

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

## Liquid Ammonia as a Solvent. VI. The Dielectric Constant of Liquid Ammonia

BY H. M. GRUBB, J. F. CHITTUM AND HERSCHEL HUNT

The dielectric constant of liquid ammonia has been determined previously only by the method of Drude.<sup>1,2,3</sup> Since the exact value of this physical constant is essential for the development of the chemistry of liquid ammonia solutions we have redetermined the dielectric constant of liquid ammonia at various temperatures.

## Experimental

**Oscillator.**—The frequency of the oscillator<sup>4</sup> was three megacycles. The circuit is shown in Fig. 1.

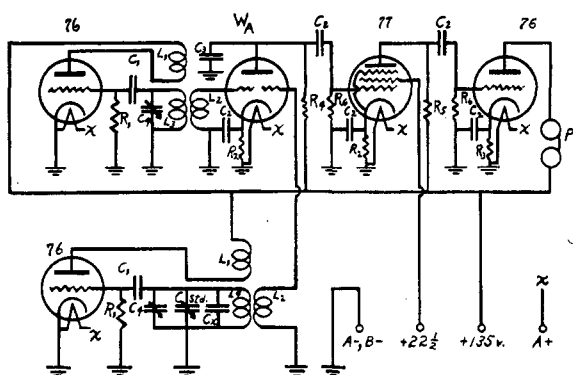


Fig. 1.—Heterodyne beat apparatus:  $W_A$  Wunderlich Type A detector,  $C$  std. 1500 mmfd. precision condenser Type 222-L,  $C_X$  cell,  $C_1$  250 mmfd.,  $C_2$  1.0 mfd.,  $C_3$  0.005 mfd.,  $C_4$  500 mmfd. variable condenser,  $R_1$  50,000 ohms,  $R_2$  3750 ohms,  $R_3$  1350 ohms,  $R_4$  20,000 ohms,  $R_5$  250,000 ohms,  $R_6$  500,000 ohms,  $L_1$  14 turns,  $L_2$  6 turns,  $L_3$  11 turns,  $L_4$  7 turns, No. 18 wire, 32 mm. form, plug in type,  $L_3$  and  $L_4$  spaced to be 19 mm. long. There is about 3 mm spacing between coils. Others wound solid.

**Standard Capacity.**—The standard capacity was a Type 222-L 1500 mmfd. General Radio precision condenser, recalibrated to permit estimation of capacities to 0.1 mmfd.

**Thermostat.**—An air-bath was used. The air was cooled and circulated by an automobile heater supplied with tap water. A 50-50 mixture of water and alcohol

was used in the regulator. This mixture did not creep by the mercury contact. The temperature was read by a Bureau of Standards thermometer and was constant to  $0.05^\circ$ .

**Cell.**—Various metals were tried for the electrodes. It was found necessary to use platinum which had been washed repeatedly with liquid ammonia. The inner electrode, a platinum wire, No. 18, was spaced with glass from the outer cylinder which was 9.525 mm. inside diameter. The cylinders were 7.62 cm. long.

The dielectric constants of the organic liquids used in calibrating this cell were determined in a variable condenser. Dry butanone (b. p.  $80 \pm 1^\circ$ ), dielectric constant 18.6, and two dry mixtures of c. p. acetone and c. p. benzene, dielectric constants 17.84 and 16.50, were used.

**Ammonia.**—The ammonia was distilled from sodium into an all-glass vacuum train containing the cell. The train had been dried at about  $400^\circ$  under a pressure of less than 0.001 mm. of mercury. The ammonia was condensed upon sodium in the first bulb of this train. The train was sealed from the iron cylinder and the system pumped out again. This method gave pure ammonia consistently (specific conductance about  $5 \times 10^{-7}$  mho). This conductivity, however, was too small to cause an error in our dielectric constant measurements. Additional drying and fractionation did not decrease the specific conductance or change the dielectric constant of the ammonia. We could only approach the specific conductance,  $1 \times 10^{-8}$  mho, reported in the literature by using point electrodes.

TABLE I

THE DIELECTRIC CONSTANT OF LIQUID AMMONIA				
$5^\circ$	$15^\circ$	$25^\circ$	$35^\circ$	$-60 \pm 10^\circ$
18.99	17.83	16.94	16.30	
18.92	17.81	16.88	16.25	26.7
18.91	17.81	16.87	16.24	
Av. 18.94 $\pm$ 0.05	17.82 $\pm$ 0.01	16.90 $\pm$ 0.04	16.26 $\pm$ 0.04	

Each of these values is an average of several measurements taken on different samples of ammonia. The data are easily reproducible so that the average values are accurate to within 0.5%.

## Summary

The dielectric constant of liquid ammonia at  $5$ ,  $15$ ,  $25$  and  $35^\circ$  has been determined.

LAFAYETTE, IND.

RECEIVED MARCH 4, 1936

(1) W. D. Coolidge, *Wied. Ann.*, **69**, 125 (1899).(2) Goodwin and Thompson, *Phys. Rev.*, **8**, 38 (1899).(3) Palmer and Schlundt, *J. Phys. Chem.*, **15**, 381 (1911).

(4) Smyth, "Dielectric Constant and Molecular Structure," Reinhold Pub. Co., New York, 1931.