sium hydroxide, and washed with water, and further purified by recrystallizing from alcohol. They are insoluble in water and moderately soluble in alcohol.

The amines, N-methylamines, benzylphenylethylamines, isoquinolines and N-methylisoquinolines were not Odealkylated as the corresponding hydroxy derivatives required for the pharmacological work have been prepared previously by demethylating the appropriate methoxy derivatives.^{1,2,14,15}

The pharmacological work will be reported in another place. Some of that previously done is reported elsewhere.^{11,18-21}

- (19) Hjort, deBeer, Buck and Ide, ibid., 55, 152 (1935).
- (20) Hjort, ibid., 52, 101 (1934).
- (21) DeBeer and Hjort, ibid., 52, 211 (1934).

Nitrogen determinations were carried out by a micro-Dumas method. Melting points are corrected.

Summary

A series of seven alkoxy- β -phenylethylamines has been prepared, and from these amines the corresponding N-methylamines, ureas, unsymmethylureas, barbituric acids, isoquinolines, Nmethylisoquinolines, benzyl- β -phenylethylamines and characterizing compounds have been made. Over one hundred and twenty of these compounds have not been described previously.

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[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Measurement of the Conductance of Electrolytes.^{1,2} VIII. A Redetermination of the Conductance of Kohlrausch's Standard Potassium Chloride Solutions in Absolute Units

By Grinnell Jones and Maurice Joseph Prendergast

Most of the experimenters who have measured the electrical conductance of solutions have calibrated their cells by means of either a 1 or 0.1 or 0.01 N solution of potassium chloride whose absolute conductance was assumed to be known from the measurements of Kohlrausch, Holborn and Diesselhorst.³ Unfortunately, Kohlrausch gives alternative definitions of these solutions. Kraus and Parker⁴ have shown that although the alternative definitions of the 1 N solution are mutually consistent, the alternative definitions of the 0.1 N and of the 0.01 N solutions are not mutually consistent. Parker and Parker⁵ have redetermined the absolute values of the conductance of the Kohlrausch solutions with substantially different results. They proposed new definitions of three different standard solutions, which they call 1, 0.1 and 0.01 demal and gave the results of measurements of the absolute conductance of these solutions. The experimental method used by Parker and Parker was in principle similar to that used by Kohlrausch although evidently improved in many details.

The Editors of the "International Critical Tables" accepted Parker and Parker's work as more reliable than that of Kohlrausch, Holborn and Diesselhorst and have applied corrections to the data in the literature based on the Kohlrausch standards to make them conform to the newer standards of Parker and Parker. As a result very few of the figures for the conductance of solutions found in the "International Critical Tables" agree with the original literature.

In the fifth paper of this series Jones and Bradshaw have described a new and more precise method of making absolute measurements and have redetermined the specific conductance of the three solutions defined by Parker and Parker at 0, 18 and 25°. These results indicate that on the whole the results obtained by Parker and Parker are not as accurate as the earlier work of Kohlrausch, Holborn and Diesselhorst, and that the corrections recommended by Parker and Parker and used by the "International Critical Tables" are unreliable. We have, therefore, undertaken to redetermine the absolute specific conductivity of three standard potassium chloride solutions used by Kohlrausch at 0, 18, 20 and 25° by the new method developed by Jones and Bradshaw. It is hoped that the re-

⁽¹⁸⁾ Hjort, J. Pharmacol., 50, 131 (1934).

⁽¹⁾ Original manuscript received August 3, 1936.

⁽²⁾ Earlier papers in this series: Grinnell Jones and R. C. Josephs, THIS JOURNAL, **50**, 1049 (1928); Grinnell Jones and G. M. Bollinger, *ibid.*, **51**, 2407 (1929); **53**, 411, 1207 (1931); Grinnell Jones and B. C. Bradshaw, *ibid.*, **55**, 1780 (1933); Grinnell Jones and S. M. Christian, *ibid.*, **57**, 272 (1935); Grinnell Jones and D. M. Bollinger, *ibid.*, **57**, 280 (1935).

⁽³⁾ F. Kohlrausch, L. Holborn and H. Diesselhorst, Wied. Ann. Physik, 64, 417 (1898).

⁽⁴⁾ C. A. Kraus and H. C. Parker, THIS JOURNAL, 44, 2422 (1922).
(5) H. C. Parker and E. W. Parker, *ibid.*, 46, 312 (1924).

sults will be helpful in reconciling the great mass of data already in the literature which is based on Kohlrausch's standards with data based on the new standards of Jones and Bradshaw.

The Definitions of the Kohlrausch Standard Solutions .- The book "Das Leitvermögen der Elektrolyte" by Kohlrausch and Holborn, published in 1898, which has probably been used by chemists more than the original article, gives the following definitions (page 76): "Normal Potassium Chloride Solution, that is 74.59 grams of KCl in 1 liter of solution at 18°. Specific gravity at 18°, 1.04492. $\kappa_{18} = 0.09822$. 74.555 grams of KC1, weighed in air, are made up to 1 liter of solution at 18° (for $\pm 1^{\circ}$ in temperature the volume is to be taken as ± 0.3 ccm. greater), or also 71.422 grams of KCl to 1000 grams of solution, weighed in air, or 76.727 grams in one liter of water at 18°...."

The actual procedure used in the preparation of the solutions which were measured is shown by a study of the original paper which says³ (p. 435) "Normal Potassium Chloride Solution. For this purpose three varieties of salt were used of which always 74.555 grams were weighed in air and dissolved at 18° to one liter The determination of the specific gravity gave the value 1.04482 at 18.31° or 1.04492 at 18° ." The conductance was measured at 0, 9, 18, 27 and 36° and the values for each 1° interval were obtained by interpolation. The specific conductivity at 18° is given as 0.09822.

The advantages of defining standard solutions in terms of grams of potassium chloride per 1000 g. of solution with both weights corrected to vacuum are discussed in the paper of Jones and Bradshaw and therefore the argument will not be repeated. In order to reproduce Kohlrausch's 1 N solution we shall have to assume that the density of the air in his Laboratory was 0.0012 g./ ml. and that he used brass weights. On these assumptions the vacuum correction for potassium chloride (d = 1.987) is +0.000461 and 74.555 g. in air is equivalent to 74.5894 g. in vacuum. Kohlrausch states that the specific gravity of his normal solution at 18° is 1.04492, but does not state definitely whether this figure is for d^{18}_{4} or d^{18}_{18} . However, we have verified this figure experimentally for d^{18}_4 and therefore conclude that Kohlrausch must have meant Therefore, one kilogram d^{18}_4 1.04492. of Kohlrausch's normal solution must have contained 74.5894/1.04492 = 71.3828 g. of potassium chloride per kilogram of solution (both weights corrected to vacuum).

The second alternative definition given in Kohlrausch and Holborn's book is 71.422 g. of potassium chloride in 1000 g. of solution (both weighed in air). Applying the vacuum corrections on the assumption stated above this is equivalent to 71.4549 g. in 1.001006 kg. of solution or 71.3831 g. of potassium chloride per kilogram of solution in vacuum. This agrees with the first definition within four parts per million. Since Kohlrausch only used five significant figures in his definition these two definitions are consistent. Most later experimenters have probably used this definition.

The third alternative definition of the 1 N solution in the book is 76.727 g. (air weight) dissolved in 1 liter of water at 18°. Applying vacuum corrections to the salt and taking 1 liter of water at 18° as 998.623 g. (vac.) this definition is equivalent to 71.3813 g. of potassium chloride per kilogram of solution. This is about 0.002% less than the first definition. These three definitions agree within the degree of precision with which the conductivity is given and therefore may be regarded as mutually consistent.

Turning now to the 0.1 N solution we find discrepancies between the alternative definitions as has been pointed out by Kraus and Parker.

The book (p. 77) says "Tenth Normal Potassium Chloride Solution. One dissolves 7.455 grams, weighed in air, to 1 liter, or 7.430 grams to 1000 grams of solution. Or one dilutes 100 ccm. normal solution to 1000 ccm. This gives $\kappa_{18} = 0.01119.$ " Here again the original paper (p. 436) reveals the actual method of preparation in the statement "Diluted Potassium Chloride Solutions. The solutions of concentration 1/10, 1/50 and 1/100 were in general prepared from the normal solutions by dilution by volume." The solutions actually measured were evidently prepared by the third alternative method given in the book. Since Kohlrausch does not describe his volumetric procedure in any detail, there is no advantage in attempting to duplicate it experimentally, but we shall have to assume that it was correct and compute the equivalent gravimetric definitions. Since the 1 N solution contained 74.5894 g. per liter the 0.1 N solution obtained by volumetric dilution should have contained 7.45894 g. per liter at 18°. Kohlrausch does not give the density of this solution but Kraus and Parker give d^{18}_4 1.00343 and we have also verified this figure experimentally. Therefore Kohlrausch's 0.1 N solution must have contained 7.45894/1.00343 = 7.43344 g. of potassium chloride per kilogram of solution (both in vacuum).

The other methods given in the book are not equivalent. 7.455 Grams in air is 7.45844 g. in vacuum which if dissolved in 1 liter of 1.00343 kg. gives 7.43294 g. per kilogram of solution (vac.). 7.430 Grams per kilogram of solution in air is equivalent, after applying the vacuum correction, to 7.43343 g. dissolved in 1.001053 kg. or 7.42561 g. dissolved in 1 kg. of solution. This definition is in error by 0.1%.

The book says (p. 77) "Fiftieth and Hundredth Normal Potassium Chloride Solution. The weighing out of 1.4860 or 0.7430 grams becomes inconvenient. Dilution according to the ratio by volume 1:50 or 1:100 from normal or 1:5 or 1:10 from tenth normal solution is the usual way. $\kappa_{18} = 0.002397$ or 0.001225."

Kohlrausch does not give the density of his hundredth normal solution but Kraus and Parker give d_4^{18} 0.99911 and we have verified this figure. A hundredth normal solution prepared by dilution of the normal solution would contain 0.745894 g. (vac.) in 999.11 g. or 0.746558 g. of potassium chloride per kilogram of solution both corrected to vacuum. The alternative definition of 0.7430 g. per kilogram in air is equivalent to 0.742557 g. per kilogram in vacuum. This definition is therefore in error by 0.54% as has already been pointed out by Kraus and Parker.

Experimental

The experimental technique need not be described in detail since it resembled very closely that used by Jones and Bradshaw with some minor improvements suggested by the earlier experience. The chief innovation was that the measurements were carried out at 20° in addition to 0, 18 and 25°, as in the earlier work. In order to avoid any question as to error due to the "Wenner Effect" as discussed in the earlier paper, the entire process of determining the cell constants by the use of mercury as a primary standard was carried through from the beginning with a cell designed so as to avoid error from this cause. Since the earlier experience showed that the cell constants of the Wenner type of cell could be determined by the use of mercury with greater precision than the other parts of the work only one primary cell was used. Most of the other cells were made from the old cells but the cell constants were altered slightly by sealing on new standardtaper ground joints to the filling tubes or new electrode tubes at the ends which made it necessary to anneal the entire cell and remove and replace the platinization. The new platinization was lighter than the old. The differences between the cell constants reported in the two papers should therefore not be interpreted as showing that either the old or new figures are in error.

The data are presented in a different form than was used in the earlier paper, which it is hoped will not only save space in printing but will more readily permit a judgment as to the precision of the data. For this purpose instead of giving the data in full we give the maximum deviation of any measurement of a series from the mean and the "probable error" of the mean, computed by the customary rules given in any book on the theory of errors. It is, of course, well known that these rules assume that the number of determinations is great enough so that the laws of probability may be used and that only accidental unsystematic errors which are as apt to be plus as minus remain. Since systematic errors can never be avoided completely. the "probable error" tends to suggest an overoptimistic judgment as to the precision of the data. We were, of course, acutely aware that the real precision of the data would depend mainly on the success in avoiding systematic errors. The earlier papers in this series explain in some detail the procedures and precautions in our technique which have a claim to novelty. We have endeavored to avoid neglecting other possible sources of systematic error, such as a shift in the ice point of thermometers, but must refrain from a detailed description of such routine matters since their general character is well known.

A very important matter of routine is to make all measurements of resistance with at least two frequencies, since many electrical sources of error which might otherwise be overlooked may be detected in this manner. By measuring each solution in two cells which differ substantially in cell constant, systematic errors in the calibration of the resistance boxes would be revealed if they were appreciable.

Table I gives the results for the cell constant of the primary cell, Z_7 , obtained by measurements on the Kelvin bridge when filled with mercury at 0° against two different standard one-ohm coils designated as H and J, each with its Bureau of Standards certificate. As will be seen the two coils give essentially identical results.

		TABLE I			
	CELL CONS	TANT OF PRIMARY	CELL AT	r 0°C.	
Cell	Based on	Cell constant	Probable error	No. of meas.	Av. dev. from mean
Z_7	Coil H	10584.02	±0.016	5	0.06
Z_7	Coil J	10584.00	± .011	5	.04

 $10584.01 \pm .01$

Table II gives the values for the cell constant ratios determined with an alternating current bridge of the new type built by the Leeds and Northrup Company⁶ in accordance with the (6) P. H. Dike, *Rev. Sci. Instruments*, **2**, 379 (1931).

Z7

Accepted av.

principles of design developed by Jones and Josephs. It was calibrated against standard coils having Bureau of Standards certificates. These ratios were determined in an oil thermostat at either 18 or 25°, or both.

Tae	BLE II					
Cell Constant Ratios						
Cell constant ratio	${ m Probable} \ { m error} \ imes 10^6$	No. of measure- ments	Av. dev. from mean $\times 10^{6}$			
0.1080923	±0.5	8	1.4			
.1043611	±1.1	8	3.6			
.0818695	±0.3	17	1.7			
.0847953	±.4	17	1.9			
.1371218	±.8	17	3.8			
.1420222	±.9	17	4.7			
.1247929	±1.1	8	4.1			
.0745097	±0.6	8	2 .0			
1219319	±1.3	8	4.5			
.0728015	±0.5	8	1.9			
	TAH CELL CONS Cell constant ratio 0.1080923 .1043611 .0818695 .0847953 .1371218 .1420222 .1247929 .0745097 .1219319 .0728015	TABLE IICELL CONSTANT RATProbable error $\times 10^6$ Cell constant ratio $\overset{Probable}{\times}$ error $\times 10^6$ 0.1080923 ± 0.5 $.1043611$ ± 1.1 ± 1.1 $.0818695$.0847953 ± 0.3 $.0847953$ $\pm .4$ $.1371218$ $\pm .8$ $.1420222$ $\pm .9$ $.1247929$ ± 1.1 $.0745097$.06 $.1219319$ ± 1.3 $.0728015$ ± 0.5	TABLE IICELL CONSTANT RATIOSCell constantProbable error ratioNo. of measure-mea			

Table III gives the values of the cell constants of the secondary cells and their probable errors,

Cell Constants of Secondary Cells						
Cell	Based on cell	°C.	Cell constant	Pro	obable error	
Y٥	Z_7	0	1144.050	± (0.006	
		18	1143.884	±	.006	
		20	1143.865	÷	.006	
		25	1143.819	±	.006	
\mathbf{Y}_4	Z7	0	1104.559	±	.012	
		18	1104.399	±	.012	
		20	1104.380	±	.012	
		25	1104.336	±	.012	
\mathbf{N}_4	\mathbf{Y}_{3}	0	93.6628	±	.0006	
N₄	\mathbf{Y}_{4}	0	93.6615	±	.0011	
N_4	Av.	0	93.6625	±	.0005	
		18	93.6489	±	.0005	
		20	93.6473	±	.0005	
		25	93.6436	±	.0005	
N_5	\mathbf{Y}_{3}	0	156.8742	±	.0012	
N_{δ}	Y4	0	156.8720	±	.0020	
	Av.	0	156.8736	±	.0010	
		18	156.8501	±	.0010	
		20	156.8481	±	.0010	
		25	156.8419	±	.0010	
Q₃	N_4	0	11.68841	±	.00012	
Q۶	N_5	0	11.68860	±	.00011	
	$\mathbf{Av}.$	0	11.68851	±	.00008	
		18	11.68682	±	.00008	
		20	11.68662	±	.00008	
		25	11.68615	±	.00008	
Q4	N_4	0	11.42045	±	.00014	
Q₄	N_5	0	11.42063	±	.00011	
	Av.	0	11.42056	±	.00009	
		18	11.41890	±	.00009	
		20	11.41871	÷	.00009	
		25	11.41825	±	.00009	

TABLE III CELL CONSTANTS OF SECONDARY CELLS which include both the influence of the error in the ratios and in the cell constants of the larger cell. The change in the cell constant with temperature is computed from the known coefficient of expansion of the glass, 8.08×10^{-6} per degree.

Tables IV, V and VI give the specific conductance, κ , (in ohm⁻¹ cm.⁻¹) of the three standard solutions at 0, 18, 20 and 25° as obtained from each of the cells together with the average deviation of the separate measurements from the mean, and the "probable error" of the mean. In the work on 1 and 0.1 N solutions the measurements at 18 and 25° were usually made in succession without removing the solution from the cells. A different series of solutions were used for the measurements at 20 and 0°, which were also made in succession without removing the solutions from the cells. With the $0.01 \ N$ solutions the procedure was different in that the measurements were made at 18, 20 and 25° without removing the solutions from the cells and an independent series of solutions was used for the measurements at 0°. The measured specific conductivity has been corrected in each case for the conductivity of the water used, amounting to about 1.1 \times 10⁻⁶ at 25°. The "probable error" of the mean is computed from the deviations of the individual measurements and the probable error of the cell constant, but any errors in the temperature scale will not be reflected in the computed probable error since such errors are systematic. The thermometers used were the same as in the previous work and have been described in the previous paper. Although these thermometers were of exceptionally good quality, it seems probable that the greatest systematic errors in the final results may be in the temperature scale. The data are possibly less reliable at 0° than at the other temperatures because of the difficulty in maintaining this temperature inside of an oil-bath. The method of maintaining the cells at 0° by packing them inside a solid block of paraffin formerly used was abandoned in favor of immersion in a liquid paraffin oil in a metal container which was completely immersed in ice. This oil cannot be stirred without causing overheating because the heat generated thereby cannot be dissipated rapidly enough. A thermometer cannot be inserted into the oil because the heat conductivity of the thermometer itself would maintain the temperature above 0°. It is necessary to be patient until the resistance

readings become independent of time. The maximum resistance obtainable was accepted. On the other hand, at the higher temperatures the thermostat can be stirred with advantage because the thermostat contained a cooling coil with cold water circulating in it and the automatic adjustment of the heat balance takes care of the heat generated by stirring.

TABLE IV

Specific Conductance \times 10⁶ of 1 Normal Potassium Chloride Solutions

Kohlrausch's 1 N KCl containing 71.3828 g. of potassium chloride per 1000 g. of solution, both weights corrected for air buoyancy and the specific conductance corrected for the conductance of the water used.

°C.	Cell	$\kappa imes 10^{6}$	Probable error × 10 ⁶	No. of solns	Av. dev. from mean X 106
0	\mathbf{Y}_{3}	65432.3	±1.3	8	4.3
0	Y₄	65428.2	± 1.4	8	3.5
0	Av.	65430	±1.0		
18	\mathbf{Y}_{3}	98201.1	±1.1	7	2.8
18	\mathbf{Y}_{4}	98200.3	± 1.4	7	2.9
18	Av.	9820	±0.9		
20	\mathbf{Y}_3	102025.5	±.9	8	2.3
2 0	Y_4	102021.7	± 1.3	7	2.1
20	Av.	102024	± 0.7		
25	Y۶	111733.8	±1.3	7	3.7
25	\mathbf{Y}_{4}	111731.2	± 1.9	7	4.6
25	Av.	11173_{3}	± 1.1		

TABLE V

Specific Conductance \times 10⁶ of 0.1 Normal Potassium Chloride Solutions

Kohlrausch's 0.1 N KCl containing 7.43344 g. of potassium chloride per 1000 g. of solution, both weights corrected for air buoyancy and the specific conductance corrected for the conductance of the water used.

°C.	Cell	$\kappa imes 10^6$	$rac{ extsf{Probable}}{ extsf{x} 10^6}$	No. of solns.	Av. dev. from mean × 10 ⁶
0	N_4	7154.26	± 0.08	7	0.19
0	N_{δ}	7154.32	± .23	8	.73
0	Av.	7154.3	± .08		
18	N_4	11191.88	± .14	8	.42
18	N_{δ}	11191.99	± .20	8	. 57
18	Av.	11191.9	± .11		
20	N_4	11667.65	±.09	6	, 16
20	N_5	11667.52	± .13	6	. 30
20	Av.	11667.6	± .07		
25	N_4	12886.04	± .16	8	.43
25	N_5	12886.30	± .12	8	.28
25	Av.	12886.2	± .10		

Although the experience gained in the earlier similar investigation in this Laboratory was very helpful and much of the same apparatus was used, nevertheless the actual experimental data are entirely independent of any measurements

TABLE VI

Specific Conductance \times 10⁶ of 0.01 Normal Potassium Chloride Solutions

Kohlrausch's $0.01 \ N \ \text{KCl}$ containing $0.746558 \ \text{g}$. of potassium chloride per $1000 \ \text{g}$. of solution, both weights corrected for air buoyancy and the specific conductance corrected for the conductance of the water used.

°C.	Cell	$\kappa imes 10^6$	Probable error × 10 ⁶	No. of f solns.	Av. dev. rom mean × 10 ⁶
0	Q3	775.144	± 0.015	6	0.04
· 0	Q4	775.114	± .009	6	.02
0	Av.	775.12	± .008		
18	Q_3	1222.721	± .020	8	.06
18	Q4	1222.641	± .025	8	.08
18	Av.	1222.69	± .016		
20	Q۶	1275.770	± .027	8	.09
20	Q4	1275.680	± .026	8	.09
20	Av.	1275.72	± .02		
25	Q۶	1411.479	± .023	8	.07
25	Q₄	1411.406	± .027	8	. 08
25	Av.	1411.45	± .02		

made by Dr. Bradshaw. Everything which could influence the numerical results, such as the calibration of the weights and resistance coils and the ice points of the thermometers, was checked independently.

Table VII summarizes the results and compares the corrections recommended by Parker and Parker and used by the "International Critical Tables'' for a systematic recalculation of the data in the literature with the corrections computed from our measurements. As will be seen our results do not confirm the reliability of the corrections recommended by Parker and Parker. In only one of the nine cases is our correction within 0.03% of that recommended by Parker and Parker. In six of the nine cases our results agree with Kohlrausch better than they do with Parker and Parker and in four of the nine cases we even differ as to the sign of the correction which should be applied to Kohlrausch's values. In attempting to apply corrections to the data in the literature due consideration must be given to the possibility of confusion caused by the alternative definitions given in the book, "Das Leitvermögen der Elektrolyte." Many authors do not make it clear which one of the alternative definitions they actually used.

Our new measurements make it probable that on the whole the accuracy of the data on the conductance of solutions given in the "International Critical Tables" has not been improved by the recalculation by the use of Parker and

		SOLUTIONS		
	0°	18°	20°	25°
1	N KCl 71.3828 g. KC	Cl per 1000 g. of solution	in vacuum	
Kohlrausch	0.06541	0.09822	0.10207	0.11180
Parker's values	.065312	.098116		.111687
Parker's corrections, %	— .150	108		<u> </u>
Our new values	.065430	.098201	. 102024	$.11173_{3}$
Recommended corrections, %	+ .031	- .019	045	060
C	0.1 N KCl 7.43344 g.	KCl per 100 g. solution	in vacuum	
Kohlrausch	0.00715	0.01119	0.01167	0.01288
Parker's values	.0071416	.0111846		.0128765
Parker's corrections, %	118	048		027
Our new values	$.007154_{3}$.0111919	.0116676	$.012886_{2}$
Recommended corrections, %	+ .060	+ .017	021	+.048
0.0	01 N KCl 0.746558 g.	KCl per 1000 g. solution	n in vacuum	
Kohlrausch	0.000776	0.001225	0.001278	0.001413
Parker's values	.00077422	.00122238		.00141037
Parker's corrections, %	229	214		186
Our new values	.00077512	.00122269	$.0012757_{2}$.00141145
Recommended corrections, $\%$	— .11 <u>4</u>	189	179	110
Parker's standards instea	d of the Kohlman	sch reference for	conductivity meas	urements have

TABLE VII

CORRECTIONS TO BE APPLIED TO CONDUCTANCE DATA BASED ON KOHLRAUSCH STANDARD POTASSIUM CHLORIDE

Parker's standards instead of the Kohlrausch standards originally used by most experimenters.

Summary

1. The absolute specific conductances of the 1, 0.1 and 0.01 N potassium chloride solutions recommended by Kohlrausch as a standard of

reference for conductivity measurements have been redetermined.

2. The results indicate that the corrections used by the "International Critical Tables" in the recalculation of the conductance data are unreliable.

CAMBRIDGE, MASS. RECEIVED FEBRUARY 26, 1937

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY SECTION, PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Kinetics of Activated Sorption of Hydrogen on Chromic Oxide Gel¹

By LOYAL CLARKE,² L. S. KASSEL³ AND H. H. STORCH⁴

Introduction

Burwell and Taylor⁵ have recently presented more than usually complete data on the kinetics of activated sorption of hydrogen on a chromium oxide catalyst as a function of pressure and temperature. The present paper derives from their data an empirical relationship which is satisfactory, except for small and for very large sorption. The form of this relation suggests a model of the sorption process, which permits derivation of the equation for moderate sorptions, and accounts at least qualitatively for its failure at extreme conditions.

When the amount of hydrogen sorbed computed by Burwell and Taylor is plotted against time and a smooth curve drawn through the points, it was found that extrapolation to the starting time would, taken naïvely, indicate an appreciable amount of sorption coincident with the beginning of the experiment. The results of these extrapolations are given in Table I. It will be seen that for all the experiments at 1 atmosphere this initial amount is about 1.3 cc., at onehalf atmosphere about 0.8, and at a quarter atmos-

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⁽⁵⁾ R. L. Burwell, Jr., and H. S. Taylor, THIS JOURNAL, 58, 697-705 (1986).