

In order to find the fundamental in the non-linear term of (2), we simply expand it in a Fourier series

$$f(x) = \sin x | \sin x | = \sum a_n \sin nx$$

and take the first term, for which $a_1 = 8/3 \pi$. Then from the point of view of the bridge detector

$$i(t) = V_m \sin \omega t (\kappa_0 + 8AV_m/3\pi) \quad (3)$$

whence

$$\kappa = \kappa_0 + 8AV_m/3\pi \quad (4)$$

Our experimental result was

$$\kappa = \kappa_0 + B\bar{V} \quad (5)$$

where B is the experimental slope and $\bar{V} = 2V_m/\pi$ is the linear average voltage. Comparison of (4) and (5) gives

$$A = 3B/4 \quad (6)$$

which brings our experimental result into exact agreement with the theoretical value.

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THE GENERAL ELECTRIC COMPANY
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The Viscosity of Liquid Ammonia

BY C. J. PLANK AND HERSCHEL HUNT

The viscosity of liquid ammonia is reported by Stakelbeck¹ to be 0.00218 g./cm. sec. at 20°, 0.00229 at 10°, 0.00238 at 0° and 0.00252 at -20°. He used the Lawaczec falling ball method. At -33.5° two values are reported, 0.002543² poise and 0.00260³ poise.

The viscosity of ammonia at room temperature is important. Since Stakelbeck's results have a small temperature coefficient, we re-determined the viscosity at 5, 15 and 25°. Our apparatus is shown in Fig. 1. The apparatus was carefully dried by heating it under reduced pressure. It was

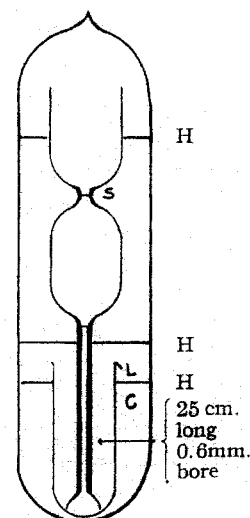


Fig. 1.—Viscometer.

calibrated with pure dry carbon disulfide and carbon tetrachloride. The following viscosities⁴ and densities of these compounds were used.

- (1) Stakelbeck, *Z. Kälte-Ind.*, **40**, 33-40 (1933).
- (2) Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).
- (3) Eelsey, *THIS JOURNAL*, **42**, 2454 (1920).
- (4) Thorpe and Rodger, *Trans. Roy. Soc. (London)*, (**A**)**185**, 397 (1895).

Temp.	Carbon disulfide Density	Carbon disulfide Viscosity	Carbon tetrachloride Density	Carbon tetrachloride Viscosity
5°	1.2856	0.004125	1.6230	0.01233
15°	1.2750	.003805	1.6037	.010476
25°	1.2554	.003565	1.5843	.009027

The constants, C and C' , of the equation

$$\eta = C\rho t - C'\rho/t$$

were determined at each temperature. The ammonia was dried over sodium and distilled under reduced pressure into the apparatus. After the outside jacket was sealed the apparatus could be rotated in order to fill the viscometer with the liquid. The supports, H's, held the viscometer perfectly vertical and rigid within the jacket when the outside jacket was placed in a vertical position.

The determinations were made in an air thermostat whose temperature was regulated to 0.05°. The time was measured with an accurately calibrated stop watch. Since the time of flow was in the neighborhood of four to eight minutes for the calibration and almost four minutes for the ammonia, the error in the measurement of time was not over 0.02%.

The apparatus was designed as shown because a closed system was necessary, and by having container C full of liquid when the meniscus passes S, a constant head was ensured. A fine lip, L, on C ensured a delivery of the liquids at the same level, so that a change in surface tension of the liquids did not interfere. The small head also increased the time of flow. It is difficult to fill the apparatus with cold ammonia by distillation and get the desired hydrostatic head when the liquid becomes warm. Two viscometers were used and the results are in excellent agreement. The viscosities and densities at the three temperatures are:

Temp., °C.	Density g./cc.	Viscometer number 1	Viscometer number 2	Viscosity of NH ₃ (av., g./cm. sec.)
5°	0.63197	0.001628	0.001607	0.001618
15°	.61821	.001468	.001446	.001457
25°	.60427	.001350	.001350	.001350

The densities were determined by the pycnometer method. These data, if we can judge by the long extrapolation, are in good agreement with the low temperature values in the literature. Stakelbeck's results would indicate that the temperature coefficient of viscosity for ammonia is much smaller than the coefficient for any other known liquid. His results agree with ours if we multiply

his values by the density of ammonia, an odd coincidence.

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The Preparation of Grignard Reagents from Magnesium Amalgams

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Magnesium amalgams have been used for the preparation of magnesium alkyls and aryls,¹ and for the coupling of ketones with chloro-esters and chloro-ethers.^{2,3,4} In view of the high reactivity of dilute amalgams of magnesium toward oxygen and water, it seemed interesting to investigate the formation of methylmagnesium halides from such amalgams, and then to follow with experiments on other less reactive halides.

The phase diagram for the system Mg-Hg shows two compounds, MgHg₂ and MgHg. Below 168° the equilibrium condition at the low magnesium end is a mixture of MgHg₂ crystals and liquid, and hence the reported solubility of magnesium in mercury (3% at 250°, 1% at 100° and probably 0.1% at room temp.) must refer to the solubility of MgHg₂. Since MgHg₂ contains 5.71% magnesium by weight, amalgams of this or greater concentration of magnesium will be solids, and amalgams in the range 5 to 0.1% magnesium will normally be mixtures of MgHg₂ with increasing proportions of liquid.

Amalgams containing from 0.1 to 1.0% of magnesium were prepared in an all-glass apparatus under an atmosphere of purified nitrogen.⁵ The dissolution of magnesium in mercury is strongly exothermic, so no external heating was required. After cooling in the stream of nitrogen, 50 cc. of a 0.1 N solution of methylmagnesium chloride was added through the condenser and methyl bromide was admitted. The purpose of the methylmagnesium chloride was to eliminate difficulties in starting, which would have confused the results obtained.

After refluxing the amalgam with the solution of methyl bromide for several hours, samples of

(1) Fleck, *Ann.*, **276**, 129 (1893).

(2) Sommelet, *Ann. chim. phys.*, (8) **9**, 484 (1906). Superficial amalgamation by addition of a trace of HgCl₂ was used here to start the reaction.

(3) Darzens, *Compt. rend.*, **151**, 883 (1910).

(4) Grignard, *Bull. soc. chim.*, **128**, 1285 (1926).

(5) The dilute amalgams are very sensitive to traces of oxygen and moisture, and it was found that the ordinary purification methods had to be supplemented by passing the gas through a 1% Mg amalgam before use.

the ether layer were withdrawn for determination of total CH₃MgX by evolution of methane with water. The increase of CH₃MgX over that added at the start was calculated as % yield based on the magnesium. Typical results were:

% Mg in amalgam	Yield of RMgX, %
0.1	0
0.5	4.1
1.0	25.3

Unreacted magnesium was evident in the mercury layer in each case as soon as the amalgam was exposed to the air. Attempts were made to displace a possible equilibrium between MgHg₂ and RMgX, but the results indicated that there was no such equilibrium. Dilute magnesium amalgams did not seem to react at all with methyl chloride, and the iodide is reported to form the R₂Mg compound under such conditions.¹

The odor of mercury dimethyl was detected in some of the experiments. Metallic mercury does not react with RMgX to form R₂Hg,⁶ but mercury halides would do so readily, and such halides might have been formed in small quantity.

The experiments indicate that the yield of RMgX from magnesium amalgams increases with the concentration of magnesium in the amalgam, and with the increasing possibility of free magnesium in the amalgam mixture. It may be concluded that MgHg₂ does not participate in the Grignard reaction as readily as magnesium, and that mercury therefore has an inhibiting effect on the reaction.

(6) Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., Chapter 4.

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Addition of Compounds of Dicyclohexylamine

BY CHARLES F. WINANS

In the hydrogenation of cyclohexanone in the presence of ammonia to form cyclohexylamine, a crystalline compound, m. p. 46°, formed in the cooled residue after distilling cyclohexylamine. This solid was found only when there was an insufficient amount of ammonia for complete reaction of the carbonyl group. Distillation of this product separated it into equivalent amounts of cyclohexanol and dicyclohexylamine, which recombined with evolution of heat to give the original crystalline material.