material crystallized when it was cooled and melted at 81–83° after recrystallization from alcohol. In all probability the product was 1-phenyl-3-(α-thienyl)-4-methylpyrazoline. *Anal.* Calcd. for $C_{14}H_{41}N_2S$: S, 13.23. Found: S, 13.34.

Compound 7.—Phenyl vinyl ketone was obtained when this compound was submitted to steam distillation and also when an attempt was made to distill the base under 18 mm. pressure; in the latter instance the yield of the unsaturated ketone was 80%. Phenyl vinyl ketone was identified by its boiling point (114–116° (18 mm.)) and by its reaction with phenylhydrazine to yield 1,3-diphenylpyrazoline (m. p. 151–152°) (Kohler, *Am. Chem. J.*, **42**, 386 (1909)); Jacob and Madinaveitia, *J. Chem. Soc.*, 1931 (1937). The picrate was formed when 3 g. of the base and 3 g. of picric acid, dissolved in 6 cc. of alcohol, were heated on a steam-bath. The product melted at 115–116° after recrystallization from alcohol which contained a small amount of acetone. *Anal.* Calcd. for $C_{19}H_{22}O_8N_4$: N, 12.90. Found: N, 12.75. Mannich (*Arch. Pharm.*, **273**, 284 (1935)) mentioned that this picrate melted at 114–115°, but he failed to describe the base.

Formation of Methyldi-(β-benzoylethyl)-amine from Phenyl Vinyl Ketone and Methylamine.—When 7.9 g. (0.06 mole) of phenyl vinyl ketone was added to 9.3 cc. (0.06 mole) of alcoholic methylamine the mixture became warm. After two hours the latter was cooled with ice whereupon 3.1 g. of the tertiary amine precipitated; m. p. 140–141°. After twelve hours at ordinary temperature, an additional 1.7 g. had separated and 0.64 g.

more was obtained after four days; total yield 61%.

Formation of Methyldi-(β-benzoylethyl)-amine Hydrochloride from Acetophenone, Paraformaldehyde and the Half Hydrochloride of Methylacetamide.—Methylacetamide,[12] dissolved in absolute ether, was treated with hydrogen chloride and the precipitated half hydrochloride[13] recrystallized from acetone; m. p. 87–89°.

Anal. Calcd. for $C_6H_{16}O_2N_2Cl$: Cl, 19.41. Found: Cl, 19.55.

A mixture of 8.8 g. (0.073 mole) of acetophenone, 3.0 g. (0.100 mole) of paraformaldehyde, 8.0 g. (0.044 mole) of methylacetamide half hydrochloride and 10 cc. of absolute alcohol was heated on a steam-bath for forty-five minutes. The mixture was cooled and the precipitated material (4.7 g.) recrystallized from alcohol. The product melted at 160–162°, the melting point of methyldi-(β-benzoylethyl)-amine hydrochloride; mixed m. p. 160–162°. After conversion of the salt into the free base, the latter melted at 140–142°.

Summary

A study has been made of the interaction of several amine hydrochlorides with formaldehyde and acetophenone, α-acetylthiophene or α-propionylthiophene.

(12) Verley, *Bull. soc. chim.*, [3] **9**, 691 (1893).

(13) This product was postulated but not described by D'Alelio and Reid, THIS JOURNAL, **59**, 110 (1937).

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Anomalies in Conductivity Measurements in Presence of Hydrogen Peroxide

BY M. BOBTELSKY AND A. E. SIMCHEN

1. Introduction.—For some years we have studied with collaborators the problem of the catalytic decomposition of hydrogen peroxide in the presence of electrolytes,[1] including the phenomena appearing in the presence of hydrogen peroxide by conductometric measurements (*e. g.*, during the catalytic action of cobalt citrate complexes). In presence of increasing quantities of hydrogen peroxide, conductometric curves were obtained with pronounced maxima and minima of conductivity that could not be accounted for by simple chemical reactions. Therefore the only explanation possible was to suppose that these "anomalous" curves were due to specific conductivity phenomena in electrolytic solutions in presence of increasing quantities of hydrogen perox-

ide; we felt quite sure that there were no chemical compounds formed between hydrogen peroxide and the simple electrolytes.

A series of conductometric titrations of pure electrolytic solutions with increasing quantities of hydrogen peroxide were carried out. The measurements were made by the visual method by means of a "lyograph" (see below) at 50 cycles/sec. Comparison experiments were carried out with a Wheatstone bridge, at 1000 cycles/sec. The experimental results reported here have largely justified our previous assumption.

Neither the aim we had put before us in this work, nor the apparatus used, admitted of a further extension of the problem in the physical direction, *i. e.*, a study of alternating current polarization. In this respect we may mention the work of Jones and Christian,[2] who investigated this question with great thoroughness and suit-

(1) M. Bobtelsky and B. Kirson, *Compt. rend.*, **199**, 573 (1934); **208**, 1577 (1939); M. Bobtelsky and L. Bobtelsky-Chajkin, *ibid.*, **201**, 604 (1935); **203**, 872 (1936); **203**, 1158 (1936); M. Bobtelsky and M. Rappoport, *ibid.*, **205**, 234 (1937); M. Bobtelsky and A. E. Simchen, *ibid.*, **208**, 1646 (1939).

(2) G. Jones and S. M. Christian, THIS JOURNAL, **57**, 272 (1935).

able apparatus. Several of their conclusions conform to the results in the present paper; Jones and Christian insist in their work on the value alternating current polarization can have in chemical problems.

We hope to be able to report in another paper how far the phenomena and regularities due to alternating current polarization can be used in the problem of hydrogen peroxide. The problem of conductivities in presence of hydrogen peroxide shall be further studied in this institute with Pt as well as with other metallic electrodes.

Pure hydrogen peroxide and its aqueous solutions are known to be poor conductors. The dissociation constant of pure hydrogen peroxide is 1.5×10^{-12} at 20°; its dielectric constant is 89.2 at 0° and has a maximum value of 121 for an aqueous solution containing 35% hydrogen peroxide.[3,5] It is thus conceivable that, when mixed with aqueous electrolytic solutions, hydrogen peroxide may have a "milieu" influence on the electrolytic conductivity of the resulting system. But it is scarcely known that a diluted solution of hydrogen peroxide may have a strong influence on electrolytic conductivity measurements made in cells of usual dimensions. Conductivity measurements of this type in presence of hydrogen peroxide were made by various investigators.[3-9] These measurements attain a peculiar importance in the investigation of peroxidized compounds, or of multivalent ions liable to appear in presence of hydrogen peroxide.[8] As we shall show they may give quite illusory results and lead to entirely false conclusions.

The various scientists who measured the conductivity of electrolytes in solutions containing hydrogen peroxide worked under different experimental conditions, but most of them observed the conductivity drop in presence of hydrogen peroxide. In trying to explain this phenomenon they supposed the formation in the solution of compounds between the electrolytes (or their ions) and hydrogen peroxide. Systematic conductivity measurements made in order to clear up the question are still lacking. In the present work it has been our principal aim to see how the conductivity drop in presence of hydrogen per-

oxide manifested itself during conductometric titrations made principally by the visual method.

The results of these measurements made with gray platinized and calcined or with smooth platinum electrodes, and with tin electrodes indicate that the already mentioned conductivity drop may not be attributed to changes in the chemical nature of the solution. It is, on the other hand, very remarkable that, with platinum electrodes, the maximum loss of conductivity occurs when small quantities of hydrogen peroxide are used; in increasing the latter the value of the conductivity loss diminishes in amounts depending on the nature of the anion in the solution. The drop of conductivity, in %, caused by hydrogen peroxide increases with increasing electrolyte concentration; at equal concentrations this action is stronger for cells with low constants than for cells with high constants. Its amount depends, moreover, on the frequency of the measuring current; at 50 cycles/sec. it is higher than at 1000 cycles/sec. In this paper we shall show the variation of the conductivity loss with changing experimental conditions: nature and concentration of the dissolved electrolyte; hydrogen peroxide concentration; cell constant; stirring velocity; frequency of the measuring current; and the material of the electrode.

2. **Apparatus.**—An important part of the measurements was made in the following way. The conductivity cell for the series of experiments was made of a vertical Pyrex glass tube of 4.3 cm. diameter the lower end of which passed into a spherical segment closed by a small ground-in glass stopper. The upper end of the Pyrex tube was fitted into a hollow ebonite head adjustable by three position screws. In the center of the ebonite head a mechanical glass stirrer (a little four-winged propeller supported by a vertical axis) was clamped in by a nickeled brass screw. The mean stirring rate was about 120 rev./min. At small distances, on both sides of the center of the ebonite head, two short brass tubes were fitted in, into which the electrode supporting glass tubes were sealed with picein. The electrodes were two platinum disks of 1.0 cm. diameter and were welded at several points to the supporting glass tubes; these tubes contained mercury and the connection wires. The distance between the electrodes was about 2.5 cm. in cell 1, the cell constant (measured with 0.02 n potassium chloride standard solution) was 0.52 at 30° and was almost insensible to temperature. The solution was stirred throughout the measurements. An aperture in the ebonite head permitted the entrance of the outlet of a microburet divided to 0.01 cc. The electrodes had been platinized and then calcined ("gray platinized"), they were washed with sulfochromic mixture before every experiment and then rinsed first with tap water and then with distilled water. Before some of the experiments the electrodes had been cathodically depolarized for five min-

(3) H. Th. Calvert, *Ann. Physik*, [4] **1**, 483 (1900).

(4) H. Th. Calvert, *Z. physik. Chem.*, **38**, 527 (1901).

(5) Cuthbertson and Maass, THIS JOURNAL, **52**, 489 (1930).

(6) Hatcher and Sturrock, *Can. J. Res.*, **4**, 35 (1931).

(7) Hatcher and Powell, *ibid.*, **7**, 270 (1932).

(8) Mayer and Pawletta, *Z. physik. Chem.*, **125**, 62 (1927).

(9) H. Menzel, *ibid.*, **105**, 413 (1923).

utes in acid solution (sulfuric). Measurements were always identical and able to be reproduced, with or without cathodic depolarization. Certain authors have used tin electrodes in order to avoid catalytic decomposition of hydrogen peroxide by the platinized platinum electrodes (see below). Now we were working with electrolytic solutions that by themselves slow down the decomposition of hydrogen peroxide or even inhibit it; and as the actual measurements took only a short time we preferred, in order to have clean-cut phenomena, to use electrodes as resistant as possible. Measurements made with tin electrodes are far more exposed to the action of supplementary factors and the reproducibility of the results—at 50 cycles/sec. at least—is worse than for platinum electrodes. As measuring apparatus we used a Lautenschlaeger (Munich) "lyograph," according to Wulff and Kordatzki,[10] working with ordinary alternating current (220 volts 50 cycles/sec.). The apparatus is designed for conductometric titrations, single measurements and continuous conductivity control. It has seven measuring ranges stretching from 50 to 50,000 ohms (50—100; 100—250; 250—1000; 1000—2500; 2500—5000; 5000—50,000 ohms) and the results (in ohms) can be read off the scale of a milliammeter. The principles of the "lyograph" are: alternating current of 220 volts, 50 cycles/sec. traverses a tension transformer and an iron–hydrogen lamp tension regulator; then it is divided into two equal and parallel transformers whence it issues at 6 volts. One of the latter transformers communicates with the measuring cell, the other with a standard resistance. Both currents after being rectified in a device of Graetz type are sent from opposing directions on a direct current measuring instrument the sensitivity of which may be varied in large limits by shunts. The measurements were accurate to a few parts per 1000. By using a constant supplementary resistance it was possible to measure with the same degree of accuracy resistances between 10 and 50 ohms, but we thought it preferable to measure resistances of less than 50 ohms by mounting a bifilar coil resistance box of Leeds and Northrup and using a constant resistance of 50 ohms out of it in series after the conductivity cell. The intensity of the alternative current traversing the conductivity cell was thus kept small. Parallel measurements made with a Wheatstone bridge (of Leeds and Northrup) and a telephone proved that the accuracy of the results was not impaired.

The visual measurements were taken with the current passing continuously through the cell; for "gray platinized" electrodes we never observed any change, neither decrease nor increase, of resistance: but when using smooth platinum electrodes, or tin electrodes (see below), we eventually let the current pass just the time necessary for the resistance value be to observed ("discontinuous measurements"); otherwise, there is a resistance shift due to electrode polarization. All of the experiments were made with 50 cc. of the electrolyte solution, to which up to 1 cc. of hydrogen peroxide solution was added from a microburet divided into 0.01 cc. and allowing exact reading to 0.005 cc. After every drop of hydrogen peroxide, the hydrogen peroxide volume on the buret and the resistance on the "lyograph" were recorded. The variation of the

(10) P. Wulff, "Anwendungen physikalischer Analysenverfahren in der Chemie," Muller and Steinicke, editors, Munich, 1936.

cell constant and the dilution produced by adding the volume of hydrogen peroxide were introduced into the conductivity computations. All the chemical substances used were pure *pro analysi* Rhône-Poulenc or Kahlbaum. The hydrogen peroxide was Merck "perhydrol" with about 30% hydrogen peroxide, the exact hydrogen peroxide content was determined by manganometry and different stock solutions varied between 9.50 and 10.20 mole g./l. Control experiments made with a British product, the "Genoxide" (about 1.07 mole gr./l.) gave exactly the same results. Investigations were undertaken only with such electrolyte solutions as were known from previous work of our department as being inactive in hydrogen peroxide decomposition or even retarding it. Investigations on alkali or alkaline reacting solutions thus do not belong here. As a rule we worked at a temperature of 30° ($\pm0.1°$) except when otherwise indicated. Some experiments were made at 0 °C. Measurements made with the "lyograph" and cell 1 could be reproduced at different times (in some cases a few months' interval) with errors of about 1% or less.

3. Results of the Measurements. In order to investigate the influence of hydrogen peroxide on the conductivity of acids, the following solutions were employed: HCl, HNO_3, $HClO_4$, H_2SO_4, H_3PO_4, tartaric, citric, acetic and trichloroacetic acids, all measurements were made with the lyograph and gray platinized electrodes (acid concentrations: 0.05, 0.10, 0.20 N). Figure 1 shows as an example the hydrogen peroxide titration curves of some electrolytes: abscissas, cc. of hydrogen peroxide, 10 mole g./l. added; ordinates, conductivity losses in per cent., the conductivity of the electrolyte solution in absence of hydrogen peroxide being taken as 100. For each experiment after the addition of small quantities of hydrogen peroxide (a few 0.01 cc.) an abrupt *maximum conductivity drop* has been observed. This loss of conductivity becomes smaller as further hydrogen peroxide is added, the rate of decrease depending on the anion of the electrolyte. In the case of hydrochloric acid, and even more of chlorides or potassium fluoride, the diminution of the conductivity loss is not so marked for further hydrogen peroxide additions. For acids the percentage value of the maximal conductivity loss is about proportional to the square root of the acid concentration. Solutions of chlorides, nitrates and sulfates of the alkali metals (at concentrations 0.1, 0.2 and 0.3 N) and solutions of some di- and tri-valent cations (Ba^{++}, Ni^{++}, Co^{++}, Al^{+++}), also were measured and gave similar results. *The situation becomes clearer if instead of considering electrolytical conductivities we compare resistances measured in absence and in presence of hydrogen peroxide* (after having intro-
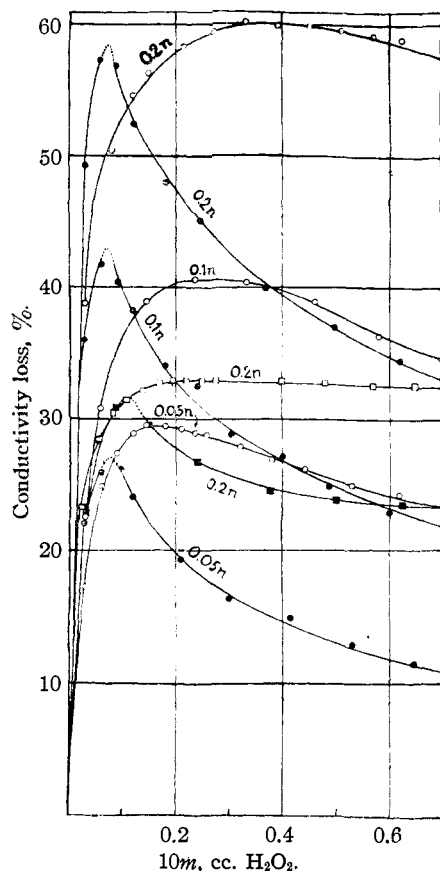
Fig. 1.—O, HCl;   ●, HNO₃;   □, NaCl;   ■, NaNO₃.

Fig. 2.—0.1 N solutions: 1, HCl O; 2, HNO₃ ●; 3, HClO₄ ϕ; 4, H₂OO₄ ·⊖·; 5, H₃PO₄ $\dot{\bullet}$.

duced the corrections for dilutions). In Fig. 2 we have plotted the difference ΔR (in ohms) between the resistance in presence of hydrogen peroxide and the initial resistance without hydrogen peroxide, against the volume of hydrogen peroxide 10 m added. It appears that ΔR reaches a maximum value $(\Delta R_{max.})$ for about 0.1 cc. of hydrogen peroxide 10 m (the concentration of hydrogen peroxide in the solution is then about 0.2 mole g./1.), it diminishes later for further hydrogen peroxide additions. The curve for hydrochloric acid shows a different feature; $\Delta R_{max.}$ is reached for a greater quantity of hydrogen peroxide and the further diminution of ΔR is less pronounced. $\Delta R_{max.}$ *can be only approximately fixed because of the abrupt form of the maximum;* it is between 7 and 10 ohms, constant for the investigated electrolytes and *independent of their concentration,* this being valid for acids as well as for salts (see Table I). Platinizing and calcining is most important for lyograph continuous measurements (50 cycles/sec.), almost immediately constant final values are obtained; when using smooth
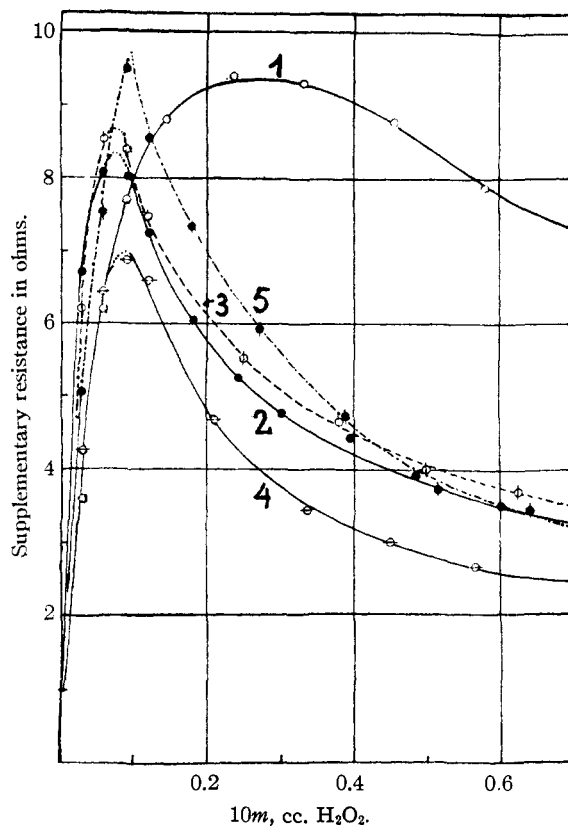
platinum electrodes and a cell of low constant "continuous" measurements are impossible because of the drifting of the measured values. By taking discontinuous measurements (see no. 2) the same values may be obtained as with gray platinized electrodes. On the other hand, by using cells of higher constants (e. g., 7.04), there is no difficulty in getting constant values, imme-

TABLE I

INFLUENCE OF ELECTROLYTE CONCENTRATION

Cell const., 0.52; temp., 30°

Solution, N	R_0 in abs. of H₂O₂, ohms	$R_{max.}$ in pres. of H₂O₂, ohms	$\Delta R_{max.}$, ohms
HCl 0.05	25.5	36.1	10.6
HCl .10	13.6	23.3	9.7
HCl .20	6.8	17.7	10.9
H₂SO₄ .05	38.6	45.8	7.2
H₂SO₄ .10	20.4	27.4	7.0
H₂SO₄ .15	14.3	21.9	7.6
H₂SO₄ .19	12.6	20.1	7.5
NaCl .1	43.9	50.5	6.6
NaCl .2	23.2	30.4	7.2
NaCl .3	14.3	21.4	7.1
Na₂SO₄ .1	54.4	61.0	6.6
Na₂SO₄ .2	30.0	37.1	7.1
Na₂SO₄ .3	21.0	28.5	7.4

diately after hydrogen peroxide additions, with smooth platinum electrodes and continuous measurements. It is seen that there is no difference in the results obtained with smooth or gray platinized electrodes. As is well known, hydrogen peroxide is decomposed readily by black platinized electrodes. It is, however, very significant that using black platinized electrodes during a titration of hydrochloric acid (stabilizer!) with hydrogen peroxide, the ΔR were but very small. During this titration while stirring, bubbles of oxygen gradually covered the electrodes.

4. Results with Different Experimental Conditions. a. Temperature.—Some experiments were carried out at 0 and at 30°; the results are given in Table II. 0° values are always about 4

Solution, N	Cell const.	Temp., °C.	R_0 in abs. of H_2O_2, ohms	R_{max} in pres. of H_2O_2, ohms	ΔR_{max}, ohms
HCl 0.05	0.52	0	44.0	58.8	14.8
HCl .05	.52	30	25.5	36.1	10.6
HCl .10	.52	0	26.3	39.6	13.3
HCl .10	.52	30	14.0	23.3	9.3
HCl .20	7.04	0	147.6	172.5	24.9
HCl .20	7.04	30	86.8	107.0	20.2
HNO₃ .20	7.04	0	147.9	163.0	15.1
HNO₃ .20	7.04	30	86.2	98.0	11.8

ohms higher than 30° values, but the ΔR are here too independent of electrolyte concentration. The temperature coefficient is in all the four cases negative and about 1% per degree, as found also by Jones and Christian.[2]

b. Cell Constant.—Table III contains the results of measurements made with cells having the following constants: 0.52 (gray platinized or smooth platinum electrodes); 7.04; and 35.5 (smooth platinum electrodes), the electrodes being in each case circular platinum disks 1 cm. in diameter. The cells having constants 7.04 and over were U-shaped and the solution was not

stirred during the measurements. It is interesting to observe that, though the ΔR_{max} are independent of the electrolyte concentration (and thus of the conductivity), a relation exists between ΔR_{max} and the cell constant, i. e., the distance between the electrodes (if the latter have the same dimensions), and perhaps the shape of the cell. It is seen from Table III that the ratio $\Delta R_{max}./\sqrt{C}$ (C = cell constant) varies only between about 4 and 10 when C varies between 0.52 and 35.5. This ratio seems to be independent of electrolyte concentration and cell constant as well and it seems that, for a given temperature and apparatus, it depends, as we shall see later, *upon the material of the electrodes.*

c. Stirring Velocity.—Conductometric titrations with hydrogen peroxide were carried out where the stirring velocity was varied from 0 to 360 rev./min. (0, 45, 120, 360 rev./min.). HCl, HNO₃, HClO₄, were investigated thus in cell no. 1 (of constant 0.52). In the case of hydrochloric acid, measured resistances were almost entirely independent of stirring velocity. With the two other acids there is a slight shift of the ΔR_{max} in the direction of higher quantities of hydrogen peroxide for experiments without stirring during the measurements. The amount of ΔR_{max} remains unchanged in any case.

d. Current Frequency.—Some comparative experiments were carried out with a Leeds and Northrup Wheatstone bridge functioning with a telephone and a General Electric Co. tuning fork oscillator giving 1000 cycles/sec. Table IV contains the results of the measurements. The ΔR_{max} obtained with 1000 cycles/sec. are but about half of the ΔR_{max} obtained with the lyograph. Anyhow, even at 1000 cycles/sec. and with cells of usual constants (0, 1 to 1.0) *one may easily get* (e. g., for 0.05 N electrolyte solutions) *errors on the conductivity value reaching tens of % if one neglects the supplementary resistances* ΔR.

Solution, N	Cell const.	Electrode surface	R_0 in abs. of H_2O_2, ohms	R_{max} in pres. of H_2O_2, ohms	ΔR_{max}, ohms	$\Delta R_{max}./\sqrt{C}$
HCl 0.2	7.04	Polished	86.8	107.0	20.2	7.6
HCl .2	35.5	Polished	437.6	477.0	39.4	6.6
HNO₃ .2	7.04	Polished	86.2	98.0	11.8	4.6
HNO₃ .2	35.5	Polished	444.2	464.5	20.3	3.4
NaCl .3	0.52	Gray plat. or polished	14.3	21.3	7.0	9.7
NaCl .3	7.04	Polished	209.3	224.3	15.0	5.6
NaNO₃ .3	0.52	Gray plat. or polished	15.1	21.9	6.8	9.4
NaNO₃ .3	7.04	Polished	228.2	246.7	18.5	7.0

TABLE IV

INFLUENCE OF THE MEASURING CURRENT'S FREQUENCY

Solution, N	Cell const.	Frequency, cycles/ sec.	R_0 in abs. of H_2O_2, ohms	R in pres. of H_2O_2 ohms	$\Delta R_{max.}$, ohms
HCl 0.2	7.04	50	86.8	107.0	20.2
HCl .2	7.04	1000	86.8	98.4	11.6
HNO₃ .1	0.52	50	12.1	20.6	8.5
HNO₃ .1	.52	1000	12.1	16.0	3.9
HClO₄ .1	.52	50	14.1	22.5	8.4
HClO₄ .1	.52	1000	14.1	17.3	3.2
NaCl .2	.52	50	23.1	30.4	7.3
NaCl .2	.52	1000	23.1	28.0	4.9

5. Experiments with Tin Electrodes.—As indicated, conductivity measurements in presence of hydrogen peroxide made with tin covered or pure tin electrodes may be found in literature, and it has been interesting to see whether the supplementary resistances ΔR observed with platinum electrodes did appear in this case too. It seems that Calvert[3] was the first to utilize tin covered electrodes. He wanted to avoid the decomposition of hydrogen peroxide by black platinized platinum electrodes in experiments where the quantity of the peroxide had to be maintained constant. He stated that his tin-covered electrodes did not decompose hydrogen peroxide. In Calvert's experiments there was a real neutralization of alkaline hydroxide solutions by hydrogen peroxide, and this neutralization manifested itself by a diminution of the conductivity of the solution. Other investigators[6,7] confirmed his observations, and so tin electrodes became currently used for conductivity measurements in presence of hydrogen peroxide. Now, these measurements with tin electrodes are rather difficult; conductivity values obtained at 50 cycles/sec. (with the "lyograph") are not well reproducible and give differences of a few ohms; those obtained at 1000 cycles/sec. (with the Wheatstone bridge and telephone) give a bad sound minimum. Thus for instance in the case of salt solutions, discontinuous measurements had to be made with the lyograph (see no. 2). Tin electrodes were made by covering heavily with pure tin little square copper plates of 1-cm side length riveted to copper rods tightly sealed into glass tubes (about 20 cm. long) with acid-proof "Cenco-Sealstix." The two glass tubes were then clamped into an ebonite head similar to the one described above (no. 2). An electrode thus devised may serve for some series of measurements with hydrogen peroxide without having to renew the tin layer. When repeating

conductometric titrations with hydrogen peroxide a number of times, initial values (before adding hydrogen peroxide) differing not more than 1-2% may be obtained. The same applies in comparing new or used tin electrodes ($t = 30°$ ($\pm 0.1°$). Stirring was maintained all throughout the measurements. Addition of hydrogen peroxide and recording were as above (no. 2).

For all the experiments after the adding of some drops of hydrogen peroxide, a maximal and *constant* resistance was observed which did not change when further quantities of hydrogen peroxide were added (for platinum electrodes the same feature had been observed only in presence of chloride and fluoride). The resistance thus obtained in presence of hydrogen peroxide remained unchanged independently of the time during which the current was allowed to pass. It has thus been possible to carry out continuous measurements with the lyograph in presence of hydrogen peroxide without recording any shift in the resistances measured. During all the measurements made with tin electrodes we observed a strong increase in the measured resistance after the addition of hydrogen peroxide. Table V shows that this resistance increase (conductivity decrease) is not related to the solution and is connected to the material of the electrode used:

TABLE V

TIN ELECTRODES

Solution, N	Frequency, cycles/ sec.	Vol. H_2O_2 corresponding to $R_{max.}$, in cc. 0.6–0.7	R_0 in abs. of H_2O_2, ohms	$R_{max.}$ in press. of H_2O_2, ohms	$\Delta R_{max.}$, ohms
Na₂SO₄ 0.05	50	0.6–0.7	171	233.6	62.6
		0.8	168	235	67
Na₂SO₄ .10	50	0.6–0.7	111	171	60
		0.4	110	172.8	62.8
H₂SO₄ .05	50	1.0	46	110.7	64.7
NaCl .05	50	0.8	137	205	68
Na₂SO₄ .05	1000	.3	114	133	19
Na₂SO₄ .10	1000	.6	68	90	22
NaCl .05	1000	.7	106	130	24

the ΔR values are independent of electrolyte concentrations—thus also of conductivity—and of the electrolyte in solution (sulfates, chlorides). For discontinuous measurements made at 30° with the lyograph (50 cycles/sec.), ΔR is about 65 ohms. Measurements made with tin electrodes and the Wheatstone bridge and oscillator (1000 cycles/sec.) yield ΔR values of about 20–25 ohms (less than half the lyograph values).

It appears from Table V that even in absence of hydrogen peroxide the resistances measured with 50 and with 1000 cycles/sec. differ from each

other (the 50 cycles/sec. values are greater than the 1000 cycles/sec. values). *It is clear that neglecting these facts when measuring conductivities in presence of hydrogen peroxide one may arrive at errors of 100% on the measured resistances and unjustified conclusions of the electrolytic solution containing undissociated molecules or complex compounds could then be drawn.*

6. **Discussion of the Results.**—It is seen from the results of the present work that the investigated phenomena are specific effects of additional alternating current polarization produced in the presence of hydrogen peroxide and do not exist in its absence. When using platinum electrodes and in absence of hydrogen peroxide at 50 and at 1000 cycles/sec., the same resistances are obtained, while in presence of hydrogen peroxide the values of ΔR are about twice as great at 50 than at 1000 cycles/sec. We have here a very interesting indicator for supplementary alternating current polarization effects appearing only in presence of hydrogen peroxide and which seems to be independent of the concentration and character of the electrolyte (excluding halogenides). We have to imagine that from the two polarization effects (hydrogen and oxygen polarization) that appear during the passage of the current in one direction, the polarization effect due to hydrogen is suppressed by hydrogen peroxide: $2H + H_2O_2 = 2H_2O$, while the polarization effect due to oxygen is given eminence. An assumption that the production of gas bubbles and its intensity may have an influence on the ΔR is impossible because this would be dependent on the character and the concentration of the electrolyte. It may also be remarked that in the studied phenomena very small quantities of reaction participants must take part for we could nowhere see at the electrodes an appreciable decomposition of hydrogen peroxide. Should such a decomposition of hydrogen peroxide take place, then the concentration of hydrogen peroxide and therefore ΔR should vary with time but we never observed anything of this kind.

Another interesting feature is the great sensitivity of ΔR to variations of the hydrogen peroxide concentration (during ΔR increase as well as during its decrease).

In all the cases the final resistance values recorded were obtained immediately after the addition of hydrogen peroxide and did not change with time. This tends to show that there can be no

question of difficulties of diffusion near the surfaces of the electrodes. Neither could we observe any change in the ΔR values when varying the stirring velocities. On the other hand, the effects can in no way influence the electrodes themselves, for at the beginning of a new experiment the ΔR values were exactly reproducible.

It is interesting to note that in the work of Jones and Christian[2] the same direction and size of temperature coefficient were found as in the present work (about 1% per degree) though experimental conditions were quite different in both cases. In both cases ΔR values are positive (although we found negative ΔR values in the special case of acetic acid) and are strongly dependent on the chemical character of the electrodes.

It is further of interest that a gray platinized electrode shows these phenomena while with a black platinized platinum electrode ΔR values are quite small.

Another question is how the maximum value of ΔR is produced and why ΔR decreases on further additions of hydrogen peroxide. It seems that this decrease depends on the character of the anions; on the other hand, the increase of ΔR and its maximum are independent of the character, the valency and the concentration of the cation. This may be connected with the fact that in presence of hydrogen peroxide cation effects are generally suppressed. The decrease of the ΔR curves is far slower than the increase; it seems to be due to the concentration effect of hydrogen peroxide.

Further experiments made with platinum and other metals will perhaps give a fuller answer to these problems.

Summary

Conductometric titrations of electrolytic solutions (salts, acids) give in presence of small quantities of hydrogen peroxide *maximal* additional resistances (ΔR_{max}) that diminish on further additions of hydrogen peroxide. These additional resistances are independent of electrolyte concentration and partly also of electrolyte character (except chlorides or fluorides). *They are conspicuous only during measurements in presence of hydrogen peroxide and disappear when measuring in absence of hydrogen peroxide.* A special clearing or a previous cathodic depolarization of the electrodes is without influence. The absolute

magnitude of the *additional resistances* (in ohms) depends, at equal working conditions, on the *chemical character* of the electrodes and on the *concentration of hydrogen peroxide.* They are smaller with platinum than with tin electrodes and are at 1000 cycles/sec. about half the value obtained at 50 cycles/sec. For a given hydrogen peroxide concentration ΔR is a constant that must be counted with in conductivity measure-

ments. If the quantities of hydrogen peroxide change during a reaction, the course of which is followed by conductometric measurements, then the ΔR will vary continuously. The temperature coefficient is negative and is about 1% per degree. *The neglect of these changing additional resistances leads to false computations and to thoroughly misleading conclusions.*

The Freezing Point of Phenothiazine*

BY L. E. SMITH AND O. A. NELSON

Most of the investigations into the properties of phenothiazine by workers in the Department of Agriculture and elsewhere have been limited to determinations of its toxicity to various types of insects, its anthelmintic properties, and its value in therapeutics. The melting point of phenothiazine as reported in the literature[1,2] or in chemical handbooks is usually 180–181°. This melting point has been taken as a criterion for the purity of the compound, and it has been common practice to recrystallize phenothiazine until the crystals gave this melting point, when the compound was accepted as pure. In the course of studies made by the authors on the vapor pressures, rates of evaporation, and freezing points of binary mixtures of phenothiazine, it was noted that repeated crystallizations gave crystals of phenothiazine having a melting point significantly higher than that previously recorded. The present study is concerned with the preparation of this compound in pure form and the accurate determination of its freezing point. ·

Experimental

Purification of Material.—A lot of recrystallized phenothiazine prepared commercially was subjected to repeated recrystallizations from toluene and butanol, decolorizing with norite. In all cases the compound after filtration was dried in an Abderhalden drier, evacuated to 16 mm. at 100°, for five to six hours. Crystallizations were repeated until no increase in melting point or freezing point was observed. A portion of the final recrystallization product was sublimed at 130° at 1 mm. pressure. Part of the resulting sublimate was again recrystallized from toluene.

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* Not copyrighted.

(1) Cumming, Hopper and Wheeler, "Systematic Organic Chemistry," second edition, 1931, pp. 325–6.

(2) Richter-Anschütz, "Chemie der Kohlenstoffverbindungen," Dritter Band, 12 Auflage, 1931.

Freezing-point Apparatus.—The apparatus shown in Fig. 1 is believed to be a decided improvement over the devices commonly used for melting-point and freezing-point determinations. The sample (approximately 1 g.) was
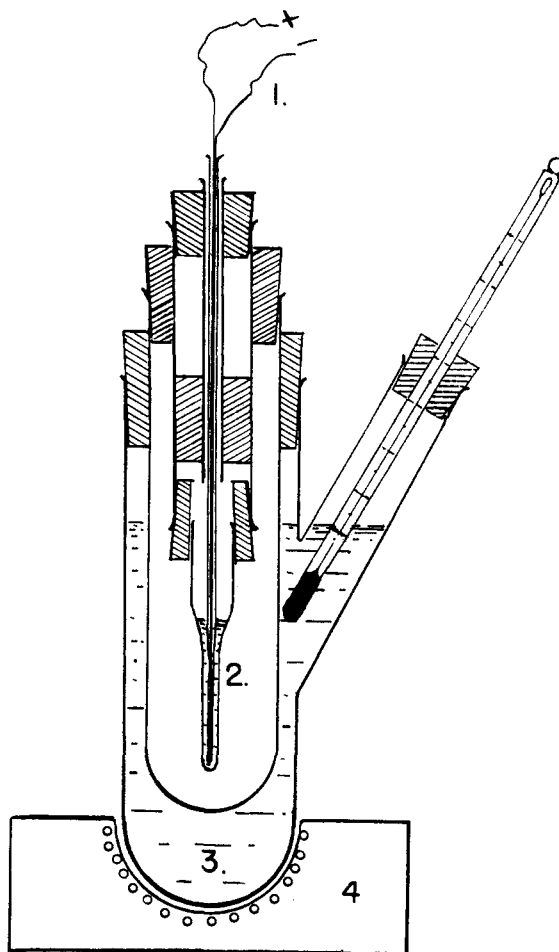

Fig. 1.—Freezing point apparatus: 1, thermocouple; 2, freezing point tube; 3, liquid bath; 4, electric heater.