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## Thermodynamic Functions of Dimethyl Selenide and Dimethyl Telluride

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The thermodynamic functions of dimethyl selenide and dimethyl telluride have been calculated in terms of the rigid rotator-harmonic oscillator approximation in the range 273.15-1500 K.

The thermodynamic functions of  $(\text{CH}_3)_2\text{Se}$  and  $(\text{CH}_3)_2\text{Te}$  were calculated in terms of the rigid rotator-harmonic oscillator approximation<sup>1</sup> from the following initial data<sup>2,3</sup>:

(CH <sub>3</sub> ) <sub>2</sub> X	M	10 <sup>17</sup> I, g <sup>3</sup> cm <sup>6</sup>	∠CXC	σ (C-X), Å	10 <sup>16</sup> I', g cm <sup>2</sup>	V <sub>3</sub> , kcal mole <sup>-1</sup>
(CH <sub>3</sub> ) <sub>2</sub> Se	109.03	187	96° 11	1.943	5.05	2.40
(CH <sub>3</sub> ) <sub>2</sub> Te	157.67	359	93° 33	2.141	5.08	2.27

Here M is the molecular weight, I the product of the principal moments of inertia, I' the reduced moment of inertia of the CH<sub>3</sub> top, and V<sub>3</sub> the barrier to internal rotation. The frequencies are as follows<sup>2,3</sup>:

ν [(CH <sub>3</sub> ) <sub>2</sub> Se], cm <sup>-1</sup>			ν [(CH <sub>3</sub> ) <sub>2</sub> Te], cm <sup>-1</sup>		
3005	2996	852	3019	3000	805
2950	1424	604	2918	1420	538
1425	890	3005	1414	820	3018
1284	3005	1424	1227	3018	1420
948	2920	911	872	2918	813
589	1434		528	1436	
158	1272		228	1225	

Table 1. Thermodynamic functions of (CH<sub>3</sub>)<sub>2</sub>Se.

T, K	S°	(G° - H° <sub>0</sub> )/T	(H° - H° <sub>0</sub> )/T	C <sub>p</sub>	(G° - H° <sub>0</sub> )/T	(H° - H° <sub>0</sub> )/T
273.15	70.1	-57.5	12.7	18.0	-71.8	-1.7
293.15	71.4	-58.4	13.04	18.7	-71.7	-0.4
298.15	71.7	-58.6	13.1	18.9	-71.7	0.0
300	71.9	-58.7	13.9	18.9	-71.7	0.1
400	77.8	-62.8	14.9	22.3	-72.6	5.1
500	83.1	-66.3	16.8	25.2	-74.1	8.9
600	87.9	-69.5	18.4	27.7	-76.0	11.9
700	92.3	-72.4	19.9	29.9	-78.0	14.3
800	96.4	-75.2	21.2	31.8	-80.1	16.4
900	100.3	-77.8	22.5	33.5	-82.1	18.2
1000	103.9	-80.2	23.7	35.0	-84.1	19.8
1100	107.3	-82.5	24.8	36.3	-86.1	21.2
1200	110.5	-84.7	25.9	37.5	-88.0	22.5
1300	113.5	-86.8	26.7	38.5	-89.8	23.7
1400	116.4	-88.8	27.6	39.4	-91.6	24.8
1500	119.2	-90.8	28.4	40.2	-93.4	25.8

Table 2. Thermodynamic functions of (CH<sub>3</sub>)<sub>2</sub>Te.

T, K	S°	(G° - H° <sub>0</sub> )/T	(H° - H° <sub>0</sub> )/T	C <sub>p</sub>	(G° - H° <sub>0</sub> )/T	(H° - H° <sub>0</sub> )/T
273.15	72.2	-59.3	12.9	18.6	-73.2	-1.1
293.15	73.5	-60.9	12.6	19.3	-73.9	-0.4
298.15	73.8	-61.0	12.8	19.5	-73.8	-0.0
300	73.9	-61.1	12.8	19.6	-73.8	0.1
400	80.1	-64.7	15.3	22.9	-74.2	5.8
500	85.5	-68.3	17.2	25.7	-75.9	9.6
600	90.4	-71.6	18.8	28.1	-77.9	12.5
700	94.9	-74.6	20.3	30.2	-80.0	14.9
800	99.0	-77.4	21.7	32.1	-82.1	16.9
900	102.9	-80.0	22.9	33.7	-84.2	18.7
1000	106.5	-82.5	24.1	35.2	-86.3	20.2
1100	110.0	-84.8	25.1	36.5	-88.3	21.7
1200	113.2	-87.1	26.1	37.6	-90.2	22.9
1300	116.2	-89.2	27.0	38.6	-92.1	24.1
1400	119.1	-91.2	27.9	39.5	-93.9	25.2
1500	121.9	-93.2	28.7	40.3	-95.7	26.2

The results of the calculation for the ideal gas state ( $P = 1$  ata) are presented in Tables 1 and 2. The units are cal mole<sup>-1</sup> deg<sup>-1</sup> (1 cal = 4.184 J).

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## The Mechanism of Nucleus Formation on the Surface of Supersaturated Solutions in an Electric Field

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The appearance of crystallization centres on the open surface of a supersaturated solution in an electric field is due to crystalline dust particles present in air. They are transmitted by the inhomogeneous electric field on to the surface of the drop, by-passing the electrodes.

The effect of the electric field on the formation of crystallization centres in supersaturated salt solutions was observed for the first time by Academician Shubnikov<sup>1</sup>, and has been explained in different ways by different workers. Some<sup>2,3</sup> attribute this phenomenon to structural changes in the solutions and others<sup>4,5</sup> to crystalline dust particles present in air. Moreover, there is no unanimous view concerning either the structural changes or the mechanism of the transport of dust particles onto the surface of the solution.

Careful analysis of the above studies and the present author's additional experiments throw some light on this problem. In the first place we shall consider the cause of the appearance of crystallization centres—processes occurring in solution under the influence of the electric field or the incidence of dust from the air. Saratovkin and Kulikov's experiments<sup>5</sup> and especially Shubnikov's study<sup>4</sup> support the latter. An unambiguous answer to this question can evidently be obtained by carrying out experiments in air freed from laboratory dust.

## EXPERIMENTAL

We placed the drop in a transparent plastic cuvette where a temperature of 40°C was maintained with the aid of a thermostat. The cuvette was closed on top by a piece

of glass. Two strips of foil (40 × 15 mm), covering the entire area of the walls and serving as electrodes, were glued on to the opposite walls of the cuvette. During the experiment, air passed through a No. 4 filter and a moist filter and dried by being passed through sulphuric acid was pumped through the chamber. This experiment ruled out an increase of the moisture content in the chamber as a result of evaporation and also the access of dust from the surrounding air.

A study was made of an  $\text{NH}_4\text{Cl}$  solution, which is the most sensitive to the effect of the electric field. The drops had a diameter of about 7 mm and the distance between the electrodes was 18 mm. A potential up to 15.5 kV, measured with an S-96 kilovoltmeter, was applied to the electrodes.

## DISCUSSION

In the purified air the drop crystallised in the same way as in the absence of a field, i.e. crystallisation centres were not formed in the dendrite-free space after the application of an electric field. When unpurified air was admitted to the drop, the appearance of a large number of crystallisation centres was observed after the application to the electrode of a potential of 5–10 kV or less. It was possible to alter the number of crystallisation centres by altering the concentration of dust particles in the atmosphere over the supersaturated drop.

Thus the earlier experimental results<sup>2-5</sup> must be explained by the effect of dust in the air surrounding the solution and not by structural changes. The electric field merely assists in the introduction of the nuclei into the drop.

We shall now show how small crystals from the air enter the drop having been repelled from the electrodes or having by-passed them. A drop of saturated  $\text{NH}_4\text{Cl}$  solution was placed in an open chamber, the walls and electrodes of which were coated by vaseline. When dendrites began to grow from the edges of the drop, the electric field was switched on, whereupon a multiplicity of crystallisation centres appeared in the drop. The implication is that dust particles entered the drop from the atmosphere, by-passing the electrodes. Otherwise they would have adhered to the electrode and the crystallisation centres should not have appeared.

In order to discover which components of the dust give rise to the crystallisation centres, we introduced artificially into a saturated drop dust collected outside the laboratory where the test substance was known to be absent. The introduction of such dust in the absence of the field gave rise to 1–2 and in the field to 4–5 crystallisation centres, while the application of the field in air containing  $\text{NH}_4\text{Cl}$  particles results in the formation of hundreds of centres. Thus our experiments confirmed the view put forward by Shubnikov and Parvov<sup>4</sup>.

The effect of the electric field on the crystallisation of a salt from solution evidently involves the generation on the surface of the drop of the solution of induced electric charges as a result of which the field set up by the electrodes greatly distorts also the lines of force concentrated at the edges of the drop. The crystals of the test salt or an isomorphous substance present in air tend to migrate to the drop either because they are themselves charged (as claimed by Shubnikov and Parvov<sup>4</sup>) or as a result of the dipole moment induced in them by the field. On entering the supersaturated drop, the crystals become

crystallisation centres. Analysis of the literature data<sup>1-5</sup> and our experiments permits the following conclusions.

In air freed from dust the electric field does not result in the appearance of crystallisation centres even when the average field strength between the electrodes is 13 kV  $\text{cm}^{-1}$  or more. Therefore the dust particles present in air must be responsible for the appearance of a large number of crystallisation centres on the open surface of a supersaturated solution following the application of the electric field. They are transported on to the surface by the inhomogeneous electric field generated near the drop, by-passing the electrodes. Crystals of the test substance present in laboratory air are mainly responsible for the appearance of the crystallisation centres.

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## The Permeability of Oxidised Aluminium to Hydrogen Mixed with Water Vapour

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The effect of the oxide film formed in the high-temperature (600°C) oxidation of aluminium in water vapour on its permeability to hydrogen has been investigated. The formation of a thick oxide film does not affect significantly the effective activation energy for the permeation of hydrogen ( $E = 27\,000 \pm 1\,000$  cal  $\text{g-atom}^{-1}$ ) and increases the permeability somewhat. The flux of hydrogen through an aluminium membrane during the oxidation of one of its sides in water vapour has been measured.

The rate of permeation of hydrogen through an aluminium membrane changes significantly in the presence of an oxide film<sup>1</sup>. According to Smithells and Ransley<sup>1</sup>, mechanical cleaning of the membrane, leading to the removal of the natural oxide film, results in a tenfold increase of the permeability and decreases the activation energy for permeation from 43 000 to 36 000 cal  $\text{g-atom}^{-1}$ . On the other hand, there are no data characterising the variation of the permeability to hydrogen of films growing on the surface of aluminium during high-temperature oxidation.