calculated. Incidental to our work we obtained a value for the composition of the water phase at 500 atmospheres and 25° as follows: 39.74 cc. of carbon dioxide (S. T. P.) per g. of water.

Summary

The composition of the phase rich in carbon dioxide, here called "vapor phase," was determined at 25°, 31.04° (critical temperature), 50° and 75° up to 700 atmospheres.

The behavior of carbon dioxide–water mixtures was discussed in connection with the general thermodynamic equation of binary mixtures.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

The Alkyls of the Third Group Elements. I. Vapor Phase Studies of the Alkyls of Aluminum, Gallium and Indium[1]

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The alkyls of boron, aluminum, gallium and indium present some interesting questions of configuration and bonding. The atoms of each of these elements possess three valence electrons and can form three single covalent bonds to alkyl groups, thus building up a sextet of electrons. There is then the possibility of the central atom accepting another pair of electrons to complete an octet, which would account for the strong tendency of these alkyls to coördinate with many donor substances. Because neither the carbon nor the hydrogen atoms in the alkyls have unshared electron pairs to donate, association is not to be expected.

Stock and Zeidler[3] have shown by vapor density measurements that boron trimethyl and triethyl are monomeric in the vapor phase. There is some evidence for the association of aluminum trimethyl and triethyl,[4] although the reports of various investigators do not agree. Krause and Toonder,[5] and Brandt[6] report vapor density data for gallium trimethyl which show definitely that it is not associated in the vapor. There have been no vapor density measurements made on gallium triethyl, but cryoscopic studies[7] of solutions in benzene gave molecular weights approaching that of the dimer. The only alkyl of indium which has been prepared is indium trimethyl,[8] which melts at the surprisingly high temperature of 89°. This suggests association, and cryoscopic measurements indicated association to the tetramer in benzene. No vapor density data have been available.

Because of the lack of data on the vapor densities of gallium triethyl and indium trimethyl, and because of the unsatisfactory and conflicting reports on the properties of aluminum trimethyl and triethyl, which were investigated at an early date when refined techniques for handling these very reactive substances were not available, the present study has been undertaken. Vapor pressure and density measurements on these alkyls have been made over wide temperature ranges in order to establish the types of molecules present in their vapors. Thermal constants have been calculated.

Apparatus and Methods.—Since these alkyls react vigorously with oxygen and moisture, being spontaneously inflammable in air, they were prepared, purified and handled in nitrogen or in an all-glass evacuated apparatus.[9] Vapor pressure and density measurements were made in an all-glass cell of the "sickle" type, as described in a previous paper.[10] Nitrogen, rather than air, was used to balance the pressures of the samples in order to eliminate the danger of explosion, should the glass diaphragm break. Samples and cells were chosen of such sizes that saturation vapor pressure data at lower temperatures and vapor density data over higher temperature ranges could be obtained for the same sample. Readings were made both as the sample was progressively heated and then cooled, to make sure that the data represented equilibrium values and that irreversible decomposition had not occurred. In all cases duplicate runs were made and the data in the table for each alkyl summarize two such runs which showed good agreement.

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(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Detroit meeting, September, 1940.

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(4) Buckton and Odling, *Ann. chim. phys.*, [4] **4**, 492 (1865); Louise and Roux, *Compt. rend.*, **106**, 602 (1888); **106**, 73 (1888); **117**, 600 (1888); Quincke, *Ber.*, **22**, 551 (1889).

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TABLE I

TEMPERATURE–VAPOR PRESSURE DATA AND THERMAL CONSTANTS

	$Al(CH_3)_3$	$Al(C_2H_5)_3$	$Ga(C_2H_5)_3$	$In(CH_3)_3$	
				Solid	Liquid
A } (for equation $\log_{10} p = -A/T + B$)	2104	3625	2222	3014	2190
B }	8.152	10.784	8.224	10.520	8.238
% Mean dev. of calcd. p from exptl. p	±0.65	±0.76	±0.80	±3.33	±0.94
Temp. range, °C. (meas. at 5° intervals)	23–70	110–140	50–80	50–88	88–135
B. p., ±0.3°C. (extrapolated)	126.1	185.6	142.8		135.8
M. p., °C.				88.4	
Molar heat of vaporization, kcal.	9.6 ± 0.1	16.6 ± 0.4	10.2 ± 0.1	13.8 ± 0.4	10.0 ± 0.1
Molar heat of fusion, kcal.				3.8 ± 0.1	
Trouton constant	24.1	36.2	24.5		24.5

TABLE II

Temp., °C.	Degree of dissociation	$K_{\text{Dis.}}$ atm. × 10^2
100.3	0.075	0.283
115.0	.118	.767
155.7	.340	9.31

Molar heat of dissociation, 20.2 ± 1.0 kcal.

Aluminum Trimethyl.—This compound was prepared by the action of mercury dimethyl on aluminum,[4] and was purified by fractional distillation in dry nitrogen. The purity of the substance was established by analysis.

Anal. Calcd.: Al, 37.44; C, 49.97; H, 12.59. Found: Al, 37.76; C, 49.85; H, 12.78.

The vapor pressure measurements and the thermal constants are summarized in Table I; the variation of the molecular weight with temperature is given in Fig. 1. The dissociation data for the equilibrium $[Al(CH_3)_3]_2 \rightleftarrows 2Al(CH_3)_3$ in the range 100–156° are given in Table II.

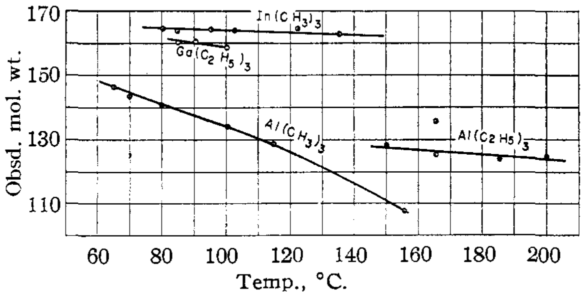

Fig. 1.—Observed molecular weights: calcd. for $[Al(CH_3)_3]_2$, 144.08; $Al(C_2H_5)_3$, 114.09; $Ga(C_2H_5)_3$, 156.8; $In(CH_3)_3$, 159.8.

The experiments prove that aluminum trimethyl is associated in the vapor state, the molecular weight observed in the neighborhood of 70° corresponding to that of the dimer. Dissociation progresses with increase in temperature and the interpolated apparent molecular weight of 115.8 at 140° agrees well with the value 114.2 calculated from Quincke's results.[4] No measurements were made above 155° because the alkyl decomposes at higher temperatures. Whatever the type of bonding involved in the association may be, it is relatively weak, the heat of dissociation being only 20.2 kcal. This is comparable to the heats of dissociation of the dimeric molecules of aluminum chloride, bromide and iodide, and of gallium trichloride, which are 29.0, 26.5, 22.5[11] and 20.0[10] kcal., respectively.

Aluminum Triethyl.—Aluminum triethyl was prepared, purified and analyzed for aluminum by methods similar to those used for aluminum trimethyl.

Anal. Calcd.: Al, 23.63. Found: Al, 23.88.

The values obtained for the vapor pressure and the thermal constants are summarized in Table I; the variation of the molecular weight with temperature is plotted in Fig. 1. Aluminum triethyl appears to be about 12% associated to the dimer at 150.6°. Association decreases with rise in temperature. It is noteworthy that the pressures measured as the samples were cooled, after having been heated to 200°, were lower than those obtained when the sample was first heated. (See Fig. 1. At 165.5° a molecular weight of 125.3 was first observed; after heating the vapor to 200° the measurement at 165.5° was repeated and the molecular weight was 135.4.) Additional experiments established the fact that if the alkyl is heated above 165° for protracted periods the pressure of the sample slowly decreases. This must mean that the sample is slowly undergoing a decomposition which involves a decrease in the number of molecules in the vapor state. Apparently at least one of the products is actually more volatile than aluminum triethyl, since the pressure in the cell at room temperature was always greater at the end of the run than at the start. The value calculated for the molar heat of vaporization is probably too high because it must include some heat of dissociation. The abnormal value for the Trouton constant is in line with this.

[11] Fischer and Rahlfs, *Z. anorg. allgem. Chem.*, **205**, 1 (1932).

Gallium Triethyl.—Gallium triethyl, prepared by P. L. Brandt[6] by the action of mercury diethyl on gallium, was purified by fractional distillation. It was shown to be very pure by spectroscopic tests.

Vapor pressure and calculated thermal data are listed in Table I; the plot of the molecular weight against temperature is given in Fig. 1. The vapor pressures are lower than those previously reported.[7] The values for the molecular weight show that, in the range 85 to 100°, the vapor of gallium triethyl is not associated, although it is reported to be associated in benzene solution.

Indium Trimethyl.—A sample of indium trimethyl, prepared and analyzed by R. W. Work,[8] was purified by distillation in the vacuum apparatus.

Vapor pressure–temperature measurements were made on large samples up to pressures of approximately one atmosphere in order to get adequate information on the solid–vapor and the liquid–vapor equilibria. Table I summarizes the results. Plotting log p against $1/T$ gives straight lines for the equilibria which intersect at the triple point; the observed vapor pressures are lower than those previously reported.[8]

Molecular weights determined for duplicate samples of indium trimethyl are shown in Fig. 1. Indium trimethyl is a monomer in the vapor state in the range 80 to 135°, showing no evidence for association like that reported for cryoscopic measurements in benzene solution.[8] If this alkyl is associated in the liquid or solid state, the values obtained for the heats of sublimation and vaporization seem surprisingly small because they should include a considerable heat of dissociation.

Discussion.—As a result of the vapor density experiments in this investigation on aluminum trimethyl and triethyl, gallium triethyl, and indium trimethyl, and of previous work on boron trimethyl and gallium trimethyl, a summary of the molecular species of these compounds found in the vapor phase is available. No association has been found for the vapors of the alkyls of boron, gallium or indium, whereas those of aluminum are definitely associated, the trimethyl strongly so.

Electron diffraction studies are now in progress on the vapors of these alkyls to determine their configurations. Cryoscopic work on their solutions in various solvents is also under way, and an attempt is being made to determine the crystal structure of indium trimethyl. It is hoped that from these studies an explanation of the apparent abnormal association of these compounds will result.

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Summary

1. The association of certain alkyls of aluminum, gallium and indium has been studied in the vapor state by making vapor density determinations in an all-glass apparatus.

2. Aluminum trimethyl exists as the dimer at 70°. It dissociates with increase in temperature, the heat of dissociation from 100 to 155° being 20.2 kcal.

3. Aluminum triethyl is 12% associated to the dimer at 150°.

4. Gallium triethyl and indium trimethyl are monomeric in the vapor state.

5. Vapor pressure and thermal data have been obtained for these substances.

6. The difficulty of accounting for the observed association of the alkyls is discussed.

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