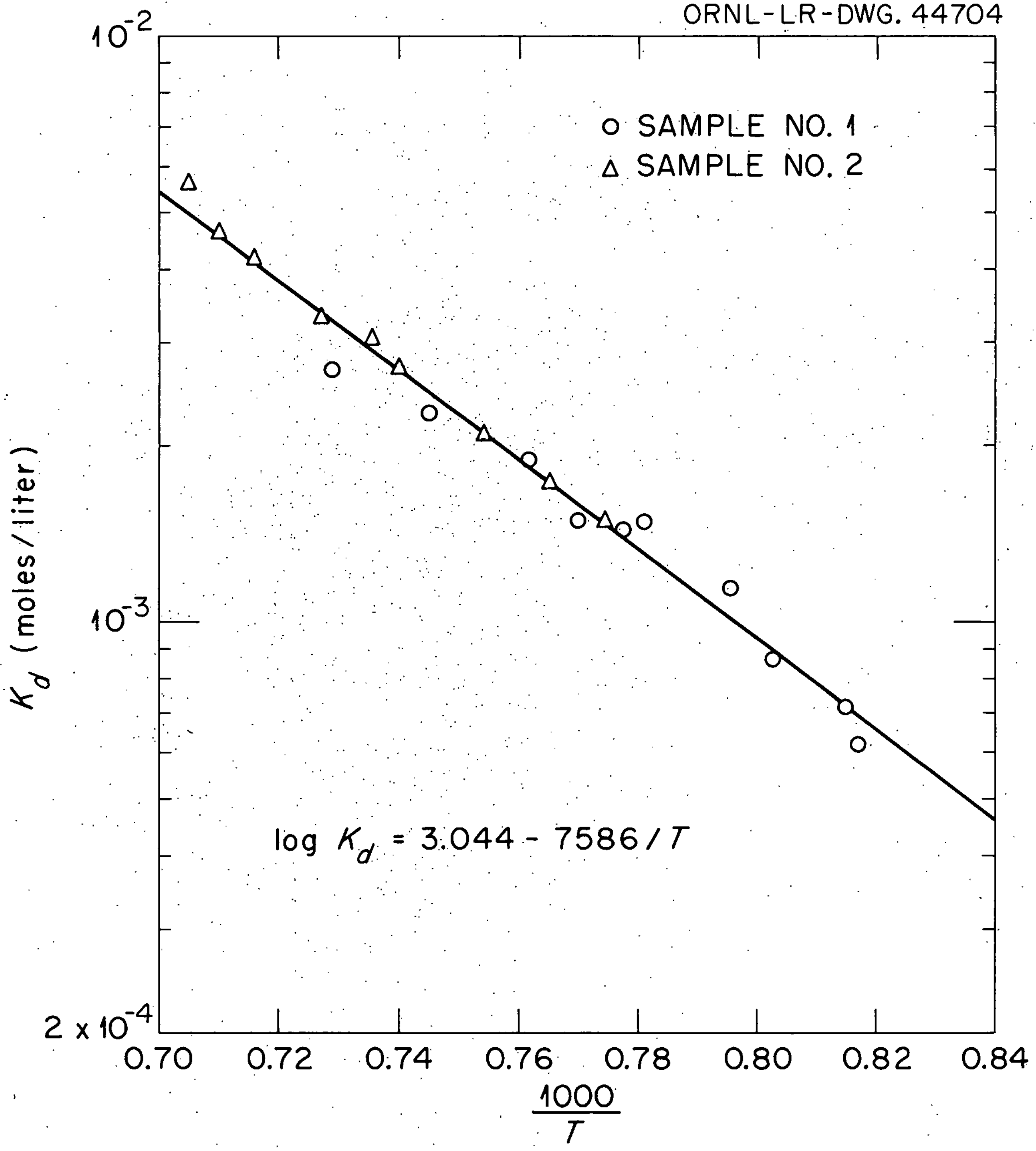

Figure 11
DISSOCIATION CONSTANT OF CESIUM CHLORIDE DIMER
vs RECIPROCAL TEMPERATURE

TABLE VIII

SUMMARY OF EXPERIMENTALLY DERIVED THERMODYNAMIC FUNCTIONS FOR DIMER DISSOCIATION

		Evaluated at 1300°K.		Standard Error of Fit
MX	ΔE^o (kcal. mole^{-1})	ΔS^o (cal. mole^{-1}deg.$^{-1}$)	$-\log K_d$	σ_f
NaCl	48.0±1.7	28.3±1.3	4.378	0.029
NaBr	42.9±1.3	28.8±0.9	3.410	0.025
NaI	40.2±1.2	27.1±1.0	3.312	0.033
KCl	41.2±2.3	27.1±1.7	3.500	0.027
KI	34.7±0.9	25.0±0.7	2.846	0.025
RbCl	39.4±2.0	27.3±1.5	3.130	0.031
CsCl	34.7±1.0	25.3±2.8	2.791	0.037

CHAPTER IV

DISCUSSION

A. The Validity of the Assumptions Used in Treating the Data

1. The Applicability of the Ideal Gas Law

Deviations from ideality of the gases studied were assumed to be due solely to chemical reaction under the conditions of pressure and temperature used in this work. The validity of this assumption may be assessed by considering those factors which would cause the greatest deviations from ideal gas behavior, namely the highest pressure (40 mm.), the lowest temperature (1200°K.), the highest polarizability ($\alpha = 10 \times 10^{-24}$ cc.), and the highest permanent dipole moment ($\mu = 10 \times 10^{-18}$ esu. cm.).

The behavior of the monomer gas may be represented by the Van der Waals equation of state,

$$(P + a/\bar{V}^2)\ (\bar{V} - b) = RT,$$

where $\bar{V}$ is the molar volume, a is the correction due to the intermolecular attraction, and b the correction due to intrinsic molecular volume. At the temperature and pressure specified above, the molar volume is 1.9×10^{6} cc. mole^{-1}, and it is clear that the deviation due to an intrinsic molecular volume of even as much as 100 cc. is negligible.

The correction due to London dispersion forces can be estimated from the relation given by Slater and Kirkwood[48]:

$$a = 1.08 \times 10^{38} \alpha^{3/2}\ n^{1/2}\ /b \text{ atm. cc.}^2 \text{ mole}^{-2},$$

where n, the number of electrons in the outer shell, is equal to eight for the alkali halides.

Even with the high estimated polarizability of α equal to 10×10^{-24} cc., the magnitude of $a/\bar{V}^2$ is 1×10^{-10} atm., which is negligible when compared with the total pressure of 5×10^{-2} atm.

The large permanent dipole moment would be expected to make the largest contribution to deviations from ideality. To determine the magnitude of this correction, it is assumed that the total interaction may be estimated by summing the contributions of strong and weak interactions. The weak interaction is defined as that for which the potential energy ϵ can be represented by[49]

$$\epsilon = - \frac{2}{3} \frac{\mu^4}{r^6 kT} ,$$

where r is the intermolecular distance and k is Boltzman's constant. This equation will be valid in the region where

$$\mu^2/r^3 < kT,$$

and, for the purposes of this calculation, it will be assumed to hold for intermolecular separations greater than 10 Å, since at this distance the interaction energy is already less than one half the thermal energy. The Van der Waals a can be obtained by summing all the interactions for a mole of gas[48,50]

$$a = 2 \pi N_0{}^2 \int_{\zeta}^{\infty} - \epsilon \, r^2 \, dr$$

where N_0 is Avogadro's number and ζ is the lower limit of the intermolecular distance for which the equation is valid. For the weak interaction, the solution is

$$a = \left(\frac{4\pi}{9}\right) \frac{N_0{}^2 \, \mu^4}{kT \, \zeta^3} = 3.62 \times 10^9 \, D^4/T\zeta^3 \text{ atm. cc.}^2 \text{ mole}^{-2},$$

where D is the dipole moment in Debyes (1 Debye = 10^{-18} esu. cm.) and ζ is in Ångstrom units. Upon inserting the parameters presently under consideration, the value of $a/\bar{V}^2$ is found to be 8×10^{-6} atm., which amounts to the negligible correction of 0.02 per cent.

In order to evaluate the contribution of forces experienced at internuclear distances of less than 10 Å (strong interactions), it is necessary to calculate the probability of finding two molecules within this distance of each other in the gas under consideration. If a random spatial distribution is assumed, the average number of molecules to be found within a sphere of radius $\bar{r}$ is given by

$$P\ (\bar{r}) = 3\pi\ N_0\ \bar{r}^{\ 3}/\bar{V}.$$

When $\bar{r}$ is 10 Å, P $(\bar{r})$ will be 3×10^{-3}. Since P $(\bar{r})$ is small compared to unity, its magnitude may be taken as the probability of two dipoles being within 10 Å of each other at any time. Hence, if the distribution were truly random, the departure from ideality due to the strong interaction is negligible. However, when two dipoles are sufficiently close to interact strongly, the randomness of the distribution is destroyed, but this is tantamount to molecular association.

Therefore, the only force which is sufficiently large to cause deviation from ideality is that which causes chemical reaction. Under these circumstances, the alkali halide gas may be considered as a reacting mixture in which each component behaves as an ideal gas.[51]

2. Probability of Trimer Formation

In the treatment of the data, it has been assumed that the only molecular species present in any appreciable concentrations have been those of momomer and dimer. If trimer molecules were also present, the derived quantities would, of course, be considerably less significant. However, two arguments can be put forth which indicate that trimer molecules are not present in appreciable concentrations under the conditions of this experiment.

First, since the equilibrium concentration of trimer should be dependent on the total pressure, it would be expected that the equilibrium constant, calculated on the assumption that only momomer and dimer were present, would vary with pressure if large amounts of trimer were present. The equilibrium constants so calculated from the measurements do not appear to be sensitive to total pressure which was varied by a factor of two by varying the sample size at constant temperature. This tends to preclude appreciable amounts of trimer.

A second and better argument can be adduced from extrapolated values of trimer concentrations measured at lower temperatures and pressures by Berkowitz and Chupka.[25] In this work, a mass spectrographic analysis of the alkali halide vapor composition was made by electron bombardment of a molecular beam emanating from an effusion cell which was maintained at a temperature corresponding to an equilibrium vapor pressure of 10^{-2} mm. If it is assumed that the ionization cross-section for the three species is the same,* an equilibrium constant for the reaction,

$$(MX)_3 \rightleftharpoons 3\ MX, \qquad (1)$$

can be calculated, at a given temperature, from

$$(K_t)_{T_1} = \frac{C_m^3}{C_t} = \frac{N_m^3}{N_t} \left(\frac{P}{RT_1}\right)^2 .$$

At any other temperature the equilibrium constant can be calculated if ΔE_t^o, the change in internal energy for this reaction, is known since

$$\ln(K_t)_{T_2} = \ln(K_t)_{T_1} + \frac{\Delta E_t^o}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right).$$

An estimate of this quantity may be obtained from the work of Milne and Cubicciotti[52] who, on the basis of a simple electrostatic model, calculated the expected energy changes for the reactions:

$$(MX)_2 \rightleftharpoons 2\ MX \qquad (2)$$

and

$$(MX)_3 \rightleftharpoons (MX)_2 + MX \qquad (3)$$

These values were calculated for sodium, potassium, rubidium and cesium chlorides, and the energy change for reaction (3) was found to be 3 to 4 kcal. less than that for corresponding reaction (2).

Since reaction (1) is simply the sum of reactions (2) and (3), it was assumed for the purposes of the extrapolation that

$$\Delta E_t^o = 2\Delta E^o - 4\ \text{kcal.}$$

where ΔE^o is the dimer dissociation energy found in the present work.

---

*It should be noted that this approximation would give higher than true values for the trimer concentration.

Of all the experimental conditions encountered in this work, the case of sodium bromide at a temperature of 1315°K. and a pressure of 35 mm. would be expected to yield the maximum value of the mole fraction of trimer. Even in this case, the mole fraction of trimer should be only 3×10^{-3}, which is negligible.

B. Calculation of Dissociation Entropies

Alkali halide dissociation entropies have been computed by previous investigators[37,38] but these calculations employed assumptions about the vibrational frequencies of the dimer that differ appreciably from the more carefully determined estimates of Berkowitz.[53*] It is, therefore, worthwhile to recalculate the entropies using these more reliable values.

The configuration of the dimer and a description of the normal modes given by Berkowitz in his previous paper[39] are pictured in Fig. 12 and the values of the parameters used in the calculation are listed in Tables IX and X.

The standard entropy changes were calculated by the usual statistical methods[50] from which the following expressions for the translational, rotational, and vibrational entropies were formulated. The translational entropy change is given by

---

[*] The author is indebted to Dr. Joseph Berkowitz of the Argonne National Laboratory for making available the results of his recent calculation of the expected dimer vibrational frequencies and for his permission to use these values prior to publication of his work.

$$\Delta S^{o}_{trans.} = R\ (3/2\ M_{MX} + 5/2\ \ln T - 5.403)$$

and the rotational entropy change by

$$\Delta S^{o}_{rot.} = 1/2R \left[1 - \ln \frac{h^2}{8\pi kT} + \ln \frac{I^4}{ABC\sigma^2} - 2 \ln \sigma \right]$$

where *h* is Plank's constant and *σ*, the symmetry number for the dimer, is equal to four. The quantity relating *I*, the moment of inertia of the momomer, to *A B C*, the product of the moments of inertia of the dimer, may be expressed as

$$\frac{I^4}{ABC} = \frac{8(M_X\ M_M)^3}{(M_{MX})^4\ (a^2 M_M + b^2\ M_X)}\ \frac{r^8}{(ab)^2}$$

where r is the internuclear distance in the monomer and *a* and *b* are the distances from the center of mass of the dimer molecule to the cation and anion respectively (Fig. 12). The vibrational entropy contribution for each mode is

$$(S^{o}_{vib.})_i = R[\mu_i(e^{\mu i} - 1) - \ln(1 - e^{-\mu i})]$$

in which $\mu_i = hc\omega_i/kT$ where c is the velocity of light and ω_i is the frequency of the i^{th} mode in cm.$^{-1}$. The vibrational entropy change is then obtained from

$$\Delta S^{o}_{vib.} = 2(S^{o}_{vib.})_m - \sum_{i=1}^{6} [(S^{o}_{vib.})_d]_i .$$

The total entropy changes obtained from

$$\Delta S^{o} = \Delta S^{o}_{trans.} + \Delta S^{o}_{rot.} + \Delta S^{o}_{vib.}$$

together with the values of the various contributions to the total entropy are listed in Table XI.

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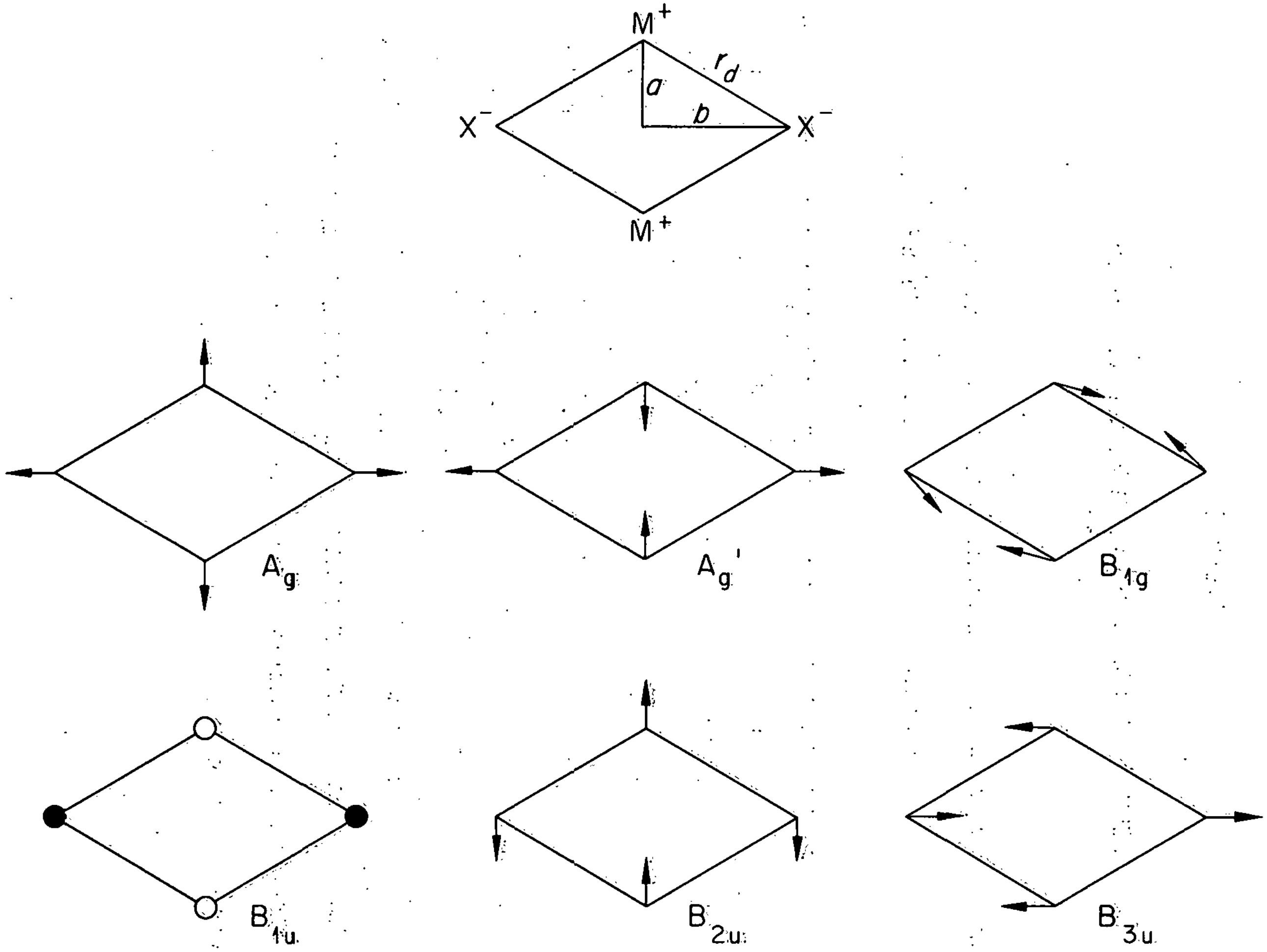

Figure 12
CONFIGURATION AND NORMAL VIBRATIONS OF ALKALI HALIDE DIMERS

TABLE IX

MOLECULAR DIMENSIONS OF MONOMER AND DIMER (in Å)

	Monomer [a]	Dimer [b]	
MX	r	a	b
NaCl	2.3606	1.536	2.128
NaBr	2.5020	1.596	2.233
NaI	2.7115	1.648	2.440
KCl	2.6666	1.868	2.260
KI	3.0478	2.000	2.608
RbCl	2.7868	2.020	2.300
CsCl	2.9062	2.184	2.308

[a] Monomer internuclear distance. See reference 5 in text.

[b] See reference 39 in text.

TABLE X

VIBRATIONAL FREQUENCIES OF ALKALI HALIDE DIMERS AND MONOMERS (ω in cm.$^{-1}$)

	Monomer[a]	Dimer[b]					
	ω_m	A_g	A_g'	B_{1g}	B_{1u}	B_{2u}	B_{3u}
NaCl	366	265	159	226	155	222	260
NaBr	302	182	120	207	134	188	228
NaI	258	143	100	202	127	173	215
KCl	281	219	108	180	104	184	206
KI	173	(130)[c]	68	(130)[c]	90	181	157
RbCl	228	169	79	148	83	156	170
CsCl	209	140	67	141	76	151	156

[a] See reference 15 in text.

[b] See reference 53 in text. The notation used is in accordance with conventions stated by E. B. Wilson, J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., Inc., New York, 1955.

[c] Bracketed values were not given by the investigation cited, but were estimated from trends in the other alkali halides.

TABLE XI

CALCULATED DISSOCIATION ENTROPIES OF ALKALI HALIDE DIMERS AT 1300°K. (in cal. mole^{-1} deg.$^{-1}$)

MX	Translational $\Delta S^o_{trans.}$	Rotational $\Delta S^o_{rot.}$	Vibrational $-\Delta S^o_{vib.}$	Total ΔS^o
NaCl	43.36	6.56	21.90	28.02
NaBr	45.05	6.24	23.28	28.01
NaI	46.16	5.97	24.09	28.04
KCl	44.09	7.24	24.05	27.29
KI	46.48	7.32	26.60	27.20
RbCl	45.53	7.10	25.82	26.81
CsCl	46.52	7.03	27.09	26.45

C. Comparison With Results of Previous Investigators

1. Normalization to 1300°K.

To facilitate comparison of the results of the present work with the measurements and calculations of previously published work, it is desirable to adjust all the reported results to their corresponding values at a single temperature. Since 1300°K. was within the temperature range of measurement for all of the salts investigated in the present work, this value was chosen as the normalized temperature. The adjustment of the other values to this temperature requires a knowledge of the heat capacities of the reactants and products as a function of temperature, in that

$$\Delta E^o_{1300} = \int_{T_1}^{1300} \Delta C_v dT + \Delta E^o_{T_1}$$

and

$$\Delta S^o_{1300} = \int_{T_1}^{1300} \frac{\Delta Cp}{T} dT + \Delta S^o_{T_1} .$$

Due to the lack of both thermal and spectroscopic data on the dimer, an exact calculation of ΔC_v is not possible. However, in this temperature range, its value may be adequately approximated by the assumption of classical equipartition of energy in all degrees of freedom. With this assumption, the corrections can be readily calculated from

$$\Delta E^o_{1300} = - 2 R (1300 - T_1) + \Delta E^o_{T_1}$$

and

$$\Delta S^o_{1300} = - 2.303 R (\log \frac{1300}{T_1}) + \Delta S^o_{T_1} .$$

The justification of this approximation can be demonstrated by estimating the maximum expected departure from classical behavior, which will occur in the vibrational mode for which the value of hcω/kT is a maximum. Of the cases under consideration, this criterion is most closely met by sodium chloride at 920°K.,* for which the value of the monomer frequency,[15] ω, is 366 cm^{-1}, and hcω/kt is equal to 0.5. The contribution of this mode to the heat capacity is 0.98 R[50] so that the error introduced even in this extreme case is only 2 per cent. Thus, even though the difference in temperature between the present measurements and those of Miller and Kusch is ca. 450°, the error in the corrections, which are ca. 1.8 kcal. to ΔE° and ca. 0.8 e.u. to ΔS°, is small.

2. Dissociation Entropies

The experimental and calculated values of the dissociation entropies obtained in this investigation are given in Table XII together with the values obtained by other investigators.

The agreement between the experimental and calculated values obtained in this investigation is quite good, the calculated values lying within the experimental standard error in all cases except potassium iodide and cesium chloride. The calculations of Bauer, Diner, and Porter,[38] and of Milne and Cubicciotti[37] are consistently higher than the present experimental values, ranging fron 2.1 to 3.2 e.u. for the former and 2.8 to 3.9 e.u. for the latter. The differences between these calculations and those calculated herein are due almost entirely to the differences in the vibrational entropy contributions.

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*One of the cases reported by Miller and Kusch.

TABLE XII

COMPARISON OF DIMER DISSOCIATION ENTROPIES AT 1300°K. (in cal. mole^{-1} deg.$^{-1}$)

	Datz[a]		Miller[b]	Bauer[c]	Milne[d]	Barton[e]
MX	(Exp.)	(Calc.)	(Exp.)	(Calc.)	(Calc.)	(Exp.)
NaCl	28.3±1.3	28.02	28.8±1.0	30.45	31.1	30.0±0.7
NaBr	28.8±1.0	28.01			31.8	
NaI	27.1±1.0	28.04	27.6±4.2	29.21	30.8	
KCl	27.1±1.7	27.29	34.1±0.8	29.62	30.8	25.5±1.0
KI	25.0±0.7	27.20	39.2±1.1	28.25		
RbCl	27.3±1.5	26.81	38.9±0.6	29.45	30.3	
CsCl	25.3±1.0	26.45			29.2	

[a] Values obtained in this work.

[b] See reference 12 in text.

[c] See reference 38 in text.

[d] See reference 37 in text.

[e] See reference 30 in text.

The large internal discrepancies found in the entropies determined by Miller and Kusch[12] were attributed by Bauer, Diner, and Porter to probable errors in the determination of the dissociation energies. The values obtained by Barton and Bloom,[30] while not in gross disagreement with other determinations, cannot be considered very reliable since in the case of sodium chloride only three points were determined and in the case of potassium chloride only seven determinations of the equilibrium constant were made, four of which were at one temperature (1416°K.). Furthermore, in treating the potassium chloride data, the authors averaged the four determinations of the equilibrium constant at 1416°K., to give a single point at this temperature, and determined the slope and intercept from this composite point and the measurements at the three other temperatures. However, when all the data are treated by the method of least squares, the value obtained for the entropy is 16.3 ± 13.3 e.u. and that for the energy is 25.9 ± 18.8 kcal. mole^{-1}.

3. Dissociation Energies

The dimer dissociation energies determined in the present work and those of other workers are listed in Table XIII.

Since the stability of the dimer is due primarily to electrostatic forces, it would be expected that the dissociation energy should be approximately proportional to the reciprocal of the anion-cation internuclear distance, and a plot of these two variables is shown in Fig. 13.

The values obtained in the present work display the expected monotonic increase with decreasing interionic separation. The lack of systematic

TABLE XIII

COMPARISON OF DIMER DISSOCIATION ENERGIES AT 1300°K.
(in kcal. mole^{-1})

MX	Datz[a] (Exp.)	Miller[b] (Exp.)	Eisenstadt[c] (Exp.)	Bauer[d] (Calc.)	Milne[e] (Calc.)	Barton[f] (Exp.)
NaCl	48.0±1.7	43.1±0.9	46.4±0.6	44.7	47.9	48.3±0.8
NaBr	42.9±1.3				46.3	
NaI	40.2±1.2	36.7±3.4		38.0	43.1	
KCl	41.2±2.3	44.2±0.7		40.2	42.2	38.0±0.6
KI	34.7±0.9	43.4±0.9		34.5	38.3	
RbCl	39.4±2.0	46.3±0.5		38.1	40.1	
CsCl	34.7±1.1				36.9	

[a] Values obtained in this work.

[b] See reference 12 in text.

[c] See reference 18 in text.

[d] See reference 38 in text.

[e] See reference 37 in text.

[f] See reference 30 in text.

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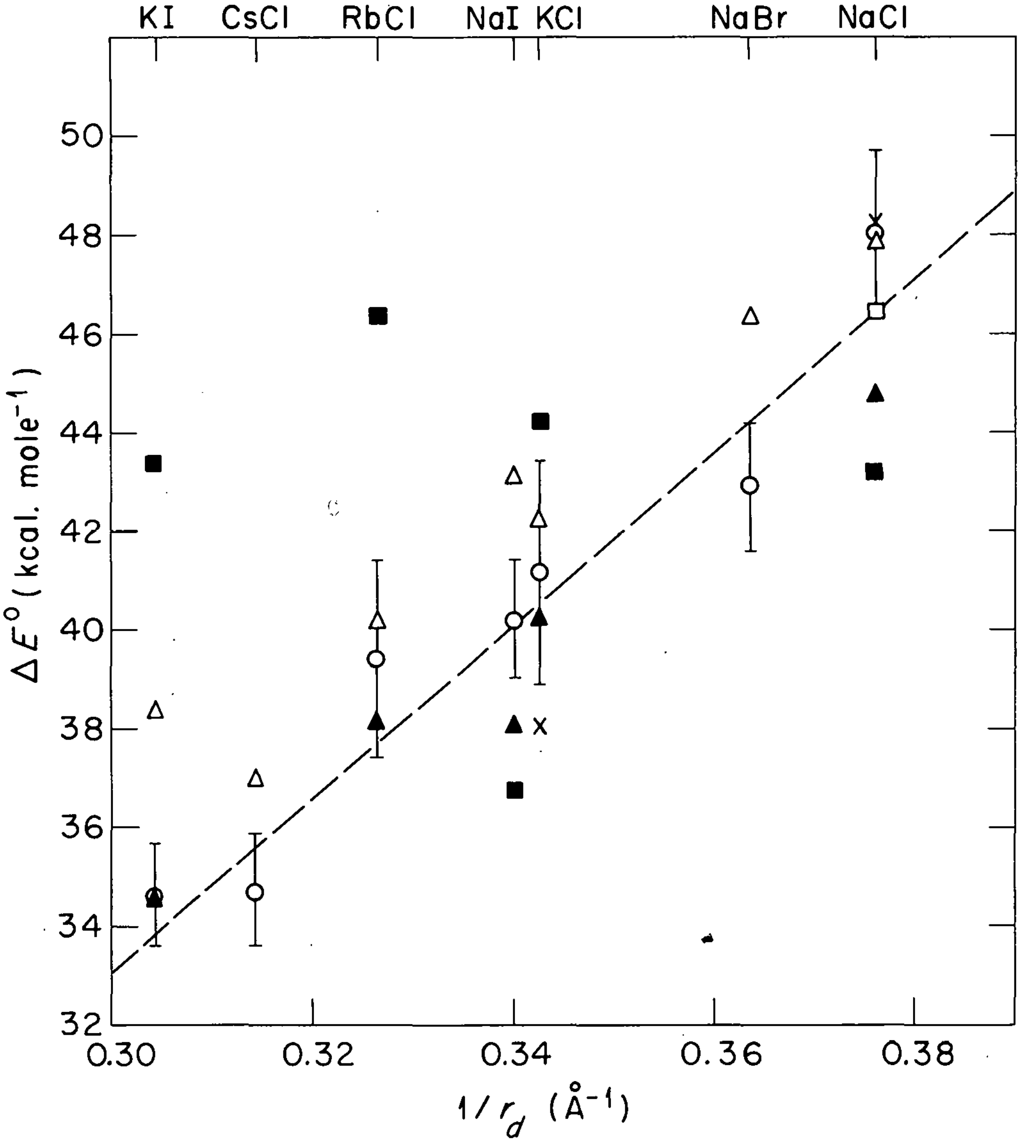

Figure 13

DISSOCIATION ENERGY vs THE RECIPROCAL OF THE ANION-CATION SEPARATION IN THE DIMER

○ Results of the Present Work
■ Miller and Kusch
▲ Bauer, Diner, and Porter
△ Milne and Cubicciotti
× Barton and Bloom
□ Eisenstadt, Rao, and Rothberg

variation in the results of Miller and Kusch[12] had been noted previously by Bauer, Diner, and Porter,[38] who proceeded to recalculate the dissociation energies, using their calculated entropy values and assuming that the equilibrium constants measured by Miller and Kusch were correct. The recalculated energies show good agreement with the present values for potassium chloride, potassium iodide, and rubidium chloride, but the values for sodium iodide and sodium chloride remain significantly lower. In the case of sodium chloride, the discrepancy has been partially mitigated by the higher value found experimentally by Eisenstadt, Rao, and Rothberg,[18] using the technique and apparatus developed by Miller and Kusch.

Although the determinations of Barton and Bloom[30] are in reasonable agreement with the present findings, the reliability of these results is questionable, for the reasons stated in the preceding section.

The dissociation energies calculated by Milne and Cubicciotti[37] agree well with the present results for sodium chloride, potassium chloride, and rubidium chloride, but are higher by ca. 2 kcal. mole^{-1} for cesium chloride and ca. 3 kcal. mole^{-1} for sodium bromide, sodium iodide, and potassium iodide.

A possible cause for this discrepancy may be found by considering the assumptions used in the calculation. The theory used by the authors was identical to the one which had been used by Pauling[36] in his treatment of gaseous alkali halide monomers. In this work, Pauling found that the binding energies of the monomers were calculable from a relatively simple formula which contained just the coulombic attractive energy and a repulsive term. The exponent of the repulsive term was defined by

$$n = n_+ + n_-,$$

where n_+ and n_- are constants characteristic of the cation and anion respectively and are independent of the particular combination of the two. These constants were empirically evaluated and a self-consistent set of binding energies for the alkali halide monomers was obtained. In their calculation, Milne and Cubiciotti have assumed that these values could be applied equally well in the calculation of the bond strengths in the dimers.

Although the contribution of polarization to the total energy is not explicitly mentioned in the Pauling formulation, it is implicitly included in the values of n_+ and n_-. Thus, the assumption made by Milne and Cubicciotti is equivalent to the supposition that the polarization energy per bond is the same in monomer and dimer. However, in the dimer the nature of the polarization interaction is considerably more complex, since each ion is interacting with three other ions and the magnitude of the polarizability for each interaction is reduced by the presence of the other interactions. The fact that the calculated energies are too high indicates that the contribution of the polarization energy per bond is less in the dimer than in the monomer and, as would be expected, the discrepancies are larger for molecules containing ions with higher polarizabilities.

D. Conclusions

The relatively small range in the values of the dissociation entropies for the series of alkali halides investigated is in accord with the predictions of previous theoretical calculations. The absolute values of the experimentally determined entropy changes are in agreement with calculations based on dimer vibrational frequencies predicted by Berkowitz, but are significantly lower than those calculated heretofore.

The trend observed in the dissociation energies is consistent with an electrostatic model for the dimer, exhibiting a monotonic increase with decreasing anion-cation internuclear distance. A comparison of the total coulombic energy of the dimer (calculated from the sum of the four anion-cation attractive energies minus the anion-anion and cation-cation repulsive terms) exhibits a similar trend. The results also indicate that a complete theoretical treatment of the dimer dissociation energies must take into account the detailed nature of the polarization interactions in the dimer.

The diminution of the dimer energy is reflected in the reduction of the bond restoring force constants and is therefore accompanied by a reduction in the vibrational contribution to the dissociation entropy. This effect is partially compensated by the increase in the translational and rotational entropy contributions due to the larger masses of the ions. However, the net effect is a decrease in the entropy so that there is a relatively small change in the equilibrium constants throughout the series of alkali halides studied (Table VIII).

CHAPTER V

Summary

Molecular association equilibria in alkali halide vapors were studied by measuring the temperature dependence of the molecular weights of gaseous sodium chloride, sodium bromide, sodium iodide, potassium chloride, potassium iodide, rubidium chloride, and cesium chloride. The molecular weights were determined by measurement of the absolute pressure exerted by a known weight of completely vaporized salt contained in an isothermal fused silica bulb of known volume. The pressure sensing element consisted of a fused silica U-tube manometer containing molten gold, and pressures were determined by measuring the argon pressure necessary to balance the gold manometer. The apparatus was used in the temperature range of 1175 to 1430°K. and pressures of from 10 to 40 mm. were measured with a precision of ± 0.05 mm.

The temperature dependence of the equilibrium constants for the reaction

$$(MX)_2 \rightleftharpoons 2MX$$

yielded dissociation energies (evaluated at 1300°K.) ranging from 48.0 kcal. mole^{-1} for sodium chloride to 34.7 for cesium chloride. The entropies of dissociation were found to fall within a small range, varying from 28.3 e.u. for sodium chloride to 25.0 for potassium iodide, and a statistical calculation of the entropy changes based on an ionic model was found to agree well with the experimental values. It is shown that these systems may be adequately described with an electrostatic model, although closer attention should be paid to the nature of polarization interactions.

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