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Abstract**Full Text**

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PHYSICS

Yu. A. GELMAN, A. M. ZATSELYAPIN, Yu. N. LYUBITOV, V. I. MIKHAILOV

ANOMALOUS EMISSION OF SODIUM CHLORIDE DIMERS FROM A TANTALUM SURFACE AND A FILM OF TABLE SALT*(Presented by Academician I. V. Obreimov, May 4, 1970)*

The literature has repeatedly considered ^(1,2) the features of evaporation of sodium chloride. In recent years special attention has been paid to the kinetics of this process ^(3,4). We shall confine ourselves only to the necessary remarks on the work of our predecessors. The work ⁽⁵⁾ on measuring the saturated-vapor pressure of sodium chloride, repeatedly checked ^(8,9) and confirmed, requires correction ^(6,7) in connection with the presence in the vapor of Na_2Cl_2 dimers, which was not known to the authors of ⁽⁵⁾. The most correct investigation of the Langmuir evaporation of NaCl is the work ⁽⁸⁾, since even in later studies ⁽³⁾ the reverse flux of particles onto the evaporating surface was poorly controlled. In view of the small temperature range, the data of work ⁽⁸⁾ have low accuracy.

A more detailed study of the kinetics of evaporation and of the interaction of a molecular beam of sodium chloride with tantalum and a film of table salt compels a new consideration of these processes. Closely related to the present study is the work ⁽¹⁰⁾ on the study of the dissociation on tungsten of molecules of sodium chloride and sodium iodide into atoms. The apparatus used by us has already been described ⁽¹¹⁾.

A beam of neutral particles Na_2Cl_2 and NaCl , issuing from source 1 (Fig. 1) onto target 3, interacted with it, and the reaction products entered chamber 6 and were detected by a mass spectrometer. Analyzer 7 allows us sharply to reduce the harmful influence of the background ⁽¹²⁾. The scheme of Fig. 1 allowed us to carry out three measurement cycles: 1) measurement, by Langmuir's method, of the evaporation rate of films of table salt previously deposited on the target; 2) measurement of the total emission of molecules from a target covered with the same film, with a flux of Na_2Cl_2 and NaCl particles incident on the target; 3) measurement of the flux of molecules from pure Ta, bombarded by a flux of Na_2Cl_2 and NaCl particles from the molecular source. In all cycles the temperatures of the target T_p were varied (600–800° K in the first two cycles, 700–950° K in the third cycle) and of the source T_c (1015 and 1044° K).

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The partial pressures of the NaCl and Na₂Cl₂ fluxes were determined from the formulas

$$P_M = K_M I_M T_p = K_M (I^{58} - l I^{81}) T_p, \quad P_D = K_D I^{81} T_p,$$

where $l = 0.34$ was determined previously ⁽²⁾, $K_M = 1.04 \cdot 10^6$ torr/a · deg, $K_D = 1.36 \cdot 10^5$ torr/a · deg (the last two coefficients were found by “splicing” our data with the data of ⁽⁸⁾ at the points $P_M = 5 \cdot 10^{-4}$ torr and $P_D = 1 \cdot 10^{-4}$ torr), and I^{58} and I^{81} are the ion currents measured by us.

The results of the first two measurement cycles processed by these formulas are shown in Fig. 2, where circles indicate the place of the “splicing.” The obtained activation heats of evaporation $E_M = 51.1 \pm 1.5$ and $E_D = 60.2 \pm 1.5$ kcal/mol agree with other data. Although we did not confirm the partial activation heats of evaporation obtained by the authors of ⁽⁸⁾, their experimental points (see Fig. 2) satisfactori-

lie on the extrapolated part of our curves. According to our data, the temperature dependence ⁽³⁾ of the evaporation coefficient α_i , determined from the formulas $\alpha_i = P_{i\lambda}/P_{ik}$, where $P_{i\lambda}$ and P_{ik} are the partial pressures of the monomer or dimer measured, respectively, by Langmuir and Knudsen, has not been confirmed.

Above points 3, 5, 7, and 9 of the branch of the second cycle merge with the curves of the first measurement cycle. But whereas the “monomer branches” 9-10 and 12-13, as the temperature is lowered, “press” against the Knudsen curve II-III, the “dimer branches” 3-4 and 5-6 intersect the Knudsen curve V-VI with a reliability exceeding the measurement errors.

Fig. 1. Physical scheme of the experiment. 1 –molecular beam with a Knudsen cell; 2 –shutter for incident molecular beams; 3 –tantalum target; 4 –shutter for detected molecular fluxes; 5 –collimator; 6 –ionization chamber of the mass spectrometer; 7 –electrostatic analyzer of detected particles by thermal velocities

Fig. 2. Partial pressures of sodium chloride monomers and dimers. I, II, III –vapor pressures of monomers and IV, V, VI –of dimers, calculated from data of ⁽⁵⁾; VII, VIII, and IX, X –partial vapor pressures of monomers and dimers according to work ⁽⁸⁾ (a –their experimental data); –our data (for monomers

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

and dimers) of the first cycle; —dimer emission at $T_c = 1015$ and 1044°K ; — the same for monomers

In the third cycle, curves were obtained (Fig. 3), where v is the fluxes of monomers and dimers reflected by tantalum (particles/cm² · sec), calculated from our experiments using the indicated calibration and according to the well-known formula

$$v_i = p_i / \sqrt{2\pi mkT}.$$

Here the dimers (as in the second cycle) behave anomalously: instead of a steep drop with increasing temperature to a level not recorded by our detector (which was observed for the same particles on tungsten in work ⁽¹⁰⁾), we found a gentle descent to a high-lying plateau. These facts are emphasized by Fig. 4, where our results (processed for all cycles) are given for the equilibrium constant of the dissociation reaction of dimers into monomers:

$$K_p = P_M^2 / P_D.$$

The heat of dissociation, calculated on the basis of Knudsen and Langmuir curves, proved to be 46 ± 3 kcal/mole, in agreement with other literature data. Sections 5—6 and 7—8 of the second cycle, and section 9—10 of the third cycle of measurements, behave anomalously.

If it is assumed that some of the dimers incident on the target are elastically reflected, then after processing curves 1—2 and 4—5 (Fig. 3) one obtains a system of points 11—12 (Fig. 4) that lie on a straight line whose slope coincides with that of straight lines 1—2 and 3—4.

Fig. 3. Fluxes of monomers and dimers from Ta (3rd cycle): 1—2 and 4—5 at $T_c = 1044^\circ\text{K}$; 2—3 and 5—6 at 1015°K

Fig. 4. Equilibrium constants. 1—2—according to data of (5), 3—4—according to the first cycle; 5—6—our data of the second cycle at $T_c = 1044^\circ\text{K}$; 7—8—the same for $T_c = 1015^\circ\text{K}$; 9—10—the same for $T_c = 1044^\circ\text{K}$ in the third cycle; a—result of allowing for partially elastic reflection

Conclusions. On the basis of the experiments carried out, it may be assumed that some fraction of the Na_2Cl_2 particles is elastically reflected from the tan-

talum target and from the sodium chloride film. To clarify the cause of the observed effects, the investigations must be continued.

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Institute of Crystallography
Academy of Sciences of the USSR
Moscow

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