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Lester, J.E.

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OF SODIUM CHLORIDE SINGLE CRYSTALS

J. E. Lester[†] and G. A. Somorjai

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
and Department of Chemistry,
University of California, Berkeley, California

ABSTRACT

The vacuum evaporation rate of the (100) of pure sodium chloride single crystals has been measured with a vacuum microbalance in the temperature range 450° to 650°C. The steady state vaporization rates of pure crystals with dislocation densities of $\sim 1 \times 10^6/\text{cm}^2$ were lower by about a factor of two than the maximum thermodynamic rate ($\bar{\alpha}_v \approx 0.5$). When the dislocation density was increased an order of magnitude (to $\sim 10^7/\text{cm}^2$) by straining the crystals, the steady state evaporation rate increased to approximately the thermodynamic rate ($\bar{\alpha}_v \approx 1.0$).

The relative vaporization rates of monomer and dimer were measured using a quadrupole mass spectrometer. Vaporization activation energies $E_D^* = 53 \pm 1$ Kcal/mole and $E_D^* = 62 \pm 1$ Kcal/mole were found for the monomer and dimer, respectively, in the temperature range of the experiments for low dislocation crystals. No dependence of the monomer to dimer ratio on the dislocation density was detected.

The presence of the divalent cation impurity, Ca^{++} , in the NaCl crystals markedly reduced the vaporization rate and increased the activation energy of vaporization. Crystals doped with 300 ppm Ca^{++} exhibited vaporization rates approximately an order of magnitude lower than the maximum thermodynamic rate ($\bar{\alpha}_v \approx 0.1$). The average activation

energy of vaporization for these crystals was $\bar{E}^* \approx 63$ Kcal/mole as computed from the total rate of vaporization. The monovalent impurities, Br^- , OH^- , O_2^- , have no detectable effect on the vaporization rate. An evaporation mechanism was postulated which could account for the experimental observation.

[†] Now with Department of Chemistry, Northwestern University, Evanston, Illinois.

INTRODUCTION

The equilibrium properties of the solid-vapor transition of the alkali halides have been well studied and the equilibrium vapor compositions of several alkali halides determined.¹⁻⁴ The kinetics of vaporization in this class of solids have received much less attention.⁵ Only two previous studies of vaporization of single crystals into vacuum have been reported.^{6,7} The purpose of this study was to thoroughly investigate the evaporation kinetics of a typical alkali halide, thus to elucidate the evaporation mechanism of the alkali halides. We chose NaCl as the subject of these investigations because reliable equilibrium vapor pressures and mass spectrometric ioni-

zation data were available. The evaporation rate from the (100) face of the single crystals was monitored in most of these studies. Use of stable faces of single crystals as vaporization sources is necessary for experimental reproducibility and interpretability.⁵

We have studied the vaporization behavior of sodium chloride into vacuum as a function of a) temperature, b) dislocation density and c) concentration of monovalent and divalent impurities in the crystal lattice. The total evaporation rates were measured with a vacuum microbalance and the vapor composition was monitored in separate experiments with a mass spectrometer. The solid vaporizes according to the dominant net reaction^{8,9}

In the temperature range of our investigation, 450° - 650°C, and under the different vaporization conditions, the dimer is roughly 5-30 mole percent of the vapor. The activation energies of vaporization of the monomer and dimer molecules were determined from the mass spectrometric data. We found that an increase in the dislocation density of the single crystals markedly increased the total steady state vacuum evaporation rate. Divalent impurities were found to decrease the

total evaporation rate and increase the activation energies of vaporization. A transient effect of dislocations on the vaporization rate of arsenic has been reported¹⁰ but, as far as we know, this is the first report of a steady-state effect. The effect of impurities on the vaporization behavior of binary semiconductors has been well documented.⁵

EXPERIMENTAL

Crystal Preparation

The majority of the crystals used in these vaporization studies were obtained from the Harshaw Chemical Company. These crystals are 99.95% pure. The major impurities are anions containing bromine and oxygen (probably Br^- , OH^- and O_2^-). Polyvalent cation impurities were present at levels not exceeding 5 ppm. In order to obtain samples of lower anion impurity concentrations crystals were grown by the Kyropoulos technique from zone refined starting materials.¹¹ These crystals had bromine and oxygen contents of less than 5 ppm. Details of the growth procedures and impurity analyses may be found in Reference 8.

Dislocation densities were determined by counting

chemically formed etch pits on a (100) cleavage face. An etching solution of 0.3g HgCl_2 in 1000 ml absolute ethanol was used.¹² With this etchant a one to one correspondance in etch pits on mating cleavage faces was observed. Most of the pure NaCl crystals had etch pit densities of $0.8 - 4 \times 10^6/\text{cm}^2$. We have assumed a constant proportionality between observed etch pits and dislocations which intersect the surface under observation and that the proportionality factor is close to one. The dislocation density of a crystal could be increased by plastically deforming it.^{13,14} Crystals with dislocation densities (etch pit counts) as high as $1.5 \times 10^7/\text{cm}^2$ were produced in this way. Etch pits in the unstrained crystals generally were uniformly distributed; however, in the strained crystals they tended to appear in "slip bands." Therefore, the etch pit density was counted in several areas on the surface and the results averaged to obtain the reported figure for these crystals.

Calcium doped NaCl crystals were grown from a melt containing CaCl_2 by the Kyropoulos technique. Crystals with calcium contents as large as 500 ppm have been grown. Oxygen doped samples were prepared by heating the crystals in an oxygen atmosphere at 750°C for

20-170 hours. It has been reported^{15,16} that oxygen enters KCl crystals in the form of O_2^- ions; similar behavior can be expected in the NaCl lattice. Sodium chloride crystals deliberately doped with OH^- anions were obtained from Harshaw Chemical Company. Bromine doped NaCl crystals were grown from the melt by the same Kyropoulos method that was used to obtain high purity sodium chloride crystals. The melt contained 0.5 mole percent sodium bromide. The crystal grown from this melt contained 0.35 mole percent Br^- . All commercial and strained crystals were annealed in evacuated sealed tubes or under dry nitrogen atmosphere before use to equilibrate the defect concentration in the crystal. The (100) cleavage plane was used in most of the experiments. After suitable preparation and/or pre-treatment the crystals were cleaved into 3 X 3 X 6 mm pieces, etched in a methanol-10% water solution and then wrapped in platinum foil so as to expose only the 3 X 3 mm face which is to be vaporized. The exposed sample surface area was measured before and after a run with an accuracy of $\sim 3\%$ ($\pm 0.3 \text{ mm}^2$).

Microbalance System

The quartz microbalance used to monitor the total

weight loss of the single crystals was built, in part, after a design by Honig and Czanderna¹⁷ and has been described in detail elsewhere.^{8, 18} It is used as a null device; the restoring force for a change in the sample weight was produced by a magnet and a solenoid. A Leeds and Northrop millivolt potentiometer with an reading accuracy of $2\mu\text{v}$ was used to measure the voltage drop due to the solenoid current across a precision resistor. The sensitivity of the balance was $\sim 18\text{ mv/mg}$. The balance was mounted on its support frame in the vacuum system as shown in Figure 1. The sample could be removed from the furnace hot zone by lifting its support fiber off the balance with a hook on the end of the linear motion feedthrough rod. This provision allowed us to introduce the crystal into the hot zone only after the furnace had reached a steady state temperature. The temperature profile of the furnace was adjusted to maintain at least a 5 cm long gradient free zone around the sample. The temperature of the furnace could be controlled to within $\pm 1^\circ$ in the range of our studies ($450^\circ - 650^\circ\text{C}$) and was measured by a Pt-10% Rh/Pt thermocouple attached to the outside wall of the sample tube. In preliminary experiments another thermocouple embedded in a sample placed in the center of the sample tube measured the actual sample temperature.

The temperature difference ($2-6^{\circ}\text{C}$) between the two thermocouples (inside the crystal and outside the sample tube) was measured simultaneously in the temperature range of our study and the outside temperature measured during the vaporization experiments was corrected to give the actual sample temperature.

Calculations of the heat balance at the vaporizing surface have been made to determine the maximum temperature gradient between the vaporizing surface and the crystal bulk.⁸ It was found that, for the rates of vaporization in our temperature range of study ($\sim 10^{-4}$ to $\sim 10^{-2}$ mg/cm²sec) and for the sample-furnace configuration, the heat flux to the sample surface could easily offset the heat loss due to vaporization.⁸ Thus, surface cooling should be negligible at the experimental vaporization rates and the surface temperature should be within 1° of the bulk temperature.

The fraction of the vapor flux which may be back-reflected onto the vaporizing surface from the tube walls is proportional to d^2/D^2 , where d is the sample cross section and D is the cross section of the reaction tube. In this experiment return flux was less than one-hundredth of the vaporization flux.⁸

The vacuum system was pumped by a liquid nitrogen trapped oil diffusion pump and a rotary forepump. The

system could be evacuated to 2×10^{-7} torr and all vaporization measurements were made in this pressure range.

The vacuum microbalance measurements yield the weight loss of the vaporizing crystal as a function of time. The rate of weight loss divided by the geometrical surface area gives the normalized rate, R_v (mg-cm²sec). This does not mean, however, that the number of vaporization sites is equal to the total number of surface sites. The vaporizing crystal surface was markedly roughened during vaporization. This roughening should produce some increase in the exposed surface area. The apparent pressure, P' , is calculated from the Hertz-¹⁸Knudsen-²⁰Langmuir²¹ (HKL) equation, $P' = R_v (2\pi RT/\bar{m})^{\frac{1}{2}}$. Since the sodium chloride vapor consists of more than one species (only the monomer, NaCl, and the dimer, Na₂Cl₂ are present in significant concentrations) $\bar{m}$ is the properly averaged molecular weight of the vapor.² If the dimer (D) to monomer (M) ratio, $D/M = a$, is known, the apparent pressures of the monomer and the dimer molecules at any temperature are given by $P'_M = \mathcal{P}' (1 + 2a)^{-1}$ and $P'_D = a\sqrt{2}\mathcal{P}' (1 + 2a)^{-1}$, where $\mathcal{P}'$ is the apparent pressure calculated by assuming that the vapor consists entirely of monomers, $\bar{m} = 58.5$ g/mole, in the HKL equation.⁶

Mass Spectrometer System

The mass spectrometer system used to determine the composition of the vapor emanating from the vaporizing crystal surface is shown in Figure 2. The quadrupole mass spectrometer (Electronics Associates, Inc. Model 200) was used in a configuration such that the molecular beam enters the ionizer chamber perpendicular to the quadrupole axis. The ions which are formed by electron impact are detected by a Cu-Be dynode electron multiplier. This type of mass spectrometer uses no magnets, is capable of rapid scan rates through its mass ranges (~50 ms scan), and transmits a larger fraction of ions than does a magnetic deflection instrument of equivalent resolution. The disadvantage of this type of analyzer is that it does not have a fixed transmission ratio as a function of ionic mass. The instrument discriminates somewhat against ions of larger mass. It can readily be calibrated, however, using an organic compound of known fragmentation pattern by comparing the results against the A.P.I. (American Petroleum Institute) published spectra.²² We have used n-heptane and n-hexane for this calibration.⁸

The sample holder is a graphite block supported by three tungsten rods. A Pt-Pt/10% RH thermocouple is held by pressure against the side of the sample. The

heating furnace is made of molybdenum wire and can be controlled to better than $\pm 2^\circ$. There is a movable slit (3 X 4 mm) approximately 10 cm above the sample which defines the molecular beam. It allows a vapor beam of the size of the crystal surface to pass through to the ionizer region. When the slit is closed the ambient background can be mass-analyzed. The vacuum system is built of stainless steel. The flanges are of the Varian-ConFlat type. The system is pumped by a large ion pump (250 l/sec) and rough-pumped by sorption pumps. After baking ($\sim 250^\circ\text{C}$) a vacuum of 10^{-9} torr can easily be obtained and 10^{-8} torr can be maintained throughout the vaporization studies. A gas handling manifold is also a part of the system.

The ion peaks detected in the mass spectrum of sodium chloride vapor were $m/e = 23(\text{Na}^+)$; 58, 60(NaCl^+) and 81, 83(Na_2Cl^+). The chlorine containing peaks had the proper chlorine isotope ratio. Berkowitz and Chupka⁸ reported the presence of Na_3Cl_2^+ ion in the mass spectrum of sodium chloride vapor from a Knudsen cell but its ion intensity was less than 1% of the NaCl^+ ion intensity at the highest temperature measured. The appearance potential plots [$I^+(23, 58 \text{ and } 81)$ vs. eV (electron energy)] show no abrupt changes of slope in the curves which would indicate the onset of some high energy fragmentation process.⁸

Thus, the possibility of direct vaporization of Na_2Cl or other Na_xCl_y molecules cannot be eliminated from this evidence alone. However, Pitzer and Snelson²³, in studying the properties of alkali halide vapor molecules by matrix isolation technique, have not reported Na_2Cl . Thus, Na_2Cl molecules should not be present in the vapor in significant concentration and the dominant vapor species are the NaCl and Na_2Cl_2 molecules.

Double oven experiments have been performed by Gorokhov, et al., to determine the contribution of the dimer fragments to each of the lower mass peaks.²⁴ The contribution of the dimer to the mass 58 (monomer) peak was reported⁴ to be less than 10%. In our experiments 23, 58 and 81 peaks were monitored during the determination of the temperature dependence of the vapor composition over the freely vaporizing crystal. The intensities reported in this paper have been corrected for isotope concentrations but not for instrumental factors. The activation energies of vaporization of the monomer obtained in this study have been corrected by the equation $E_M^* = 0.99 E_M^*$ (measured) which results from the elimination of the contribution of the dimer to the monomer peak.⁸ This correction (~ 0.5 kcal) is of the order of the experimental error. The mass 81 peak was assumed to be due entirely to the dimer. The ion current, I_1 , due to

a molecular species, i , may be related to the evaporation rate, R_i , by $R_i = a_i I_i T^{\frac{1}{2}}$, or to the apparent pressure by $P_i = k_i I_i T$ where k_i is a constant, dependent on geometry and species but not on P_i or T . The activation energies of vaporization of both the monomer and the dimer molecules were calculated from the slope of the $\log(IT)$ vs. $1/T$ curves by least square analysis.

The monomer-dimer ratios are computed from the ion current ratios by using the relative ionization cross sections derived by Kishin, Gorokhov and Sidorov from their equilibrium data.⁴ Let

$$I_M/I_D = (I_{23} + I_{58} + I_{80})/(I_{81} + I_{83}),$$

then the monomer to dimer ratio $M/D = I_M \sigma_D \tau_D / I_D \sigma_M \tau_M$, where σ_M and σ_D are the relative ionization cross sections and τ_D and τ_M are the transmission probabilities for the ions through the quadrupole analyzer. From our calibration, $\tau_D/\tau_M \sim 0.4/0.8$. The best agreement between our equilibrium data and that of Gorokhov⁴ was obtained using $\tau_D \sigma_D / \tau_M \sigma_M \sim 1$ in calculating the monomer to dimer ratios.

In these experiments we have measured the composition of the sodium chloride vapor flux emanating from the different sodium chloride single crystals as a function of temperature. Because of the large number of samples used in the determination of the temperature dependence of the vapor composition, the experimental

data will be tabulated by the least square parameters of the equation $\log (IT) = A + B/T$ fitted to the experimental data. The monomer to dimer ratio data are reported by tabulating the parameters A_{MD} and B_{MD} of the equation $\log(I_M/I_D) = A_{MD} + B_{MD}/T$.

This ratio may be converted into pressure ratios using applicable relative ionization cross sections and transmission factors for the various molecules.⁸ Thus, in this study, $\log(P_M/P_D) \sim A_{MD} + B_{MD}/T$.

RESULTS

Microbalance Measurements

a. Effect of dislocations on the evaporation rate:

The (100) face of sodium chloride was used in these studies. This face remained stable throughout the vaporization run, i.e. it did not exhibit faceting to other low index crystal planes. Thus, steady state evaporation rates could readily be obtained at a given temperature. Initial experiments showed large variations in the total evaporation rates from crystal to crystal (factor of three). In every case, however, steady state vaporization rates for a given sample could readily be achieved and maintained. It was discovered that the total evaporation rate of sodium

chloride crystals depends on the dislocation density in the sample. Figure 3 shows a plot of the logarithm of the evaporation rates of sodium chloride crystals with two different dislocation densities ($\sim 1 \times 10^6 \text{ cm}^{-2}$ and $\sim 1 \times 10^7 \text{ cm}^{-2}$) as a function of reciprocal temperature. Here we also plot the maximum evaporation rate as calculated from equilibrium vapor pressure measurements. The steady state evaporation rate was approximately doubled by increasing the dislocation density by an order of magnitude. Sodium chloride crystals with dislocation densities of $\sim 10^6 \text{ cm}^{-2}$ gave evaporation rates which were lower than the equilibrium rate by about a factor of two. The crystals with larger etch pit counts ($\sim 10^7 \text{ cm}^{-2}$) had evaporation rates equal to the maximum equilibrium rate. Except for dislocation density these crystals should be identical (impurities and preparation technique). These curves give an average activation energy of vaporization of approximately 55 kcal/mole. It should be noted that this value is a weighted average of the activation energies of vaporization of the monomer and dimer molecules for the different dislocation density crystals. The accurate values of the activation energies will be given in the section on the results of our mass spectrometric studies. In Table I we have

listed the measured experimental evaporation rates at the different temperatures for the different dislocation density crystals. These tabulated values are representative of results obtained from many sodium chloride samples. Since steady state evaporation rates could be maintained even after vaporizing more than one-half of the samples it appears that the dislocation density does not change appreciably in the crystals during vaporization at the evaporation temperatures.

b. Effect of divalent impurities (Ca^{2+}) on the evaporation rate.

Sodium chloride single crystals containing 330 ± 50 ppm Ca^{2+} ions used in these studies show the effect of divalent impurities on the vacuum evaporation rate of NaCl. Figure 4 shows the evaporation rates of these crystals as a function of the reciprocal temperature on a semilogarithmic plot. There is a large decrease of the total evaporation rate (by factor of five) for crystals doped with calcium. These Ca^{++} doped crystals not only show drastically reduced evaporation rates but also a marked increase of the average activation energy of vaporization. While the average vaporization coefficient has dropped to $\bar{\alpha}_v \sim 0.5$ obtained for the pure low

dislocation density sodium chloride crystals, the average activation energy of vaporization has increased to $\bar{E}^* \approx 63$ kcal/mole with respect to that obtained for the pure crystals ($\bar{E}^* \approx 55$ kcal/mole).

There is experimental evidence indicating that the concentration of calcium ions slowly increases at the vaporizing sodium chloride surface as a function of time during vaporization. The evaporation rate was found to decrease slowly for a given sample during the experiment. Simultaneously, the apparent activation energy of vaporization also increases. The effect of the changing divalent ion surface concentration on the vacuum evaporation rate will be described in detail elsewhere. The vaporization data given in Figure 4 are representative of the results obtained early in the measurements using several calcium-doped samples. In Table II we have listed representative values of the measured evaporation rates at the different temperatures for the calcium doped crystals.

We have also plotted in Figure 4 the vacuum evaporation rates reported by Rothberg, Eisenstadt and Kusch⁶ for sodium chloride single crystals. They have reported an average activation energy of vaporization of $\bar{E}^* = 62 \pm 4.6$ kcal/mole, which is the same within the accuracy of their experiment as the value we have obtained for the

calcium-doped crystals, The agreement between the vaporization rates and the activation energies reported by Rothberg, et al.⁶ and here may suggest that the sodium chloride crystals used in their studies contained divalent impurities, possibly Ca^{2+} in appreciable concentrations (>100 ppm). The large scatter in their data may also reflect the effect of slowly changing calcium surface concentrations.

c. Effect of monovalent impurities on the evaporation rate.

Sodium chloride samples doped with Br^- ion showed vaporization characteristics which were identical to undoped high purity single crystals of the same dislocation density. This result was comforting since some of the commercially obtained optical grade crystals contained relatively large amounts of this impurity.⁷ The presence of oxygen or OH^- ions in the crystals also had no observable effect on the evaporation rates in the temperature range of this study. For some of the oxygen doped samples a change in vaporization characteristics were observed when the evaporation rates of these crystals before and after the heat treatment were compared. In every case, however, these changes could be traced to a

change in the dislocation density of the sample.

Mass-spectrometric Studies

The accuracy of the mass-spectrometer system was tested by measuring the ion intensities, $I_1(T)$, as a function of temperature and heats of evaporation of the monomer and dimer molecules of sodium chloride from an equilibrium source (Knudsen effusion cell). The results can be expressed by the equations, $\log(I_{23}T) = 7.07 \pm 2 - 1.133 \pm .02 \times 10^4/T$, $\log(I_{58}T) = 7.42 \pm .3 - 1.58 \pm .02 \times 10^4/T$ and $\log(I_{81}T) = 8.38 \pm .3 - 1.277 \pm .02 \times 10^4/T$. Thus, the measured heats of evaporation for the monomer and dimer were 52.4 ± 1 and 58.4 ± 1 kcal/mole at 800°K . The accepted values are 52.1 and 59.5 kcal/mole at this temperature.¹ This agreement is good; therefore, the activation energies of vaporization should also be reliable. The monomer to dimer ratio in the NaCl vapor emerging from the effusion cell is given by, $\log I_M/I_D = 0.7 \pm .2 - 1.2 \pm .1 \times 10^3/T$. At $T = 1000^\circ\text{K}$ this equation yields $I_M/I_D = 2.6 \pm$. The only reported value at 1000°K for the pressure ratio, is $M/D = 3.0$.

The ion currents due to the vapor emanating from the freely vaporizing (100) face of all of the high

purity and pre-treated crystal samples have been monitored as a function of temperature. A representative curve showing the logarithm of the ion intensities (Na^+ , NaCl^+ , Na_2Cl^+) as a function of the reciprocal temperature is given in Figure 5. These slopes were used to calculate the activation energies of vaporization for both $\text{NaCl}(\text{vapor})$ and $\text{Na}_2\text{Cl}_2(\text{vapor})$. We also plot representative values of the computed monomer to dimer ratio on a semilogarithmic scale as a function of temperature.

We have also monitored the vapor composition from the (111) crystal face of sodium chloride as a function of temperature. Within the accuracy of our measurements both the monomer to dimer ratio and the activation energies of vaporization, E_D^* and E_M^* were identical to those for the (100) face of sodium chloride crystals of similar dislocation density. Inspection of the (111) face after the vaporization studies revealed the development of facets of (100) orientation. It is likely that after a short transient the unstable (111) surface has virtually disappeared and the largest fraction of the vapor flux came from the freshly formed (100) facets.

Table III lists the parameters, A and B, of the intensity equation $[\log(IT) = A + B/T]$ for the vaporization of the different dislocation density crystals. In

the same table we also list the activation energies of vaporization for the monomer and the dimer from crystals of different dislocation density. The parameters A_{MD} and B_{MD} which can be used to calculate the temperature dependence of the monomer to dimer ratio, are also tabulated. It is apparent that the activation energies vary somewhat for crystals with different etch pit densities. There seems to be a small increase in the activation energies with increasing dislocation density which is not significantly outside our experimental error. The monomer to dimer ratio appears not to change appreciably with increasing dislocation density in the crystals. There may be a small increase in the monomer concentration relative to the dimer for the highly strained samples ($1 \times 10^{-7} \text{cm}^{-2}$).

The vaporization parameters and activation energies of vaporization E_M^* and E_D^* have also been measured for sodium chloride crystals doped by a variety of impurities. The activation energies of vaporization for the dimer and monomer are the same as those of the undoped crystals for monovalent impurities investigated. There is an increase in the activation energies of vaporization of crystals doped with even small concentrations of divalent impurities.⁸

DISCUSSION

The following statements summarize the experimental results which could be used to determine the vaporization mechanism of sodium chloride single crystals.

1. The vacuum vaporization rates of the high purity (100) crystal faces of sodium chloride were lower than the maximum rates calculated from the equilibrium vapor pressure by about a factor of two for samples of low dislocation density ($\sim 1 \times 10^6 \text{ cm}^{-2}$). Their activation energies of vaporization [$E_M^* = 52.6 \pm 1 \text{ kcal/mole}$, $E_D^* = 62.1 \pm 1 \text{ kcal/mole}$] are comparable to the equilibrium heats of vaporization [$\Delta H_M = 52.1 \text{ kcal/mole}$, $\Delta H_D = 59.5 \text{ kcal/mole}$].

2. The total steady state evaporation rate increases with increasing dislocation density in the samples. Crystals with high dislocation density ($\sim 1 \times 10^7 \text{ cm}^{-2}$) showed evaporation rates which are equal to the maximum equilibrium rate.

3. Divalent ion impurity (Ca^{2+}) in the sodium chloride crystals in concentration $\sim 10^2 \text{ ppm}$ has markedly decreased (by a factor of five) the total steady state evaporation rates. Simultaneously, the average activation energy of vaporization has increased to $\bar{E}^*$ (Ca^{2+} -doped) $\approx 63 \text{ kcal/mole}$ from $\bar{E}^*$ (pure) $\approx 55 \text{ kcal/mole}$.

4. Monovalent ion impurities (OH^- , O_2^- , and Br^-)

had no effect on the vaporization characteristics of sodium chloride.

5. The monomer and dimer molecules are the dominant species in the vapor flux. The ratio of monomer to dimer molecules remains unchanged for the different pure sodium chloride crystals within the accuracy of the experiments. The ratio, M/D , seems to be little effected by doping treatments or moderate straining. Crystals with the highest dislocation density ($\sim 1 \times 10^7 \text{ cm}^{-2}$) show somewhat increased monomer concentration relative to that of the dimer.

Dislocations are known to affect markedly the condensation of thin metal films on sodium chloride crystals.²⁵ It has also been reported that changes in the concentration of dislocations cause an initial transient evaporation rate from arsenic and antimony single crystal surfaces.¹⁰ We find, however, that the steady state vacuum vaporization rate of the solid is determined by the dislocation density. These results indicate that the dislocation density in the sodium chloride crystals remains largely unchanged throughout the vaporization and that dislocations control the concentration of surface sites from which vaporization is to occur. An order of magnitude increase in the dislocation density increased the evaporation rate by a factor of two or the average evaporation

coefficient from $\bar{\alpha}_v \sim 0.5$ to $\bar{\alpha}_v \sim 1.0$. The variations in the evaporation rates of crystals with different dislocation densities are greater than the estimated error in our measurements by about a factor of three. The overall vaporization rate, J , (moles/sec) can be expressed by $J = K_0(S) \exp(-E^*/RT)$ where K_0 is a constant related to the frequency of motion of a molecule over the energy barrier, E^* , and (S) is the concentration (moles/cm²) of molecules in the surface sites from which vaporization proceeds. The activation energies of vaporization exhibit a small upward trend with increasing dislocation densities and corresponding increased rates of vaporization. This change in activation energy is less than 3 kcal (about 3 X average error). It should be noted that an increase of two kilocalories in E^* would decrease the evaporation rate of NaCl by a factor of three at 800°K if there were no accompanying changes in the pre-exponential factor. We observed an increase in the rate by a factor of two (2 X). Thus the pre-exponential factor would have to increase by a factor of six to accommodate the increased evaporation rate in this case. If all dislocations are equally effective in producing vaporization sites then one would expect the pre-exponential factor to increase linearly with dislocation density. There is an increased roughening of the sodium

chloride surface during vaporization which is probably due to enhanced evaporation around dislocations, in addition to ledge motion from crystal edges. It is apparent from our data that an etch pit density of 10^7 cm^{-2} corresponds to a dislocation density sufficient to establish the maximum equilibrium vaporization rate. We cannot say what is the lower limit on the vaporization rate of high purity crystals as we were not able to prepare samples with dislocation densities lower than $\sim 8 \times 10^6 \text{ cm}^{-2}$.

The monomer to dimer ratios were essentially unchanged for all of the sodium chloride crystals within the accuracy of the measurement (with the exception of the crystals of the highest dislocation density which showed larger relative monomer concentrations). If the dimers formed by an equilibrium association of two monomer molecules adsorbed on the surface then the monomer to dimer ratio, M/D , should decrease as a function of the increasing monomer concentration, i.e., $M/D \propto 1/M$, at a given temperature. This does not happen. For crystals which have high vaporization fluxes (and high dislocation densities) there are more monomer molecules on the surface, but, if anything, the monomer to dimer ratio increases with respect to the lower vaporization rate crystals (low dislocation density). Thus, there is no equilibrium between the monomer and dimer molecules on the vaporizing sodium chloride surface. It seems that the monomer

to dimer ratio is fixed by the relative energies necessary to remove a monomer or dimer, respectively, from a surface site. The absence of any appreciable equilibrium interaction between the absorbed monomer and/or dimer molecules could be due to the short residence time of these molecules on the vaporizing surface prior to desorption into vacuum. The mean free path ($\bar{X}$) of molecules away from the ledge depends on the activation energies of surface diffusion, E_{diff}^* , and of desorption, E_{des} , from the free surface and can be estimated by the equation $\bar{X} = a \exp [(E_{\text{des}} - E_{\text{diff}}^*)/2kT]$ where a is the interatomic distance.²⁶ For KCl these energies have been calculated to be $E_{\text{des}} = 0.35$ eV and $E_{\text{diff}}^* = 0.23$ eV.²⁷ These energies should be similar to NaCl. Using these values, at $T = 800^\circ\text{K}$, we have $\bar{X} = 0.4a$. Thus, at the vaporization temperature the mean free path of the sodium chloride molecule would not be more than a few lattice spacings. This implies that most of the monomer and dimer molecules vaporize near ledges and that surface diffusion cannot play an important role in the vaporization reaction.²⁸ The lack of any appreciable surface diffusion also inhibits the establishment of a steady state ledge concentration at the vaporizing surface which could be approximated by the equilibrium value. Thus, an increased ledge density

and, therefore, an increased kink concentration would be established locally around dislocations, and the vaporization rate could be increased with increasing dislocation density.²⁹

Monovalent anion impurities had no effect on the vaporization characteristics. Divalent calcium ions, introduced into the crystal lattice in low concentrations (~400 ppm), markedly increased the activation energies of vaporization ($\bar{E}^* = 63$ kcal/mole) and decreased the total evaporation rate by about a factor of five. The value of the average evaporation coefficient decreased from $\bar{\alpha}_v \sim 0.5$ to $\bar{\alpha}_v \sim 0.1$. It is apparent that the removal of a sodium chloride molecule from a surface site became more difficult in the presence of neighboring divalent ions. Such a marked effect on the evaporation rate by doubly charged impurities indicates that the breaking away of sodium chloride molecules from lattice sites (kinks) on the vaporizing surface is a rate controlling step. Since only monovalent anion impurities have been used we cannot determine whether divalency at either a cation or anion site or only at a cation site controls the evaporation rate. One may consider the different ionic size of the impurity resulting in lattice strain as being the cause of the decreased evaporation rate.

However, Ca^{2+} (radius of 0.99Å, only 0.04Å larger than the Na^+ radius) affects the evaporation rate while Br^- (radius of 1.95Å, or 0.17Å larger than the Cl^- radius) has no effect seems to indicate against this explanation.

These vaporization characteristics of the sodium chloride single crystals can be explained in terms of the stepwise model of vaporization of the heterogeneous solid surface.³⁰ We postulate a possible mechanism of vaporization of sodium chloride which can explain most of the data.

1. Ledges (of approximately monatomic height) are formed in large concentrations at positions where dislocations intersect the surface (and at the edges of the crystal).

2. Both monomer and dimer molecules are formed at the same sites (kinks) on these ledges.

3. The desorption rate of both monomer and dimer molecules from the proximity of the ledges is rapid. Thus, the equilibrium ledge concentration cannot be established at the freely vaporizing surface.

The first step explains the observed increase of the evaporation rate of sodium chloride surfaces with increased density of dislocations. Dislocations have been

shown to be nucleation sites for crystal growth and thermal etch pits have been observed on alkali halide crystals at the point of emergence of dislocations at the surface.¹³ Increasing the dislocation density will increase the number of ledge nucleation sites and thus, increase the density of kinks on the surface. The increase in kink density will increase the total evaporation rate.

The second step, the breaking away of both monomer and dimer molecules independently from the kinks, explains the insensitivity of the monomer to dimer ratio to increased dislocation density. The marked decrease of the evaporation rate (factor of five) of calcium doped crystals and the simultaneous large increase in the activation energy of vaporization indicate that the breaking away of sodium chloride molecules at ledges is a rate determining step in the vaporization process.

There are several complementary research results available which support this postulated mechanism. Knacke, Stranski and Schmolke³¹ have monitored the evaporation rate of KCl and KJ as a function of pressure.. They have also made electron micrographs of the surface after evaporation at different pressures. At high undersaturations (free vaporization conditions) the

vaporizing surface was completely roughened and the distance between microscopic steps was about 10^{-6} - 10^{-5} cm. For the same vaporization conditions the evaporation coefficient was in the range $1/3 < \alpha_v < 2/3$. These observations are in agreement with our results. At low undersaturation ($P \rightarrow P_{eq}$, near equilibrium) the surface becomes smooth, i.e., the distance between ledges increases. Simultaneously, the evaporation coefficient, α_v , decreases. Bradley⁷ measured the vacuum evaporation rates of different faces of potassium chloride single crystals. The reported evaporation characteristics are similar to those of pure sodium chloride crystals determined in this study. He also found that the activation energy of vaporization is virtually identical to the heat of evaporation just as we find for pure sodium chloride crystals.

It is expected that other divalent cation impurities would affect the activation energies of vaporization and the total evaporation rate of sodium chloride in a manner similar to calcium. Other alkali halides may show similar mechanisms of vaporization to that of sodium chloride, i.e., their evaporation characteristics should be sensitive to the concentrations of line defects and divalent impurities in the crystals. Experiments are in progress to test the presence of these effects.

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TABLE I: Representative values of the total evaporation rates of different dislocation density sodium chloride crystals.

Dislocation Density	T (°K±6)	Rate (mg/cm ² sec)	P' (torr)
$1.2 \times 10^6 \text{ cm}^{-2}$	749	$5.0 \pm .1 \times 10^{-5}$	3.07×10^{-6}
	827	$1.66 \pm .1 \times 10^{-3}$	1.06×10^{-4}
	838	$2.58 \pm .1 \times 10^{-3}$	1.68×10^{-4}
	846	$3.16 \pm .14 \times 10^{-3}$	2.07×10^{-4}
	850	$4.45 \pm .1 \times 10^{-3}$	2.92×10^{-4}
	865	$7.7 \pm .2 \times 10^{-3}$	5.05×10^{-4}
	880	$1.31 \pm .1 \times 10^{-2}$	8.69×10^{-4}
	899	$2.16 \pm .1 \times 10^{-2}$	1.47×10^{-3}
$1.2 \times 10^6 \text{ cm}^{-2}$	822	$1.4 \pm .1 \times 10^{-3}$	8.86×10^{-5}
	828	$1.9 \pm .15 \times 10^{-3}$	1.24×10^{-4}
	834	$2.5 \pm .11 \times 10^{-3}$	1.61×10^{-4}
	834	$2.54 \pm .12 \times 10^{-3}$	1.63×10^{-4}
	836	$2.6 \pm .1 \times 10^{-3}$	1.68×10^{-4}
$1.6 \times 10^7 \text{ cm}^{-2}$	821	$4.1 \pm .15 \times 10^{-3}$	2.62×10^{-4}
	833	$5.0 \pm .15 \times 10^{-3}$	3.26×10^{-4}
	851	$1.04 \pm .05 \times 10^{-2}$	6.84×10^{-4}
	865	$1.67 \pm .05 \times 10^{-2}$	1.10×10^{-3}
	899	$4.7 \pm .1 \times 10^{-2}$	3.21×10^{-3}

TABLE I: (continued)

Dislocation Density	T (°K±6)	Rate (mg/cm ² xec)	P ¹ (torr)
1.6 X 10 ⁷ cm ⁻²	824	2.7 ± .1 X 10 ⁻²	1.75 X 10 ⁻⁴
	847	8.2 ± .1 X 10 ⁻³	5.37 X 10 ⁻⁴
	861	1.5 ± .06 X 10 ⁻²	9.59 X 10 ⁻⁴
	865	1.42 ± .1 X 10 ⁻²	9.15 X 10 ⁻⁴
	867	2.3 ± .06 X 10 ⁻²	1.54 X 10 ⁻³
	884	2.3 ± .06 X 10 ⁻²	1.54 X 10 ⁻³
	892	2.1 ± .07 X 10 ⁻²	1.42 X 10 ⁻³
	919	3.2 ± .1 X 10 ⁻²	2.1 X 10 ⁻³

TABLE II: Total evaporation rates for Ca^{+2} -doped sodium chloride single crystals.

T (°K±6)	Rate (mg/cm ² sec)
864	1.86×10^{-3}
864	2.25×10^{-3}
874	2.13×10^{-3}
876	2.54×10^{-3}
876	3.31×10^{-3}
880	2.46×10^{-3}
888	3.59×10^{-3}
894	5.91×10^{-3}
897	1.02×10^{-2}
908	8.93×10^{-3}
917	1.28×10^{-2}

TABLE III: Representative mass spectrometric results, activation energies of vaporization for NaCl crystals with different dislocation densities.

Dislocation Density	.8 X 10 ⁶	1 X 10 ⁶	2 X 10 ⁶	~4 X 10 ⁶ /cm ²	~6 X 10 ⁶	>15 X 10 ⁶ /cm ²
A _{2s}	7.61 ± .2	8.41 ± .3	8.28 ± .2	9.05 ± .3	8.50 ± .3	8.88 ± .3
-B _{2s} X 10 ⁻⁴	1.116 ± .015	1.144 ± .03	1.188 ± .01	1.222 ± .02	1.190 ± .02	1.249 ± .02
A _{5s}	7.63 ± .2	8.69 ± .3	8.03 ± .2	8.76 ± .4	8.08 ± .4	8.62 ± .3
-B _{5s} X 10 ⁻⁴	1.1018 ± .02	1.150 ± .03	1.169 ± .02	1.211 ± .01	1.164 ± .02	1.223 ± .02
A ₈₁	9.155 ± .2	10.59 ± .3	9.68 ± .1	11.06 ± .3	10.30 ± .3	9.75 ± .3
-B ₈₁ X 10 ⁻⁴	1.2725 ± .02	1.345 ± .03	1.354 ± .01	1.433 ± .01	1.383 ± .02	1.373 ± .02
-A _{MD}	.96 ± .2	-----	-1.2 ± .2	-1.8 ± .3	-1.6 ± .3	-.8 ± .3
-B _{MD} X 10 ⁻³	1.4 ± .2	-----	1.8 ± .2	2.2 ± .2	2.0 ± .2	1.4 ± .2
E _M [*]	50.7 ± 1	52.4 ± 1.5	54.0 ± 1	55.6 ± .6	53.8 ± 1.1	56.6 ± .7
E _D [*]	58.2 ± 1	61.5 ± 1.6	62.0 ± .4	65.6 ± .6	63.3 ± .8	62.8 ± .9

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28. Similar calculations gave for the binding energy of a positive ion $E_{des}^* = 0.86$ eV on the alkali halide surface.²⁷ Thus, the ion mean free path on the surface is much larger than the mean free path for a neutral molecule. This result may explain the absence of ions in the vapor flux. Due to their long residence time on the surface ions can easily be attached again to a ledge before their desorption can take place.
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FIGURE CAPTIONS

- Fig. 1 Scheme of the experimental arrangement used in the microbalance studies of the total vaporization rate.
- Fig. 2 Scheme of the mass spectrometer system.
- Fig. 3 Evaporation rates of low and high dislocation density sodium chloride single crystals as a function of temperature. Etch pit densities, $\circ - 1 \times 10^6 \text{cm}^{-2}$; $\Delta - 1 \times 10^7 \text{cm}^{-2}$. Equilibrium data from Zimm and Mayer.³²
- Fig. 4 Evaporation rates of calcium-doped sodium chloride crystals ($\circ$) as a function of temperature. Evaporation rates (Δ) reported by Rothberg et al.^{5,23} The evaporation rates of pure low dislocation density crystals and the maximum equilibrium rates³² are also shown in comparison.
- Fig. 5 Representative curves of the ion intensities, $\text{Na}^+(\square)$, $\text{NaCl}^+(\odot)$ and $\text{Na}_2\text{Cl}^+(\blacksquare)$ and the monomer to dimer ratio, M/D , as a function of temperature.

XBL671-1-A

Fig. 1

XBL671-2

Fig. 2

XBL682-2101

Fig. 3

XBL682-2100

Fig. 4

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