

is the same for isomers. Thus, the consideration of the ν values of Table VI leads to a comparison of the force constants k of the isomers. The force constants involved in these stretching vibrations can be used as a measure of the strength of the binding between X^- and R^+ .

This binding is the resultant of the attraction exerted on X^- by C^{4+} and the repulsion due to the other three negative groups surrounding the latter. Hence, the same factors which were assumed to cause an increase of refractivities and dipole moments of isomers can, on the basis of these simplified deductions, be expected to lead to the observed diminution of the stretching frequencies.

The analogy in the gradation of different properties is, however, not complete. For instance, the ΔR values of the bromides are larger, but their absolute $\Delta\nu$ values are smaller than the corresponding values of the chlorides. It is premature to attempt a clarification of these details, but a general remark should be added here.

Fajans⁵ recognized in 1921 that the difference in properties of chain isomers cannot be understood if one considers merely interactions within bonds connecting two adjacent atoms and that forces between more remote atoms have also to be taken into account. Now, on the basis of the quanticule formulations, it is evident that the

force between C^{4+} and X^- depends on the nature of the other three R^- groups. And *vice versa*, the properties of $(R^-)_3C^{4+}$ depend on the nature of X^- due to the coulombic forces as well as to mutual polarization effects. Thus it is not surprising to find that the complicated interactions among the quanticules do not influence different properties of isomers in an identical manner.

Acknowledgments.—The author wishes to thank Professor H. Rheinboldt, Director of this Department, and especially Professor K. Fajans and Dr. B. Cook Hillig, of the University of Michigan, for valuable discussions and criticism.

Summary

Densities and refractive indices, at 25°, for eleven spectral lines, of highly purified samples of the isomeric propyl and butyl mercaptans were determined.

From the results obtained, the molar refractivities, dispersivities and volumes were calculated. The extrapolated values for R_∞ were derived by the graphical method of Wulff.

An attempt was made to correlate these data, and those for analogous isomeric halides, as well as dipole moments and Raman frequencies, from the point of view of the quanticule theory of molecular structure.

SÃO PAULO, BRAZIL

RECEIVED JULY 22, 1949

[CONTRIBUTION FROM THE ALUMINUM RESEARCH LABORATORIES]

The Alleged Complexity of Solid Aluminum Chloride

BY L. M. FOSTER

The complex nature of solid aluminum chloride was reported by Smits and Meijering.¹ In brief, their observations were as follows: 1. By fractionally subliming pure solid aluminum chloride, a residue could be obtained which had a vapor pressure as much as 50% lower than the equilibrium vapor pressure at the same temperature. 2. By rapidly condensing aluminum chloride vapor, a solid condensate could be obtained which had a vapor pressure considerably higher than the equilibrium pressure. 3. The vapor pressure of these residues and condensates always reverted to the normal equilibrium values on long standing at constant temperature. 4. A "distorted" phase obtained as in 1, was observed to melt several degrees higher than the accepted melting point of aluminum chloride (192.6°). Once the material melted, its vapor pressure immediately reverted to the normal value for that temperature. 5. Only one phase could be detected by X-ray examination of solid aluminum chloride.

(1) A. Smits and J. L. Meijering, *Z. physik. Chem.*, **B41**, 98-111 (1938); see also A. Smits, "Die Theorie der Komplexität und der Allotropie," Verlag Chemie, Berlin, 1939, lithographed by Edwards Brothers, Inc., Ann Arbor, Michigan, 1944.

The explanation offered by Smits and Meijering for this anomalous behavior was that pure solid aluminum chloride is a mixture of two "pseudo-phases," each of which has a characteristic vapor pressure.

With the exception of Smits and Meijering's vapor pressure work, no measurement on aluminum chloride has indicated the possibility of separating the substance into two forms.²

The purpose of the present investigation was to extend the work of Smits and Meijering and to seek an explanation for the anomalous behavior they reported.

Experimental

Materials.—The aluminum chloride used for the vapor pressure measurements was made by the reaction of pure hydrogen chloride gas at about 400° with 99.99% aluminum contained in a pure alumina boat. The hydrogen chloride was made by adding concentrated hydrochloric acid dropwise to concentrated sulfuric acid. The gas was dried by passing it over phosphorus pentoxide. The

(2) The "International Critical Tables," Vol. 5, p. 98, and a number of handbooks, list alpha and beta forms of aluminum chloride having different specific heats. This was an editorial error, however. The reference cited dealt with ammonium rather than aluminum chloride.

aluminum chloride used for the melting point experiments was Eimer and Amend C. P. grade, resublimed twice in vacuum.

Vapor Pressure Measurements.—To investigate the vapor pressure anomaly, apparatus was constructed as follows: A Pyrex glass sickle-type gage was constructed (Fig. 1) which permitted the comparison of two pressures, the vapor pressure of freshly sublimed aluminum chloride and that of the residue remaining after the sublimation. The inner chamber was constructed with three sickle bulbs in tandem. This provided a sensitive gage which nevertheless would withstand a large pressure difference between the two sides without breaking. Bulb A, Fig. 1, communicates with the inside of the sickle. Initially, the two bulbs also communicate with each other through a by-pass, C, constructed from 2-mm. i. d. capillary tubing. The large chamber and the sickle within it are kept at 225 to 250° by means of nichrome heating wire wound around the former. Deflection of the needle of the sickle is observed with the aid of a telescope equipped with an internal scale.

Aluminum chloride, resublimed twice in vacuum after its preparation, was condensed into one bulb of the apparatus. The apparatus was sealed off in vacuum from the aluminum chloride preparation train and the vacuum pump at the points D. The under structure of the apparatus, comprising the two bulbs and the by-pass tube, was then immersed in a beaker of oil³ maintained at 170 to

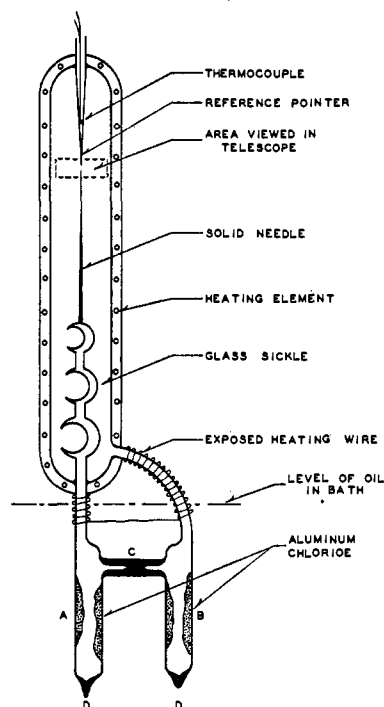


Fig. 1.—Apparatus for comparing aluminum chloride vapor pressures.

TABLE I
DEPENDENCE OF PRESSURE DIFFERENCE BETWEEN RESIDUE AND SUBLIMATE ON TEMP. AND TIME—EXPERIMENT 1

Observation ^a	Temp., °C.	Δp , cm.	Time, min.
a	179.5	+ 2.5	0
b	180	+ 1.6	2
Cooled Rapidly			
c	173	- 8.3	4
e	173.5	- 4.2	6
h	173	- 1.1	13
i	173	- 0.4	16
Heated Rapidly			
j	192	+31.3	25
p	192	+30.3	49
r	192	+28.5	54
u	192	+22.2	65
v	192	+ 9.7	70
x	192	+ 5.1	75
z	192	+ 3.7	80
bb	192	+ 3.0	88
Cooled Rapidly			
cc	170	-44.5	92
dd	170	-27.1	94
ff	170	-10.4	97
gg	170	- 6.6	98
ii	170	- 1.4	102
kk	170	- 0.4	107
Heated Rapidly			
ll	192	+25.0	117
nn	192	+12.5	122
pp	192	+ 8.0	125
rr	192	+ 4.4	131
tt	192	+ 3.7	143
vv	192	+ 2.5	153

^a About twice as many observations were taken as indicated here. The values reported are representative.

(3) Kronitex (technical tricresyl phosphate) obtained from Ohio Apex, Inc., Nitro, West Virginia.

180° for a minimum of three hours. This period of heating was deemed sufficient to establish any internal equilibrium as proposed by Smits and Meijering. After the heating period, the oil-bath was removed, and before the bulbs had cooled appreciably, part of the aluminum chloride was sublimed through the by-pass to the other bulb. The two bulbs were then isolated from each other by rapidly collapsing the by-pass with a gas-oxygen flame. The beaker of vigorously stirred oil was placed around both bulbs again and measurements were started immediately. Temperatures were read from a calibrated mercury thermometer immersed in the oil. If the vapor pressure of the residue and sublimate were equal, the needle of the gage would show no deflection. If there were a difference in the vapor pressure of the two parts, the needle would deflect accordingly. The apparatus was previously calibrated so that needle deflections could be converted to cm. of mercury pressure difference.

For the first experiment, all of the aluminum chloride was condensed in Bulb B initially. Then, after partial sublimation, the residue remained in this bulb, while the sublimate was in Bulb A.

When the oil-bath was first placed around the bulbs, an appreciable deflection of the needle was observed. About 10 minutes was required to get the telescope in place and adjusted after that time, however, so that only a 2.5 cm. pressure difference remained when the readings were started (observation a, Table I). The general procedure, after noticing that a considerable pressure difference could exist, was to keep the bath at a constant temperature until the pressure in the two bulbs became essentially equal, then to raise or lower the temperature a few degrees as rapidly as possible. In every case on raising the temperature a rather large positive deflection was observed corresponding to a higher pressure in Bulb A (sublimate). In every case on lowering the temperature, a comparable negative deflection was observed corresponding to a lower pressure in Bulb A. Regardless of whether the initial deflection was positive or negative, the pressure in the two bulbs became essentially the same after standing at constant temperature from about fifteen minutes to more

than an hour depending upon the magnitude of the initial difference. Because of the construction of the apparatus it was not possible to tell whether the pressure in one bulb was higher than the "equilibrium" pressure curve of Smits and Meijering or the pressure in the other bulb was lower, since either situation would result in differences observed.

The data of this experiment are contained in Table I. The value of Δp (the difference in pressure between the two sides) marked (+) signify higher pressures in Bulb A (sublimate). Values marked (-) signify higher pressures in Bulb B (residue).

For Experiment 2 a new charge of aluminum chloride was made. The experiment was set up in the same manner as Experiment 1 with the important exception that the residue and sublimate were interchanged in the bulbs. That is, all of the material was initially condensed in Bulb A. After aging for more than three hours at 170 to 180°, a part was distilled into Bulb B leaving the residue in A. Measurements were carried out as before. The results are given in Table II. Again Δp values marked (+) signify higher pressures in Bulb A (this time the residue).

The results are in qualitative agreement with those of Experiment 1 with the difference that in this case the higher pressure observed on rapid heating (+ deflections) was associated with the residue instead of the sublimate in exact contradiction to the observations of Smits and Meijering.

After completion of Experiment 2, the aluminum chloride in both bulbs was allowed to come to room temperature. The next day the experiment was repeated with the same aluminum chloride, still divided between the two bulbs. The effect had not diminished in magnitude and, in fact, even greater pressure differences could be observed between the two sides by heating or cooling the bulbs more rapidly than had been done before.

Melting Point Determination.—Smits and Meijering offered as additional proof for their complexity hypothesis their observation that aluminum chloride could be obtained as a phase which melted several degrees higher than the "equilibrium" melting point of 192.6°. Their experiment consisted of carrying out their phase separation, by rapidly subliming away part of a quantity of aluminum

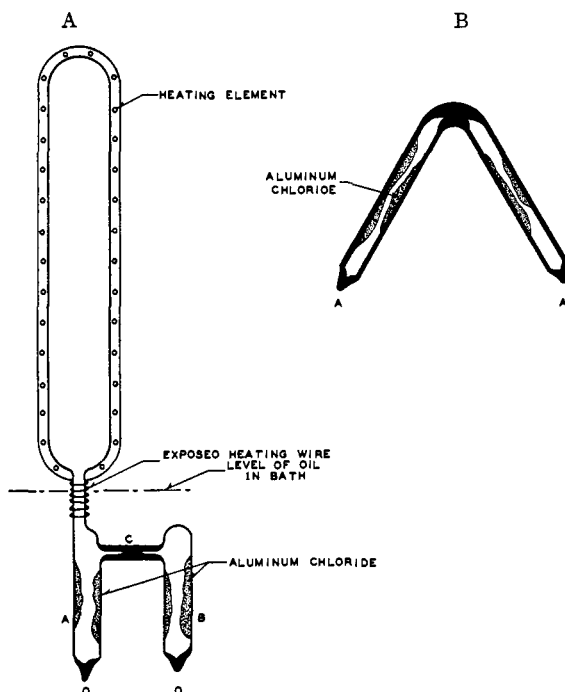


Fig. 2.—Apparatus for comparing aluminum chloride melting points.

TABLE II
DEPENDENCE OF PRESSURE DIFFERENCE BETWEEN RESIDUE AND SUBLIMATE ON TEMPERATURE AND TIME—EXPERIMENT 2

Observation ^a	Temp., °C.	Δp , cm.	Time, min.
a	180.5	+24.7	0
c	180.8	+ 8.6	8
e	179.8	+ 2.4	16
Cooled Rapidly			
f	175	- 8.3	22
h	175	- 1.1	33
j	175	- 0.3	38
Heated Rapidly			
k	190	+29.2	61
Cooled Rapidly			
l	175	-19.2	66
n	175	- 7.2	69
p	175	- 3.2	72
q	175	- 2.1	74
u	175	0.0	130
Heated Rapidly			
v	190	+27.9	205
w	190	+29.2	207
y	190	+26.7	210
aa	190	+22.2	214
cc	190	+19.0	217
ee	190	+13.8	223
gg	190	+10.4	228
kk	190	+ 6.8	241
mm	190	+ 5.7	245
pp	190	+ 5.1	256
rr	190	+ 4.6	268
Cooled Rapidly			
ss	175	-16.5	272
tt	175	-11.3	273
uu	175	- 6.3	276

^a See footnote after Table I.

chloride, and watching the residue for evidence of melting as the temperature was increased. They reported that in one case the aluminum chloride was still solid at 195.4-2.8° above the equilibrium melting temperature.

An experiment was carried out to check their observation in the following manner. A "U" tube was constructed from 4-mm. i. d. heavy-walled Pyrex tubing. About one gram of aluminum chloride was condensed into one arm, then the tube was sealed off in vacuum from the preparation train and the vacuum pump at points A (Fig. 2-B). The unit was left in an oven at 175 to 180° for about eighteen hours to "age." Immediately after the aging period about half of the material was sublimed into the other arm of the tube; then the connecting tube between them was sealed shut. The unit was immediately placed into the vigorously stirred oil-bath at 191°. The temperature of the bath was raised slowly while the material in both arms was observed for evidence of melting. The aluminum chloride in both arms started to melt at the same temperature (192.5 ± 0.2°) and at the same time, as closely as could be observed. Only five minutes had elapsed from the time the tube was removed from the oven to the time that first melting was observed, so it cannot be argued that equilibrium was reestablished in each arm of the tube before melting started. All of the material in one arm was melted after three minutes, and that in the

other arm after five minutes, roughly in proportion to the amount of material in the respective arms.

The experiment was repeated with a different type of apparatus as shown in Fig. 2-A. This consisted of two bulbs of about 7.5-ml. capacity connected by means of a capillary tube. Bulb A also communicated with a large heated tube so that the total volume in this side was about 75 ml. The experiment was carried out in the same manner as before. The aluminum chloride was initially condensed in Bulb A where it was aged for eighteen hours. Part of it was then distilled to Bulb B and the connecting tube was sealed shut. The large heated tube was kept at 210 to 235° to prevent condensation in it. Because of the additional clamping and adjusting required to get this experiment started, about thirteen minutes had elapsed from the time the unit was removed from the oven until it was placed in the bath and the temperature increased to 192.5°. After three minutes at that temperature the material in Bulb B started to melt, but there was no sign of melting in Bulb A. The oil-bath was maintained at 192.5 to 192.7° and only after sixteen minutes more did melting begin in Bulb A. Melting continued at constant temperature in both bulbs until all the material became liquid.

It is important to note that had the temperature been allowed to increase slowly throughout the experiment in order to determine the "melting point" of each "phase" the residue in Bulb A would have appeared to melt several degrees higher than the sublimate in Bulb B. It is possible that this was the manner by which Smits and Meijering obtained the high value they reported.

Discussion

It was possible to qualitatively reproduce the observations of Smits and Meijering concerning the apparently anomalous vaporization and melting of aluminum chloride. Further, it was possible to get exactly the opposite effects by simply reversing the aluminum chloride residues and sublimes in the apparatus.

The vaporization behavior has a possible explanation based on a slow rate of volatilization of aluminum chloride at constant temperature as suggested by Fischer and Rahlfs.⁴ In the first vaporization experiment, the volume available to the residue was about 70 ml. The volume available to the sublimate was only 21 ml. On increasing the temperature of both the residue and the sublimate, the sublimate reached saturation pressure first since it had the smaller volume to fill with vapor. On cooling both residue and sublimate, the residue retained a high pressure longer than the sublimate because of the larger volume of vapor to condense. By reversing the position of the residue and sublimate in the apparatus in Experiment 2, the sublimate had the larger volume to fill and hence required the longer time to reach saturation pressure, etc.

Such behavior is not surprising and, of course, would be exhibited to a degree by all substances. What is surprising, however, is the extremely long time required for saturation pressure to be at-

tained in these systems. It does not seem reasonable that an hour or more should be required for a substance to saturate a 50 to 100-ml. volume, in spite of its high heat of vaporization. It, therefore, seems necessary to assume that the heat transfer from the oil-bath, through the various heterogeneous layers, to the surface of the crystals is so poor that there is an appreciable temperature lag from the bath to the evaporating surface. During condensation, the large heat of condensation must be conducted away through the same poorly conducting media. This point of view was taken by Ruff and Bergdahl.⁵ Olbrich⁶ observed a similar slow rate of volatilization of aluminum fluoride.

The view that heat transfer is determinative is supported by the melting point experiments. The fact that in the first melting experiment both sublimate and residue melted at the same temperature is in sharp contradiction to the predictions of the complexity theory.

Smits and Meijering stated that the anomalous vaporization effects that were observed disappeared at the melting point. This can easily be attributed to the attainment of thermal equilibrium by better contact of the liquid with the walls, and by the agitation resulting from convection currents.

A number of manifestations of the lack of equilibria in these systems have been observed in this Laboratory. In one instance it required more than an hour for aluminum chloride vapor at one atmosphere, contained in a heated, 200-ml. spectroscopic adsorption tube, to completely condense into a 12-mm. diameter side arm held at room temperature. Incidental to another experiment, it was observed that aluminum chloride evaporating into a vacuum from a furnace held at 125° had a pressure corresponding to only about 90°.

Summary

The vaporization and melting of aluminum chloride have been investigated. The complexity theory advanced by Smits and Meijering to explain their observations on similar systems does not satisfactorily explain our results. They can be explained by assuming a very slow rate of evaporation of aluminum chloride together with a lack of thermal equilibrium in the solid state.

No evidence has come forward to indicate that aluminum chloride consists of more than one component or can be separated into two pseudo-phases as proposed by Smits and Meijering.

NEW KENSINGTON, PA.

RECEIVED JULY 13, 1949

(5) O. Ruff and B. Bergdahl, *ibid.*, **106**, 76-94 (1919).

(4) W. Fischer and O. Rahlfs, *Z. anorg. allgem. Chem.*, **205**, 1-41 (1932).

(6) W. Olbrich, Dissertation, Breslau, 26 (1929); see Fischer and Rahlfs, ref. 4.