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THE STABILITIES OF GASEOUS SODIUM CHLORIDE TRIMERS AND TETRAMERS

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ABSTRACT

Measurements of the ion intensities attributable to NaCl(g) and $Na_3Cl_3(g)$ as functions of temperature in a mass spectrometer yield vaporization data for the monomer that are in good agreement with the average of eight previous investigations. The enthalpy and entropy of sublimation for the trimer at 937°K are 62.2 ± 3 kcal/mole and 30.5 ± 3 eu/mole, respectively.

The measured enthalpy for the trimer agrees well with the prediction made by applying a normalization factor to calculations from an ionic model of Milne and Cubicciotti. The experimentally observed intensity of $Na_4Cl_3^+$ ion is combined with the stability predicted for Na_4Cl_4 when the ionic model is extended to tetramers to calculate an entropy for the reaction - $4NaCl(g) = Na_4Cl_4(g)$.

INTRODUCTION

Good thermochemical data are available for gaseous alkali halide monomers and dimers in equilibrium with their condensed phases (1,2), while data for trimers and higher polymers are scant. It is of interest, therefore, to obtain as accurate data as possible for these higher polymers, not only for their intrinsic value, but to allow comparison with ionic models (3-7) which work well for predicting the stabilities of gaseous alkali halide monomers and dimers.

We have used a mass spectrometer to measure the enthalpy and entropy for the reaction $3NaCl(s) = Na_3Cl_3(g)$ and have obtained the first intensity measurement for the $Na_4Cl_4(g)$ molecule. The value of the enthalpy of dissociation of the trimer to a monomer and a dimer calculated by Milne and Cubicciotti (4) from an ionic model is compared to the experimental data and their model is extended to tetrameric molecules to permit the calculation of thermodynamic data for Na_4Cl_4 from the measured concentration.

EXPERIMENTAL

This study was carried out with a 60° sector, 24 cm radius, magnetic deflection Atlas mass spectrometer, which was equipped with a 16-stage electron multiplier using Cu-Be dynodes. Sodium chloride was purchased from the J. T. Baker Chemical Co. The only spectroscopically detectable impurities were .001% Ca and .0005% Mg.

All effusion experiments were carried out in copper Knudsen cells. Temperatures were measured with a chromel-alumel thermocouple which had been previously calibrated at the freezing point of aluminum. The thermocouple was securely clamped inside a hole drilled in the bottom

of the cell. The cell was heated by radiation from a tungsten filament which was inside copper-clad tantalum heat shields.

Runs were made using copper cell lids with two different orifice sizes in order to be sure that equilibrium had been achieved. Orifice diameters were .034 cm and .100 cm while channel lengths were .017 cm and .100 cm, respectively.

Preliminary experiments indicated that ion intensities associated with the trimer decreased below the equilibrium values when the mean free path to diameter ratio, as calculated by the hard sphere approximation, fell below ~1.7. It is interesting to note that, over the same temperature range, the ion intensities associated with the monomer were unaffected. We have observed similar differences in behavior between the dimer and monomer species in mass spectrometric studies of lanthanum trifluoride and cerium trifluoride vaporization (8,9). All subsequent trimer data were taken with $\lambda/D > 1.7$ to insure that molecular flow conditions prevailed.

Shutterable ion intensities corresponding to Na^+, $NaCl^+$, Na_2Cl^+, $Na_3Cl_2^+$, and $Na_4Cl_3^+$ were observed and identified by means of the background spectra and their isotopic abundances. A fragmentation pattern at 968°K with 70 eV ionizing electrons is reported in Table 1 where the ion intensities relative to Na^+ have been corrected for isotopic abundances. No ions attributable to products of reaction with the cell were observed.

Na^+, Na_2Cl^+, and $Na_3Cl_2^+$ are the principal ion fragments arising from electron impact with NaCl(g), Na_2Cl_2(g), and Na_3Cl_3(g), respectively (10-12). $Na_4Cl_3^+$ is the expected principal product of Na_4Cl_4(g)

ionization. It has been suggested by Milne and Klein (12) that $NaCl^+$ may originate partly from polymer in addition to the monomer. Higher polymers than the dimer are very improbable sources of a significant fraction of the observed $NaCl^+$ ion intensities due to their low concentrations. If $NaCl^+$ were the product of dissociative ionization of $Na_2Cl_2(g)$, the $Na^+/NaCl^+$ ratio would decrease by ∿35% in going from 870°K to 1020°K. The results of two consecutive measurements of the temperature dependence of the $Na^+/NaCl^+$ ratio (Fig. 1), however, indicate that the intensity ratio is constant between 870°K and 1020°K. We conclude, as Berkowitz, Tasman, and Chupka (13) did for the LiCl, LiBr, and LiI systems, that simple ionization of NaCl(g) is the only source of the observed $NaCl^+$ ion intensities.

It should be pointed out that the relative proportion of Na^+ to $NaCl^+$ ion was observed to vary, depending on which mass peak we chose to maximize our ion intensities. This effect is apparent when the data in Table 1 are compared to the intensity ratio data in Fig. 1. The data in Fig. 1 are particularly significant since they are the results of consecutive runs in which only the beam focusing voltages were altered. Similar variations in ion intensity ratios have been noted for LiF by Berkowitz et al. (13), who attributed the phenomenon to the formation of Li^+ fragments with excess kinetic energy.

The intensities of the Na^+ and $Na_3Cl_2^+$ ions were followed as functions of temperature using 70 eV ionizing electrons. Temperatures were varied up and then down to minimize temperature dependent errors and approximately 20 minutes were allowed between data points to insure that equilibrium had been achieved.

The electron multiplier gain of $Na_3Cl_2^+$ ion was assumed to be equal to that for Na^+ ion (14,15). The additivity rule of Otvos and Stevenson (16) was used to estimate an ionization cross section of 3.0 for the trimer relative to the total cross section of the monomer. It was assumed the total cross section of NaCl(g) remains constant relative to the polymer species while the $Na^+/NaCl^+$ ratio may vary. Since Na^+ comprises ~66% of the total number of Na^+ and $NaCl^+$ ions produced by electron impact of neutral NaCl(g) (Table 1), we estimate the ionization cross section of the trimer for $Na_3Cl_2^+$ production relative to that of the monomer for Na^+ production to be 4.5. The appearance potential of $Na_3Cl_2^+$, measured by the method of extrapolated differences from Hg^+, is 9.9 ± .5 eV.

RESULTS AND DISCUSSION

Nine separate monomer runs and eight trimer runs were performed to measure the temperature dependences of the respective ion intensities. The data presented in Fig. 2 are the results of the best two mass spectrometer runs. The arithmetic average of the calculated enthalpies from all monomer and trimer runs agree to within .05 kcal with the enthalpies calculated from the data in Fig. 2.

The ln I^+T vs. 1/T plots for Na^+ ion from cells with .034 cm and .1 cm orifices were made to coincide at 937°K, the midpoint of the experimental temperature range. All Na^+ data were then normalized to agree with the pressure accepted in the JANAF (1) tables for the monomer at 937°K.

An arithmetic average of the least square analyses of all nine monomer runs gives a second law enthalpy of sublimation at 937°K of 51.5 ± .8 kcal/mole where the reported error is the average deviation from the mean. The value accepted by JANAF at the same temperature is 52.0

kcal/mole. The good agreement between the experimental and accepted values indicates that temperature dependent errors were small during the experiments.

From the average of the least square fits of the data for $Na_3Cl_3(g)$, the enthalpy and entropy of sublimation at 937°K were calculated to be 62.2 ± 2.3 kcal/mole of trimer and 30.5 ± 2.3 eu/mole of trimer, respectively. The value for the enthalpy of sublimation for the trimer is only in fair agreement with the second law value of 71.3 kcal/mole at 1002°K reported by Akishin, Gorokhov, and Sidorov (17).

Combining the enthalpy and entropy of sublimation for the trimer with the corresponding JANAF data for the monomer at 937°K, we calculate the enthalpy and entropy of trimerization to be -93.8 ± 2.3 kcal/mole and -67.7 ± 2.3 eu/mole, respectively. This entropy is consistent with the entropies reported by JANAF at 937°K for the corresponding gaseous reactions in the LiF(g) and LiCl(g) systems — -70.5 eu and -69.2 eu, respectively.

It is of interest to compare the experimental enthalpy of sublimation for $Na_3Cl_3(g)$ with the enthalpy predicted from the ionic model calculations of Milne and Cubicciotti (3,4). Table 2 presents their calculated enthalpies at 0°K for the reaction $M_2X_2(g) = 2MX(g)$ where their estimated differences in zero point energies have been neglected. Table 3 lists the results of Milne and Cubicciotti's (4) calculations for dissociation of a trimer into a monomer and dimer. A comparison of the ΔH_0° (calc.)/ΔH_0° (exp.) ratios in Tables 2 and 3 indicates that, within experimental error, the ratio calculated for dissociation of the dimeric alkali halide can be applied to the dissociation of a trimer of the same

system to a monomer and a dimer. Following this approach, we have divided the calculated enthalpy for the reaction $Na_3Cl_3(g) = NaCl(g) + Na_2Cl_2(g)$ by 1.10 to give a predicted enthalpy at 0°K of 45.5 kcal/mole of trimer. Neglecting the small difference in $\Delta H^\circ_{1000}-\Delta H^\circ_0$ (Table 3) and combining this result with the JANAF enthalpies of formation at 1000°K for the monomer, dimer and condensed NaCl, we calculate a predicted enthalpy of sublimation for the trimer of 62.0 kcal/mole which is in good agreement with the value of 62.2 ± 2.3 kcal/mole obtained experimentally.

Our measured $Na_4Cl_3^+$ ion intensities were too low to permit experimental determination of the enthalpy of sublimation, but the data can be used to calculate thermodynamic data by extending the ionic model of Milne and Cubicciotti to the tetramer. The customary procedure in obtaining thermodynamic values from a single vapor pressure determination is to estimate the entropy of sublimation and then use the third law method to calculate the enthalpy. Because of the difficulty in estimating the entropies of complex polymers and the success of the ionic model correlations in predicting the enthalpies of the lower alkali halide polymers, we suggest that the better procedure for Na_4Cl_4 may be to estimate the enthalpy from the ionic model and calculate the entropy from the single vapor pressure determination.

Our ionic model calculations incorporated the same assumptions as did Milne and Cubicciotti's (3,4) for monomers, dimers, and trimers. We employed a computerized, iterative technique which involved fixing the Cl-Cl distances and allowing the Na-Na distances to vary in .05 Å increments. This process was repeated until a minimum energy was achieved with respect to the gaseous ions at infinite separation.

Calculations were performed for two different molecular structures -- a planar ring and a dodecahedron. Figure 3 illustrates these structures with their minimum energy configurations. The minimum enthalpies of formation for the planar ring and dodecahedral structures relative to the gaseous ions at infinite separation are -645.9 kcal/mole and -649.8 kcal/mole, respectively. The difference in these calculated values is too small relative to uncertainties in the model to permit us to conclude that the dodecahedral structure can be definitely assigned to the tetramer, but we can use its calculated stability to estimate the heat of sublimation of the tetramer.

Combining this value with the calculated stability for $Na_2Cl_2(g)$ of Milne and Cubicciotti (3), we calculate an enthalpy of 45 kcal for the reaction:

$$Na_4Cl_4(g) = 2Na_2Cl_2(g)$$

Dividing this result by 1.10, as was done previously for the trimer, and estimating $\Delta H^\circ_{1000}-\Delta H^\circ_0$ for the reaction to be $\sim$0 we calculate the enthalpy of the reaction to be 40.9 kcal at 1000°K. Combining this value with the JANAF data for the enthalpy of sublimation of the dimer at 1000°K yields a predicted enthalpy of sublimation for $Na_4Cl_4(g)$ of 70.9 kcal/mole.

Estimating an ionization cross section of 6.0 for the tetramer relative to Na^+ and assuming the electron multiplier gains of the ions to be equal, we calculate the pressure of Na_4Cl_4 to be 4.3×10^{-10} atmospheres at 968°K. This pressure, combined with the estimated enthalpy of sublimation and the JANAF data for the monomer, gives an entropy of -99.8 eu for the reaction:

$$4NaCl(g) = Na_4Cl_4(g)$$

This value is in satisfactory agreement with the value of -110.4 ± 20 eu which we calculated for the analogous reaction in the TlF system from the data reported at 595°K by Cubicciotti (18).

It will be interesting to examine the validity of this technique and of this extension of the ionic model to tetrameric alkali halide molecules as experimental data become available with which to compare the calculated results. The data of Berkowitz and Chupka (10) indicate that significant concentrations of tetrameric molecules are produced by vaporization of the lithium halides and sodium fluoride which make them of interest for such a study.

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Table 1. Relative Ion Intensities at 968°K.

Ion	Relative Intensity
Na^+	1.00
$NaCl^+$	.49
Na_2Cl^+	.88
$Na_3Cl_2^+$	.0068
$Na_4Cl_3^+$	.00010

Table 2. Comparison of Calculated and Experimental Enthalpies for the Reaction $M_2X_2(g) = 2MX(g)$

System	ΔH_0° (calc.) kcal	ΔH_0° (exp.)[1] kcal	$\frac{\Delta H_0^\circ \text{ (calc.)}}{\Delta H_0^\circ \text{ (exp.)}}$
LiF	57.6	61.8	.93
LiCl	54.7	48.9	1.12
LiBr	52.3	45.7	1.14
LiI	48.9	42.7	1.15
NaF	55.9	56.0	1.00
NaCl	53.0	48.4	1.10
NaBr	51.6	47.4	1.09
NaI	48.2		
KF	48.2	49.5	.97
KCl	47.4	45.1	1.05
KBr	46.8	43.3	1.08
KI	44.4	39.3	1.13

Table 3. Comparison of Calculated and Experimental Enthalpies for the Reaction: $M_3X_3(g) = MX(g) + M_2X_2(g)$

System	ΔH_0° (calc.) kcal	ΔH_0° (exp.)[1] kcal	$\frac{\Delta H_0^\circ \text{ (calc.)}}{\Delta H_0^\circ \text{ (exp.)}}$	$\Delta H_{1000}^\circ - \Delta H_0^\circ$
LiF	65	59.5	1.09	-1.091
LiCl	56	49.3	1.14	- .003
NaCl	50			

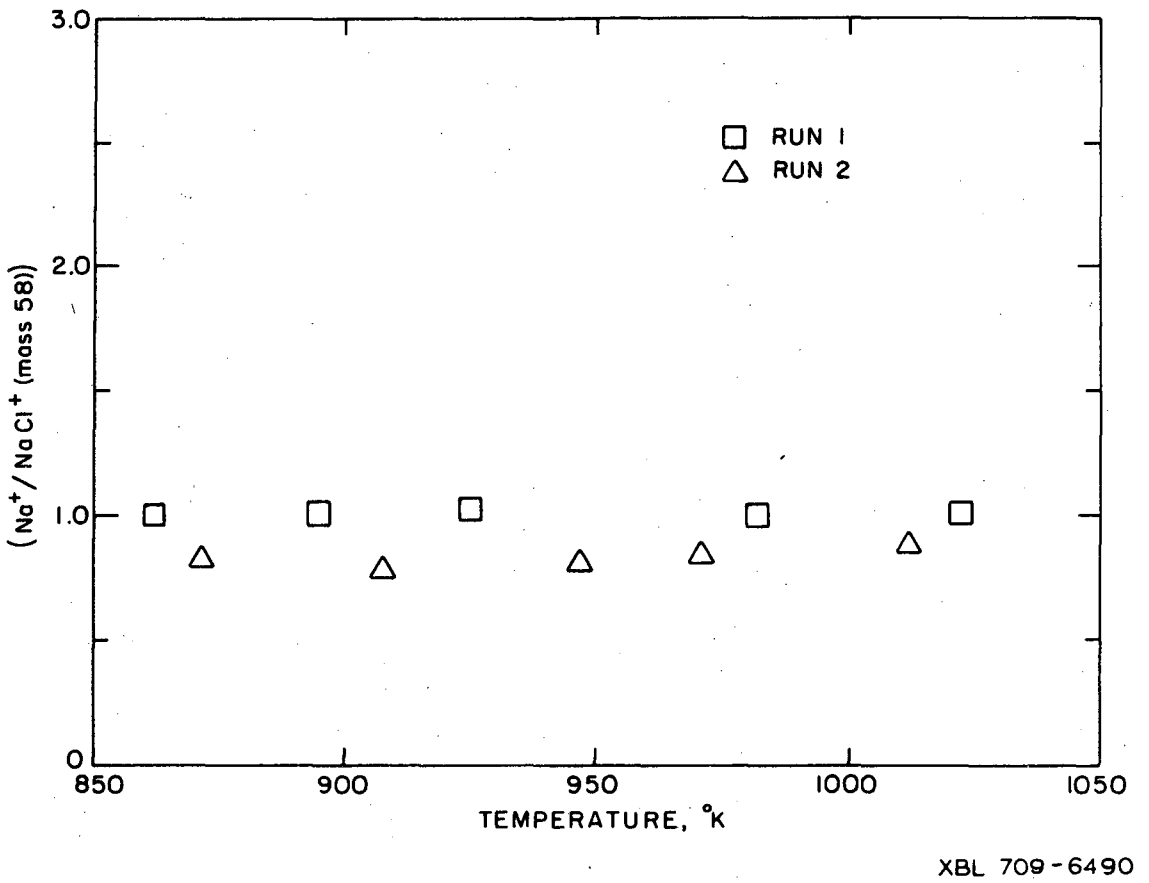


Fig. 1. The monomer fragmentation ratio ($Na^+/NaCl^+$) as a function of temperature.

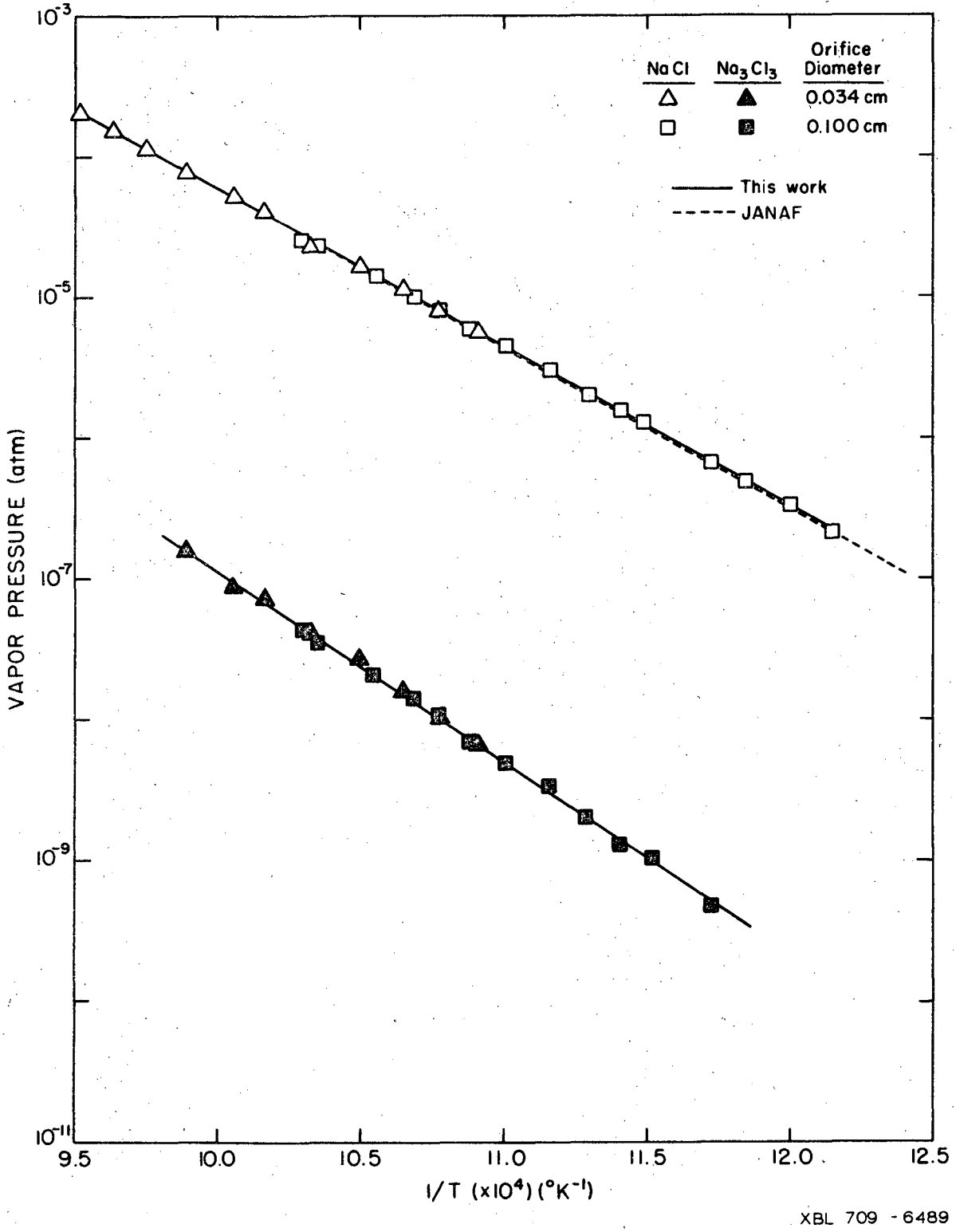
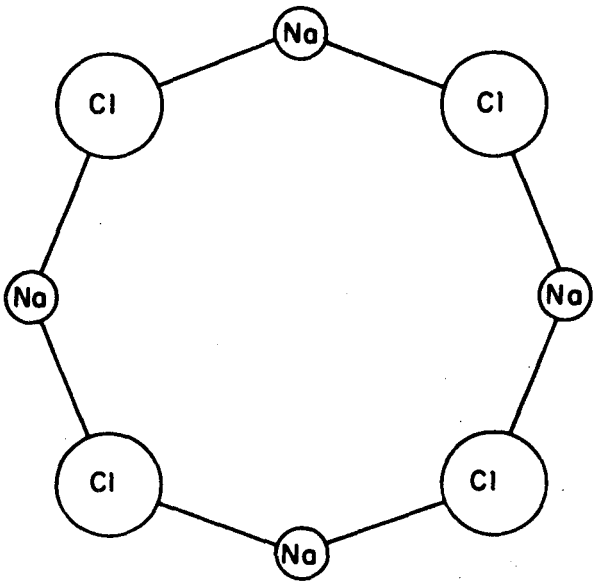


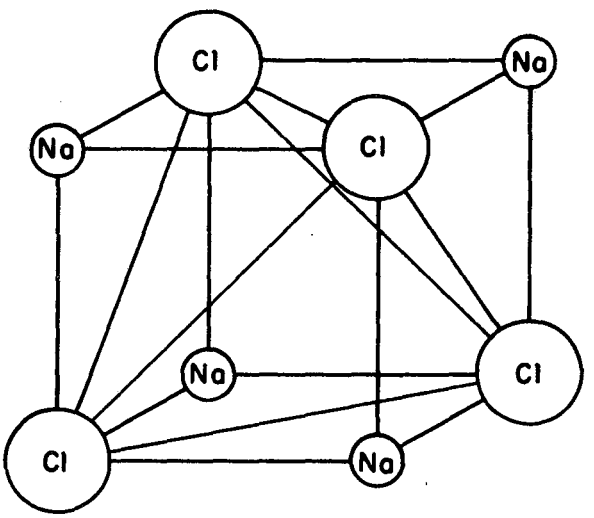
Fig. 2. Vaporization data for sodium chloride.



PLANAR RING

INTERATOMIC DISTANCE

Na - Na	4.55 Å
Cl - Cl	4.60 Å
Na - Cl	2.47 Å



DODECAHEDRON

INTERATOMIC DISTANCE

Na - Na	3.65 Å
Cl - Cl	3.80 Å
Na - Cl	2.63 Å

XBL 709-6491

Fig. 3. Sodium chloride tetramer structures.

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