

[CONTRIBUTION FROM ALUMINIUM LABORATORIES LIMITED]

Vapor Pressures of the System Sodium Chloride-Aluminum Chloride

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The vapor pressures of liquid mixtures of sodium chloride and aluminum chloride have been measured over a range of compositions from 50 to 67 mole % aluminum chloride. The results have been correlated with the published phase diagram. A compound, presumed to be NaAlCl_4 , exists in the gas phase above mixtures containing around 50 mole % aluminum chloride.

Introduction

This work was undertaken to investigate the reliability of the vapor pressures reported by Naryshkin,¹ and to provide additional data on the sodium chloride-aluminum chloride system.

Vapor pressures were determined at high temperatures with a metal transference apparatus and at low temperatures by means of a glass static system.

Experimental

Materials.—The starting materials were sodium chloride of analytical grade and commercial grade aluminum chloride supplied by the Aluminum Company of Canada Limited and redistilled in a metal evaporator-condenser system. The redistilled material was yellow or orange due to the presence of iron chloride and was available as lumps or powder. The lumps were preferable since they seemed to contain less water and hydrochloric acid. The necessary quantities of the constituents were weighed directly and were melted together in glass vessels. Melting commenced readily at temperatures close to the eutectic temperature, considerable gas evolution occurring as the aluminum trichloride dissolved. The solutions thus obtained were deep orange in color and contained dissolved hydrochloric acid. This could be removed by adding pieces of aluminum, which caused effervescence; when this ceased metallic iron began to be precipitated although the rate was slow unless the temperature was above 200°. Any iron remaining after this treatment could be removed by adding metallic sodium; this left a water-white solution from which the precipitated material could be removed by filtration through glass wool. A rough check on the composition could be obtained from the temperature at which freezing commenced, although many of the purified mixtures would supercool to a large extent, on occasion right down to room temperature.

Apparatus and Procedure. 1. **For Vapor Pressure Measurements at Low Temperatures.**—A static method was employed whereby the pressure exerted by the liquid in an otherwise evacuated space was balanced against a known air pressure. The essential part of the apparatus was a container about 1 cm. i.d. and 7 cm. long with a central tube leading to the exterior, and with provision for sealing it under vacuum once it had been filled. The external pressure was applied to the central tube and adjusted until the menisci in the tube and container were level. Capillary rise effects were negligible.

The apparatus was made of Pyrex glass. Since it was necessary to remove as much permanent gas as possible from the system, the mixtures were purified under vacuum and then transferred to the measuring vessel without exposure to the atmosphere. To this end the mixture, purified as described under the section headed "Materials," was sucked up into a separate vessel where it could be outgassed under reduced pressure in contact with small pieces of aluminum. These served to remove any traces of hydrochloric acid and helped to reduce bumping when the liquid was heated at low pressure. (The pressure at which it was possible to work depended on the composition of the mixture used.)

When outgassing appeared complete, the liquid was pushed over into the measuring vessel and allowed to freeze. (This operation was carried out with the apparatus inverted to prevent liquid entering the central tube.) It was subsequently sealed off under reduced pressure with the liquid boiling gently.

After sealing, the vessel was transferred as quickly as possible to a bath of a eutectic mixture of potassium nitrate and sodium nitrite stirred with a stream of air and heated electrically. Its temperature was measured with a Chromel "P"-Alumel thermocouple. The bath was contained in a glass tube so that the meniscus in the innermost tube could be observed. The pressure regulating system was operated by pumping against a capillary leak. Pressures were measured with a mercury manometer, atmospheric pressure being obtained from a mercury barometer.

After completion of an experiment, the mixture was allowed to freeze, sealed off in the vessel and sent for analysis.

2. **For Vapor Pressure Measurements at High Temperatures.**—The transference apparatus used in this work was made of mild steel and consisted of a cylindrical vessel to hold the melt, with a tube through which helium could be bubbled extending below the surface of the liquid. The exit tube ran from the gas space above the melt through the bottom of the vessel and into a water-cooled condenser. The furnace surrounding the vessel was made from a 4 in. i.d. steel pipe wound with Chromel "A" heating wire and insulated with a thick layer of asbestos powder. Power was regulated with a Variac. A Chromel "P"-Alumel thermocouple was placed in a well dipping into the liquid.

The gas, after leaving the condenser, passed to a water-filled aspirator bottle through a calcium chloride tube which prevented back-diffusion of water vapor. The flow of gas was measured by the weight of water run from the aspirator and its pressure and temperature by a mercury manometer and thermometer. Atmospheric pressure was read from a barometer.

During the time that the furnace was heating, a by-passing system allowed a stream of helium to flow backwards through the condenser to prevent aluminum chloride diffusing into it.

After a run, the exit tube of the vessel and the condenser were washed out and the washings sent for analysis. In calculations it was assumed that the gas was saturated with aluminum chloride vapor when it left the vessel and that the gas in the aspirator bottle was at all times saturated with water.

Results

From Static Experiments.—In spite of the precautions taken to remove permanent gas from the materials used in the static measurements, a non-reversible increase in pressure took place at the higher temperatures used. On lowering the temperature, results higher than those found earlier, but in themselves reproducible over all but the highest part of the temperature range, were obtained. By comparing the initial and final pressures at the lowest temperature an estimate of the quantity of gas evolved usually could be made and a correction for it applied to the readings taken as the temperature was lowered. The corrected values then normally coincided with the earlier values at the lower temperatures. The corrected values did not coincide with the earlier ones at higher temperatures since the latter were becoming progressively more in error due to gas evolution as the temperature was raised.

The results for the mixture containing 58.1 mole % AlCl_3 may be considered as an example of this procedure. The first measurement made showed a

(1) I. I. Naryshkin, *J. Phys. Chem. (U.S.S.R.)*, **13**, 690 (1939).

pressure of 12 mm. at 155°. The temperature was then raised stepwise to 338° where the pressure was 530 mm.; the measurements made as the temperature was raised are represented by circles on the sigma-plot in Fig. 1. The sample was then cooled stepwise to 165° where the pressure was 35 mm. Interpolation of the first measurements showed a pressure of 16 mm. at this temperature; it was consequently assumed that 19 mm. of permanent gas had been evolved. Assuming that this gas obeyed the ideal gas law, the corresponding correction at other temperatures was calculated and the values resulting are represented by triangles in Fig. 1. It can be seen that the agreement with the earlier values is good.

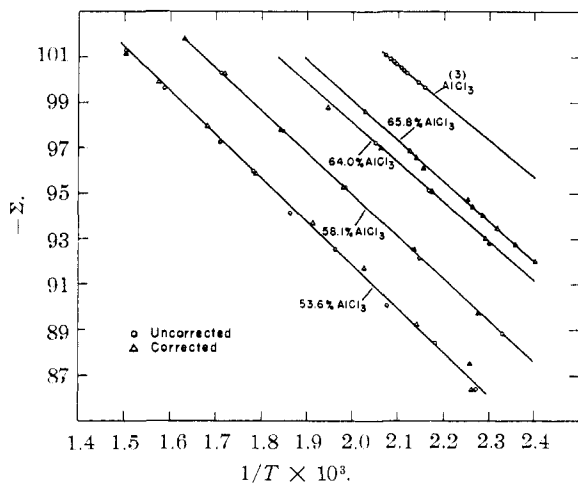


Fig. 1.—Sigma plot of vapor pressures from static experiments.

The largest correction that it was found necessary to apply was 81 mm. at 168° in the case of the mixture containing 53.6 mole % AlCl_3 . This was large probably because the temperature reached was the highest in these measurements (433°), but in spite of this the agreement between the corrected and uncorrected values can still be seen to be quite good.

In one case (65.8 mole % AlCl_3) it was not possible to reach a temperature low enough to obtain a reliable estimate of the permanent gas correction; several values were tried and the one which gave the straightest sigma-plot accepted. These results are thus not as reliable as the others, but since the correction was small (5 mm. at 143°) they should not be very much in error.

Figure 1 shows a sigma-plot ($\Sigma = -4.576 \log P_{\text{atm}} + 2.303 \Delta C_p \log T$) of the results from this series of experiments computed with a value of $\Delta C_p = -16 \text{ cal./}^\circ\text{C}$. (A value of $C_p = 60 \text{ cal./}^\circ\text{C}$. has been taken for Al_2Cl_6 in solution and $C_p = 44 \text{ cal./}^\circ\text{C}$. for Al_2Cl_6 gas. The latter includes the full contribution from the vibrational specific heat and will be correct at high temperatures. It seemed better to use this than the value of $C_p = 34 \text{ cal./}^\circ\text{C}$. adopted by Kelley.²) The results of Smits

(2) K. K. Kelley, "Contributions to the Data on Theoretical Metallurgy. III. The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances," United States Government Printing Office, Washington, D. C., 1935, p. 16.

and Meijering³ for pure liquid aluminum chloride are included for comparison.

From Transference Experiments.—Early runs using a salt melt containing about 56 mole % aluminum chloride gave somewhat erratic results, but showed that no volatile sodium compounds were present in the gas phase. However, with a melt containing about 50 mole % aluminum chloride, distillates obtained above 550° contained significant quantities of sodium. For the purpose of calculation, it has been assumed that this was transferred as a compound NaAlCl_4 ; discussion of this point is given below.

The results are given in Fig. 2.

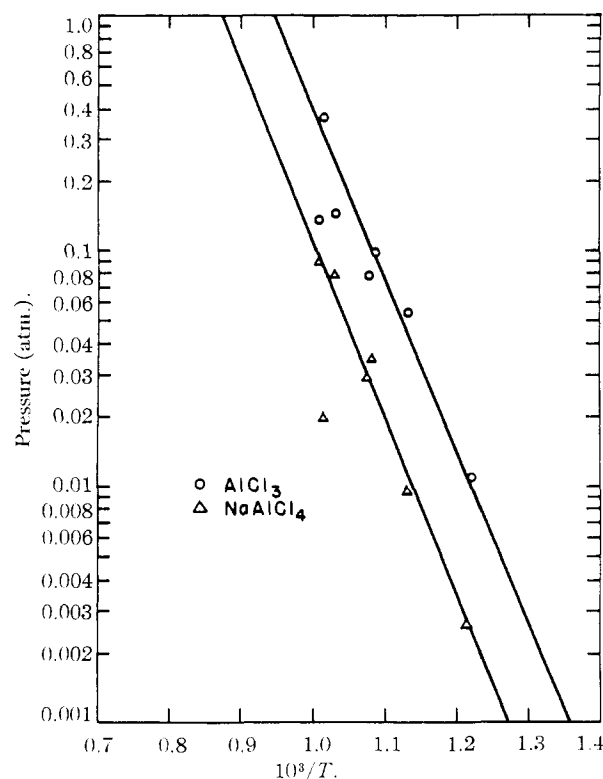


Fig. 2.—Vapor pressures derived from transference experiments (49.5 mole % AlCl_3).

Discussion

The vapor pressures found are much higher than those reported by Naryshkin¹; there is no obvious explanation of the discrepancy.

From the sigma-plots (Fig. 1) and the values of Smits and Meijering³ for pure aluminum chloride, the differential heats and entropies of solution of Al_2Cl_6 are obtained, and these are shown in Fig. 3. The line drawn to represent the entropies is the calculated ideal entropy of mixing of Al_2Cl_6 molecules with NaAlCl_4 molecules, *i.e.*, $R \ln n_{\text{Al}_2\text{Cl}_6}$, when the molar fractions are expressed in terms of Al_2Cl_6 and NaAlCl_4 . In constructing the curve to represent the heats, use has been made of the phase diagram of Kendall, *et al.*,⁴ in the region from 62 to 82 mole % AlCl_3 where solid aluminum chloride is in equilibrium with the liquid. Using the vapor pres-

(3) A. Smits and J. L. Meijering, *Z. physik. Chem.*, **B41**, 98 (1938).

(4) J. Kendall, E. D. Crittenden and H. K. Miller, *THIS JOURNAL*, **46**, 963 (1923).

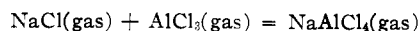
sure equation for the solid given by Stull⁵ and the entropies of solution calculated, the heats of solution are derived. The fact that the measured heats of solution are so close to those calculated may be taken as confirming the vapor pressure measurements.

The results may be represented by the equation

$$\log P_{\text{atm}} = -\frac{17,070 - \Delta\bar{H}}{4.576T} + \frac{136.60 - \Delta\bar{S}}{4.576} - 8.052 \log T$$

In selecting values of $\Delta\bar{S}$ from Fig. 3 for use with this equation, a correction should be applied for compositions between 50 and 60 mole %. It will be noted that the two points in this region, although only slightly displaced from the theoretical curve, (and that within the experimental error) are vertically as much as 0.5 cal./°C. from the line. Values in this range should therefore be corrected proportionately for the discrepancy if correct vapor pressures are to be calculated.

The phase diagram⁴ shows a compound NaAlCl₄ to exist in the solid; the entropy measurements above suggest that it exists in the liquid also. The most reasonable assumption concerning the transfer of sodium in the gas phase is that the same compound is responsible. (Since this work was completed, Howard⁶ has shown that the analogous fluoride, NaAlF₄, is stable in the gas phase). Owing to the lack of precision in the results given in Fig. 2 and uncertainties regarding the activities of sodium chloride in the liquid mixtures and the entropy of NaAlCl₄(gas) it is not possible to make precise calculations, but a ΔH of the order of -50 kcal. is indicated for the reaction



This is unexpectedly high. In order to confirm that the transfer of sodium was in fact due to a volatile compound and not to spray or liquid films creeping over the inner surfaces of the apparatus a few additional experiments were made.

(5) D. R. Stull, *Ind. Eng. Chem.*, **39**, 540 (1947).

(6) E. H. Howard, *THIS JOURNAL*, **76**, 2041 (1954).

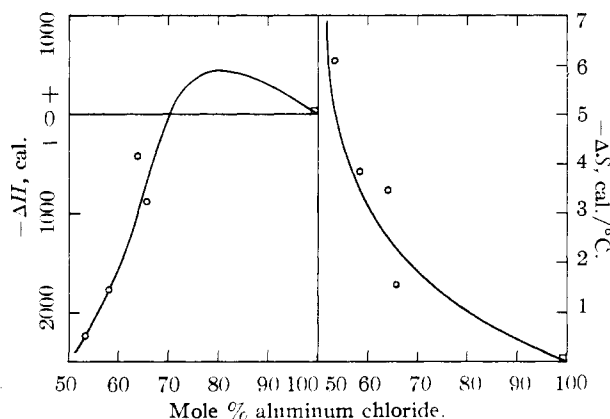


Fig. 3.—Differential heats and entropies of solution of Al₂Cl₆ in sodium chloride-aluminum chloride mixtures.

(1) Gas was passed over the liquid instead of bubbled through it—sodium was still transferred in large quantity.

(2) Some barium chloride was put in the melt—the ratio sodium:barium in the distillate was 10 times higher than in the melt.

(3) From pure liquid sodium chloride very little sodium was distilled.

(4) Distillation from one limb to the other of an inverted U-tube showed that transfer was faster in an evacuated tube than in one filled with argon at atmospheric pressure.

(5) It was shown that condensation of a liquid phase could occur at a temperature only a little below that of the liquid being distilled; this implies that the vapor was saturated.

All these results point plainly to the conclusion that distillation of sodium is by means of a volatile compound and, although there is no evidence as to its composition, the assumption that it is NaAlCl₄ is by far the most reasonable that can be made.

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The Crystal Structures of RhTe and RhTe₂

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The crystal structures of three rhodium tellurium phases have been determined from X-ray powder diffraction data. RhTe has the NiAs(B8) type structure. The high temperature form of RhTe₂ has the Cd(OH)₂(C6) type structure and the low temperature form has the pyrite (C2) type structure. The latter which has the lower volume per RhTe₂ is a superconductor at 1.51°K. discovered by Matthias, *et al.*¹

Introduction

Recently, Matthias reported¹ that the compound RhTe₂ is superconducting with a superconducting transition temperature of 1.51°K. Although not pointed out by Matthias at the time, there exist two RhTe₂ phases, only one of which is

superconducting² above 1.06°K. Also there is a phase of composition RhTe which is not superconducting above 1.06°K.² The purpose of this paper is to report the crystal structures of the aforementioned rhodium-tellurium phases.

Apparently, Wöhler, Ewald and Krall³ were the

(1) B. T. Matthias, E. Corenzwit and C. E. Miller, *Phys. Rev.*, **93**, 1415 (1954).

(2) B. T. Matthias, private communication.

(3) L. Wöhler, K. Ewald and H. G. Krall, *Ber.*, **66**, 1638 (1933).