TRANSACTIONS

OF THE

Moda Scotian Enstitute of Science.

SESSION OF 1912-1913.

ON THE ELECTRICAL RESISTANCE OF ACETIC ACID IN THE SOLID AND LIQUID PHASES.—By J. H. L. JOHNSTONE, B. Sc., Dalhousie University, Halifax, N. S.*

Read, March 9, 1914.

In a previous paper^I the writer published some results on the electrical resistance of ice, showing how it varied with the temperature. Its temperature-coefficient was found to be unexpectedly large and a further investigation of this point was thought desirable.

As it had been difficult to obtain satisfactory regulation of temperature below 0° C, it was decided to choose for the present investigation some substance with a melting-point so high, that with the substance in the solid state, the temperature could be regulated in a thermostat. Acetic acid appeared to fulfil these conditions; and it can be easily obtained in a comparatively pure state.

The method of measurement used in the previous investigation was inconvenient. It was also felt to be unsatisfactory as it was a direct current method and so introduced the danger of polarization effects. It seemed desirable therefore to obtain some alternating current method.

^{*} Contributions from the Science Laboratories of Dalhousie University (Physics).

¹ Trans. N. S. I. S. Vol., XIII, 2, pp. 126-144.

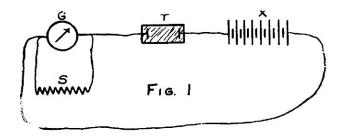
THE OBJECTS OF THIS WORK WERE:-

- 1. To determine a satisfactory method for the measurement of large electrolytic resistances.
- 2. To measure the electrical resistance of acetic acid in the solid and liquid phases at different temperatures and to find the causes of the variations which occur.
- 3. To determine the effect of small quantities of water on the resistance.

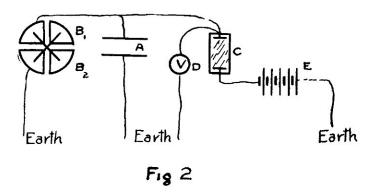
In the measurement of electrolytic resistances the effects of the electro-motive force of polarization are in general quite marked. This polarizing effect consists of two parts; one of which is a function of the current, f(i), and is in fact, a variable resistance, increasing with time due to the deposition of gas on the electrodes. The other part, e, is a true polarization e. m. f. which is independent of the value of the current passing thru the electrolytic cell. It seldom amounts to more than 1 or 2 volts. Any alternating current method should practically eliminate both of these effects.

Using the well known method of Kohlrausch, resistances greater than 10⁵ ohms, cannot be measured with any great accuracy. For satisfactory measurements of resistances ranging between 10⁴ and 10⁸ ohms another alternating current "bridge" method is suitable. In this method the telephone or galvanometer of the Kohlrausch apparatus is replaced by an electrometer and two of the resistances by capacities.

To measure resistances greater than 10^8 ohms, a direct current method may be used. The f(i) term of the polarization effect will be very small as compared with the total resistance because the current flowing thru the cell will be minute, and furthermore as the applied e. m. f. is large the " ϵ " term will be a small fraction of the total e. m. f. Using a sensitive galvanometer, connected as in figure 1, resistances ranging from 10^8 to 10^{10} ohms may be conveniently measured.

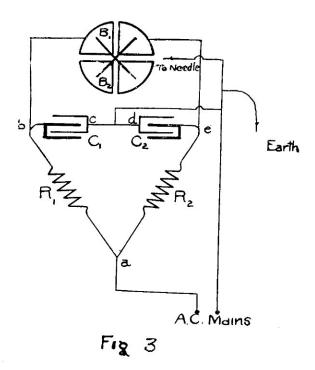


For greater values of resistance than 10¹⁰ ohms, the electrometer may be substituted for the galvanometer and the apparatus connected as in figure 2.



The A. C. Bridge method¹ referred to, was used considerably in this work. It consists of a network of two resistances and two condensers connected with a source of alternating current, (110V), as shown in figure 3. The electrometer was of the *Dolezalek* type but was fitted with an aluminium needle.

¹ Journal de Physique; Series 5, III, Jan. '13.



In fig. 3:-

B₁ and B₂ are two quadrants of the electrometer.

C₁ and C₂ are two capacities.

 $R_1 \equiv an adjustable known resistance.$

 R_2 \equiv the unknown resistance.

A. C. = terminals of A. C. circuit.

Applying Kirchoff's second law to the circuit.

$$\begin{split} & I_1 \text{ Rin. } \omega t - \frac{I_1}{\omega C_1} \text{ Cos. } \omega t \\ &= I_2 \text{ Rin. } (\omega t + \Phi) - \frac{I_2}{\omega C_2} (\text{Cos. } \omega t + \Phi) \end{split}$$

where I_1 is the maximum current flowing in branch ac. I_2 " " ad.

At the instant t, the difference in potential between the two pairs of quadrants is:

If $\Phi = 0$ and if the above potential difference be zero, then there will be no deflection of the electrometer needle. Then:

$$\frac{I_1}{I_2} = \frac{C_1}{C_2}$$
 that is, $C_1 \, R_1 = \, C_2 \, R_2$

which is the condition for no deflection. Hence if C_1 , R_1 and C_2 be so chosen that with a given R_2 , no deflection of the electrometer results, it is possible from the above equation to obtain the value of R_2 . It is well to remark, that the most sensitive conditions for a balance exist when the reactances of condensers C_1 and C_2 are respectively equal to the resistances

 R_1 and R_2 . In practice if the ratios $\frac{C_1}{R_1}$ and $\frac{C_2}{R_2}$ are each between 5 and $\frac{1}{5}$ comparatively good working conditions exist. This method is given in some detail, as it may be set up with ease and it will give very satisfactory results. Furthermore, it does not involve any knowledge regarding the absolute value of the capacities. It is the writer's belief that it deserves more general attention than it has hitherto received.

A standard $\frac{1}{3}$ M. F. condenser, manufactured by Leeds and Northrup, was used for capacity C_1 .

The reactance of this condenser is 8000, approx.. for a 60 cycle E. M. F. Four adjustable resistance boxes, manufactured by the same firm and having a combined resistance of 40,000 ohms were used for R₁. The values of R₂, which were measured by this method, ranged from 10⁵ to 10⁸ ohms and as considerable accuracy was desirable, it was necessary to manufacture three capacities having approximate reactance values of 10⁶, 10⁷ and 10⁸ respectively. Two mica condensers

and a cylindrical condenser were made and their capacities were determined as follows:

If C₁, R₁ and R₂ be known, C₂ may be accurately measured, provided the condition for sensitivity be adhered to. A known resistance as great as 106 ohms was necessary for the calibration of the smallest capacity. A subdivided megohm was not obtainable, so three Hittorf1 resistances were constructed. type of resistance is non-polarizable and is made by filling a glass tube, fitted with Cadmium electrodes, with a 10% solution of cadmium iodide in amyl alcohol. The tube was then sealed off and placed in a larger test-tube filled with oil. Leads were then soldered to the electrodes and passed thru a cork, which closed the tube. (see figure 4).

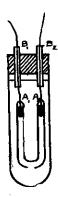


Fig. 4

The $\frac{1}{8}$ M. F. condenser was used as capacity C_1 in the network, thru-out the work.

I Making $C_2 \equiv .05$ M. F. of a "L and N" subdivided condenser.

and $R_1 \equiv 3000$ ohms,

 R_2 was adjusted for a balance and C_2 was obtained in terms of C_1 .

II Making $C_2 \equiv .05$ M. F.

and $R_2 \equiv N_0$. 1 resistance,

then R₁ was adjusted for a balance,

and No. I resistance was obtained.

III Making $C_2 \equiv Mica$ condenser No. I,

and $R_2 \equiv No$. I resistance,

then R₁ was adjusted,

and No. I capacity was obtained.

IV Making $C_2 \equiv No$. I condenser,

No. 2 resistance was determined in a similar way.

V Making $C_2 \equiv No$. I condenser,

No. 2 capacity was measured.

¹ Stewart and Gee, Pract. Physics, Vol. II, pp. 494.

VI Making $C_2 \equiv No. 2$ condenser,

No. 3 resistance was measured.

VII Making $C_2 \equiv No. 3$ condenser,

No. 3 condenser was measured.

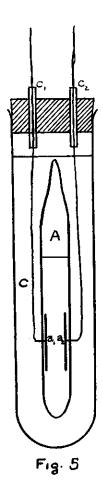
Table I gives the values obtained for the different condensers and resistances. The above series of measurements were made every few days and it was found that the capacities remained remarkably constant, never showing variations greater than 1%.

To find if this method was reliable, the resistances were measured by a direct current method, (see fig. 1), and a very good agreement was found to exist in the two methods. These measurements were made when the tubes had remained in a thermostat for at least 15 minutes. The thremostat consisted of an inner and outer vessel. The outer was constructed so that cold water could be used to circulate about the inside vessel. A heating coil was placed in the latter and using electromagnetic regulation, temperatures ranging from 10 degrees above room temp., to 10 degrees below could be maintained to the tenth part of a degree.

 $\mathbf{C}_{\mathbf{i}}$ C, R, QUANTITY MEASURED. $\mathbf{R_i}$ 3000 05 M.F. 20494 .05 M. F. = .0487 M. F.1/3 0487 M.F. R No. 1 1/3 26440 Res. No. $1 = 1.81 \times 10^5$ o h m s 4225 C. No. 1 1/3 No. 1 Cond. No. $1 = .00783 \, \text{M}$. F. 1/3 16970 No. 1 No. 2 Res. No. $2 = 7.22 \times 10^{6}$ 1/3 3170 No. 2 No. 2 Cond. No. 2 = .001461/3 36220 No. 2 No. 3 Res. No. 3 @ 9° C. = 8.27×10° 1/3 5930 No. 3 No. 3 Cond. No. 3 = .000238

TABLE No. 1.

Bakers' acetic acid, (99.55% guaranteed), was used. To eliminate water the acid was fractionally frozen and the mother liquor was then poured off. The resistance of a sample was measured after each separation and it was found



that the specific resistance increased greatly after each freezing. The greatest number of freezings attempted in any one case was five. With more freezings, a purer sample could, no doubt, be obtained. However there is a limit to the purity obtainable in this manner as you can't prevent the absorption of moisture from the air; and there is also some dissociation. It was thought that the traces of water might be eliminated by adding acetic anhydride (Kahlbaum's C. P.) to the acid. This was tried but it was found that the specific conductivity of the anhydride was greater than that of the acid. Traces of HCl. were afterwards found in the anhydride, which would account for its conductivity.

The resistance vessel, A, (see figure 5), was blown from glass tubing of 0.7 cm. bore and mane about 12cm. long Into the tube were sealed two platinum electrodes, a_1 and a_2 , each of which had an area of about 2 sq. cm. and a chromicsulphuric acid cleaning solution was used. NaOH was then used and finally alcohol to remove grease etc. After washing many times with distilled water, the vessel was dried care-

fully. To ensure the removal of as much moisture as possible from the glass, the tube was connected to a mercury pump and heated to about 160° C in an oil bath for several hours. The pump was exhausted at intervals over a period of two days.

The "cell constant" was determined by measuring the resistance of a $\frac{1}{10}$ N. solution of Kcl on a $Kohlrausch\,bridge^1$ The tube was then sealed off and suspended in a test tube filled with oil, which was placed in the thermostat. On account of capacity effects it is essential that the thermostat be well earthed.

¹ Kohlrausch, F., Physico. Chem. Measurements.

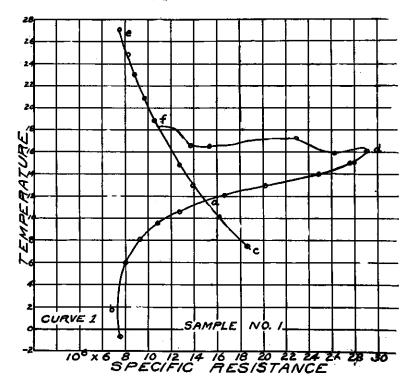
Measurements of the resistance of sample I were made at different temperatures ranging from -7° C. to the melting point. It was found possible to supercool to temperatures as low as 0° C with comparative ease, so measurements were made in the liquid phase at temperatures ranging from 25°C to 0° C.

TABLE 2.

		Sample 1. ≈ Cell Constant 0.166 ≈ M. P. 15.9° C.					
Темр.	State.	Sp. RESISTANCE					
−.7°C.	Solid	7.48×10*					
+.6.0	"	7.95×10°					
8.0	"	9.25×10 ^s					
9.5	"	1.10×10°					
10.5	"	1.27×10^7					
12.0	"	1.66×10					
12.9	. "	2.01×10 ⁷					
14.0	66	2.48×107					
15.	"	2.76×10 ⁷					
15.0	"	2.79×10 ⁷					
15.9	"	2.95×10^{7}					
16.0	Liquefying	2.91×10 ⁷					
15.9	. "	2.62×10^{7}					
17.2	и.	2.29×10 ⁷					
16.5	i.	1.53×107					
16.5	"	1.37×10'					
18.0	"	1.23×10 ⁷					
27.0	Liquid	7.48×10*					
24.9	"	8.24×10 ⁸					
23.	"	8.83×10°					
20.9	"	9.72×10°					
18.9	"	1.05×107					
14.8	"	1.27×107					
13.0	"	1.39×10 ⁷					
10.0	"	1.61×10 ⁷					
7.3	"	1.85×10 ⁷					
−80°C.	Solid	1.02×1018					

In table 2 are given values of the specific resistance for sample I, in the liquid and solid phases at temperatures ranging from 27° C to -7° C. Curve 1 shows how the specific resistance in each phase varies with the temperature. Starting at the point, c, on curve 1, the resistance at first decreases very slowly with rising temperature, then it begins to in-

crease slowly and then with great rapidity until the temperature has risen to the melting point, d. Liquefaction then begins and the resistance decreases very irregularly until finally the liquid phase alone exists in the tube, and the point f, is reached. It is well to state here, that the points on the curve between the eutectic temperature and the melting point, really do not represent the specific resistance of the solid phase, but the resistance of the tube multiplied by the cell constant. The specific resistance in the liquid phase increases with falling temperature. This is indicated by the part of the curve, e a c, which is quite normal as was to be expected. It is seen that there exists a point, a, at which the specific resistance in the liquid phase is equal to the so called specific resistance in the solid phase at the same temperature. This point was not found to exist in the case of acids which had been more carefully purified.



It was found that the specific resistance of the samples used, changed considerably with time and according to the previous history of the tube. This is to be expected, because, the action of the acid on the glass tube will result in the addition of impurities, which will continually decrease the value of such a high resistance as is being dealt with.

The change in resistance of the solid acid with change in temperature is evidently not a true temperature coefficient. It is due in a large part to three factors which are functions of the temperature.

There exists in the tube what may be regarded as a solution of a minute quantity of water in the acetic acid as sol-As the temperature is lowered the acid gradually crystallizes out, with the result that the freezing point of the liquid portion is gradually lowered and the concentration of the water in the acetic acid is increased. specific resistance of the liquid portion decreases on account of the increasing concentration of water. On the other hand, the effective cross section of the liquid between the electrodes gradually decreases and as a result the specific resistance tends to increase. Thirdly, the resistance tends to increase with decreasing temperature because of a true temperature effect. Examining the curve it is evident that the concentration factor is predominant above O°C. to be expected as the increase in the concentration of the water in the solution part of the mixture, will be very rapid at first but will gradually decrease. The effect of the second factor, at temperatures near the melting point, will be small compared to the effect of the first factor. With decreasing temp., the volume of the liquid decreases more rapidly and so the second factor will have a gradually increasing effect until finally a temperature is reached when this effect will be equal and opposite to the effect of the first factor. At this point the curve bends and with lower temperatures the second factor is the predominant one, the resistance increasing with

decreasing temperature. The true temperature effect is to make the resistance increase with decreasing temperature, but as the temperature coefficient of this liquid is small, the shape of the curve is not materially affected by this factor.

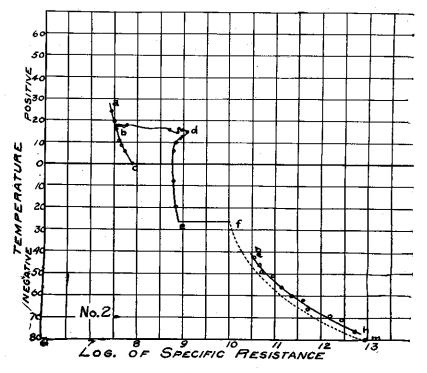
From the temperature of the bending point, down to the eutectic point, the resistance increases with the decreasing temperature. At the eutectic point, $(-26.55^{\circ}\text{C})^{1}$, the solution of water in acetic acid suddenly becomes solid, this mixture containing 59% of solid acid and 41% of ice. A considerable change in the resistance of the tube might be expected to occur at this temperature, and as the temp. is further decreased, the solid mixture should be found to have a true temperature coefficient.

To verify the last supposition, the resistance tube was surrounded by solid carbon dioxide and a temperature of -80°C2 was finally obtained. This was measured by means of a thermocouple placed in the oil bath. As the temp, decreased rapidly it was noted that at some temperature between -25° and -30°C the resistance suddenly increased from approx. 8 x 10⁸ to a value impossible to measure in the "network". The tube was then connected with an electrometer and condenser, as shown in figure 2. When the temperature of the resistance tube became equal to the temp. of the surrounding solid CO2, -80°C, an E. M. F. was applied and the current passing thru the acetic acid was measured by the electrometer. The specific resistance of sample I was found equal to 1.00 x 1013 @ -80°C. Another sample No. 2, somewhat purer than No. I, was measured in a different tube @ -80°C and had a value of 9.92 x 10¹². Sample 2 was removed from the surrounding CO2 and placed in a Dewar bulb. As the tube heated, resistance measurements were made at intervals, the thermocouple being read at the instant an electrometer

¹ Dahms, Wied. Ann 60, 123, 1897.

² Landolt und Bornstein, Tabellen page 76.

reading was made. In this manner values of the resistance at temperatures ranging from -80° to -47° C were obtained. Above -46° C the resistance was such that it was impossible to use the electrometer as a current measurer, so it was replaced by a D'Arsonval galvanometer. This instrument had a sensitivity of $3.52 \times 10^{\circ}$ amperes for one scale division and a resistance of 1900 ohms at room temperature. As the specific resistance of sample 2 varies from 9.92×10^{12} @ -80° C to 2.67×10^{7} @ $+24^{\circ}$ C, it is impracticable to plot these values by the direct method, so in curve No. 2, the logarithms of the specific resistance are shown plotted with the temperatures.



As the thermocouple indicates the temperature of the oil bath, the actual value of the temp. of the acetic acid, corres-

ponding to a particular electrometer reading will be lower than this. However the true temp. resistance curve shown as the dotted line, drawn from m to f, parallel to h.g. The part of the curve ef indicates clearly the discontinuity in resistance at the eutectic point; it shows that when -26.55° C is reached the resistance of sample 2, changes suddenly from 10^{10} to 8.8×10^{3} ; this change being due to the solidification of the liquid portion between the electrodes.

When the temperature reaches 15°C, melting of the substance was apparent and the specific resistance decreases very rapidly from 1.27 x 10° to 3.52 x 10° @ 17.5°C, when liquefaction is complete. The part of the curve ac, shows the variation of the specific resistance with temp. in the liquid phase. Values of the specific resistance in the solid and liquid phases of sample No. 2, are given in table 3.

TABLE 3.

Sample 2 = Cell. const. \equiv 4.8 \approx M. P. \equiv 16.4°C.					
Темр.	STATE.	Sp. Resistance			
24.0	Liquid	2:67×10 ⁷			
19.4	`"	3.22×10 ⁷			
17.8	44	3.34×10 ⁷			
15.7	"	3.60×10 ⁷			
10.8	"	4.48×10 ⁷			
6.0	**	5.55×10 ⁷			
0.	"	7.55×10 ⁷			
-19.9	Solid	6.48×10*			
- 8.0	44	6.14×10 ⁸			
+ 6.8	"	5.55×10*			
9.8	46 ·	6.86×10°			
11.8	46	8.57×10°			
12.2	u	9.64×10 ²			
14.8	"	1.27×10°			
13.4	"	1.07×10°			
15.5	Melting	5.16×10*			
17.4	· · · ·	6.23×10 ⁷			
17.5	u	4.40×10			
17.5	"	3.65×10'			
17.5	Liquid	3.65×10 ⁷			
-80	Solid	9.90×1012			
-79.1	"	5.55×10 ¹²			
-74	"	2.82×1012			
-73	" .	1.51×10 ¹²			
-69	"	5.45×10 ¹¹			
-65	ш	4.19×10 ¹¹			
63	16	2.41×10 ¹¹			
-59		1.45×10"			
-54	41 .	9.26×10 ^D			
-52	••	5.50×10 ¹⁰			
-46		3.55×10 ¹⁰			

At temperatures below the eutectic point no liquid exists between the electrodes and as the amount of ice present is very small in comparison with the acetic acid (solid); there should exist a true temperature coefficient of resistance for the solid acid. Defining this as $\frac{1}{R_t} \frac{dR_t}{dT}$ it can be determined from the curve 2, by graphical methods and it is found to vary from 0.3 @ -43°C to 0.25 @ -70°C. The writer found the temp. coeff. of ice to vary from 0.6 @ -2° to 0.12 at -12° and with lower temperatures it increases in value. It thus appears that solid acetic acid is like ice in that it has a very great temperature coefficient of resistance. The temp. coeff. for sample 2 in the liquid phase was calculated in a similar manner and found equal to 0.04 @ 14°C.

To determine the effect of adding considerable quantities of water to the acid, the tube was filled with a 2% solution of water in acetic acid, (sample No. 3), and measurements were made at different temperatures.

A comparison of the specific resistance, temp. coeff. and the melting points for samples 1, 2 and 3 is given in table 4.

TARLE 4

IABLE 4.							
Sample.	STATE.	М. Р.	Темр.	RES. Sp.	Темр Соетт.		
1	Liquid	15.9	14° c.	1.3×10 ⁷	.04		
2	"	16.4	14	3.8×10⁵	.04		
3	"	13.2	14	1.2×10°	.03		
1	Solid		12	1.7×10 ⁷			
2	"		12	8.9×10 ⁸			
3	"		12	2.2×17	*		
1	"		-80	1.0×10 ¹¹	25		
2	"		-80	9.9×1011			
3	 "		-80	8.4×10 ¹¹			
	L	•					

1 Trans. N. S. Ins. of Sc. XIII., part 2, page 143.

The evidence appears to be conclusive, that at temperatures above the eutectic, practically all the current passing thru the acid is conducted by the liquid portion of the mixture between the electrodes. So the term, specific resistance of the solid at temperatures above the eutectic is meaningless, and the values obtained for the specific resistance and plotted on curves 1 and 2 merely indicate the resistance of thin columns of the solution of acid and water between the electrodes, multiplied by the cell constant. To obtain a true value for the specific resistance of the solid acetic acid, the temperature must be kept below the eutectic point.

Comparing the values of the specific resistances in table 4, it may be seen that small variations in the quantity of water present greatly affect the specific resistance at temperatures above -26.55 in the solid and liquid phases, while below the eutectic point, the specific resistance is not materially affected by the presence of small quantities of water. At-80°C the specific resistance of sample 3 is considerably smaller than that of samples 1 and 2 at the same temperature. This might be expected and it is probably due to the comparatively large amount of water in the solid form, stretching from one electrode to the other, thus increasing the conductivity of the mixture of ice and acetic acid, as the former has a greater conductivity than the latter. In tubes 1 and 2, the amount of water present is so small, that when frozen, it does not occupy sufficient volume to materially affect the sp. resis.ance.

Summary.

- 1. Three satisfactory methods have been investigated and used in the measurement of high electrolytic resistances.
- 2. The specific resistance of acetic acid in the solid and liquid phases, has been measured at temperatures ranging from -80°C to +27°C and sudden changes were found at the melting and eutectic points.

- 3. The resistance in the solid phase above the eutectic point is found to vary in a peculiar manner, as the temperature changes. This variation has been explained.
- 4. The effect of small quantities of water on the resistance of the acid has been investigated and explained and it has been shown that the conductivity of the acid in the solid state above the eutectic point, is due almost entirely, to the presence of this water.
- 5. The temperature coefficient in the liquid phase was found to be nearly constant and equal to 0.04. In the solid phase it varies from 0.30 @ -43°C to 0.25 @ -70°C.

In conclusion I wish to thank Dr. Bronson for the inspiration and help which made this work possible.

Dalhousie University, Halifax.

March 9th, 1914.