

weight of germanium, calculations being based on the assumption that chlorine is 35.46, fluorine, 19.00, and potassium, 39.10.

In conclusion, the above investigation suggests that an examination of other double halides of germanium and the alkalis might give desirable compounds for accurate analysis by a similar volatilization of the germanium content, and thus furnish a check upon the results obtained in this work.

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CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF PARIS.]

A NEW METHOD OF MEASURING ELECTROLYTIC CONDUCTANCE.

BY CHARLES MARIE AND W. ALBERT NOYES, JR.

Received March 8, 1921.

Since the original researches by Kohlrausch,¹ the alternating current Wheatstone bridge has been universally accepted as the basis for measurement of electrolytic conductance. This method has been improved by various investigators, until Washburn² claims that this method, with the precautions proposed by him, is limited only by the ability to keep the temperature constant.

The present work was undertaken, therefore, to compare conductivities as measured by the ordinary Kohlrausch method with those measured under exactly similar circumstances on the same bridge by a direct-current method. Newbery³ has done some work on direct-current conductivities by a direct-current method, using two calomel electrodes to determine the potential drop along an electrolytic conductor. He finds slight differences from values obtained by Kohlrausch's method, but offers no satisfactory explanation of the differences.

Since the work described in the present paper was completed, Eastman⁴ has published an article on "Conductivity and Frequency" in which he discusses the form of the conductivity-frequency curve. His results with direct current show variations but slightly greater than the experimental error from values obtained with alternating currents, but are smaller, as would be expected.

The present work is a continuation of research started before the war by the senior author.⁵ The principle of the apparatus is not complicated. Two hydrogen electrodes of exactly equal potential are placed in the solution in question and an ordinary direct-current Wheatstone bridge is used to determine the resistance.

¹ Kohlrausch and Holborn, "Leitvermögen der Elektrolyte."

² Washburn, *THIS JOURNAL*, **35**, 177 (1913); **38**, 2431 (1916); **39**, 235 (1917).

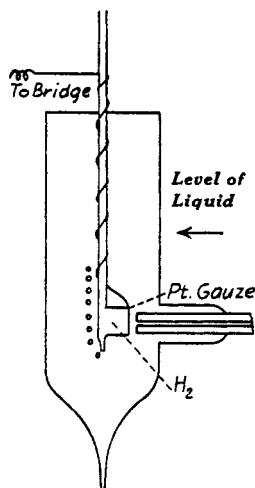
³ Newbery, *J. Chem. Soc.*, **113**, 701 (1918).

⁴ Eastman, *THIS JOURNAL*, **42**, 1648 (1920).

⁵ C. Marie, *Soc. chim. phys.*, July 1910; cf. *J. chim. phys.*, **8**, 699 (1910).

Experimental.

The form of hydrogen electrode adopted is that shown in the figure. The main conditions affecting the equilibrium of this electrode may be summed up as follows: (a) pressure of the gaseous hydrogen; (b) platinization of the electrodes; (c) temperature; (d) perturbation of the electrolyte (especially by the passage of bubbles); (e) purity of the hydrogen.



The pressure of the hydrogen was very carefully regulated by means of 2 stopcocks placed in parallel. The hydrogen was obtained electrolytically, using an anode of platinum and a cathode of mercury and was well washed with potassium permanganate and potassium hydroxide solutions, and was finally bubbled through a solution of the same composition as that being measured.

All of the measurements were made at 18°, and the measurements were made on a Wheatstone bridge which could be used with either direct or alternating current by means of a double throw switch.

Before making measurements with direct current, the hydrogen pressure of the electrodes was regulated until the two electrodes gave no deflection of the galvanometer. In making the measurement the current was allowed to pass only long enough to determine the direction of the deflection. Polarization effects were thus reduced to a minimum. The source of current for the Kohlrausch method was a buzzer, which undoubtedly gave a wave very far from that of a pure sine wave. Several readings were always made with sufficient lapses of time to equalize temperature differences, so that heating effects were undoubtedly reduced to a minimum.

The sulfuric acid was purified by heating for 8 hours at 260° in a current of hydrogen chloride after adding some organic matter. It was then fractionally distilled 3 times in a platinum retort. The other acids were the best chemically pure acids obtainable. The sodium chloride was purified several times by precipitation with hydrogen chloride.

The equivalent conductivities were calculated from the dimensions of the tube connecting the 2 electrodes, and there is a slight error due to the resistance between the surface of the electrode and the end of the tube, but calculation showed this error to be less than 0.1%.

The "standard" values were obtained by extrapolation from the values given in the "Receuil de Constantes Physiques" and in the "Conductivity of Aqueous Solutions" by Noyes and others, and are sometimes considerably in error. They are given only as a means of comparison.

The results obtained by the hydrogen-electrode method are compared below with those by the Kohlrausch method and the accepted values of the equivalent conductance as obtained from Tables.

Conc.	Our Kohlrausch. Mhos.	Stand. Kohlrausch. Mhos.	D. C. meth. Mhos.	Diff. %.
Sulfuric Acid. $t = 18^\circ$.				
1.583	187.3	189.3	182.7	2.5
1.2372	195.7	194.5	192.5	1.7
0.6358	206.9	204.1	203.2	1.8
0.2868	215.1	215.0	213.7	0.7
0.0719	247.1	245.0	247.1	0
0.01294	309.1	304.8	309.1	0
0.00293	346.6	346.9	346.6	0
Hydrochloric Acid.				
2.6135	230.5	229.4	226.1	1.9
1.3068	285.0	286.0	281.6	1.2
0.4222	335.0	331.5	335.0	0
Oxalic Acid.				
0.4229	79.0	80.6	79.0	0
0.1107	115.8	115.9	115.8	0
0.0277	146.2	146.9	146.2	0
Citric Acid.				
0.6576	6.3	6.6	6.3	0
0.05205	21.7	21.7	21.7	0
Succinic Acid.				
0.3177	3.34	...	3.34	0
0.08164	6.5	...	6.5	0
Sodium Chloride.				
0.8825	75.0	75.8	75.0	0

Discussion of Results.

It will be seen from the results that differences between the two methods are obtained only in concentrated solutions of strong acids. Since the experimental difficulties were larger for these solutions, due to their lower resistance, there may be some doubt as to their validity in spite of the precautions taken.

Newbery,¹ at 25° in *N* sulfuric acid, obtained a value of 3% lower by his direct current method than the value of Kohlrausch, and this result is roughly verified by our experiments. Eastman, on the other hand, in maximum conducting sulfuric acid, found a difference of only about 0.2% between his values and the values of Kohlrausch. It is somewhat difficult to offer an acceptable explanation of this discrepancy without more experimental results.

Summary.

1. A method for measuring electrolytic conductance by a direct-current method, using hydrogen electrodes, is described.

¹ *Loc. cit.*

2. Measurements of equivalent conductance of various acids and of sodium chloride have been made and negligible differences between the direct current values and the values by Kohlrausch's method are found except for solutions over 0.5 *N* in sulfuric and hydrochloric acids.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF MCGILL UNIVERSITY.]

SOME PHYSICAL PROPERTIES OF HYDROCARBONS CONTAINING TWO AND THREE CARBON ATOMS.

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Received March 10, 1921.

Introduction.—As some of the simpler hydrocarbons had been prepared in the pure state for an investigation on molecular compound formation and as the surface tensions, previously measured by one of us¹ are not exact in the light of Richards'² recent work, it has been considered worth while to measure their physical properties. The interest lies principally in the fact that the particular compounds investigated, ethane, ethylene, acetylene, propane, propylene and allylene, are the first members of homologous series of which the physical properties of the higher members only are well known. The effect on these properties of passing from saturation to various degrees of unsaturation is brought out by this investigation. Densities and surface tensions have been measured over a wide temperature range and the melting points determined in every case. With compounds where doubt existed as to the true boiling point, vapor-pressure and critical-temperature determinations have been made.

Preparation of Hydrocarbons.—Ethane and propane were prepared by the action of the zinc-copper couple on ethyl iodide and propyl iodide, respectively; ethylene and propylene by the catalytic influence of aluminum oxide on the corresponding purified alcohols at a temperature of 350°; and acetylene by the action of water on calcium carbide. An especially pure sample of allylene was available for this work. It had been prepared for a previous investigation by the action of methyl iodide on sodium acetylide in liquid ammonia; reference to this method of preparation, which was first used by Lebeau and Picon,³ has been made in greater detail in another paper.⁴

Purification of Hydrocarbons.—The hydrocarbons were collected by displacement of water in large gasometers and subjected to a very careful purification. Ethane and propane were passed through spirals cooled to -78°, then a number of times over the zinc-copper couple moistened with alcohol at 50° until free from iodide, then through conc. silver nitrate and conc. alkali solutions, finally dried by phosphorus pentoxide, and condensed.

The ethylene and propylene, saturated with water vapor, when dried by phosphorus pentoxide and condensed was still found to contain a considerable amount of impurity. After boiling off the ethylene from a large amount of distillate a sufficient

¹ McIntosh and Maass, *THIS JOURNAL*, **36**, 737 (1914).

² T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1656 (1915).

³ Lebeau and Picon, *Compt. rend.*, **156**, 1077 (1913).

⁴ To be published later.