

A FEW MEASUREMENTS ON THE ELECTRICAL CONDUCTIVITY OF ACETOPHENONE SOLUTIONS OF CERTAIN ORGANIC BASES AND ACIDS.—By H. JERMAIN MAUDE CREIGHTON, M. A., M. SC., DR. SC., Lecturer on Physical Chemistry, Dalhousie University, Halifax, N. S.

Read May 13th, 1912.

In an investigation¹ recently carried out by the author, it was found that the degree in which the decomposition of bromcamphor-carboxylic acid, in acetophenone solution, was accelerated by various alkaloids and other organic bases, was in most cases parallel to their affinity constants. As these affinity constants are for water solutions, it seemed desirable to determine whether the same order held when the conductivity of the bases was measured in acetophenone solution. Accordingly the following measurements were made.

Measurements on the conductivity of a number of substances in acetophenone have been made by *Dutoit* and *Friderich*², by the ordinary method of Kohlrausch. With the substances under investigation, however, it was found that this method was not sufficiently accurate, on account of the self-induction and electrostatic capacity effects that arose with the large resistances it was found necessary to employ.

The method employed, therefore, was the condenser method used by Nernst³ and Miss Maltby⁴. By this method the resistance of the electrolyte is determined through substitution in one arm of a Wheatstone bridge arrangement, which consists of four electrolytic resistances. Here the disturbance arising from electrostatic influences is eliminated by means of two condensers of variable capacity. The procedure is the same as in the determination of the dielectric constant, wherein the galvanic conductivity is compensated.

1. Creighton, H. J. M. : Dissertation, Zürich, 1911.

2. Dutoit, P. and Friderich L. : Bull. Soc. Chim., 19, 321, (1898).

3. Nernst, W. : Zeitschr. f. phys. Chem., 14, 622, (1894).

4. Maltby, M. E. : *ibid.*, 18, 133, (1895).

The apparatus used consisted of the following:

1. An induction coil and accumulator.
2. Liquid resistances (electrolytic).
3. Two variable condensers.
4. An electrolytic cell for the liquid being investigated.
5. A telephone.

The glass vessel used to hold the electrolytic resistances was of the form shown in figure 1. The arms AB and CD are about 10cm. long, the internal diameter of the former being 5mm. and of the latter 0.8mm. The platinum electrodes which fit inside these arms may be raised or lowered by turning. Both

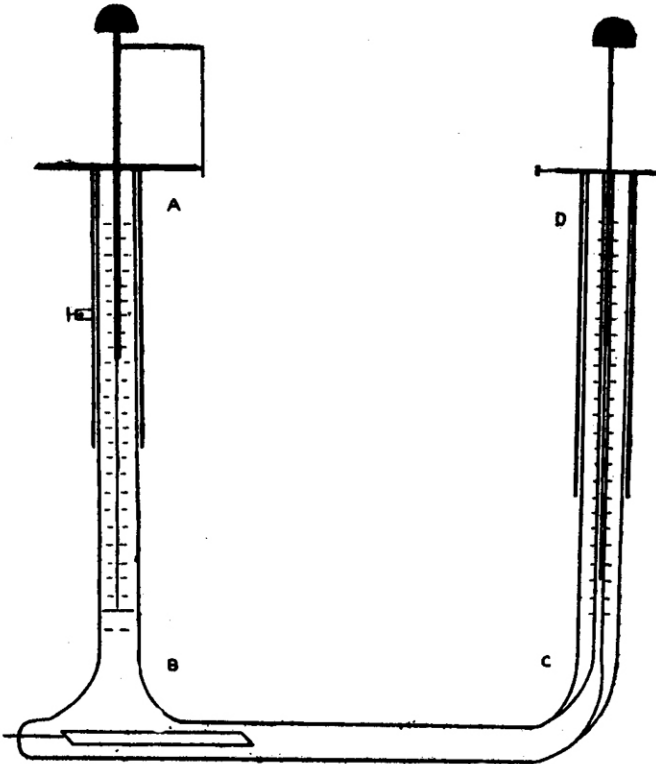


FIG. 1.

arms of the tube, as well as the metal disc at the top of AB, are graduated; AB in half millimeters and CD in millimeters. One complete turn of the larger electrode raises it 0.45mm., and since the metal disc at the top is divided into 100 parts, it is possible to read a change in the height of the electrode to a few $45/10000$ mm. The narrow arm of this resistance tube is used for measuring very high resistances, while the wider arm is used for smaller. By placing the unknown resistance behind the measuring resistance, or in shunt with it, it is possible to measure resistances varying from one hundred to thirty million ohms, within a few per cent.

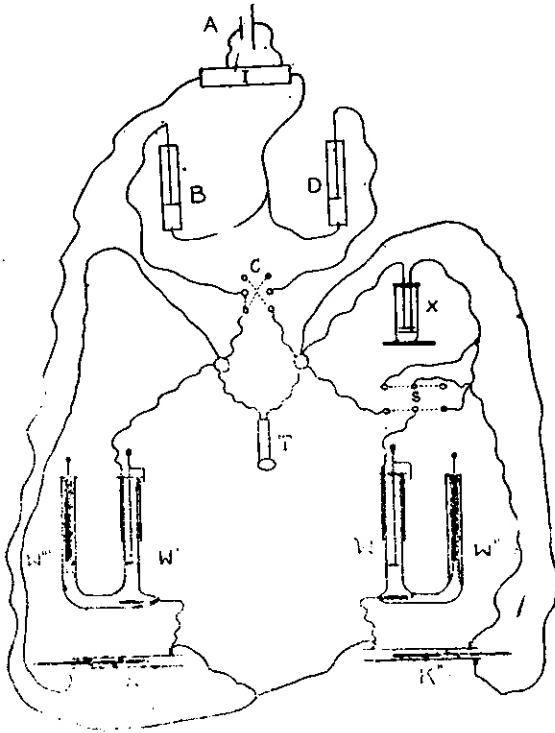


FIG. 2.

A $\frac{2}{3}$ -normal solution of mannite and boric acid, whose small negative temperature coefficient was compensated with potassium chloride (0.06g. per liter of the mannite solution), was used as the electrolytic resistance.

A diagram of the complete apparatus is shown in figure 2. A and I are the accumulator and induction coil. W, W', W'' and W''' are the arms of the bridge (W and W' are 5 mm. in diameter, and W'' and W''' are 0.8mm.); D and B are two resistances which remain constant during an experiment; K' and K'' are variable condensers; T is the telephone; X is the cell for the unknown resistance; S is a two-way switch for introducing X behind W or in shunt with it, and C is a commutator used for making D and B equal.

The resistances W, W', W'', and W''' were calibrated by means of a known electrolytic resistance in the cell X. By using the same cell, for the acetophenone solutions of the substances under investigation, their resistances were readily calculated from the length of resistance W required to give a balance¹.

In order to test the accuracy of this method, the conductivity of a sample of ordinary distilled water, the conductivity of which was also measured by the Kohlrausch method, was determined. By the first method it was found that at 15°.0 $\kappa = 1,23 \cdot 10^{-5}$, and by the second method, at the same temperature, that $\kappa = 1,17 \cdot 10^{-5}$.

The acetophenone used in the following measurements was first purified by distillation and recrystallization. This acetophenone had a specific conductivity of $\kappa = 2,02 \cdot 10^{-7}$.

The measurements given in the following tables were all made at room temperature (16-17°).

1. For a detailed description of the method, apparatus, etc., see Maltby, M. E. loc. cit.

TABLE I.

Conductivity of some Substances in Acetophenone.

Liter per Mol. V.	Spec. Conductivity corr. $\kappa \cdot 10^7$	Mol. Conductivity corr. $\mu \cdot 10^4$
Piperidine*		
2	5.37	10.74
4	4.54	18.16
8	3.76	30.08
Camphor-carboxylic acid		
2	29.1	58.2
4	19.9	79.6
8	12.5	100.0
16	6.7	107.5
32	3.5	111.7
Bromcamphor-carboxylic acid		
2.75	30.7	84.4
5.50	19.1	105.0
11.00	11.5	126.5
22.00	6.0	132.0
Piperidine camphor-carboxylate		
2	172.4	344.8
4	87.6	350.4
8	50.8	406.4
16	30.8	492.8
32	18.3	585.6

* The acetophenone used with piperidine had a specific conductivity of $\kappa = 2.87 \cdot 10^{-7}$.

On account of the readiness with which acetophenone solutions of bromcamphor-carboxylic acid decompose in the presence of small quantities of organic bases¹, it was not possible to measure the conductivity of salts of this acid. In order to obtain some idea of the order of the conductivity of the salts of bromcamphor-carboxylic acid with weak bases, an acetophenone solution, which was 0.3305 molar with respect to acid and 0.0113 molar with respect to conine, was prepared and its conductivity immediately determined. The specific conductivity of this solution was found to be $65.0 \cdot 10^{-7}$; its molecular conductivity was, therefore, $196.6 \cdot 10^{-4}$.

The conductivities given in the foregoing table have been corrected for the conductivity of the solvent.

In the following table there is given the specific conductivity of half normal acetophenone solutions of a number of weak organic bases; the specific conductivity of half normal acetophenone solutions of the salts of these bases with camphor-carboxylic acid and, lastly, the specific conductivity of half normal water solutions and the dissociation constants of some of the bases. In this table the bases are placed in the order of their dissociation constants in water solution.

1. Creighton, H. J. M. : loc. cit.

TABLE II.

BASE.	Half normal acetophenone solution.				Half normal aqueous solution.	Dissociation constant ² at 25° (water solution.)
	Spec. conductivity of the base.		Spec. conductivity of the carboxylate.		Specific conductivity of the base ¹ .	
	$\kappa \cdot 10^7$.	$\kappa \cdot 10^7$.	$\kappa \cdot 10^7$.	$\kappa \cdot 10^7$.		$\kappa \cdot 10^8$.
	uncorr.	corr.	uncorr.	corr.		
Aniline	2.13	very small.	38.1	36.1	$4.0 \cdot 10^{-9}$
Quinaldine	2.11	"	71.8	69.8
Quinie	2.79	0.77	88.5	86.7
Quinidine	2.83	0.81	88.2	86.2
Nicotine	3.72	1.70	258.4	256.4
Benzylamine	5.86	3.84	176.3	174.3	0.94	$2.4 \cdot 10^{-5}$
Triisobutylamine	2.75	0.73	566.1	564.1	$2.6 \cdot 10^{-4}$
Diisobutylamine	2.42	0.40	salt not	soluble.	$4.8 \cdot 10^{-4}$
Isoamylamine	6.82	4.80	salt not	soluble.	4.2	$5.0 \cdot 10^{-4}$
Tripropylamine	2.30	2.28	721.7	719.7	$5.5 \cdot 10^{-4}$
Conine	3.90	1.88	37.3	36.3	6.9	$1.3 \cdot 10^{-3}$
Piperidine	8.24^3	5.37	175.3^3	173.3	7.3	$1.6 \cdot 10^{-3}$

1. The numbers in this column have been obtained by extrapolation of measurements by G. Bredig (*Zeitschr. f. phys. Chem.*, 13, 289, 1894), after converting the values expressed in units based on Siemens unit into values expressed in the international unit.

2. Bredig, G.: *loc. cit.*

3. The acetophenone used with the piperidine preparation had a specific conductivity, $\kappa = 2.87 \cdot 10^{-7}$.

From the foregoing conductivity measurements, it will be seen that, where conductivities were measured at different dilutions, the molecular conductivities increased with dilution, as in aqueous solutions; that the "electrolytic dissociation"¹ of the above bases must be exceedingly small; and, also, that the "electrolytic dissociation" of their salts with camphor-carboxylic acid, although twenty to several hundred times greater, is still of the same small order. There is reason to believe that the salts of these bases with bromcamphor-carboxylic acid are probably "electrolytically dissociated" to a much greater extent.

It was hoped to have been able to determine the dissociation constants of the different bases in acetophenone solution, but this was found to be impossible, owing to the large errors introduced by the extreme smallness of the conductivities and the rapidity with which the specific conductivities of the solutions approached the specific conductivity of the solvent, even at small dilutions. From the last two columns of table 2, it will be seen that the specific conductivities of equi-molar aqueous solutions of benzylamine, isobutylamine, conine and piperidine, are relatively proportional to their dissociation constants. In view of this it is possible that the specific conductivities of equi-molar acetophenone solutions of the different bases, which are about ten thousand times smaller than for water solutions of the same concentrations, are also a measure of their dissociation constants in this solvent. From the measurements made it would appear, then, that the dissociation constants of the different substances employed are *very much smaller in acetophenone solution than in water*. This supposition is in harmony with the Nernst-Thomson rule, which shows clearly the close parallelism between the dielectric constant of the solvent and its dissociating power, since Walden has recently

1. Here by "electrolytic dissociation" and "electrolytically dissociated" are meant any condition of good electrolytic conduction, without necessarily assuming that the relations are as simple as those which occur in water solution.

found the dielectric constant of acetophenone¹ to have the small value of 18.1-18.6 at room temperature. It is further to be observed that if our conjecture be correct, namely, that with equi-molar acetophenone solutions the specific conductivity is an approximate measure of the dissociation constant of the solute, then the relative strengths in acetophenone of the bases used above differ somewhat from those in water. Thus conine which, in water solution, is a stronger base than isoamylamine, for example, is weaker than the latter in acetophenone. On the other hand the relative position of piperdine is the same in either solvent.

The measurements embodied in this paper were carried out at the Laboratorium für electro und physikalische Chemie, der eidgenössischen technischen Hochschule, Zürich, Switzerland, in February, 1911, at the suggestion of Professor G. Bredig.

1. Walden, P. : Zeitschr. f. phys. Chem., **70**, 573, (1910).

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May 3rd, 1912.