

TABLE IV
"FREE ENERGY" OF GASEOUS HYDROGEN (NUCLEAR SPIN
ENTROPY INCLUDED)

$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0}{T}\right)$	$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0}{T}\right)$	$T, ^\circ\text{K.}$	$-\left(\frac{F^\circ - E_0}{T}\right)$
2100	40.800	3100	43.746	4100	45.959
2200	41.144	3200	43.992	4200	46.154
2300	41.475	3300	44.234	4300	46.345
2400	41.793	3400	44.467	4400	46.532
2500	42.100	3500	44.696	4500	46.716
2600	42.396	3600	44.919	4600	46.897
2700	42.684	3700	45.136	4700	47.073
2800	42.962	3800	45.349	4800	47.246
2900	43.232	3900	45.557	4900	47.417
3000	43.493	4000	45.761	5000	47.584

should be used to supplement Giauque's¹ table, which is reliable up to 2000°. In order that this table may be consistent with that of Giauque we have *included* the effect of nuclear spin. We wish to point out that this is inconsistent with our own custom of publishing both free energy and entropy tables with nuclear spin *excluded*. The values in Table IV may be converted to values with the spin *excluded* by reducing (arithmetically) each number by $R \ln 4$ ($= 2.755$).

Probable Errors.—The reliability of the spectroscopic values of the molecular constants of hydrogen is so high that it is probable that the small uncertainty in the molar gas constant contributes more to the probable errors of the entries in the tables than do the spectroscopic uncertain-

ties. One or two hundredths of a calorie should, therefore, cover the probable error in either free energy, entropy or heat capacity at any temperature while the error in $E^\circ - E_0^\circ$ might attain five to ten calories.

We wish to acknowledge the assistance of the National Research Council, through its committee on grants in aid, which provided the calculating machine used in making these calculations.

Summary

Accurate values of the heat capacity, of the entropy and of the "total energy" of hydrogen are calculated for the temperature interval 250 to 5000°K., and are tabulated. A corrected table of the free energy function between 2100 and 5000°K. is also included.

The influence of anharmonic vibration is particularly large in hydrogen and amounts, at 5000°K., to about 0.5 cal./mole/degree. The influence of molecular stretching is also relatively large and goes through a maximum at about 3500°K., at which temperature it makes a contribution, to the heat capacity, of about 0.18 calorie.

A table is included which shows the percentage distribution of H₂ molecules among the various vibrational levels, as a function of the temperature.

COLUMBUS, OHIO

RECEIVED JANUARY 19, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Indium Trimethyl¹

By L. M. DENNIS, R. W. WORK AND E. G. ROCHOW, WITH MICROSCOPICAL STUDY BY E. M. CHAMOT

In the Third Group of the Periodic Table from boron to thallium, either the normal trimethyl or triethyl compounds, or both, of all the elements with the exception of indium have been prepared. The present article deals with the synthesis and study of indium trimethyl.

Experimental

Pure indium was prepared by dissolving the commercial metal in nitric acid, precipitating indium hydroxide with ammonium hydroxide, dissolving the hydroxide in sulfuric acid and depositing the indium by electrolysis.² The

(1) The investigations upon which this article is based were supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

(2) Mathers, *THIS JOURNAL*, **29**, 485 (1907).

metal was then redissolved in sulfuric acid and redeposited electrolytically. Spectroscopic examination by Professor Papish of the final deposit showed that it contained about 0.001% cadmium but no other foreign metal.

Metallic indium, 34 g., mercury dimethyl, 54 g., and mercuric chloride, 0.1 g., were brought into bulb A, Fig. 1, and the air in the apparatus was displaced by dry carbon dioxide which was introduced through B. Around the neck of A was coiled a rubber tube through which cold water was passed to return the Hg(CH₃)₂ (b. p. about 95°) to A during the heating of the bulb. A was heated to about 100° for eight days, stopcocks B, D and E being closed. The heating was then discontinued, A was surrounded by an ice-bath, and the mercury dimethyl that had not reacted was distilled into the reservoir C by immersing that bulb in liquid air. The stopcock D was then closed.

The U-tube G, which had been weighed, was attached

to the side-arm F by the ground slip-joint S and was evacuated, H being then closed. Liquid air was brought up around G and the stopcock E (bore 6 mm.) was opened.

The crystalline product in A slowly sublimed into G. When a sufficiently large sample had collected in G, the bath of liquid air was removed and was brought around A to distil back any traces of mercury dimethyl that might have passed over into G. The stopper K was then turned to close, the U-tube was detached and weighed, and was then attached by the slip-joint to the vacuum fractionation apparatus.³ Water vapor, allowed to enter the U-tube from a bulb attached to the chain, caused, at room temperature, the evolution of a gas and the formation of a white solid. A sample of the gas, burned in a Dennis and Hopkins combustion pipet,⁴ was found to be pure methane. The addition of more water caused no further action at room temperature, but when the U-tube was surrounded by hot water, a violent reaction and liberation of gas resulted. The white solid remaining in the U-tube was identified as indium hydroxide.

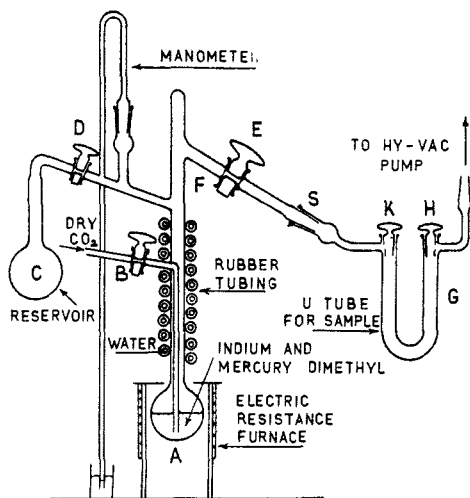


Fig. 1.

The experiment was repeated quantitatively to obtain a complete analysis of the substance and to ascertain the extent of the reaction with cold water.

A sample of 0.1661 g. was sublimed into the U-tube G and water was distilled into the tube. The gas that was evolved was pumped off into a mercury-filled gas buret, and was measured and analyzed. Dilute sulfuric acid was then run into the U-tube. There was further evolution of gas which was removed and analyzed as before. The indium was determined by precipitation with ammonium hydroxide, and weighing this, after ignition, as In_2O_3 .

Anal. Subs., 0.1661. Calcd. for $\text{In}(\text{CH}_3)_3$: In, 0.1193 = 71.81%. Found: 0.1190 = 71.65%. CH_3 , calcd., 0.0468 = 28.19%. Found: 0.0467 = 28.12%.

Evolution of methane: (a) On treatment of $\text{In}(\text{CH}_3)_3$ with cold water: millimoles $\text{In}(\text{CH}_3)_3$, 1.039; millimoles CH_4 , 2.081; molar ratio $\text{In}(\text{CH}_3)_3:\text{CH}_4 = 1.000:2.003$. (b) On treatment of residue from (a) with dilute sulfuric acid: millimoles CH_4 , 2.16; molar ratio of residue from

(a): $\text{CH}_4 = 1.000:1.004$. (c) Molar ratio of $\text{In}(\text{CH}_3)_3:\text{CH}_4$, sum of (a) and (b), 1.000:3.007.

Molecular Weight.—Since the normal methyl and ethyl alkyls of the elements boron, aluminum, gallium and thallium are gaseous or liquid at room temperature, it was expected that $\text{In}(\text{CH}_3)_3$ would prove to be a low-boiling liquid. To ascertain the extent of association evidenced by its solid crystalline form under ordinary conditions, its molecular weight was determined by measuring the depression of the freezing point of dry benzene. Sample, 0.0809, 0.0851 g.; lowering of freezing point, 0.021°, 0.022°. *Mol. wt.* [$\text{In}(\text{CH}_3)_3$]_n, calcd., 639.48, found, 604, 628. In solution in benzene, the compound therefore consists of four associated molecules.

Physical Properties

Melting Point.—The melting point of crystalline indium trimethyl under its own vapor pressure lies between 89 and 89.5°. The boiling point of the compound could not be determined because of thermal decomposition at higher temperatures.

Indium trimethyl vaporizes without formation of a liquid phase, and it sublimes slowly in a vacuum at room temperature. In a dry, evacuated, sealed tube, it can be vaporized repeatedly and condensed without decomposition.

Vapor Pressure.—At room temperature indium trimethyl develops a vapor pressure of about 3.5 mm. Its vapor pressure from 25 to 127° was measured at intervals of 3° in the vacuum apparatus. The results may be plotted as a straight-line function of $\log P$ and $1/T$, the equation of this line being

$$\log P = -2535 (1/T) + 9.2197$$

The pressures from 25 to 70° agree with the equation; at 30°, calcd. 7.15 mm., obs. 7.2 mm.; at 50°, calcd. 23.5 mm., obs. 23.8 mm.; at 70°, calcd. 67.44 mm., obs. 72.1 mm. The difficulties in making the measurements cause deviations from the linear function that increase with rise of temperature.

Density.—The density of indium trimethyl was measured by the pycnometric method, using mercury as the immersion liquid. The alkyl was fused in the evacuated pycnometer bulb in order to obtain a compact mass, and the bulb was then filled with mercury. The gas adhering to the crystals was removed by pumping. The density of the alkyl was then calculated from the weight of the sample and the weight of the displaced mercury: $d_{19}^{19} 1.568$.

Chemical Properties

Indium trimethyl is readily decomposed by moisture with the removal, at room temperature,

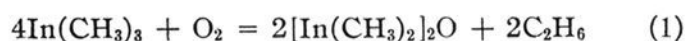
(3) Laubengayer and Corey, *J. Phys. Chem.*, **30**, 1043 (1926).

(4) Dennis and Hopkins, *THIS JOURNAL*, **21**, 398 (1899).

of two CH_3 groups, the third being expelled by dilute acids.

When either dry air or dry oxygen was brought into contact with the alkyl at 0° , violent oxidation was found to take place if the pressure was above 400 mm. At lower pressure, 200 mm. or less, the oxidation of the alkyl proceeded somewhat more slowly with the formation of a variety of products—a viscous, unstable liquid, an opalescent solid, and a mixture of volatile substances among which ethane, methane and methyl ether were identified. No carbon dioxide was formed.

Since the proportion of methane decreases with more intensive drying of the apparatus and of the oxygen that is used, it appears that the methane is formed by the action of moisture and not by that of oxygen. When the crystalline alkyl was allowed to stand in contact with oxygen at -78° for 250 hours, the gas mixture from the reaction bulb was found to consist of 92% oxygen and 8% ethane. This would indicate that the reaction is



To ascertain whether this supposition was correct, the white, non-volatile residue in the bulb was freed from the excess of unchanged alkyl by distillation, and dilute sulfuric acid was run in upon it. Methane was liberated and the indium was determined in the resulting solution in the usual manner.

Anal. Subs., 0.078. Calcd. for $[\text{In}(\text{CH}_3)_2]_2\text{O}$: CH_4 , 22.8 cc. = 19.66% CH_3 ; In_2O_3 , 0.0707 = 75.11% In. Found: CH_4 , 22.5 cc. = 19.37% CH_3 ; In_2O_3 , 0.0692 = 73.5% In.

Although the results deviate appreciably from the theoretical, doubtless because of the smallness of the sample, they suffice to show that the first stage of the oxidation is essentially as given in equation (1).

Indium trimethyl reacts with anhydrous methyl alcohol at room temperature, releasing two CH_3 groups as methane. The reaction is not as violent as that with water. The ratio of alkyl to methane produced was found to be 1.000:1.997. Ethyl alcohol reacts similarly, but more slowly. Pure methane is evolved.

Indium trimethyl is soluble in liquid ammonia, but there was no indication of the formation of an ammine at -35° .

Indium trimethyl is soluble in ethyl ether, but appears to form no etherate stable above -40° . However, since volatile gallium triethyl mono-

etherate is formed in the reaction of gallium bromide with the Grignard reagent, it was possible that a volatile etherate of the indium alkyl might similarly be synthesized, but no such product resulted from the action of methylmagnesium iodide upon indium trichloride.

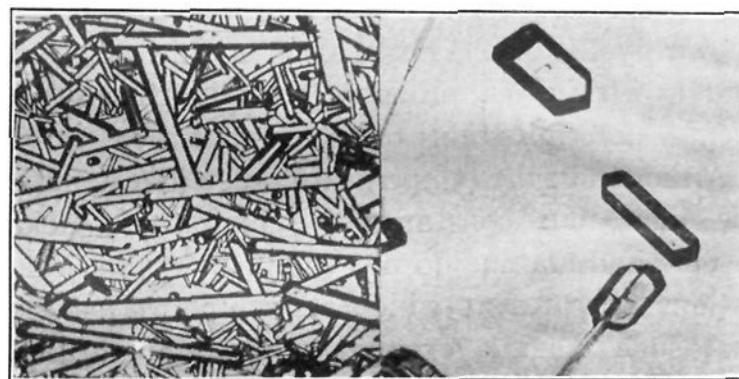
The alkyl is very soluble in dry acetone and dry benzene, and is readily soluble in ether and carbon tetrachloride.

Microscopical Examination

Since the indium trimethyl is instantly oxidized on exposure to air, the crystals could be examined under the microscope only through the wall of a flat-sided, exhausted glass tube.

Rapid sublimation within the tube gives rise to long, slender, acicular crystals. If sublimed more slowly, long, thin, lath-shaped prisms are formed. Upon still slower sublimation, large, beautiful, well-formed prisms with square, beveled or truncated ends, and short, thick, many-faced tablets are produced.

The crystals are highly refractive, strongly birefringent, with polarization colors of the first order. Extinction is parallel. The prisms are probably orthorhombic, but in several preparations the habit appeared to be monoclinic. In no case was the orientation such as to exhibit oblique extinction.



A

B

Fig. 2

Photographs taken through the wall of the glass tube show, A, crystals formed on rapid sublimation and, B, on slow sublimation.

Summary

This article describes the preparation and properties of indium trimethyl, $\text{In}(\text{CH}_3)_3$, a colorless, crystalline solid. In solution in benzene it has the formula $[\text{In}(\text{CH}_3)_3]_4$. A microscopical study of the crystals is included.

ITHACA, N. Y.

RECEIVED JANUARY 22, 1934