

Summary

Potassium cyanide vapor at 875° absorbs light in two regions, the long wave length boundaries of which are approximately 2175 (5.7 v.) and 2900 Å. (4.3 v.). The latter absorption region is interpreted, according to Franck, Kuhn and Rollefson, as representing dissociation of the *ionic* molecule into a normal potassium atom and a normal CN radical and agrees within 0.5 v. with the calorimetric data, supplemented by an estimate of the heat of sublimation (48.8 k. cal.). The former absorption act takes place at an energy 1.4 v. greater and represents dissociation into a normal and an excited dissociation product (K excitation 1.6; CN, 1.8 v.). The change with temperature in stability of the two molecular forms postulated by Franck and Kuhn is explained in the light of the free energy.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE MEASUREMENT OF THE CONDUCTANCE OF ELECTROLYTES.¹ III. THE DESIGN OF CELLS

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Historical Introduction

In 1923 H. C. Parker² published two papers which challenge a fundamental postulate of the Kohlrausch method for the measurement of the conductance of electrolytes, by the observation that "cell constants" are apparently not really constant but vary with the resistance being measured. If a solution of specific conductance, κ , is placed in a cell, A, whose length is l and whose cross section is a , then the fundamental premise of the Kohlrausch method is that the resistance, R_A , is given by the equation

$$R_A = \left(\frac{l}{a}\right)_A \frac{1}{\kappa} \quad (1)$$

$(l/a)_A$ is designated as the "cell constant"³ and has been assumed to have a fixed value for any given cell at a given temperature, and this assumption is vital for the Kohlrausch method.

If we have two different cells, A and B, and fill them with the same solution and designate the corresponding resistances and cell constants by

¹ The first two papers in this series are: Grinnell Jones and R. C. Josephs, *THIS JOURNAL*, **50**, 1049 (1928); Grinnell Jones and Giles M. Bollinger, *ibid.*, **51**, 2407 (1929).

² H. C. Parker, *ibid.*, **45**, 1366, 2017 (1923).

³ If the cross section is not uniform the cell constant is $\int_0^l \frac{dl}{a}$.

suffixes, we may eliminate the specific conductance of the solution used giving

$$\frac{R_A}{R_B} = \frac{(l/a)_A}{(l/a)_B} \quad (2)$$

Therefore, if Equation 1 is valid, the ratio of the resistances of any pair of cells when filled with the same solution should be the same as the ratio of the cell constants, and should be independent of the composition and concentration of the solution used and hence of the resistance being measured. This ratio should also be independent of the frequency and the voltage used in the measurements.

Parker compared the resistances of two cells, sealed together so as to facilitate filling them with a common solution, and found that the ratio of the resistances, instead of being constant, varied in a complicated but systematic manner with the specific conductance of the solution chosen for the comparison. Parker has recorded data and drawn curves for seven cases. In these curves the ratios of the resistances are plotted as ordinates and the resistances of the cell having the lower cell constant as abscissas. The lines depicting the resistance ratio, instead of being horizontal and straight, have a varied shape. All show a steep negative slope at low resistances. Three of his curves show both a maximum and a minimum, two a minimum but no maximum, and two show a gentle negative slope at high resistances but no maximum or minimum. The phenomena are evidently very complicated. He has not determined the influence of variations in frequency on the cell resistance ratios. Although the variations are apparently exaggerated in his figures because the zero on the ordinate scale is not shown, the variations are substantial. In one case recorded by Parker the deviation amounts to 0.33%. If, as seems probable, the errors in the two cells are in the same direction, this figure is the difference in the errors, and the actual error in using Equation 1 may be greater by a considerable and unknown amount. All measurements were made with solutions of potassium chloride.

Parker regards polarization as the cause of the steep negative slope of these curves at low resistances. He is doubtless correct in this interpretation although he makes no attempt to show that the shape of his curves is in conformity with the known facts about polarization. In view of the earlier literature on polarization this interpretation lacks novelty.

On the other hand, Parker appears to have been the first to observe the more gentle and usually positive slope of these curves at resistances above the range in which polarization predominates. At any rate he was the first observer with the courage to record his data, and we shall therefore call this anomaly the Parker Effect to distinguish it from polarization. This positive slope at moderate resistances is ascribed by Parker to adsorption of electrolyte at the electrodes, although the arguments in favor of this suggestion

are extremely weak. He is unable to account for the peculiarities of his various cases by the aid of this hypothesis. He offers no explanation of the appearance of a maximum and a negative slope at very high resistances and gives it little consideration because it does not appear in all of his cases.

Randall and Scott⁴ have confirmed the existence of the Parker Effect. They used a single pair of cells only, not sealed together, and a single frequency (1000 cycles), but used four electrolytes, potassium chloride, barium nitrate, sodium sulfate and sulfuric acid. For potassium chloride their results are similar to those of Parker. The steep negative slope at low resistances, which Parker ascribed to polarization, is absent for the other three electrolytes. The Parker Effect, represented by a positive slope of the resistance ratio curves, was obtained with barium nitrate as well as with potassium chloride. They concluded from their experiments that the Parker Effect is absent in the case of sodium sulfate and sulfuric acid and regarded this alleged difference in behavior of these electrolytes as supporting the hypothesis advanced by Parker that adsorption is the cause of the phenomena since it is characteristic of adsorption to vary greatly in different cases. It should be noted, however, that when the cells were filled with sulfuric acid and with sodium sulfate, measurements at high resistances were omitted. Whereas with potassium chloride the highest resistance measured in the longer cell was about 64,000 ohms, when using sulfuric acid the upper limit was only 5100 ohms, and, therefore, these experiments do not prove that the curves might not have been similar if comparable resistances had been used. In the case of sodium sulfate the upper limit was about 31,000 ohms, a little less than half that used with potassium chloride. The result with this most dilute solution does show a rise of about 0.10%; nevertheless this rise is ignored by Randall and Scott in drawing their curves and in the interpretation of their data. Randall and Scott offer no reason for ignoring the evidence of their data on the highest resistance they measured or for not extending the measurements on sodium sulfate and on sulfuric acid to as high resistances as were used with the other salts. The only suggestion for a remedy of the Parker Effect that they offer is that sodium sulfate would be a better substance than potassium chloride for standard solutions for the determination of cell constants. But this suggestion, even if it were based on unquestionable premises, would not give a means of obtaining accurate conductance data if adsorption of the salt being measured can cause an error.

Some recent experiments by F. A. Smith⁵ are of interest as an extreme example of the Parker Effect. His cell contained three electrodes consisting of coaxial cylinders open at the ends, two of which were concentric and

⁴ M. Randall and G. N. Scott, *THIS JOURNAL*, 49, 636 (1927).

⁵ F. A. Smith, *ibid.*, 49, 2167 (1927).

close together and the third at some distance from the others, presenting its edge to an edge of the others. By using the two electrodes positioned close together, a cell of low cell constant was available, and by using one of the close electrodes and the distant electrode a second cell having a cell constant about two hundred times greater was available. Smith's data afford comparison between two cells of widely different cell constant, covering a great range in concentration and extending to very high resistances under conditions that insure identity of composition of the solution in the two cells. Smith reports a change in the apparent cell constant ratio between the most concentrated solution and the most dilute amounting to more than 50%. This is an extreme case of the Parker Effect. Smith reports such data on three cases, ammonium chloride dissolved in liquid ammonia, ammonium nitrate dissolved in liquid ammonia, and potassium chloride in water. The data on these three cases, when plotted as resistance ratio against resistance in one cell, all fall on the same curve. This creates a presumption that the cause of the effect is purely electrical, rather than due to adsorption. If the effect is to be explained as due to adsorption it will have to be maintained that the adsorption in these three cases and the variation thereof with the concentration cause an identical effect on the conductance, which is hardly plausible. Smith used a single frequency of 1000 cycles only. His cells were closely shielded and without proper grounding of the bridge, which probably contributed to the very large errors, so that errors of this magnitude are not to be regarded as common or unavoidable.

O. Redlich⁶ has devised a radically different method of measuring conductance in an effort to avoid errors due to electrode processes (polarization, adsorption, etc.). His apparatus may be regarded as a double alternating current potentiometer instead of a Wheatstone-Kohlrausch bridge. His cell contained three platinized platinum electrodes of the usual type which served as current electrodes, and near each a small platinum potential electrode through which no current flows when the measurements were being made. With a given solution in the cell he made measurements by the Kohlrausch method between three pairs of large electrodes and also by his new method between three pairs of small electrodes. The solution was replaced by another of different specific conductance and the measurements repeated. In this way several cell resistance ratios were compared using two radically different methods of measurement. He varied the specific conductance of the solution used by about ninetyfold and when using the large electrodes and the Kohlrausch method found no variation in cell constant ratio greater than 0.03%. Just what difference in cell design or bridge design or manipulation as compared to Parker's is responsible for the comparatively small Parker Effect in his experiments is

⁶ O. Redlich, *Z. physik. Chem.*, 136, 331 (1928).

not discussed by Redlich and is not immediately obvious. So long as the resistances being measured did not exceed 2300 ohms the results by the new method agreed with those of the older method within about 0.03%. At higher resistances discrepancies up to 0.1% occurred.

Recently Shedlovsky⁷ has designed, built and tested a new form of cell intended to eliminate any effects at the electrodes which would disturb conductance measurements, especially polarization and adsorption. In Shedlovsky's cell the two end electrodes, which carry the current and are subject to electrode effects, were in different adjacent arms of the bridge and hence electrode disturbances tended to compensate each other. The midpoint of the bridge was inside the cell itself and consisted of a loop of fine smooth platinum wire. Since the loop composing the midpoint was nearer to one of the end electrodes than to the other, the difference of the resistance of the portions in the two arms had to be balanced by a resistance box in the same arm as the short portion of the cell. Shedlovsky provided three different midpoint loops at different positions which could be used in turn. He made measurements at three different frequencies, 1000, 2000 and 3000 cycles. He filled his cell with four different solutions (0.005 *N* KCl, 0.001 *N* HCl, 0.002 *N* HCl, 0.004 *N* HCl) and on each filling measured each electrode combination at each of his three frequencies. By subtracting the readings obtained by the use of the three different loops he attempted to eliminate the electrode effects entirely. Although the individual readings show deviations from the mean up to a maximum of 0.08%, the results indicate that the differences obtained as described above are probably reliable to within 0.01%. It should be pointed out, however, that the specific conductance of the solutions used in these tests only covered a fourfold range, so that the test was not as severe as if a wider range had been used. This range is inconveniently small for the practical use of the cell. The necessity of taking multiple readings and subtracting the results is a disadvantage in the routine use of the cell; nevertheless Shedlovsky's cell is evidently a distinct step in advance in eliminating polarization and other electrode effects. It would be interesting to have

⁷ T. Shedlovsky, *THIS JOURNAL*, 52, 1806 (1930). During the course of our experimental study of the problem we learned that Dr. Theodore Shedlovsky of the Rockefeller Institute for Medical Research in New York was engaged in a study of the same problem. We have kept in touch with each other's work by occasional visits and frank discussion and correspondence while attacking the problem along different lines. Dr. Shedlovsky's paper has been published after the completion of our experimental work but before the completion of our manuscript. We wish to compliment Dr. Shedlovsky on his literary skill in writing his paper so as to embody only ideas already in the literature and his own new ideas with a complete exclusion of ideas based on our work which we had disclosed to him in advance of publication. Since Dr. Shedlovsky's paper has now been published it is not necessary for us to attempt the same difficult task, but we cordially acknowledge Dr. Shedlovsky's priority on all points covered in his recent paper on cell design.

data obtained with the Shedlovsky cell on concentrated solutions in which polarization is a more serious difficulty.

It is evident that the Parker Effect, unobserved or at least unreported until 1923, throws suspicion on the data on the conductance of electrolytes obtained by the Kohlrausch method. The work cited above appears to show that the concept of a fixed and definite cell constant is invalid. Although there is no certain criterion for estimating the magnitude of the error, since the method of intercomparison of cells shows only the differences in the errors in two cells and not the absolute error in either, it is evident that errors up to at least 0.3% are likely to be present with cells of the type commonly used in spite of precautions which eliminate errors due to polarization. In one case with a cell of unusual design an error of 50% was reported. Moreover, there is no adequate theory to account for the error or errors. The hypothesis that adsorption is responsible fails to account for the known facts and has not suggested to anyone a practical remedy.

The general consistency of the data in the literature makes it seem improbable that errors of as much as 0.3% are commonly present in the results of the more careful and experienced investigators. This may indicate that some faulty detail of design may have aggravated the error in the cases cited above. But an adequate understanding of the nature and causes of the Parker Effect is urgently needed to permit an estimate of the reliability of the great mass of data now available, and, more important still, to guide the design of cells which may be relied on to have a fixed and definite cell constant.

The Determination of Phase Displacement in Conductance Cells.—All of the earlier experimenters on the Parker Effect, except Shedlovsky, have been content to use a single frequency, but our experience in the study of the errors in the bridge made it probable that the study of the influence of variations in frequency would be a great aid in understanding the nature of the phenomena. Accordingly, at least two frequencies were used in each case except in some of the preliminary trials.

Although nearly all experimenters on conductance since the time of Kohlrausch have used a capacitance in parallel with the resistance box to obtain a sharp balance, very few have recorded these capacitance readings, C_p , or made any attempt to interpret them. This is doubtless due to the fact that there was so much reactance in their circuits outside the cells (such as inductance in a helically wound slide wire, capacitance and inductance in the resistance boxes and in the bridge, and capacitance introduced by shields) that the capacitance required to obtain a balance did not depend solely or even largely on the reactance in the cell itself and, therefore, it was not to be expected that the parallel capacitance required could be correlated with the design of the cell, the frequency, specific conductance,

or chemical nature of the solutions used. Some of the investigators of polarization in cells, beginning with Wien, have obtained significant information from the study of the reactance in their cells, but none of the experimenters on the Parker Effect has published the capacitance required to obtain a balance. Our bridge was designed to avoid inductance and capacitance as much as possible and it was therefore hoped that the capacitance required in parallel with the resistance box would depend primarily on the reactance in the cell and give a clue to the nature of the error responsible for the Parker Effect. We, therefore, recorded the capacitance required to obtain a balance in each of the readings, by the use of a calibrated condenser in parallel with the resistance box. The precision of these capacitance readings was much less than the precision of the resistance readings because the capacitance in most cases was very low (commonly under 100 micromicrofarads at resistances over 1000 ohms, where the Parker Effect becomes serious, and in some cases it was even below 5 micromicrofarads) and because the bridge was not designed as a capacitance bridge; nevertheless, the results did prove to be helpful in the interpretation of the data.

Since the phase displacements in the ratio arms of the bridge have been made as nearly equal as possible, we can regard the phase displacement, θ , in the arm of the bridge containing the resistance box and parallel condenser as equal to the phase displacement in the cell itself.⁸ This can be computed from the well-known formula for a parallel combination of resistance and capacitance

$$\tan \theta = C_p \omega R \quad (3)$$

where f is frequency in cycles per second and $\omega = 2\pi f$.

Five cells differing greatly in design were selected or especially built and sealed together by their filling tubes, as had been done by Parker, to facilitate filling them with a common solution. These cells are shown somewhat diagrammatically in Fig. 1. Cells I, II, III had approximately the same cell constants but differed greatly in dimensions. The electrodes in cells I and II were made interchangeable by means of ground joints.

⁸ Grinnell Jones and R. C. Josephs, *THIS JOURNAL*, 50, 1070 (1928).

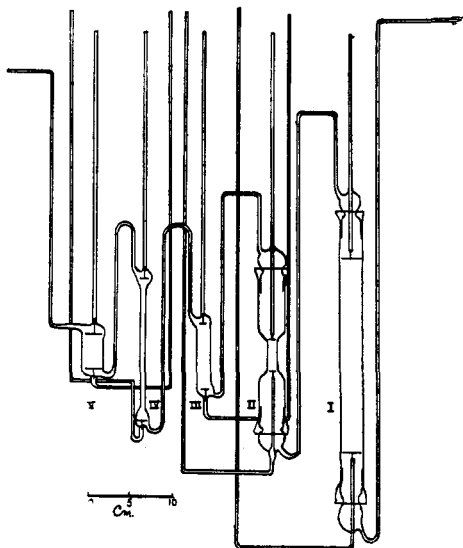


Fig. 1.—Pipet type cells, I-V.

These joints were very carefully ground and made perfectly tight by means of a trace of pure, soft paraffin around the outer edge. The upper joints were protected from the oil by a layer of mercury and the lower joints by the air trapped under the rim. Cells IV and V differed greatly in dimensions and cell constants from the others. The dimensions of these cells are shown in Table I.

TABLE I
CELL DATA
Dimensions of the cells used in the cell comparisons

Cell	Cell constant	Area of electrode, sq. cm.	Distance between electrodes, cm.	Diam. of tube, cm.	Light Milliampères per sq. cm.	Platinization data		Min.
						Heavy Milliampères per sq. cm.	Min.	
I	4.39	3.8	20	2.2	7.9	20	25	75
II	4.29	0.8	3	1.0	6.2	19	31	25
III	4.32	1.5	7	1.4
IV	51.47	2.0	16	0.5	4.0	22.5	22.5	40
V	1.232	3.1	4	2.5	6.5	20	30	45

If adsorption plays a significant part in the Parker Effect, it would be expected that lightly platinized electrodes should give less Parker Effect than heavily platinized electrodes. We, therefore, determined to make a series of measurements to test the Parker Effect with light platinization, and then give the cells a heavy platinization and repeat the measurements. But in order to have a fixed standard of reference, cell III was given a heavy platinization in advance and remained unaltered during both series. The other four cells were treated with aqua regia to remove an old platinization and were then given a light platinization using a solution of platinum chloride and hydrochloric acid (with no lead acetate) as shown in Table I. At this stage the platinization was so slight as to be barely perceptible to the eye as a slight tarnish or dimming of the bright electrode. The first series of measurements on cell resistance ratios was then carried out. For this purpose a potassium chloride solution of suitable concentration was prepared in a large "Non-Sol" bottle and thence forced into the five cells in series by compressed air. The cells were filled and emptied repeatedly to ensure thorough rinsing. In order to avoid changes in concentration of the solution by evaporation, the air used was first bubbled through some of the same solution before it entered the stock bottles. The cells were then placed in the thermostat and, after waiting for at least one-half hour for temperature equilibrium, the resistance of each cell was measured with 1090 cycles and with 2280 cycles. The capacitance required across the box in the other arm of the bridge to secure a balance was also determined from the reading of the condensers and recorded for each measurement. The solution was then replaced by a more concentrated solution and the measurements repeated. Twelve different solutions covering the range 0.0005 to 1.0 *N* were used. The cells, except No. III, were then given a much

heavier platinization on top of the light platinization, as is shown in Table I. The electrodes at this stage did not have the deep sooty black color which can be obtained by using platinizing solutions containing a trace of lead acetate but were black with a slightly grayish or metallic appearance. Then the second series of measurements on cell resistance ratios was carried out.

The solutions used in the second series were approximately of the same concentration but not identical with the solutions used in the first series. The ratio of the specific conductance of these solutions can be computed from the data on cell III because in this case the cell itself was unchanged.

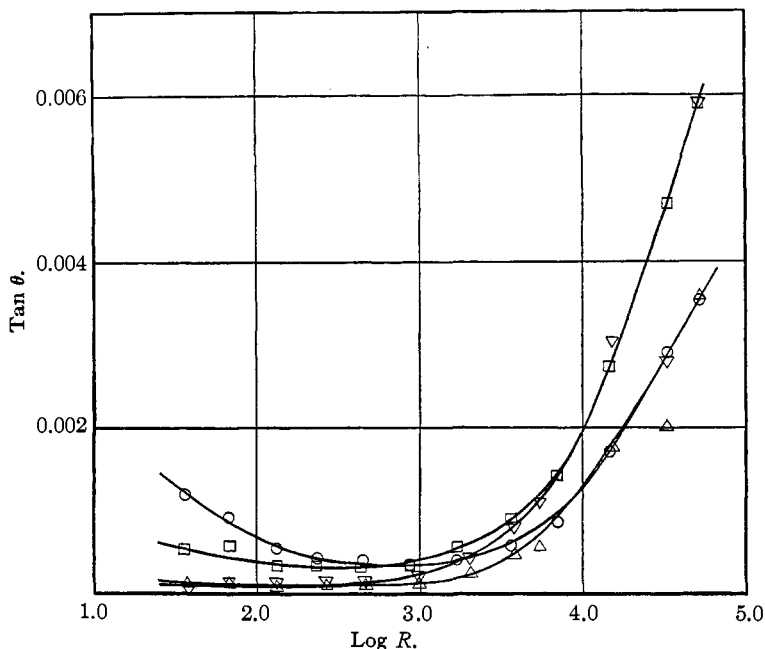


Fig. 2.—Cell I: ○, 1090 L; □, 2280 L; △, 1090 H; ▽, 2280 H.

but no direct comparison can be made between the first and second series without making due allowance for the difference in specific conductance, and for the fact that the cell constants may have been slightly changed by the additional platinization.

The primary data of these cell comparisons are shown in Tables II to VI, inclusive, in which the successive columns have the significance: (1) the number of the solution of potassium chloride used; (2) the approximate concentration; (3) the resistance in ohms when measured with 1090 cycles, R' ; (4) the capacitance in micromicrofarads required in parallel with the resistance box in the other arm of the bridge to give a balance, C_P , when using 1090 cycles; (5) the tangent of the phase angle, $\tan \theta = C_P \omega R$, when using 1090 cycles; (6) the resistance with 2280 cycles, R'' ; (7) the

parallel capacitance at 2280 cycles; (8) the tangent of the phase angle at 2280 cycles; (9) the change in resistance caused by changing the frequency from 1090 to 2280 cycles, $-(R''-R')$, with sign reversed for convenience; (10) the percentage change in resistance with reversed sign, $-100(R'' - R')R'$.

The Significance of Phase Displacement in Cells.—Figures 2 to 6 give plots of $\tan \theta$ against $\log R$ for each of the five cells at two frequencies and

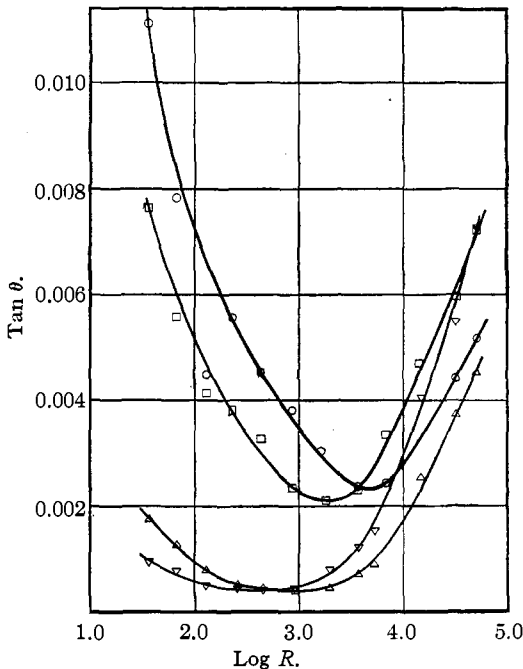


Fig. 3.—Cell II.

with two degrees of platinization. The $\log R$ is plotted as abscissa instead of R merely to avoid confusion due to crowding of the points at the lower resistances. In the legend under Figs. 2-10 the numbers 1090 and 2280 designate the frequency used, L signifies light platinization, and H heavy platinization.

In these curves the outstanding feature is that the phase displacement goes through a minimum which indicates that there are two phenomena superimposed on each other. At low resistances the phase angle is undoubtedly one aspect of polarization. These data and curves make it evident

that there is another and distinct disturbing effect which causes a phase displacement and which increases rapidly with the resistance being measured. This disturbance apparently also causes an error in the resistance which is responsible for the Parker Effect. Our task is, therefore, to analyze the data for the purpose of elucidating the nature of this disturbing effect and to ascertain the sign of the error in the resistance caused thereby and the factors controlling its magnitude and, if possible, to find a means of eliminating this error. From a study of these data and curves the following general conclusions may be drawn.

(1) The measured resistance with 2280 cycles, R'' , is always less than with 1090 cycles, R' , when all other conditions remain unchanged. Tables II-VI give 109 instances of this without a single exception and this conclusion is in accord with much other experience in this Laboratory.

TABLE II
CELL COMPARISON DATA. CELL I

Soln.	Approx. concn.	Light Platinization			Light Platinization			$R' - R''$ ohms	$\frac{(R' - R'')}{R'}$ %
		R' , ohms	C_p , $\mu\mu\text{f.}$	$\text{Tan } \theta$ $C_p \omega R$	R'' , ohms	C_p , $\mu\mu\text{f.}$	$\text{Tan } \theta$ $C_p \omega R$		
		$f = 1090$			$f = 2280$				
1	0.0005	51,623.7	10	0.0035	51,512.0	8	0.0059	111.7	0.217
2	.0009	32,876.7	13	.0029	32,824.2	10	.0047	52.5	.160
3	.0019	14,717.7	17	.0017	14,704.7	13	.0027	13.0	.089
4	.0040	7,008.92	18	.00086	7,005.8	14	.0014	3.12	.045
5	.0077	3,677.98	23	.00058	3,677.23	17	.00090	0.75	.020
6	.016	1,675.4	35	.00040	1,675.13	23	.00055	.27	.016
7	.033	871.711	60	.00036	871.626	28	.00035	.085	.010
8	.065	447.96	130	.00040	447.913	50	.00032	.047	.010
9	.13	235.553	270	.00044	235.509	100	.00034	.044	.019
10	.25	133.295	600	.00055	133.276	180	.00034	.019	.014
11	.5	67.935	2000	.00093	67.916	590	.00057	.019	.028
12	1.0	36.380	4800	.00120	36.368	1050	.00055	.012	.033
Heavy Platinization									
21	0.0005	51,808.8	10	0.0035	51,675.3	8	0.0059	133.5	0.258
22	.0009	32,721.4	9	.0020	32,681.1	6	.0028	40.3	.123
23	.0020	15,161.1	17	.0018	15,148.4	14	.0030	12.7	.084
24	.005	5,456.20	15	.00056	5,454.47	14	.0011	1.73	.032
25	.008	3,836.87	18	.00047	3,836.14	15	.00082	0.73	.019
26	.013	2,046.77	18	.00025	2,046.61	15	.00044	.16	.008
27	.031	941.065	20	.00013	941.015	15	.00020	.050	.005
28	.065	470.156	33	.00011	470.14	23	.00015	.016	.003
29	.13	267.620	65	.00012	267.613	36	.00014	.007	.003
30	.25	132.529	83	.00007	132.523	88	.00009	.006	.005
31	.50	68.853	315	.00015	68.849	145	.00014	.004	.006
32	1.00	37.774	500	.00013	37.771	210	.00011	.003	.008

TABLE III
CELL COMPARISON DATA. CELL II

Soln.	Approx. concn.	Light Platinization			Light Platinization			$R' - R''$, ohms	$\frac{(R' - R'')}{R'}$, %
		R' , ohms	C_p , $\mu\mu\text{f.}$	$\text{Tan } \theta$	R'' , ohms	C_p , $\mu\mu\text{f.}$	$\text{Tan } \theta$		
		$f = 1090$			$f = 2280$				
1	0.0005	50,411.4	15	0.0052	50,317.7	10	0.0072	93.7	0.185
2	.0009	32,109.7	20	.0044	32,059.4	13	.0060	50.3	.157
3	.0019	14,380.0	14,361.6	23	.0047	18.4	.128
4	.0040	6,851.96	52	.0024	6,846.12	28	.0033	5.84	.085
5	.0077	3,597.36	95	.0023	3,594.87	45	.0023	2.49	.070
6	.016	1,640.08	270	.0030	1,638.60	90	.0021	1.48	.090
7	.033	854.19	650	.0038	853.14	190	.0023	1.05	.120
8	.065	439.536	1500	.0045	438.811	520	.0033	0.725	.165
9	.13	231.68	3500	.0055	230.987	1150	.0038	.693	.300
10	.25	131.180	5000	.0045	130.904	2200	.0041	.276	.211
11	.50	67.235	17000	.0078	67.000	5800	.0056	.235	.348
12	1.0	36.175	44800	.0111	36.025	14800	.0076	.150	.415

TABLE III (Concluded)

Heavy Platinization

Soln.	Approx. concn.	$f = 1090$			$f = 2280$			$R' - R''$, ohms	$\frac{(R' - R'')}{R'}$, %
		R' , ohms	C_P , $\mu\text{f.}$	$\text{Tan } \theta$	R'' , ohms	C_P , $\mu\text{f.}$	$\text{Tan } \theta$		
21	0.0005	50,593.7	13	0.0045	50,497.7	10	0.0072	96.0	0.190
22	.0009	31,959.2	17	.0037	31,914.3	12	.0055	44.9	.141
23	.0020	14,814.7	25	.0025	14,795.2	19	.0040	19.5	.132
24	.005	5,332.59	25	.00091	5,330.39	20	.0015	2.20	.041
25	.008	3,749.84	28	.00072	3,748.91	23	.0012	0.93	.025
26	.013	2,000.48	33	.00045	2,000.26	28	.00080	.22	.011
27	.031	919.930	65	.00041	919.833	33	.00043	.10	.011
28	.065	459.691	140	.00044	459.646	65	.00043	.045	.045
29	.13	261.761	300	.00054	261.726	120	.00045	.035	.035
30	.25	129.698	890	.00079	129.678	280	.00052	.020	.020
31	.5	67.460	2750	.00127	67.448	810	.00078	.012	.012
32	1.0	37.080	6900	.00175	37.070	1800	.00096	.010	.010

TABLE IV

CELL COMPARISON DATA. CELL III

Heavy Platinization

Soln.	Approx. concn.	$f = 1090$			$f = 2280$			$R' - R''$, ohms	$\frac{(R' - R'')}{R'}$, %
		R' , ohms	C_P , $\mu\text{f.}$	$\text{Tan } \theta$	R'' , ohms	C_P , $\mu\text{f.}$	$\text{Tan } \theta$		
1	0.0005	50,920.5	8	0.0028	50,888.5	8	0.0058	32.0	0.063
2	.0009	32,415.1	9	.0020	32,402.1	8	.0037	13.0	.040
3	.0019	14,502.1	14	.0014	14,499.6	11	.0023	2.5	.017
4	.0040	6,905.92	10	.00047	6,904.2	9	.00089	1.72	.025
5	.0077	3,623.70	12	.00030	3,623.24	10	.00052	0.46	.013
6	.016	1,650.54	18	.00020	1,650.46	13	.00031	.08	.005
7	.033	858.755	21	.00012	858.74	12	.00015	.015	.002
8	.065	441.218	45	.00014	441.205	20	.00013	.013	.003
9	.13	231.999	100	.00016	231.992	33	.00011	.007	.003
10	.25	131.296	260	.00024	131.288	70	.00013	.008	.006
11	.50	66.897	1000	.00046	66.893	230	.00022	.004	.006
12	1.00	35.824	2900	.00071	35.819	520	.00027	.005	.014

Heavy Platinization									
21	0.0005	51,118.8	6	0.0021	51,081.8	6	0.0044	37.0	0.072
22	.0009	32,268.8	8	.0018	32,249.9	6	.0028	18.9	.059
23	.0020	14,942.8	14	.0014	14,936.5	12	.0026	6.3	.042
24	.005	5,376.34	10	.00037	5,375.56	9	.00069	0.78	.014
25	.008	3,780.46	13	.00034	3,780.11	11	.00060	.35	.009
26	.013	2,016.60	10	.00014	2,016.51	9	.00026	.09	.004
27	.031	927.141	14	.00009	927.111	9	.00012	.030	.003
28	.065	463.221	34	.00011	463.204	16	.000106	.017	.004
29	.13	263.665	75	.00013	263.657	29	.00011	.008	.003
30	.25	130.571	200	.00018	130.563	40	.000075	.008	.006
31	.50	67.834	700	.00032	67.828	170	.00016	.006	.009
32	1.0	37.217	1900	.00048	37.212	320	.00014	.005	.013

TABLE V
CELL COMPARISON DATA. CELL IV
Light Platinization

Soln.	Approx. concn.	$f = 1090$			$f = 2280$			$R' - R''$, ohms	$(R' - R'')/R'$, %
		R' , ohms	C_P , $\mu\mu\text{f.}$	$\text{Tan } \theta$	R'' , ohms	C_P , $\mu\mu\text{f.}$	$\text{Tan } \theta$		
5	0.0077	43,101.1	23	0.0068	43,019.3	20	0.0123	81.8	0.190
6	.016	19,657.2	25	.0033	19,644.2	23	.0065	13.0	.066
7	.033	10,230.3	21	.0015	10,228.0	19	.0028	2.3	.023
8	.065	5,257.42	21	.00076	5,256.41	18	.0014	1.01	.019
9	.13	2,764.51	26	.00049	2,764.26	21	.0008	0.25	.009
10	.25	1,564.88	35	.00038	1,564.72	20	.00045	.16	.010
11	.5	797.53	60	.00033	797.45	30	.00034	.08	.010
12	1.0	427.183	130	.00038	427.159	60	.00037	.024	.006
Heavy Platinization									
25	0.008	45,017.9	19	0.0059	44,959.5	18	0.0116	58.4	0.13
26	.013	24,025.0	20	.0033	24,013.0	18	.0062	12.0	.050
27	.031	11,046.2	21	.0016	11,044.9	21	.0033	1.3	.012
28	.065	5,519.75	15	.00057	5,519.50	15	.0012	0.25	.004
29	.13	3,142.14	17	.00037	3,142.04	15	.00067	.10	.003
30	.25	1,555.96	21	.00022	1,555.93	18	.000403	.03	.002
31	.50	808.493	20	.00011	808.480	14	.000106	.018	.002
32	1.00	443.632	40	.00012	443.625	21	.000103	.007	.002

(2) For any given cell and frequency the change in apparent resistance caused by a change in frequency, $-(R'' - R')$, increases in magnitude with the resistance being measured throughout the range from 19 to 51,000 ohms.

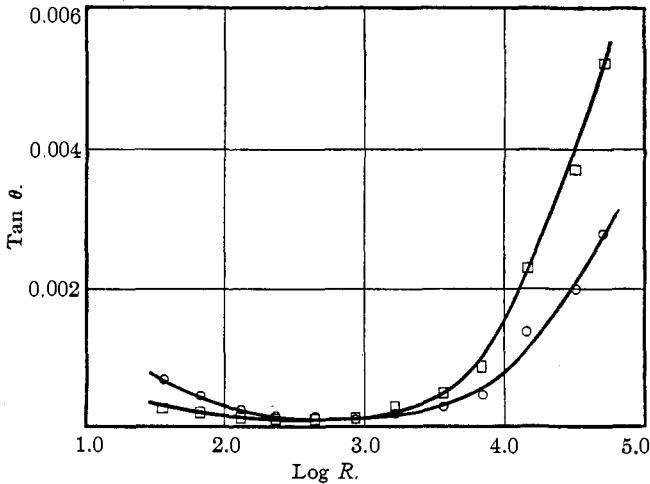


Fig. 4.—Cell III: \circ , 1090; \square , 2280.

(3) For any given cell and frequency the numerical value of the percentage change in resistance caused by a change in frequency, $-100(R'' -$

TABLE VI
CELL COMPARISON DATA. CELL V
Light Platinization

Soln.	Approx. concn.	$f = 1090$			$f = 2280$			$R' - R''$, ohms	$(R' - R'')/R'$, %
		R' , ohms	C_P , $\mu\mu\text{f.}$	$\tan \theta$	R'' , ohms	C_P , $\mu\mu\text{f.}$	$\tan \theta$		
1	0.0005	14,544.2	16	0.0017	14,541.5	16	0.0033	2.7	0.019
2	.0009	9,256.1	11	.00070	9,255.2	10	.0013	0.9	.010
3	.0019	4,139.3	23	.00065	4,138.88	11	.00065	.42	.010
4	.0040	1,970.06	60	.00081	1,969.74	23	.00065	.32	.016
5	.0077	1,033.74	130	.00092	1,033.46	42	.00062	.28	.027
6	.016	470.895	130	.00088
7	.033	245.249	1000	.0017	245.048	350	.0012	.201	.08
8	.065	126.09	2000	.0017	125.969	870	.0016	.121	.09
9	.13	66.349	4300	.0019	66.292	1850	.0018	.057	.09
10	.25	37.588	10000	.0026	37.551	4300	.0023	.037	.10
11	.5	19.160	26000	.0034	19.148	7000	.0019	.012	.06
Heavy Platinization									
21	0.0005	14,595.2	12	0.0012	14,593.1	12	0.0025	2.1	0.014
22	.0009	9,206.04	8	.0005	9,205.5	8	.0011	0.54	.006
23	.0020	4,262.19	9	.00026	4,261.99	8	.00049	.20	.005
24	.005	1,533.04	19	.00020	1,532.95	13	.00028	.09	.006
25	.008	1,077.93	22	.00016	1,077.86	13	.00020	.07	.007
26	.013	575.117	43	.00017	575.08	22	.00018	.037	.006
27	.031	264.381	130	.00023	264.361	55	.00021	.020	.008
28	.065	132.095	320	.00029	132.090	100	.00019	.005	.004
29	.13	75.202	930	.00048	75.188	310	.00033	.014	.019
30	.25	37.241	2600	.00066	37.231	700	.00037	.010	.027
31	.50	19.352	6900	.00091	19.345	1750	.00048	.007	.036

R''/R' , goes through a minimum at intermediate values of the resistance. (This is not shown by Cell IV, for which data at very low resistances are not available.)

(4) For any given cell and frequency the phase displacement, $\theta = \tan^{-1}C_P\omega R$, goes through a minimum at intermediate values of the resistance being measured. This minimum is shown in nineteen cases in the tables. In the case of Cell IV at 2280 cycles when heavily platinized the minimum was not observed but it would probably be found below the lowest resistance measured.

(5) Increasing the frequency or increasing the platinization causes the minimum in the phase angle to occur at a lower resistance.

At low resistances, where polarization has the predominating influence, the following characteristics appear.

(6) For any given cell and frequency the parallel capacitance always has its greatest value at the lowest resistance measured, and decreases rapidly from this high value with increasing resistance.

(7) The parallel capacitance is much less at 2280 cycles than at 1090.

(8) For any given cell and frequency the phase angle is reduced by increasing the resistance being measured.

(9) The phase angle is reduced by increasing the frequency.

(10) The effect of increasing the platinization is to reduce greatly the parallel capacitance, the phase angle, and the change in resistance caused by a change in frequency. This drop in parallel capacitance is doubtless due to an increase in the series capacitance since the two are related by the equation

$$C_s = \frac{1}{C_{p\omega^2} R^2} \quad (4)$$

(11) A comparison of the curves for the different cells indicates that polarization and the related effects are reduced by increasing the area of the electrodes and increasing the distance between them.

At high resistances, where polarization becomes relatively insignificant and the disturbance responsible for the Parker Effect predominates, the phenomena are very different.

(12) The parallel capacitance becomes nearly independent of the resistance and of the frequency.

(13) The phase angle is increased by increasing the resistance or by increasing the frequency.

(14) The parallel capacitance and phase angle are not influenced by the degree of platinization.

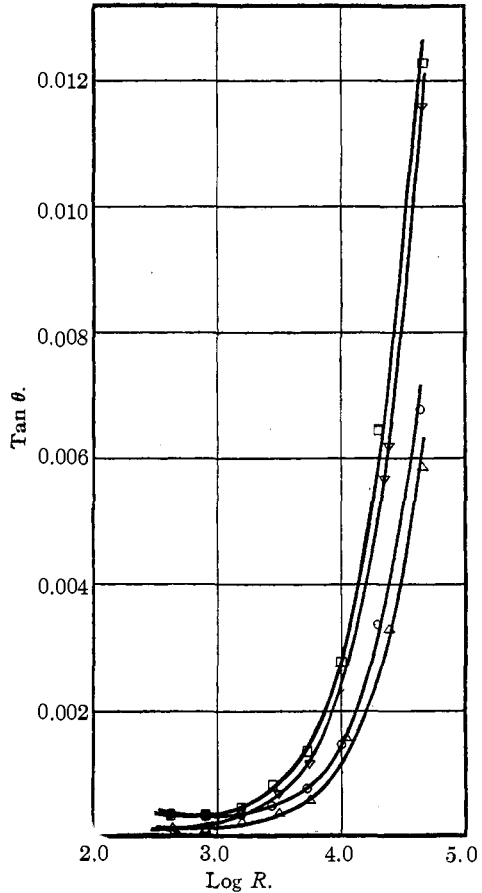


Fig. 5.—Cell IV: O, 1090 L; \square , 2280 L; \triangle , 1090 H; ∇ , 2280 H.

The Cell Resistance Ratios—

Polarization and Parker Effect.—From these data on five cells we can obtain ten intercomparisons similar to Parker's, each at two frequencies and with two degrees of platinization. All of the possible forty curves have been drawn but since they are not all mathematically independent, we have selected illustrative examples of the different types for reproduction in Figs. 7 to 10. The cell resistance ratios from which these curves

are drawn are not printed, in order to save space, because they can be readily computed by anyone interested from the data in Tables II to VI.

The curves obtained are of varied types.⁹ The curve depicting the ratio V/III shows a steep fall with increasing resistance at low resistance (especially when unplatinized) and a steep rise at high resistances, giving a sharp minimum. I/III, on the other hand, has a negative slope throughout—gentle at low resistances but steep at high resistances. II/III is like I/III in showing a negative slope throughout, but is much steeper at low resistances than at high resistances. Attention is called to the fact that in drawing curve II/III it was necessary to use a vertical scale only about $\frac{1}{20}$ of that used in the other cases. In the case of V/IV [not printed]

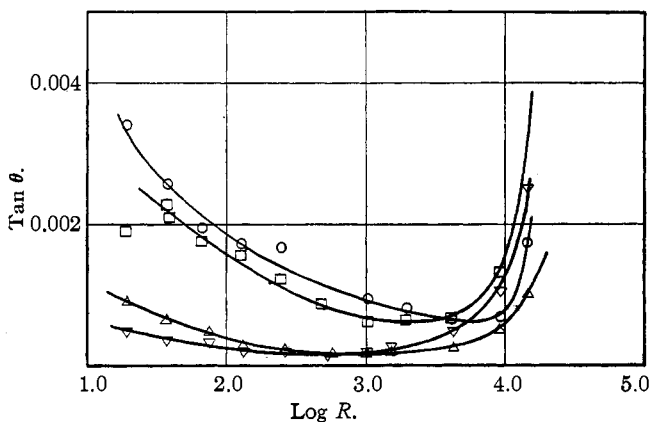


Fig. 6.—Cell V: ○, 1090 L; □, 2280 L; △, 1090 H; ▽, 2280 H.

when lightly platinized both frequencies give curves with a sharp minimum similar to V/III; when heavily platinized and using 1090 cycles there is a minimum although a flat one, but with 2280 cycles the minimum disappears entirely, giving a positive slope throughout.

This variation in the shape of curves in different cases is clearly due to the fact that there are errors in both cells and the location of the points above or below the true cell constant ratio depends on the sign of the error and on which of the two cells has the greater fractional error. With only resistance ratio curves as a guide it would be extremely difficult to decide as to which of the two cells has the predominating influence and as to the sign of the error. Indeed, as will be shown, Parker himself reached

⁹ In comparing these curves with those of Parker it should be noted that we have plotted $\log R$ as abscissa instead of R , to avoid undue crowding of points at low resistances. It should also be noted that Parker always puts the cell of lowest cell constant in the numerator, whereas we have found it desirable in all cases in which cell III was used to put this cell in the denominator to facilitate comparison of the different curves.

an erroneous conclusion on these questions at resistances high enough so that polarization ceases to be the controlling influence; but by using our $\tan \theta$ curves as an indication of the quality of the cells, together with a consideration of the influence of the frequency and of the degree of platinization, we hoped to be able to unravel the nature of the disturbances and to determine the sign and perhaps the magnitude of the errors.

These data confirm Parker's results in showing that the ratio of the resistances of two cells when filled with a common solution is not independent

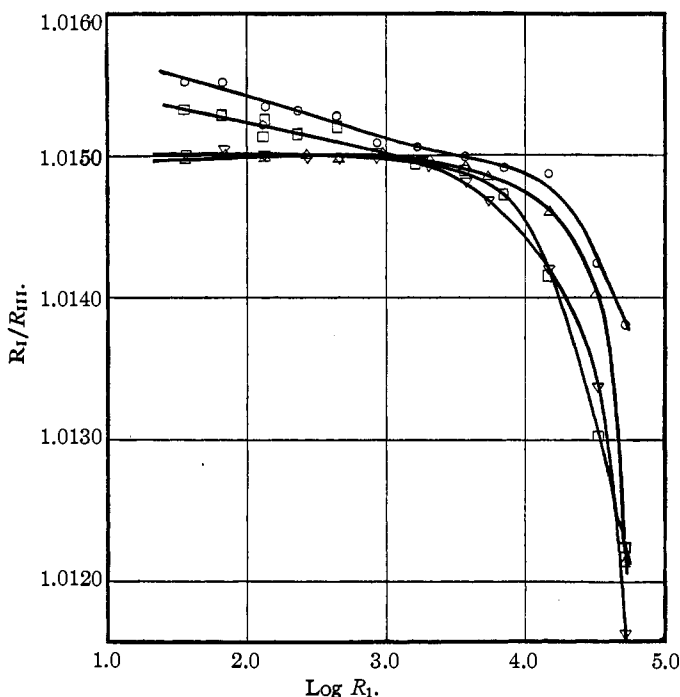


Fig. 7.—Cell resistance ratios, I/III: ○, 1090 L; □, 2280 L; △, 1090 H; ▽, 2280 H.

of the concentration of the solution used. An extreme example is given by a comparison of cells V and II when both were lightly platinized. When using 1090 cycles and with both cells filled with a normal potassium chloride solution, the ratio of the resistances was 0.28497, whereas when both were filled with a 0.0005 *N* solution the ratio was 0.28851, a difference of 1.25%.

Although our various curves differ among themselves greatly in slope and curvature, none of them shows both a maximum and a minimum, as do some of Parker's. His curves indicate clearly that in some of his experiments there were at least three disturbances present, but ours show indi-

cations of only two causes of error. It seems probable that this simplification of the problem has been accomplished by the improvements in our bridge as compared to that used by Parker. These improvements have been described in the first and second papers of this series. Of the two disturbances which remain, the one which predominates at low resistances is clearly polarization and the other is presumably responsible for the Parker Effect.

Polarization has long been known and has been the subject of many investigations. One of the effects of polarization is to cause a capacitance

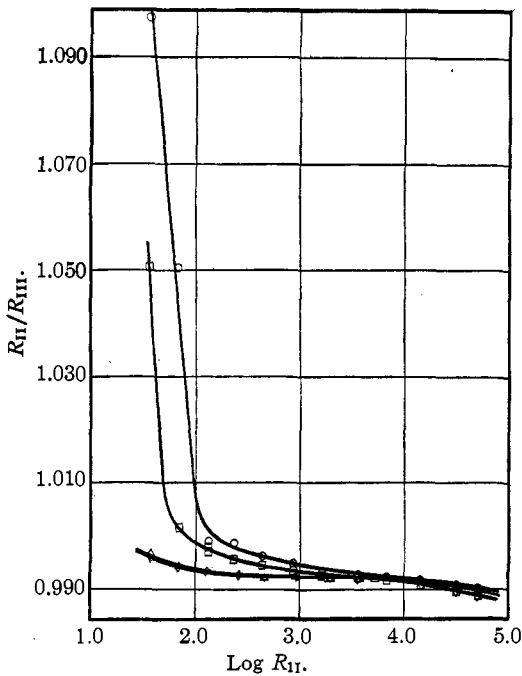


Fig. 8.—Cell resistance ratios, R_{II}/R_{III} : \circ , 1090 L; \square , 2280 L; \triangle , 1090 H; ∇ , 2280 H.

in series with the resistance of the cell, as is clearly shown by the phase displacement. If this were a pure capacitance and followed the harmonic laws characteristic of geometric capacitance, it could be compensated without causing an error in the resistance measurements. But it has been demonstrated by Wien,¹⁰ Miller,¹¹ and others that one aspect of polarization is an added polarization resistance in series with the true electrolytic resistance of the solution in the cell. The error in the measured resistance of a cell due to polarization is always positive. The polarization resistance is independent of the distance between the

electrodes and therefore the percentage error caused by polarization resistance can be decreased by using cells of high cell constant. Of two cells which are alike except in the distance between the electrodes, the shorter cell will have the relatively greater polarization error when both are filled with the same solution. Polarization can also be minimized, as was suggested long ago by Kohlrausch, by platinization of the electrodes, by the use of high frequencies and by the use of large electrodes. The behavior of our cells at the lower resistances as shown in the tables and curves and

¹⁰ M. Wien, *Wied. Ann.*, **58**, 37 (1896).

¹¹ C. Miller, *Phys. Rev.*, [2] **22**, 622 (1923).

summarized above (see pp. 424–425, paragraphs numbered 6–11) is clearly consistent with this interpretation. Increasing the platinization or increasing the frequency at low resistances always causes a decrease in the phase angle and tends to make the cell resistance ratios more nearly constant. From the consideration of the dimensions of our cells we should expect that the influence of polarization would be the greatest in cell II and decrease in the order V, III, I, IV. It will be apparent from these curves, data and discussion that in order to minimize errors due to polarization it is desirable to use a high frequency and to use a cell of high cell constant so that the resistance being measured will be high; but both of the expedients aggravate the disturbance responsible for the Parker Effect and, therefore, do not furnish a satisfactory solution of the problem unless and until the cause of the Parker Effect can be ascertained and a remedy for it invented.

The disturbance which predominates at the higher resistances and is presumably responsible for the Parker Effect is clearly different from polarization. It is independent of the degree of platinization and is aggravated rather than cured by an increase of frequency.

The hypothesis that adsorption is responsible, as suggested by Parker¹² and supported by Randall and Scott,¹³ is discredited by the fact that the effect was not increased by a tenfold increase in the amount of spongy platinum present. This disturbance is like polarization in causing the current to lead the voltage but it differs in that the phase displacement increases rapidly with increased resistance being measured, whereas the

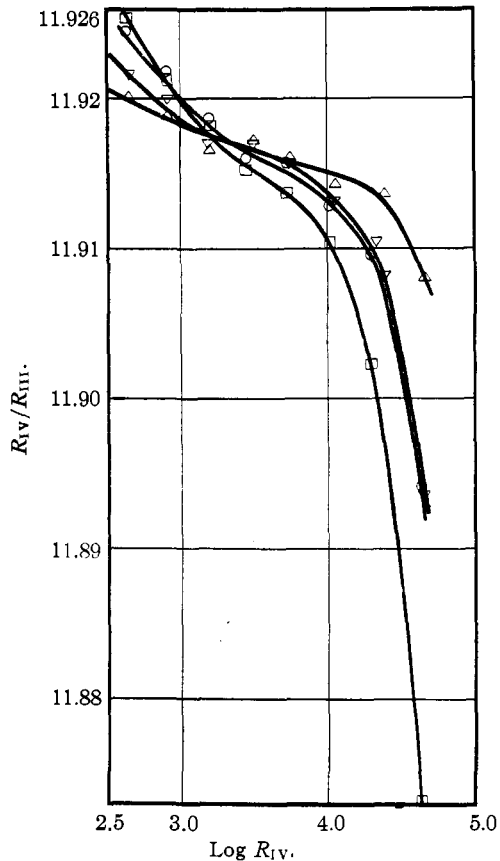


Fig. 9.—Cell resistance ratios, IV/III: ○, 1090 L; □, 2280 L; △, 1090 H; ▽, 2280 H.

¹² H. C. Parker, *THIS JOURNAL*, **45**, 1378 (1923); **45**, 2021 (1923).

¹³ M. Randall and G. N. Scott, *ibid.*, **49**, 642 (1927).

phase displacement due to polarization decreases with the resistance, as is shown by the occurrence of a minimum in the phase displacement and the rapid rise at the higher resistances. It also differs from polarization in that the phase displacement corresponds to a parallel capacitance which is independent of the frequency and the resistance. This suggests that we are dealing with a real parallel capacitance instead of a series capacitance.

We now come to the question of the sign of the error in the resistance which is responsible for the Parker Effect. Parker accounted for the

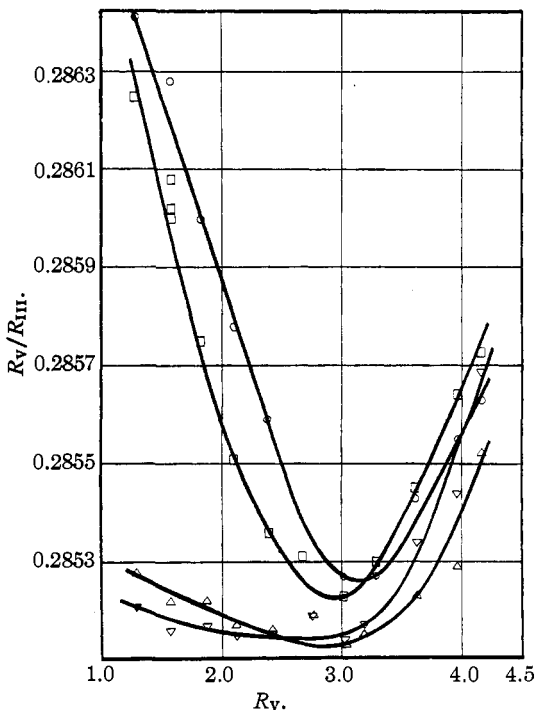


Fig. 10.—Cell resistance ratios, V/III : \circ , 1090 L; \square , 2280 L; \triangle , 1090 H; ∇ , 2280 H.

positive slope in his resistance ratio curves in the following manner. "It is evident from the direction of the effect in the more dilute solutions that if the correction which should be applied to the resistances to give a constant ratio, is *relatively* greater for the shorter cell, then the correction is negative." . . . "The facts gathered thus far indicate that the effect is in the cell itself and that the correction is negative, that is, that the resistances, R , should be corrected by an amount ΔR , which should be subtracted from the apparent resistance."¹⁴ But our cells show both positive and negative slopes in the resistance ratio curves at the higher resistances. The rapid increase in the phase displacement at the higher resistances and the increased slope of the resistance ratio curves at the high resistances are clearly related. Both the phase displacement and the slope of the resistance ratio curves are increased by increasing the frequency, thus clearly showing that the disturbance responsible for the Parker Effect is increased by increasing the frequency. But since increasing the frequency always decreases the apparent resistance at high resistance as well as at low resistances, it follows that the error in the resistance due to the Parker Effect must always be negative and increase in magnitude with the frequency and

¹⁴ H. C. Parker, *THIS JOURNAL*, 45, 1375 (1923).

the resistance being measured. Hence, contrary to Parker's conclusion, the correction must be positive. The fact that the error is always negative suggests a shunt path for the current which is electrically in parallel with the solution between the electrodes. A shunt is much more effective across a high resistance than across a low resistance, which is the case for the disturbance responsible for the Parker Effect. The clear indication of a parallel capacitance given by a study of the data suggests that the shunt is not a pure resistance but contains the equivalent of a condenser. The influence of a shunted condenser would increase with the frequency, which accords with our experience. But if the impedance in the shunt were due solely to capacitive reactance, it could be fully compensated by a condenser shunted across the resistance box without causing an error in the resistance, which is not the case. We must, therefore, infer that the shunt contains resistance as well as reactance. And now a renewed inspection of the pipet cells with the vision thus sharpened reveals the shunt clearly; it consists of the resistance in the filling tube, and the capacitance through the glass walls of the cell and the thermostat oil between the solution in the filling tube and the mercury in the contact tube of opposite polarity; together with distributed capacitance between the electrolyte in the cell proper and the filling tubes and contact tubes, as shown diagrammatically in Fig. 11. Having once seen the shunt we wonder why no one ever saw it before, and are chagrined that our eyes had been blind so long.

Since according to this hypothesis the disturbance causing the Parker Effect is not primarily an electrode effect, it would be expected that the degree of platinization will have little if any influence, which is in accord with our experience.

The earlier investigators who came the nearest to the solution of this problem appear to be Morgan and Lammert.¹⁵ They measured the resistance of a series of solutions covering a wide range of resistance at two different frequencies in several cells with unplatinized electrodes. They have observed points (1), (2), and (3) listed above (pp. 420-423). They say: "Throughout the work the capacities were measured and found to be

¹⁵ J. L. R. Morgan and O. M. Lammert, *THIS JOURNAL*, **45**, 1693-1697 (1923). This paper was published only one month after the first paper of Parker [*ibid.*, **45**, 1366 (1923)] and therefore Morgan and Lammert must have written their manuscript before they had an opportunity to read Parker's paper.

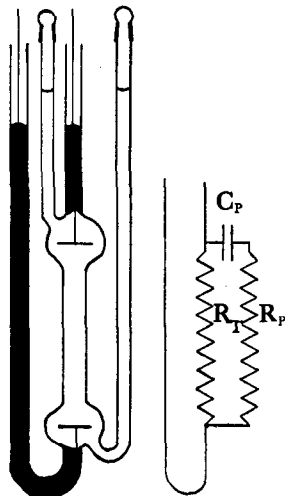


Fig. 11.—Capacitance by-paths in pipet cell.

greater at 500 cycles than at 1000 cycles, but as the difference in the resistance at the two cycles [*sic*] increased, the difference in the capacities decreased. Inasmuch as the condensers were of the type used to balance out capacity in the cell and were not standardized, the actual values are qualitative and are not given." They evidently anticipated our point (7) above without publishing the proof; but they did not interpret the capacitance readings either in terms of phase displacement in the cells or as an indication of a capacitative shunt which could cause an error in the resistance which is a function of the frequency, nor did they distinguish between errors in resistance due to polarization and errors due to capacitative shunt or offer any interpretation of or cure for the Parker Effect.

Mathematical Analysis of Errors Due to Shunt.—In the pipet cells as usually designed the electrodes are placed horizontally one above the other and the electrical contact to the electrodes is made by means of wires dipping into the glass tubes which are commonly filled with mercury to the level of the liquid in the thermostat. These contact tubes and the filling tubes through which the electrolyte is added to the cell are commonly brought out of the thermostat vertically and in close proximity to each other, thus creating capacitance between them as indicated diagrammatically by C_P in Fig. 11. This arrangement provides an additional path for the current through the resistance of the electrolyte in the filling tube, R_P , and the capacitance between the filling tubes and the contact tubes, C_P . If the thermostat is filled with water instead of oil the resistance in the thermostat liquid will be part of the shunt resistance, but since it is known that the use of water introduces errors, this case will not be considered further here. In an oil-filled thermostat the glass parts of the cell with the intervening oil may be regarded as a pure capacitance, and all of the shunt resistance is in the filling tubes and contact tubes. This shunt across the cell obviously tends to make the apparent resistance of the cell less than the true resistance of the electrolyte between the electrodes. The capacitance in the shunt is of course distributed along the resistance and therefore a precise analysis of the problem in the case of any given cell would require a precise knowledge of the geometrical form, the dielectric constant, and power factor of the glass used and of the thermostat liquid; and, even with all of these data at hand, would be a mathematical problem of great complexity.¹⁶ For the sake of analyzing the effects of this shunt we can assume that a shunt composed of a resistance, R_P , and a capacitance, C_P , in series across the electrodes is electrically equivalent to the distributed capacitance and resistance actually present, and that dielectric

¹⁶ See Shedlovsky, *THIS JOURNAL*, 52, 1793 (1930), for an interesting attempt to solve a similar problem for a simpler case in which the capacitance is assumed to be uniformly distributed along the resistance.

losses in glass and oil are negligible in comparison with the losses in the filling tube. The reactance of the shunt is

$$X_P = \frac{1}{\omega C_P} = \frac{1}{2\pi f C_P} \quad (5)$$

and the impedance of the shunt is

$$Z_P = R_P + jX_P \quad (6)$$

Let R_T be the true resistance of the cell;¹⁷ R be the measured resistance of the combination of cell and shunt at the frequency of f ; X , the measured reactance of the combination at frequency f ; $Z = R + jX$, the impedance of the combination at frequency f . Then by the law of parallel branches

$$\frac{1}{Z} = \frac{1}{R_T} + \frac{1}{R_P + jX_P} = \frac{R_T + R_P + jX_P}{R_T(R_P + jX_P)} \quad (7)$$

$$Z = \frac{R_T(R_P + jX_P)}{R_T + R_P + jX_P} = \frac{R_T(R_P + jX_P)}{(R_T + R_P + jX_P)} \times \frac{R_T + R_P - jX_P}{R_T + R_P - jX_P} \quad (8)$$

$$Z = \frac{R_T^2 R_P + R_T R_P^2 + R_T X_P^2}{(R_T + R_P)^2 + X_P^2} + \frac{jX_P R_T^2}{(R_T + R_P)^2 + X_P^2} \quad (9)$$

Therefore $R = R_T \frac{(R_T R_P + R_P^2 + X_P^2)}{(R_T + R_P)^2 + X_P^2} = R_T \left(1 - \frac{R_T R_P + R_T^2}{(R_T + R_P)^2 + X_P^2} \right)$ (10)

and $X = X_P \frac{R_T^2}{(R_T + R_P)^2 + X_P^2}$ (11)

Let ΔR designate the error due to the shunt, then

$$R = R_T + \Delta R \quad (12)$$

and hence the error

$$\Delta R = - \frac{R_T(R_T R_P + R_T^2)}{(R_T + R_P)^2 + X_P^2} \quad (13)$$

or the fractional error

$$\frac{\Delta R}{R_T} = - \frac{R_T R_P + R_T^2}{(R_T + R_P)^2 + X_P^2} \quad (14)$$

Since none of the terms in this equation can ever have a negative real value, the error is always negative. But

$$X_P = \frac{1}{\omega C_P} \quad (5)$$

$$\frac{\Delta R}{R_T} = - \frac{(R_T R_P + R_T^2)\omega^2 C_P^2}{(R_T + R_P)^2 \omega^2 C_P^2 + 1} \quad (15)$$

When working under such conditions that polarization is negligible, unless the cell is of poor design, C_P will be about 20 $\mu\mu\text{f.}$ or less. If C_P has this

¹⁷ It will be noted that in this mathematical analysis of the effect of the shunt, the cell proper (the electrodes and the electrolyte between them) is treated as a pure resistance. This is strictly true only if the reactance of the cell $X_C = 0$, that is, if the reactance due to polarization is negligible. An inspection of Curves 2-6 indicates clearly that for well-platinized electrodes the phase angle and hence the reactance falls rapidly with increasing resistance and would become negligible above 1000 ohms if the Parker Effect were not present.

value, 2×10^{-11} farads, and the measurement is made with 5000 cycles ($\omega = 31,400$; $\omega^2 = 10^9$) or less, and if the total resistance of $R_T + R_P$ does not exceed 100,000 ohms, the value of $(R_T + R_P)^2 \omega^2 C_P^2$ will not be greater than $10^{10} \times 10^9 \times 4 \times 10^{-22} = 4 \times 10^{-3}$. Under these circumstances if we ignore this term in the denominator of Equation 16, the error in $\Delta R/R$ will not be greater than 0.4%. With a frequency of 1000 (which is that most commonly used) and $C_P = 20 \mu\mu f.$ and $R_T + R_P = 100,000$, the error in $\Delta R/R$ due to using the simpler form cannot exceed 0.02%. Therefore, at audio frequencies, except in the case of cells of abnormally bad design, $(R_T + R_P)^2 \omega^2 C_P^2$ will be small in comparison with 1 and therefore it will be approximately true that

$$\Delta R/R_T = -(R_T R_P + R_T^2) \omega^2 C_P^2 \quad (16)$$

A further simplification is possible for the case of measurements made with an equal arm bridge which has been designed so that the capacitances between the arms are small and properly balanced by the earthing device, which is the case in our bridge, and if the conditions are such that polarization is negligible. In such a case the condenser shunted across the resistance box when adjusted so as to give a phase angle equal to that of the cell will have a capacitance, C_R , very nearly equal to the capacitance in the shunt across the cell, and the fractional error due to this capacitance¹⁸ on the resistance box will be $-R_R^2 \omega^2 C_R^2$ which will be substantially equal to the $-R_T^2 \omega^2 C_P^2$ and thus will compensate for one term in the equation for the error in the cell, leaving as the net fractional error due to capacitance and resistance in the shunt across the cell approximately

$$\Delta R/R_T = -R_T R_P \omega^2 C_P^2 \quad (17)$$

The actual error is therefore approximately

$$\Delta R = -R_P R_T^2 \omega^2 C_P^2 = -R_P \tan^2 \theta \quad (18)$$

Combining Equations 18 and 12 gives

$$R = R_T - R_P R_T^2 \omega^2 C_P^2 = R_T - R_P \tan^2 \theta \quad (19)$$

Experimental Verification of the Shunt Theory.—For any given cell filled with a given solution, R_T and R_P are constants, and ω can be held constant during a series of measurements. If now we vary C_P it may be predicted from Equation 19 that an increase in C_P will result in a decrease in the measured resistance, R , which will be proportional to the square of the total capacitance in the shunt. In order to make this test the capacitance in the shunt was artificially increased by connecting one lead wire from a variable air condenser to the mercury in one of the contact tubes, and connecting the other lead wire to a small piece of platinum foil dipping into the filling tube of opposite polarity. The total capacitance in the shunt due to the cell itself and to the condenser was then measured as usual by the capacitance required in parallel with the resistance in the

¹⁸ See Grinnell Jones and R. C. Josephs, THIS JOURNAL, 50, 1076 (1928).

other arm of the bridge. Resistance measurements were made with 500 and 2280 cycles at various settings from 0 to 25 $\mu\mu\text{f.}$ of the variable air condenser which was in parallel with the cell.

The actual data are omitted for the sake of abbreviation and because the actual values are dependent on the particular cell and solution used. The variation of the apparent resistance with the capacitance, which alone is important for our present purposes, is shown in Fig. 12, in which we have plotted the measured resistance as ordinate against the square of the capacitance as abscissa. It will be observed that the experimental points at each frequency are on a straight line within the limit of error of the data. The intercept of each of these lines on the resistance axis should be the true resistance. It will be observed that the intercepts of the lines for the two frequencies are the same.

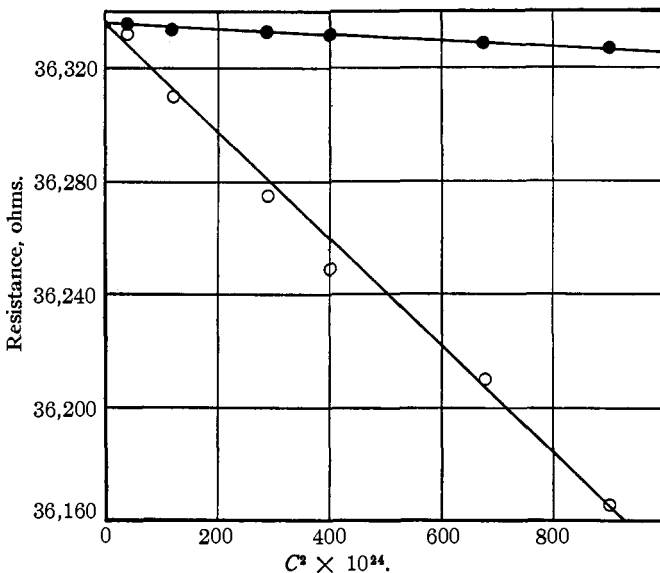


Fig. 12.—For upper curve $f = 500$; for lower curve $f = 2280$.

We next made a series of measurements in which the frequency was varied while the other factors were kept constant. In order to magnify the capacitance effect, 25 $\mu\mu\text{f.}$ was added across the cell in the manner just described and the resistance determined at ten different frequencies within the range from 500 to 2280 cycles. In addition, the resistance was determined at several lower values of the capacitance at three frequencies. The actual results are omitted for the reasons explained above but they are shown in Fig. 13, in which the measured resistance is plotted against the square of the frequency. As will be seen, the results at each frequency are on a straight line and these lines all have a common intercept on the axis of

zero frequency which should be the true resistance. The value for the true resistance thus obtained is the same as that shown in the previous plot.

A special experiment was carried out to determine whether or not a significant change in capacitance and in resistance could be produced merely by a change in the relative position of the filling tube and the cell without any change in the electrodes or in the cell proper. A cell of the pipet type similar in shape to that shown in Fig. 11 was filled with potassium chloride solution and its resistance determined at several frequencies. The capacitance was 6 micromicrofarads. The filling tube was then extended and bent so as to conform with the shape of the cell and fitted closely to the cell.

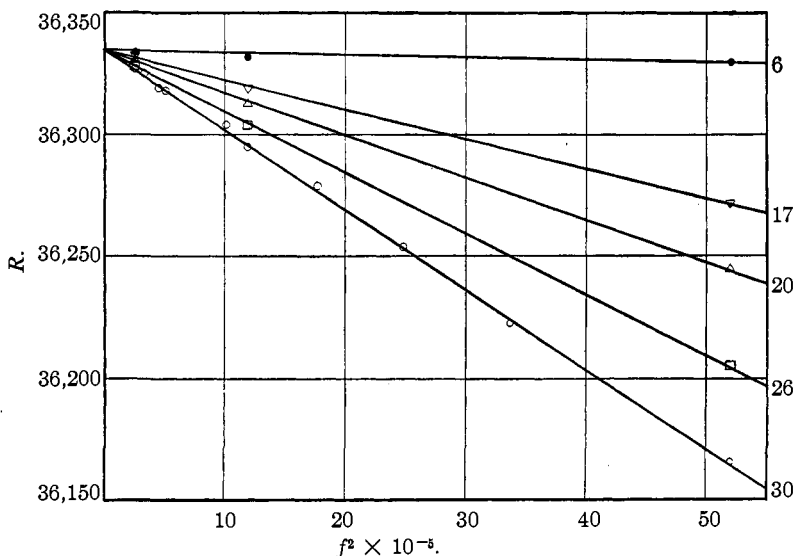


Fig. 13.—The values of C_p for these curves are given on the right-hand margin.

The effect was an increase in parallel capacitance to 14 micromicrofarads and a great increase in the variability of the resistance readings with change in frequency as shown in Table VII.

TABLE VII
CHANGE IN RESISTANCE CAUSED BY ALTERATIONS IN FILLING TUBE

Frequency, cycles	(Frequency) ²	Original filling tube $C_p = 6\mu\mu\text{f.}$ Resistance ohms	New filling tube $C_p = 14\mu\mu\text{f.}$ Resistance ohms
500	2.50×10^5	36,308	36,306
710	5.05		36,303
1090	11.9	36,306	36,295
1575	24.8		36,285
2280	52.0	36,304	36,258

The resistance readings when plotted against the square of the frequency give a straight line similar to that shown in Fig. 13. This experiment

definitely proves that altering the relative position of filling tubes and cell influences the parallel capacitance and that the resistance changes caused thereby vary with the frequency in accordance with our theoretical equation.

We next consider the effect of varying R_P while keeping the other factors constant. For this purpose we must use Equation 15 instead of the simplified form (17) because we wish to consider the influence of values of R_P greater than the upper limit assumed in deriving the simplified form. By differentiating Equation 15 with respect to R_P and holding all other factors constant and placing $\partial(\Delta R/R_T)/\partial R_P = 0$, it is possible to show that $\Delta R/R_T$ rises with increasing R_P to a maximum when $R_P = 1/C_P\omega$ and then falls again. The value of R_P which produces the maximum error is very large. Thus, for example, if $C_P = 10^{-11}$ farads, and $f = 2280$, $R_P = 1/(2 \times 3.14 \times 2280 \times 10^{-11}) = 7,000,000$ ohms. R_P will be far below this value in pipet cells of the usual design and the partial derivative indicated above will be positive. It will, therefore, be advantageous to design the cell so as to keep R_P low, provided this can be accomplished without increasing C_P .

In order to vary R_P while keeping all other factors constant, we devised a suitable expedient. A pipet type of cell was filled with a solution giving a resistance of about 50,000 ohms with both filling tubes filled as usual. Measurements were made at 500, 1090 and 2280 cycles and the true resistance ascertained by the method indicated in Fig. 13, and thus the error at 2280 cycles due to the shunt was estimated to be 0.02%. Then one of the filling tubes was emptied, leaving the inner wall wet with the solution, thus enormously increasing the resistance in the shunt without altering anything else. The error at 2280 cycles, estimated in the same manner, was now 0.10%. The inner wall of the filling tube was then dried by inserting a capillary tube and applying suction so that a stream of air passed down through the filling tube until it appeared to be dry. The error at 2280 cycles as determined in the same manner was now reduced to 0.025%. Apparently in this case the resistance in the filling tube was in excess of that which gave the maximum error. Although, owing to a lack of knowledge of the value of the resistance in the filling tube, the evidence of these experiments in support of our equation is not of the same quantitative nature as was obtained by varying the frequency and the capacitance, these experiments do support in a qualitative manner the predictions of our mathematical analysis.

Parker reported a difference in his cell constant ratios when the tube connecting his two cells was filled with the solution and when the solution in the tube was interrupted by an air bubble but could offer no explanation of this fact or reconcile it with his hypothesis that the error was due to adsorption. Our experiment just cited indicates that the reason for the

influence of the bubble in the connecting tube was that the resistance in the shunt was changed thereby.

An interesting and important corollary of the analysis of the influence of the magnitude of the resistance in the shunt is that capacitance between the two lead wires and the mercury in the contact tubes in the pipet form of cell can do no harm provided an oil thermostat is used, because it is in effect a pure capacitance and can be compensated by a pure capacitance across the box without error in the resistance. In this case the resistance in the mercury and in the copper wires is negligible and the resistance in the oil enormously greater than the value $R_P = 1/C_P\omega$ which gives the maximum error. On the other hand, if water is used as the thermostat liquid, this water forms a part of a shunt between the contact tubes and may have a resistance which will cause a substantial error.

Parker Effect Due to Capacitative Shunt.—The expression for the error due to a capacitative shunt also accounts for the Parker Effect. If we use subscripts A and B to designate two different cells, in which the subscript A refers to the cell of lower cell constant, then the ratio of the measured resistance will be

$$\frac{R_A}{R_B} = \frac{R_{TA} + \Delta R_A}{R_{TB} + \Delta R_B} \quad (20)$$

Since ΔR is very small in comparison with R_T this can be developed into a power series and the higher terms neglected, giving

$$\frac{R_A}{R_B} = \frac{R_{TA}}{R_{TB}} \left(1 + \frac{\Delta R_A}{R_{TA}} - \frac{\Delta R_B}{R_{TB}} + \dots \right) \quad (21)$$

Then by Equation 17

$$\frac{R_A}{R_B} = \frac{R_{TA}}{R_{TB}} [1 - (R_P R_T \omega^2 C_P^2)_A + (R_P R_T \omega^2 C_P^2)_B + \dots] \quad (22)$$

For any given cell, R_P will be proportional to R_T , since both are proportional to the specific resistance of the solution used, so that we may write $R_P = kR_T$, where the value of k will depend on the dimensions of the cell and of the filling tube and

$$R_T = (l/a) (1/\kappa)$$

and hence

$$\frac{R_A}{R_B} = \frac{R_{TA}}{R_{TB}} \left[1 - \left\{ \left(\frac{kl^2}{a^2} C_P^2 \right)_A - \left(\frac{kl^2}{a^2} C_P^2 \right)_B \right\} \frac{\omega^2}{(\kappa)^2} \right] \quad (23)$$

It is thus evident that the variation of the resistance ratios R_A/R_B with increase in the specific resistance (or decrease in κ) will be positive if $(kl^2/a^2 C_P^2)_B > (kl^2/a^2 C_P^2)_A$ and negative in the converse case.

Our data, depicted in part in Curves 7 to 10, give examples of both positive and negative slope of the resistance ratio curves, and we have been able to correlate at least qualitatively the slope of these curves with the dimensions of the cells, which determine k , l/a and C_P , but the detail of this correlation must be omitted to save space. It may also be predicted

from this equation that the slope of the resistance ratio curves (in the region where polarization is avoided), regardless of its sign will increase in magnitude with an increase in frequency and with an increase in the specific resistance of the solution used, which is fully in accord with our experience, and for a given pair of cells the slope can never change in sign with variation in frequency or variation in the specific conductance of the solution used, which is in accord with our experience.

Since sealing the cells together, as was done by Parker and in our experiments described above, would probably increase the capacitance,¹⁹ it is to be expected that the error would be increased thereby, and it therefore seemed worth while to determine whether or not the effect is present in disconnected cells of the pipet type.

We therefore made another series of cell comparisons similar to those recorded above, using four separate disconnected cells of the pipet type, all heavily platinized, using 500, 1090 and 2280 cycles. The results are not published in detail, because they are similar in all respects to those given in Curves 7 to 10, except that the slopes are more gentle. The maximum variation in the resistance ratios observed in these experiments was only 0.05%, but the deviations are systematic and show in milder form the characteristics already observed with the connected cells.

This demonstration that Parker's expedient of sealing his two cells together to facilitate filling them with a common solution aggravates the error is important because it increases the reliance which may be placed on the great mass of data in the literature which were usually obtained with single cells.

Cell Design to Avoid Errors Due to Polarization and Shunt.—The theory of errors due to capacitative shunt has not only given a complete explanation of the nature and cause of the Parker Effect but has guided us in the design²⁰ of cells in which the error is eliminated. From the equation for the error due to a capacitative shunt, $\Delta R = -R_P R_T^2 \omega^2 C_P^2 = -R_P \tan^2 \theta$, it is evident that it will be well to keep each of the factors in this equation as low as other considerations permit.

It would of course be possible to design a cell without filling tubes as an integral permanent part of the cell but the filling tubes serve a useful purpose in facilitating the filling of the cells without contamination or evaporation of the solutions and should not be sacrificed except as a last resort. The resistance in the filling tubes might be reduced by making them of large diameter, but this tends to increase the capacitance, which

¹⁹ There is a certain analogy between capacitance shunt errors in cells which are sealed together and the effect of appended coils in a resistance box. See Grinnell Jones and R. C. Josephs, *THIS JOURNAL*, 50, 1084 (1928).

²⁰ See E. W. Washburn [*THIS JOURNAL*, 38, 2431 (1916)] for a mathematical analysis of cell design including a discussion of several considerations not taken up in detail in this paper.

offsets the gain. The filling tube should, however, be kept full of solution to avoid the high resistance of the surface film wetting the inner wall. The resistance in the filling tube will of course be proportional to the specific resistance of the solution being measured, and therefore this factor helps to set an upper limit to the resistance which can be measured accurately in any given cell.

It should be pointed out that although dipping electrode cells as commonly designed have no filling tube at all, nevertheless they do have a capacitative shunt. As usually designed, the electrodes are supported by two vertical contact tubes which are commonly close together. These electrodes should be immersed to a considerable depth in order that the lines of flow of the current may not be cut off by the surface of the solution and thus make the effective cell constant too greatly dependent on the depth of immersion of the electrodes. This creates a shunt across the path between the electrodes, through the glass walls of the contact tubes acting as a condenser and the resistance of the solution between these tubes. The impedance of this shunt will be a function of the frequency and errors due to capacitative shunt may therefore be expected with dipping cells, in spite of the fact that they have no filling tubes, especially when used with dilute solutions.

For any given solution the working value of the resistance will depend on the cell constant of the cell used, and can therefore be controlled within wide limits provided a sufficient number and variety of cells are available. But there is a limit below which it is not safe to go with R_T because of errors due to polarization. The limit will of course depend on the precision desired, on the frequency used, and on the dimensions and platinization of the electrodes. As the result of our experience we have set the lower limit of the resistance to be measured at about 1000 ohms when using well-platinized cells (see Figs. 2-6). But unless the upper limit can be many times the lower limit, a very great number of cells of closely graded cell constants will be needed to cover the whole range of specific conductance from that of very good conductivity water, 1×10^{-7} , up to about 0.5 for the best conducting aqueous solutions at room temperatures. Washburn²¹ recommends that the upper limit be placed at 10,000 ohms, which with a lower limit of 1000 ohms would require seven cells to cover the entire range. To cover this range with four cells will require that the upper limit be placed at nearly 50,000 ohms, which is the upper limit which we have thought it desirable to strive for. It is, therefore, apparent that there are serious practical difficulties in any attempt to solve the problem by restricting the measurements to low values of the resistance to be measured.

An attempt to solve the problem by lowering the frequency would be

²¹ E. W. Washburn, *THIS JOURNAL*, 38, 2450 (1916).

defeated by the fact that errors due to polarization increase rapidly with decrease in the frequency. Lowering the frequency tends to raise the safe lower limit of the resistance which can be measured without the appearance of an error due to polarization, which would defeat any attempt to make a substantial reduction in the shunt error by any considerable reduction of the frequency below 1000 cycles. Moreover, in the practical routine of conductance measurements it is possible with a suitable oscillator to change the frequency instantly by a mere turn of a dial and repeat the measurement at another frequency in a moment. If the measured resistance proves to be substantially independent of the frequency it shows that many of the possible errors, including polarization, shunt errors, and errors due to capacitance and inductance in the bridge and resistance boxes which have been discussed in the first paper of this series, have been eliminated. On the other hand, if there is a significant variation in the apparent resistance with variation in frequency it proves that some error is present and gives a clue as to the magnitude and nature of the error. Therefore, if it is possible to do so there will be a great advantage in avoiding the error due to a shunt by some other means than lowering the frequency, and judging of the success or failure of the attempt by noting the effect of variations in frequency.

The capacitance in the shunt can be reduced to a very small value by designing the cell so as to avoid close proximity of the filling tubes and the portions of the cell of opposite polarity. Each of the filling tubes should be placed at a safe distance from the other filling tubes and from the contact tube at the other end of the cell.

This is most conveniently done by making the cells of the form shown in Fig. 14. Our experience indicates that a separation of 15 cm. between parts of the cell of opposite polarity is adequate. Shields placed close to any part of the cell should be avoided.

New Cells—Description and Tests.—Four cells of the new form, designated K, L, M, N, which are depicted in Fig. 14 and whose dimensions are shown in Table VIII, were constructed and thoroughly tested.

These new cells were at first given a light platinization and then tested. The results of these tests will be omitted, because no new conclusions could be drawn from them. The cells when lightly platinized showed the

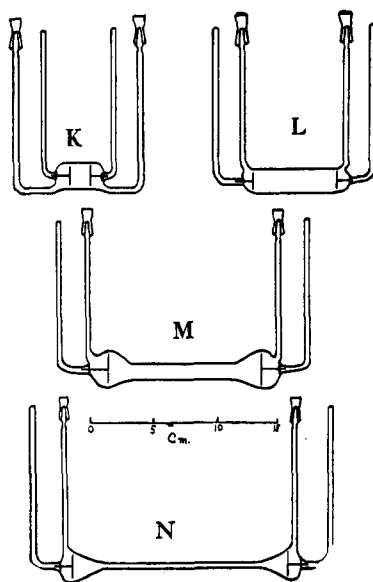


Fig. 14.—New cells.

TABLE VIII
CELL DIMENSIONS

Cell	Dimensions of the new cells			Electrodes			
	Cell constant	Diam. inside, cm.	Distance between electrodes, cm.	Diam. of disk, cm.	Thick. of disk, cm.	Diam. of rod, cm.	Length of rod, cm.
K	0.67503	1.8	1.5	1.4	0.033	0.011	1.6
L	2.6268	1.6	6	1.3	.033	.011	1.6
M	11.7066	1.0	11.5	2.3	.033	.011	2.0
N	126.722	0.33	16.5	1.9	.025	.011	2.0

characteristic behavior of cells in which errors due to polarization are present even up to high resistances. The cells were then given a heavy platinization, using a platinizing solution containing a trace of lead acetate.

TABLE IX
CELL COMPARISON DATA. CELL K. (KCl AS ELECTROLYTE)

KCl	Heavy Platinization						
	Approx. concn.	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$		
Soln.		R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$
41	0.0001	57,066.6	14	0.0025	57,060.0	12	0.0047
43	.0003	15,982.7	18	.00090	15,981.0	17	.0018
44	.0003	13,847.3	20	.00087	13,846.1	17	.0016
42	.0005	9,762.1	17	.00052	9,761.4	11	.00073
45	.0009	5,344.66	23	.00038	5,344.16	14	.00051
46	.0016	2,891.94	43	.00039	2,891.63	20	.00040
47	.0035	1,346.72	90	.00038	1,346.55	38	.00035
48	.0075	662.13	200	.00042	662.03	75	.00034
49	.017	294.253	700	.00065	294.204	210	.00042
50	.03	158.106	1400	.00069	158.076	480	.00052
51	.07	75.664	4300	.00102	75.653	1325	.00069
52	.2	30.009	21500	.00203	30.005	4900	.00101

Soln.	$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$			$f = 4000$ $\omega = 25133$		
	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$
41	57,050.1	12	0.0098	57,044.1	12	0.0192	57,036.1	12	0.0172
43	15,979.0	15	.0034	15,978.5	15	.0045	15,977.5	15	.0060
44	13,844.8	17	.0034	13,844.2	17	.0044	13,843.6	18	.0063
42	9,760.8	10	.0014	9,760.6	9	.0017	9,760.4	9	.0022
45	5,343.66	12	.00092	5,343.4	11	.0011	5,343.2	11	.0015
46	2,891.42	14	.00058	2,891.35	13	.00071	2,891.26	12	.00087
47	1,346.42	21	.00041	1,346.39	18	.00046	1,346.35	17	.00057
48	661.95	33	.00031	661.93	23	.00029	661.90	18	.00030
49	294.151	90	.00038	294.136	70	.00038	294.123	55	.00041
50	158.044	200	.00045	158.034	140	.00041	158.026	100	.00041
51	75.638	550	.00060	75.632	400	.00057	75.626	300	.00057
52	30.001	1200	.00052	29.999	670	.00038	29.997	300	.00023

The cells were filled with common solutions of potassium chloride and the resistance and capacitance of each measured as before, except that the readings were taken not only with 1090 and 2280 cycles, but also with 500, 3000, and 4000 cycles as well. The results are recorded in Tables IX to XII. A consideration of the values of $\tan \theta$ at high resistances indicates that cell K, in which the electrodes are 1.5 cm. apart, is superior to cells II and IV, about the same as cells I and V, and inferior to cell III. In cell K the electrodes are comparatively close together, but the disadvantage of this close proximity is partly avoided by the design which places the filling tubes outside the contact tubes (see Fig. 14). The separation of electrodes and filling tubes is apparently inadequate in this cell. In this cell the capacitance which makes trouble is probably that between the portion of the cell between the electrodes and the filling tubes and contact tubes.

TABLE X
CELL COMPARISON DATA. CELL L. (KCl AS ELECTROLYTE)

Heavy Platinization								
$f = 500$ $\omega = 3142$					$f = 1090$ $\omega = 6849$			
Soln.	Approx. concn.	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	
44	0.0003	53,876.3	4	0.00068	53,872.0	4	0.0015	
42	.0005	37,985.6	5	.00060	37,982.8	5	.0013	
45	.0009	20,796.3	7	.00046	20,795.3	6	.00085	
46	.0016	11,253.7	11	.00039	11,253.2	9	.00070	
47	.0035	5,240.5	6	.000099	5,240.29	3	.00011	
48	.0075	2,576.47	20	.00016	2,576.33	8	.00014	
49	.017	1,144.88	50	.00018	1,144.83	18	.00014	
50	.03	615.151	110	.00021	615.116	38	.00016	
51	.07	294.378	370	.00034	294.360	120	.00024	
52	.2	116.751	1900	.00070	116.744	480	.00038	
53	.5	49.906	10400	.00163	49.900	2430	.00083	
54	1.0	25.195	37000	.00293	25.184	8100	.00140	

$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$			$f = 4000$ $\omega = 25133$			
Soln.	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R = \tan \theta$
44	53,867.3	4	0.0031	53,864.7	4	0.0040	53,861.6	4	0.0054
42	37,980.7	5	.0027	37,979.1	5	.0036	37,977.6	4	.0038
45	20,794.4	6	.0018	20,794.0	6	.0023	20,793.6	6	.0031
46	11,252.8	8	.0013	11,252.5	8	.0017	11,252.4	7	.0020
47	5,240.04	3	.00022	5,240.03	3	.00029	5,239.88	3	.00040
48	2,576.23	5	.00018	2,576.20	4	.00019	2,576.19	3	.00019
49	1,144.79	9	.00015	1,144.76	7	.00015	1,144.74	5	.00015
50	615.079	14	.00012	615.061	10	.00012	615.049	6	.00009
51	294.339	55	.00023	294.333	38	.00021	294.327	32	.00024
52	116.738	160	.00027	116.734	120	.00026	116.730	70	.00021
53	49.896	760	.00054	49.895	530	.00050	49.895	400	.00050
54	25.182	1750	.00063	25.181	900	.00042	25.180	420	.00027

TABLE XI
CELL COMPARISON DATA. CELL M. (KCl AS ELECTROLYTE)

Heavy Platinization									
$f = 500$ $\omega = 3142$					$f = 1090$ $\omega = 6849$				
Soln.	Approx. concn.	R	C _p μf.	C _p ωR = tan θ	R	C _p μf.	C _p ωR = tan θ		
46	0.0016	50,156.1	0	0	50,154.9	0	0		
47	.0035	23,354.9	3	0.00022	23,354.5	3	0.00047		
48	.0075	11,482.0	6	.00022	11,482.1	6	.00047		
49	.017	5,102.2	0	0	5,102.20	0	0		
50	.03	2,741.25	0	0	2,741.26	0	0		
51	.07	1,311.76	8	.000033	1,311.77	3	.000026		
52	.2	520.277	38	.000062	520.270	9	.000032		
53	.5	222.399	190	.000133	222.392	55	.000083		
54	1.0	112.261	720	.000254	112.259	170	.00013		
55	3.0	38.257	6300	.00076	38.254	1425	.00037		

$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$			$f = 4000$ $\omega = 25133$			
Soln.	R	C _p μf.	C _p ωR = tan θ	R	C _p μf.	C _p ωR = tan θ	R	C _p μf.	C _p ωR = tan θ
46	50,154.6	0	0	50,154.6	0	0	50,154.6	0	0
47	23,354.2	3	0.0010	23,353.7	3	0.0013	23,353.8	3	0.0018
48	11,481.8	6	.00099	11,481.7	6	.0013	11,481.8	6	.0017
49	5,102.1	0	0	5,102.2	0	0	5,102.2	0	0
50	2,741.23	0	0	2,741.24	0	0	2,741.2	0	0
51	1,311.77	3	.000056	1,311.76	3	.000075	1,311.76	3	.000098
52	520.265	0	0	520.261	0	0	520.266	0	0
53	222.389	19	.000060	222.392	12	.000050	222.391	7	.000039
54	112.256	38	.000061	112.255	22	.000046	112.254	9	.000025
55	38.253	320	.000175	38.253	180	.000130	38.253	90	.000086

We infer that in cells having electrodes as close together as this it would have been better to extend the filling and contact tubes in the direction of the axis of the cell for several centimeters before bending them upward.

Cell L, in which the electrodes are 6 cm. apart, shows a definite improvement over all of our older cells in having a lower phase angle at high resistances than any of the older cells. Nevertheless, cell L does have a measurable parallel capacitance at high resistances and therefore a slight although reduced error due to capacitive shunt.

However, in cells M and N, in which the separation of the electrodes is 11.5 and 16.5 cm., respectively, the parallel capacitance is so low that it is no longer measurable with our bridge, since it is of the same order of magnitude as the unavoidable capacitance in bridge, boxes, lead wires and in the condensers at their zero setting. Readings of less than 5 micromicrofarads have little significance in our apparatus. But these capacitance readings, in spite of their lack of precision, do prove that cells M and N have a lower phase angle at high resistances than any of the other cells and therefore by

TABLE XII
CELL COMPARISON DATA. CELL N. (KCl AS ELECTROLYTE)
Heavy Platinization

Soln.	Approx. concn.	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$		
		R	C_p $\mu\text{f.}$	$C_p\omega R =$ $\tan \theta$	R	C_p $\mu\text{f.}$	$C_p\omega R =$ $\tan \theta$
49	0.017	55,225	0	0	55,224	0	0
50	.03	29,672.6	0	0	29,671.8	0	0
51	.07	14,199.2	3	0.00013	14,199.0	3	0.000284
52	.2	5,631.9	0	0	5,631.8	0	0
53	.5	2,407.8	2	.000015	2,407.65	0	0
54	1.0	1,215.25	15	.000051	1,215.25	0	0
55	3.0	414.23	140	.00018	414.225	29	0.000082

Soln.	$f = 2280$ $\omega = 14326$			$f = 3000$ $\omega = 18850$		$f = 4000$ $\omega = 25135$	
	R	C_p $\mu\text{f.}$	$C_p\omega R =$ $\tan \theta$	R	C_p $\mu\text{f.}$	R	C_p $\mu\text{f.}$
49	55,221	0	0	55,221	0	55,221	0
50	29,670.9	0	0	29,670.5	0	29,670.3	0
51	14,198.8	3	0.00061	14,198.6	3	14,198.5	3
52	5,631.8	0	0	5,631.9	0	5,631.9	0
53	2,407.65	0	0	2,407.65	0	2,407.65	0
54	1,215.25	0	0	1,215.25	0	1,215.25	0
55	414.218	8	0.000048	414.218	3	414.216	0

virtue of Equation 17 the error due to capacitance shunt has been greatly reduced and probably made negligible.

A surer test of the quality of the new cells is the variation in the apparent resistance with variation in frequency, because this is not dependent on the capacitance measurements of low precision. It will be recalled that with the old cells the variation of resistance with frequency increased rapidly with the resistance being measured and at about 50,000 ohms a change in the frequency from 1090 to 2280 cycles caused the following decreases in resistance: cell I, 133.5 ohms; II, 96 ohms; III, 37 ohms; IV, 58.4 ohms. These figures may be compared with the corresponding values for the new cells: cell K, 9.9 ohms; cell L, 4.3 ohms; cell M, 0.3 ohm: cell N, 3 ohms. When the frequencies increased to 4000, cell K shows a further drop of 4 ohms, cell L of 6 ohms and cells M and N are unchanged.

It is apparent that the effect of variation in frequency has been greatly reduced in the new cells and the effect which remains is not proportional to the square of the frequency, which has been demonstrated to be characteristic of errors due to a capacitative shunt. The slight remaining frequency effect must therefore be ascribed to some other cause, probably polarization.

Attention is called especially to cell M, which shows an apparent variation between 1090 and 4000 cycles of only 0.3 ohm which is less than

0.001%. An error of this magnitude might be caused by a change in temperature of less than 0.0005° . The change of 1.2 ohms in cell M between 500 and 1090 cycles is probably due to some polarization at the lower frequency. It may therefore be regarded as established that there is no real change in the conductance of electrolytes with a change in frequency up to 4000 cycles. The slight frequency effect remaining in the other new cells and the much greater frequency effect reported by other experimenters is due to errors caused by polarization or faulty design of bridge or cells.

Debye and Falkenhagen²² have made a theoretical study of the effect of variation in frequency on the conductance of dilute solutions based on the Debye-Hückel interionic attraction theory of electrolytes. One of the most important theoretical deductions of Debye and Hückel is that the electric forces between the ions tend to maintain a space lattice structure and oppose the motion of an ion under the influence of an outside electric field and thus cause a decrease in conductance which is proportional to the square root of the concentration. Debye and Falkenhagen conclude that at extremely high frequencies the influence of the interionic forces in retarding the motion of an ion in an electric field tends to disappear, so that the conductance increases with increasing frequency. Thus, for example, with 0.001 *N* potassium chloride solution and a wave length of 14.9 meters, corresponding to a frequency of 20 million cycles per second, the retardation by the interionic attraction is reduced to one-half of its value at zero frequency.²³ Falkenhagen and Williams²⁴ have reviewed the paper referred to and interpreted it by the computation of numerical values for numerous specific cases as a function of the mobility and valence of the ions, the concentration, temperature, nature of solvent, and the frequency. It is apparent from this analysis that the theory predicts no measurable change of conductance with variations in frequency within the audio range. Neither of these papers contains any experimental verification of the theoretical deductions.

Sack,²⁵ in a brief preliminary notice, claims to have demonstrated the variation of resistance with variation of frequency at frequencies from 6 million to 20 million cycles but the effect is not much, if any, greater than the experimental errors in the method.

A third test of the quality of the cells is the constancy of the cell resistance ratios. These ratios are not given here since they may be computed readily by anyone interested, from the data in Tables IX to XII; they are shown in Fig. 15. These ratios are much more nearly constant than those

²² P. Debye and H. Falkenhagen, *Physik. Z.*, 29, 121 (1928).

²³ Debye and Falkenhagen, *Ref. 22*, p. 131.

²⁴ H. Falkenhagen and J. W. Williams, *J. Phys. Chem.*, 33, 1121 (1929).

²⁵ H. Sack, *Physik. Z.*, 29, 627 (1928).

given by any of the older cells. Considering only the values at resistances above 1000 ohms in order to avoid the effects of polarization, it will be seen that the Parker Effect has been substantially eliminated with the new cells. The ratio of L to M and of M to N remains within 0.01% of the mean except at the lower resistances, where the $\tan \theta$ - $\log R$ curves show that polarization plays a part. The elimination of the Parker Effect by the avoidance of capacitative shunt in the design of the cells furnishes additional evidence as to the validity and usefulness of our new theory that the Parker Effect is due to the shunt. This test agrees with the first two tests in showing that cell K is not quite so good as the others.

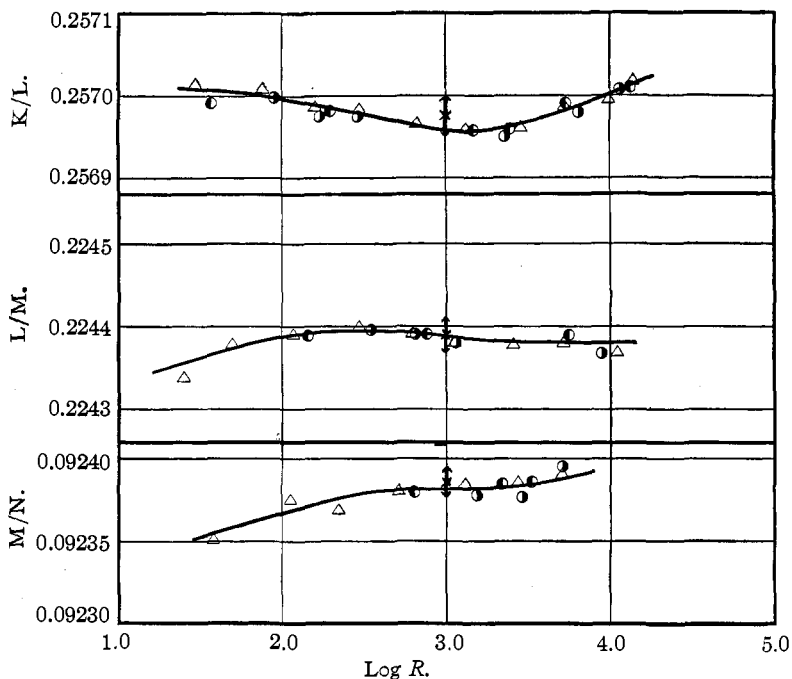


Fig. 15.— Δ , KCl ; \bullet , Na_2SO_4 ; \blacksquare , $Ba(NO_3)_2$.

Effect of Change of Electrolyte.—It now remains to compare the behavior of other electrolytes with that of potassium chloride. For this purpose we have selected barium nitrate and sodium sulfate because Randall and Scott have reported experiments with these salts which they interpret as showing a specific effect of the salt used. We, therefore, made a series of cell comparisons using these two salts, similar to those reported above with potassium chloride, although less extensive. The results are shown in Tables XIII to XVI.

We have plotted the $\tan \theta$ - $\log R$ curves (although they are not reproduced here) and find that the points fall on the same curves as the data

TABLE XIII
CELL COMPARISON DATA. CELL K
Heavy Platinization

Soln.	Approx. concn. Na ₂ SO ₄	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$			$f = 3000$ $\omega = 18850$		
		R	C _P $\mu\mu\text{f.}$	C _P ω R = tan θ	R	C _P $\mu\mu\text{f.}$	C _P ω R = tan θ	R	C _P $\mu\mu\text{f.}$	C _P ω R = tan θ
56	0.0002				13,249.9	15	0.00136			
60	.0005	5317.35	22	0.00037	5,316.80	13	.00047	5316.50	10	0.0010
59	.001				2,505.78	18	.00031			
58	.002	1472.71	86	.00040	1,472.56	36	.00038	1472.39	17	.00047
57	.018	193.496	1075		193.462	380	.00050	193.414	110	.00040
62	.10	36.876	15000	.00065	36.873	4000	.00101	36.862	1000	.00069
Ba(NO ₃) ₂										
67	0.0003				11,649.9	14	0.00112			
61	.0005	6379.6	20	0.00040	6,379.3	11	.00048	6378.9	9	.0011
66	.0012	2297.91	40	.00029	2,297.76	20	.000315	2297.41	10	.00043
65	.01				290.059	190	.00038			
64	.02				169.262	420	.00049			
63	.04	88.878	3000	.00084	88.869	1000	.00061	88.848	320	.00054

TABLE XIV
CELL COMPARISON DATA. CELL L
Heavy Platinization

Soln.	Approx. concn. Na ₂ SO ₄	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$			$f = 3000$ $\omega = 18850$		
		R	C _P $\mu\mu\text{f.}$	C _P ω R = tan θ	R	C _P $\mu\mu\text{f.}$	C _P ω R = tan θ	R	C _P $\mu\mu\text{f.}$	C _P ω R = tan θ
56	0.0002				51,554	4	0.0014			
60	.0005	20,689.5	7	0.00046	20,688.6	6	.00085	20,687.7	6	0.0023
59	.001				9,751.6	3	.00020			
58	.002	5,731.00	6	.000109	5,730.75	4	.00016	5,730.55	3	.00033
57	.018	752.85	95	.000224	752.82	27	.00014	752.74	6	.000085
62	.10	143.483	1300	.000585	143.479	340	.00033	143.466	300	.00082
Ba(NO ₃) ₂										
67	0.0003				45,329.0	5	0.00155			
61	.0005	24,825.1	6	0.00047	24,824.1	5	.00085	24,822.9	5	0.0023
66	.0012	8,943.0	0	0	8,942.4	0	0	8,942.4	0	0
65	.01	1,128.70	15	.000053	1,128.74	28	.00022	1,128.67	2	.000043
64	.02				658.669	30	.00014			
63	.04	345.812	240	.00026	345.797	75	.000178	345.780	25	.00016

obtained with potassium chloride. The cell resistance ratios for all three salts also were found to be alike within 0.01%, as is shown in Fig. 15. With none of the three salts is there any variation in resistance with variation in frequency from 1090 to 3000 cycles per second greater than 0.01%. We conclude, therefore, that the hypothesis, first suggested by Parker and later supported by Randall and Scott, that adsorption is responsible for the Parker Effect is without a sound theoretical or experimental basis and is unnecessary to account for the known facts. Of course, this does not preclude the possibility that a real adsorption effect may be demonstrated in the future with some other electrolyte or in extremely narrow tubes.

On the other hand, our hypothesis that the Parker Effect is due to a shunt

TABLE XV
CELL COMPARISON DATA. CELL M
Heavy Platinization

Soln.	Approx. concn., Na ₂ SO ₄	$f = 500$ $\omega = 3142$			$f = 1090$ $\omega = 6849$			$f = 3000$ $\omega = 18850$		
		R	C _P $\mu\mu\text{f.}$	C _P ω R= tan θ	R	C _P $\mu\mu\text{f.}$	C _P ω R= tan θ	R	C _P $\mu\mu\text{f.}$	C _P ω R= tan θ
59	0.001				43,461.5	0				
58	.002	25,540.4	6	0.00049	25,539.9	4	0.00069	25,539.9	3	0.0015
57	.018	3,355.02	0	0	3,355.02	0		3,355.02	0	
68					2,205.62	1	.000015			
62	.1	639.440	25	.000051	639.444	4	.000017	639.440	4	.000048
Ba(NO ₃) ₂										
66	0.0012	39,857.5	0	0	39,856.0	0	0	39,856.3	0	0
65	.01				5,030.54	0	0			
64	.02				2,935.38	0	0			
63	.04	1,541.02	8	.000039	1,541.01	0	0	1,540.97	0	0

TABLE XVI
CELL COMPARISON DATA. CELL N
Heavy Platinization

Soln.	Approx. concn., Na ₂ SO ₄	$f = 500$ $\omega = 3142$		$f = 1090$ $\omega = 6849$		$f = 3000$ $\omega = 18850$
		R	C _P $\mu\mu\text{f.}$	R	C _P $\mu\mu\text{f.}$	R
57	0.018	36,315.9	0	36,315.3	0	36,313.0
68				23,874.2	0	
62	.1	6,921.9	0	6,921.86	0	6,921.8
Ba(NO ₃) ₂						
65	0.01			54,445.8	0	
64	.02			31,776.1	0	
63	.04	16,681.7	3	16,681.6	0	16,682.6

across the electrodes containing resistance and capacitance is in accord with all of the known facts. It has led to an equation for the error due to the shunt which has been confirmed quantitatively as to the influence of frequency and capacitance on the error and has guided the design of a new type of cell in which capacitance between parts of the cell of opposite polarity is made negligible, with the result that the new cells have a very low phase angle and show no Parker Effect and no variation of resistance with frequency.

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Summary

1. The observation of Parker that the ratio of the resistances of two conductance cells when filled with a common solution and measured with an alternating current bridge is not independent of the specific conductance of the solution used, has been confirmed experimentally with cells of the

type commonly used. The curves obtained are, however, of simpler form than those obtained by Parker and this simplification of the problem is ascribed to the use of a superior bridge, thus avoiding some causes of error present in Parker's work.

2. By using an unshielded bridge carefully designed to avoid inductance and capacitance, the phase angle between the current and the voltage in conductance cells has been measured and made significant in the study of errors in conductance measurements and in the design of cells. The phase angle in the cells depends on the frequency used, the resistance being measured, the degree of platinization, and the dimensions of the cell.

3. The conclusion of earlier investigators that the error due to polarization is positive in sign and can be minimized and made practically insignificant by a combined use of proper platinization, large electrodes, high frequency, and high resistance, is confirmed.

4. It is demonstrated for the first time that with cells of the type commonly used there is a capacitive shunt between parts of the cell of opposite polarity, which has the effect of making the measured resistance lower than the true resistances of the electrolyte between the electrodes.

5. By the use of alternating current theory the error due to the capacitive shunt is shown to be approximately $\Delta R = -R_P R_T^2 \omega^2 C_P^2 = -R_P \tan^2 \theta$. The validity of this equation has been demonstrated by special experiments. The error due to capacitive shunts differs from that due to polarization in sign and in being increased by an increase in the frequency used and in the resistance being measured. The error due to capacitive shunt varies as the square of the capacitance in the shunt and as the first power of the resistance in the shunt whereas neither of these influences the error due to polarization. On the other hand, the degree of platinization, which has a great influence on the polarization, is without influence on the error due to capacitive shunt.

6. The equation for the error due to capacitive shunt has guided the design of new cells in which close proximity of parts of the cell of opposite polarity is avoided.

7. It has been demonstrated by measurements of phase angle and by intercomparisons of cells that the new cells are greatly superior to the forms commonly used. The new cells can be used at frequencies and resistances so high as to make errors due to polarization negligible without introducing errors due to capacitive shunt so that results which seem to be reliable within 0.01% may be obtained with them.

8. Although earlier experimenters have reported a variation in the conductance of electrolytes with change in frequency, it has been demonstrated experimentally that no change greater than a few thousandths of one per cent. occurs between the limits of 1090 and 4000 cycles per second when errors due to polarization and capacitive shunt are avoided.

9. The most convenient test of the quality of cells is the observation of the variation in apparent resistance with variation in frequency.

10. It has been shown experimentally that the ratio of the resistances of a pair of cells when filled with a common solution is independent of the electrolyte used for three different electrolytes. This does not confirm observations of earlier experimenters and removes the only experimental support for the hypothesis of Parker that adsorption is responsible for the Parker Effect.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF RUTGERS UNIVERSITY]

THE VAPOR PRESSURE OF PYRIDINE¹

BY P. A. VAN DER MEULEN AND RUSSELL F. MANN

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In the course of a study of certain complex compounds containing pyridine, a search made of the literature revealed that the vapor pressure curve of this substance below the normal boiling point has been only partially determined. Kahlbaum² determined the vapor pressure at six temperatures below 51°. Zawidzki³ reports a single value at 80°; the "International Critical Tables"⁴ give the boiling point as 115.3°, but the vapor pressure as 760 mm. at 115.50°. ^{5,6} The present study was undertaken to fill the gaps between these data.

Experimental Work

Pyridine c. p. brand of Baker was purified as recommended by Arndt and Nachtwey.⁷ This involves preparation of the pyridine perchlorate, purification of the perchlorate by crystallization, and liberation of the pyridine. The product was dried over solid potassium hydroxide, and was distilled with a fractionating column. The first and last quarters were rejected. The middle fraction, passing over between 115.1 and 115.3° was collected. This was redistilled as required.

The apparatus used was similar to that employed by Mortimer and Mur-

¹ This paper is based on a thesis submitted by Russell F. Mann to the faculty of Rutgers University in partial fulfilment of the requirements for the degree of Master of Science.

² G. W. A. Kahlbaum, "Siedetemperatur und Druck," Leipzig, 1885, p. 67.

³ J. v. Zawidzki, *Z. physik. Chem.*, **35**, 129-203 (1900).

⁴ "I. C. T.," McGraw-Hill Book Co., Inc., New York, 1926, Vol. I, p. 190.

⁵ *Ibid.*, 1928, Vol. III, p. 219.

⁶ K. G. MacKensie, *Ind. Eng. Chem.*, **1**, 360-362 (1909); Robert Schiff, *Ber.*, **19**, 560-568 (1886); W. Louguinine, *Compt. rend.*, **129**, 366-369 (1899); H. Hartley, N. G. Thomas and M. P. Appleby, *J. Chem. Soc. (Trans.)*, **93**, 538-563 (1908); W. R. Innes, *ibid.*, **79**, 261-266 (1901); E. J. Constam and J. White, *Am. Chem. J.*, **29**, 1-49 (1903); J. v. Zawidzki, *Chem.-Ztg.*, **30**, 299 (1906).

⁷ F. Arndt and P. Nachtwey, *Ber.*, **59A**, 448-455 (1926).