# 49. *The Dissociation Constants of Organic Acids. Part V. The Mobility of the Hydrogen Ion at 18° and at 25°.*

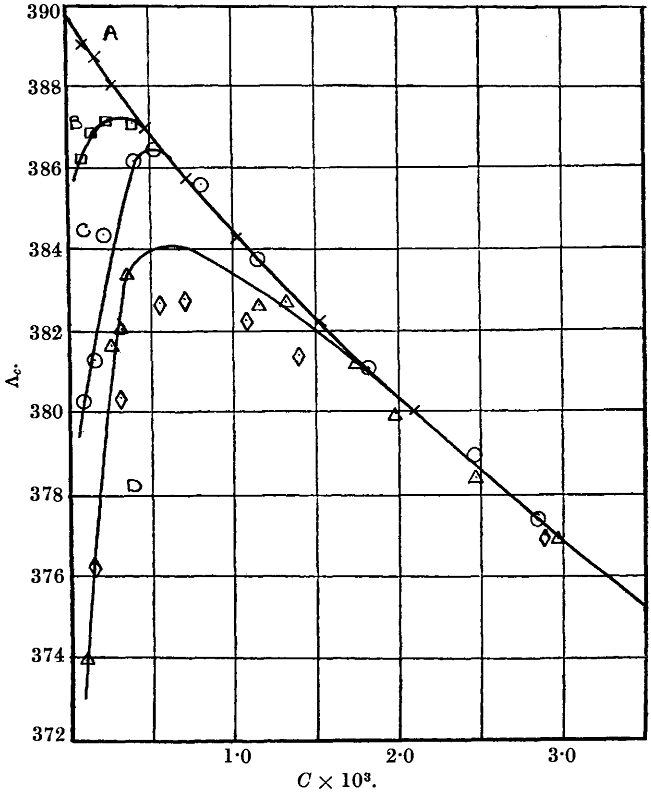
By George Harold Jeffery and Arthur Israel Vogel.

The most important datum for the calculation of dissociation constants at any temperature is the mobility of the hydrogen ion at that temperature; this value is, however, known with but little accuracy; *e.g.*, for 25°, at which temperature most conductivity measurements are now carried out, the most trustworthy figures range from $347{\cdot}2 \pm 0{\cdot}4$ (Kendall, J., 1912, **101**, 1275; compare Derick, *J. Amer. Chem. Soc.*, 1914, **36**, 2268) to 351·5 (Ulich, *Trans. Faraday Soc.*, 1927, **23**, 390). Other values which have been given are 342 (Ostwald, *Z. physikal. Chem.*, 1888, **2**, 842; this figure was employed in his calculations of the dissociation constants of weak acids, *ibid.*, 1889, **3**, 172), 347 (*idem*, " Lehrbuch der allgemeine Chemie," 1893, **2**, 675), 352 (Kohlrausch, " Leitvermögen de Elektrolyte," 1898, pp. 107—110), 365 (Noyes and Sammet, *Z. physikal. Chem.*, 1903, **43**, 49), 346 (Drucker, *Z. Elektrochem.*, 1907. **13**, 81), 348 (Kohlrausch, *ibid.*, p. 333; " Gesammelte Abhandl.," 1911, **2**, 1119), 353 (Gorke, *Z. physikal. Chem.*, 1908, **61**, 495), 348 (Noyes and Kato, *ibid.*, 1908, **62**, 420), 349·93 (Kraus and Parker, *J. Amer. Chem. Soc.*, 1922, **44**, 2449), 349·89 (Parker, *ibid.*, 1923, **45**, 2033), 349 (Hartley and Raikes, *Trans. Faraday Soc.*, 1927, **23**, 390), 349·05 (Ferguson and Vogel, *Phil. Mag.*, 1927, **4**, 305; see, however, *ibid.*, 1931, **27**, 289), 351 (Murray-Rust, Gatty, MacFarlane, and Hartley, *Ann. Reports*, 1930, **27**, 351), and 348·6 (Jeffery and Vogel, Part IV of this series, J., 1931, 1723). The best figures at 18° appear to be $313{\cdot}9 \pm 0{\cdot}4$ (Kendall, J., 1912, **101**, 1296), 315 (Kohlrausch and Holborn, " Leitvermögen der Elektrolyte," 1916, p. 214), 315·62 (Kraus and Parker, *loc. cit.*), and 317·0 (Jeffery and Vogel, *loc. cit.*); a full bibliography of the earlier results is given in Kendall's paper (*loc. cit.*).

The necessity for obtaining a trustworthy figure for the mobility of the hydrogen ion at 18° and at 25° is therefore obvious. For accurate work with dilute solutions of acids it is now recognised that the use of silica conductivity cells is essential (compare Kraus and Parker; Parker; Jeffery and Vogel, *locc. cit.*). By a comparison of their results with iodic acid in Pyrex cells at 25° with those of Kraus and Parker in silica cells, the present authors have shown (J., 1931, 1720) that excellent agreement is obtained at concentrations greater than $1{\cdot}5 \times 10^{-3}N$, but the conductivities below this concentration pass through a maximum at about

$1 \times 10^{-3}N$. Ferguson and Vogel (*Trans. Faraday Soc.*, 1931, **27**, 289) have computed the value of the conductivity at infinite dilution of iodic acid at 25° from Kraus and Parker's determinations with water of specific conductivity of about 0·1 gemmho, and find that the conductivity–concentration curve is represented by

FIG. 1.



*Iodic acid at 25°.*

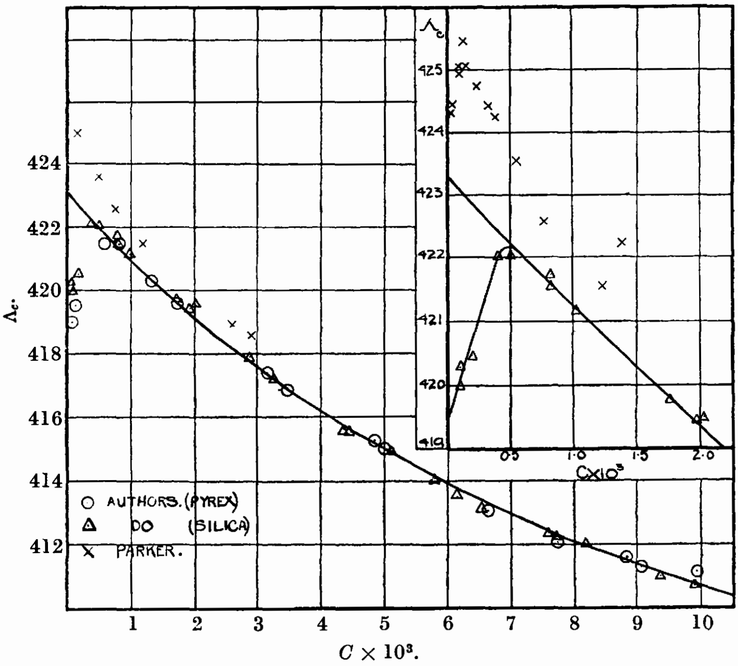
⊙ *Authors* (*Silica:* $H_2O$, $\kappa=0·8$). ⊡ *Kraus and Parker* (*Silica:* $H_2O$, $\kappa=0·5$).
△ ,, (*Pyrex:* ,, ). × ,, ,, ( ,, $H_2O$, $\kappa=0·1$).
◇ *Kraus and Parker* (*Lime-glass:* $H_2O$, $\kappa=0·8$).

$\Lambda_0 = \Lambda + 2187C^{0·880}$, leading to $\Lambda_0 = 389·61$. We have repeated the measurements upon iodic acid at 25° in a silica cell of the Hartley and Barrett type with equilibrium water and find good agreement with Kraus and Parker's determinations at concentrations above $0·0005N$. The conductivity–concentration curve passes through a maximum below this concentration—an effect obviously due to the use of less pure water. The $\Lambda$–$C$ curve of our own results above 0·0005$N$ is expressed by the equation $\Lambda_0 = \Lambda + 1735C^{0\cdot837}$, leading to a mean value of $\Lambda_0$ of 389·99. This is in satisfactory accord with that deduced from Kraus and Parker's figures, and it seems reasonable to assert that trustworthy conductivity values are obtained with equilibrium water in quartz cells at concentrations above *ca.* 5 × $10^{-4}N$. Fig. 1 illustrates well the influence of the nature of the material of the cell and of the specific conductivity of the water used upon the conductivity–concentration curve for iodic acid at low concentrations. Curves *A* and *B* represent Kraus and Parker's determinations in a silica cell with water of $\kappa$ = *ca.* 0·1 and 0·5 gemmho respectively (only one run is shown for the sake of clarity), curve *C* the authors' figures with water with $\kappa$ = *ca.* 0·8 gemmho (present research), and curve *D* depicts similar measurements but with Pyrex cells (J., 1931, 1720). Kraus and Parker's results with lime-glass cells are also indicated. The above comparison is legitimate since both Kraus and Parker's and the present authors' determinations of cell constants are based upon Kohlrausch and Maltby's figures for potassium chloride at 18° (" Gesammelte Abhandl.," 1911, **2**, 826).

The value for the mobility of the hydrogen ion at 25° is 349·0 or 348·0 according as the figure 41·0 or 42·0 is employed for the mobility of the iodate ion (Jeffery and Vogel, Part IV, *loc. cit.*).

Since accurate data are now available from which the mobility of the chloride ion at 25° can be calculated (Jeffery and Vogel, *loc. cit.*), new measurements on hydrogen chloride have also been made in a silica cell. The most noteworthy previous work is that of Parker (*J. Amer. Chem. Soc.*, 1923, **45**, 2017; this paper contains a full bibliography of earlier work). Our figures cover the concentration range 1—100 × $10^{-4}N$, those of Parker extend over the range 1—30 × $10^{-4}N$. The results are plotted in Fig. 2. Our method for the preparation of the solutions by weight is based upon the use of constant-boiling hydrochloric acid, the concentration of which is known with great accuracy from the work of several investigators (compare Hulett and Bonner, *J. Amer. Chem. Soc.*, 1909, **31**, 390; Foulk and Hollingsworth, *ibid.*, 1923, **45**, 1223; Bonner and Titus, *ibid.*, 1930, **52**, 633; Bonner and Wallace, *ibid.*, 1930, **52**, 1747). This method is susceptible of great accuracy and would seem to be preferable to that employed by Parker, which consisted of generating the hydrogen chloride from sodium chloride and sulphuric acid, passing the gas through a wash-bottle containing concentrated sulphuric acid, drying it by means of one tube filled with phosphoric oxide, and then passing it into about a kilogram (accurately weighed) of conductivity water contained in a quartz flask, the connexion to the quartz absorption flask being made with rubber tubing. No precautions were taken to remove sulphuric acid spray; the use of phosphoric oxide, unless very highly purified, is not entirely satisfactory (compare Richards, *J. Amer. Chem. Soc.*, 1909, **31**, 6; Gray and Burt, J., 1909, **95**, 1639). The discrepancies between the experimental results of the present authors and those of Parker are probably to be attributed to these causes, and not to the actual conductivity measurements, which are beyond criticism.

FIG. 2.



*Hydrochloric acid at* 25°.

The $\Lambda$–$C$ curve above $5 \times 10^{-4}N$ is expressed by the equation $\Lambda_0 = \Lambda + 1380C^{0·929}$, which gives a mean value of $\Lambda_0$ for hydrogen chloride at 25° of 423·67. This leads to a value for the mobility of the hydrogen ion of 348·3 or 347·3 according as 75·4 or 76·4 is taken for the mobility of the chloride ion (Jeffery and Vogel, Part IV, *loc. cit.*).

Measurements have also been carried out with hydrochloric acid in Pyrex cells with equilibrium water. The $\Lambda$–$C$ curve passes through a maximum at about $0·0008N$ and is expressed at concentrations exceeding $0·001N$ by the equation $\Lambda_0 = \Lambda + 576·1C^{0·788}$, which gives a mean value of $\Lambda_0 = 423{\cdot}66$, in satisfactory agreement with the figure deduced above.

As a further check on the value for the mobility of the hydrogen ion at 25°, conductivity measurements have been made on benzenesulphonic acid in a silica cell, and on its sodium salt in Pyrex cells.* In view of the indirect proof of the purity of the benzenesulphonic acid and its extremely hygroscopic character, the results for this acid are not considered to be as trustworthy as those for iodic and hydrochloric acids. The $\Lambda$–$C$ curve for the acid above $0{\cdot}0005N$ is expressed by $\Lambda_0 = \Lambda + 527{\cdot}1C^{0{\cdot}740}$, giving $\Lambda_0 = 385{\cdot}26$. For the sodium salt, $\Lambda_0 = \Lambda + 240{\cdot}8C^{0{\cdot}711}$, leading to $\Lambda_0 = 86{\cdot}33$; $l_0$ for the hydrogen ion is 349·7 or 348·7 according as $l_0$ for the sodium ion at 25° is taken as 50·8 or 49·8 (J., 1931, 1723).

The results for the three acids are collected in Table I. The two alternative values for the mobilities of the anions are due to the use of two kation transport numbers for potassium chloride, *viz.*, 0·497 (the formerly-accepted figure of Kohlrausch and Maltby, *op. cit.*, p. 906) and 0·490 (the recent value of MacInnes and Dole, *J. Amer. Chem. Soc.*, 1931, **53**, 1362).

TABLE I.

| | $HIO_3$. | | HCl. | | $C_6H_5{\cdot}SO_3H$. | |
|---|---|---|---|---|---|---|
| $\Lambda_0$ | 389·99 | | 423·67 | | 385·26 | |
| $n_c$ for KCl | 0·497 | 0·490 | 0·497 | 0·490 | 0·497 | 0·490 |
| $l_0$ of anion | 41·0 | 42·0 | 75·4 | 76·4 | 35·5 | 36·5 |
| $l_0$ of $H^+$ ion | 349·0 | 348·0 | 348·3 | 347·3 | 349·7 | 348·7 |

The mean value for the mobility of the hydrogen ion at 25° is $349{\cdot}0 \pm 0{\cdot}7$ ($n_c = 0{\cdot}497$) or $348{\cdot}0 \pm 0{\cdot}7$ ($n_c = 0{\cdot}490$), or a maximum deviation from the mean of 0·2%.

Conductivity measurements in a quartz cell have also been made for iodic acid at 18° over the range $0{\cdot}0001$—$0{\cdot}01N$. The $\Lambda$–$C$ curve above $0{\cdot}0005N$ is expressed by the equation $\Lambda_0 = \Lambda + 690{\cdot}5C^{0{\cdot}719}$, giving a mean value for $\Lambda_0$ of 348·05. This figure differs by about 1% from the preliminary value previously deduced (Part IV, *loc. cit.*) from measurements in Pyrex cells at concentrations above $0{\cdot}002N$, and illustrates that extrapolation to zero concentration from results at relatively high concentrations for acids may be only approximate. The mobility of the hydrogen ion at 18° is 314·1, that for the iodate ion being assumed to be 34·0 (Ferguson and Vogel, *Phil. Mag.*, 1925, **50**, 971). The latter is based on a transport number for potassium chloride of 0·497; if MacInnes

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* The early work of Ostwald (*Z. physikal. Chem.*, 1888, **2**, 845), and of Wightman and Jones (*Amer. Chem. J.*, 1911, **46**, 56) (compare Boyle, J., 1919, **115** 1505) must be regarded as approximate.

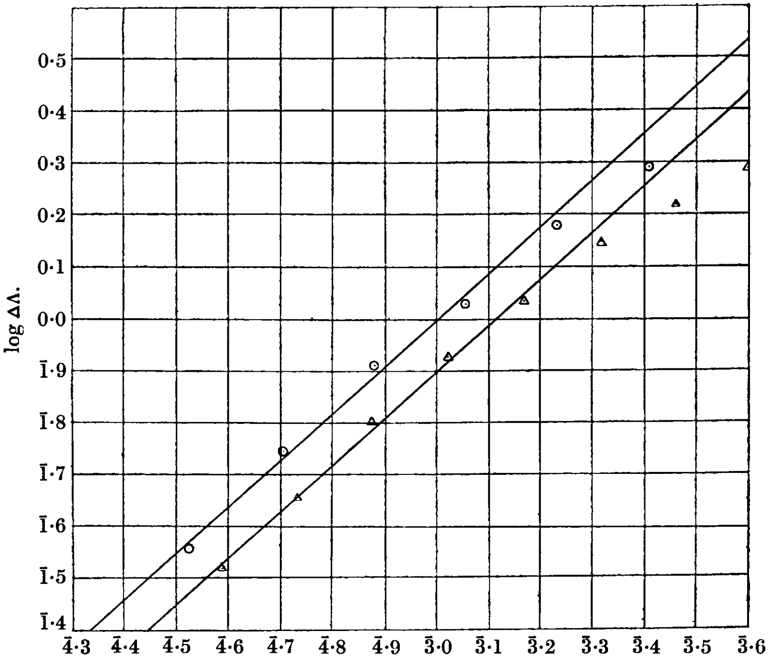
and Dole's figure (*loc. cit.*) be employed, $l_0$ for the iodate ion is 34·7, and that for the hydrogen ion is 313·4.

All the above calculations are based upon the use of Ferguson and Vogel's formula (*Phil. Mag.*, 1925, **50**, 971)

$$\Lambda_0 = \Lambda + BC^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for extrapolation to $\Lambda_0$. A slight variation of the usual procedure has been introduced. It has been found that by making two plots of log $\Delta\Lambda$ (ordinates) against log $C$ (abscissæ) with common ratio $r$ of 1·4 and 1·5 respectively, the exact position of the straight line—upon which the values of $B$ and $n$ depend—can be very easily fixed. A typical example for hydrochloric acid in silica at 25° is shown in Fig. 3.

FIG. 3.



*Hydrochloric acid at* 25° (*silica*).

⊙ $r = 1·5$. △ $r = 1·4$.

It is of interest to compare the results for acids with those predicted by the Debye–Hückel–Onsager theory of complete ionisation, according to which the $\Lambda$–$C$ relation at concentrations below about 0·002$N$ is of the type

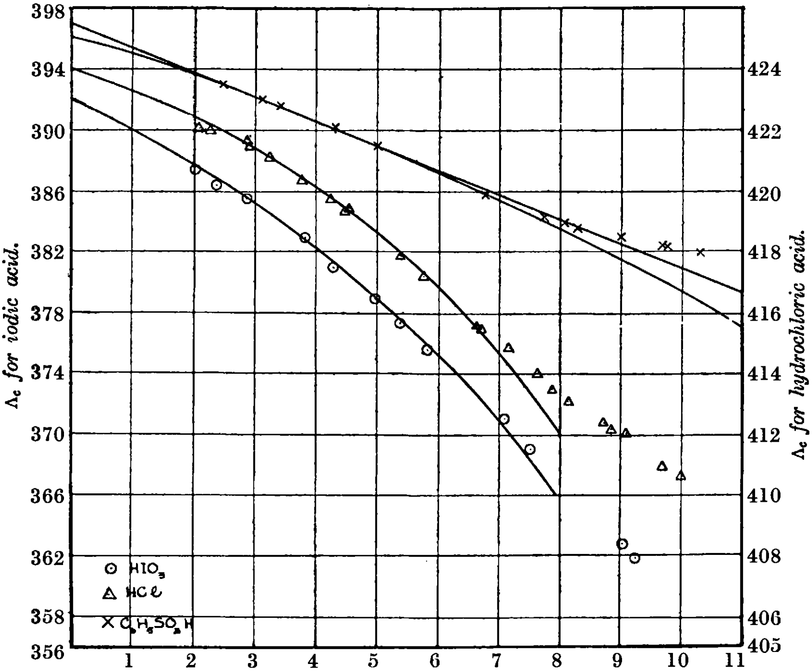
$$\Lambda_0 = \Lambda + PC^{0·5} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Onsager's actual equation for a $z$-valent binary electrolyte (*Physikal. Z.*, 1927, **28**, 277; *Trans. Faraday Soc.*, 1927, **23**, 344; compare Hartley, *Ann. Reports*, 1930, **27**, 331) is

$$\Lambda_0 = \Lambda + \left[\frac{0\cdot986 \times 10^6}{(DT)^{3/2}}(2 - \sqrt{2})z^2\Lambda_0 + \frac{58\cdot0}{(DT)^{\frac{1}{2}}\eta}z\right]\sqrt{2zC} \quad . \quad (3)$$

where $D$ is the dielectric constant of the solvent at $T°$ Abs., and $\eta$ is the viscosity of the solvent. For uni-univalent electrolytes in water, this reduces to :

FIG. 4.



$\Lambda$–$C^{0\cdot5}$ *Plot for acids at* 25°.

$$\text{At } 18° \quad \Lambda_0 = \Lambda + (0\cdot224\Lambda_0 + 50\cdot5)C^{0\cdot5} \quad . \quad . \quad . \quad (4)$$
$$\text{At } 25° \quad \Lambda_0 = \Lambda + (0\cdot228\Lambda_0 + 59\cdot8)C^{0\cdot5} \quad . \quad . \quad . \quad (5)$$

The plots of $\Lambda$ against $C^{0\cdot5}$ are shown in Fig. 4. The ordinate scales for iodic and hydrochloric acids respectively are indicated on the extreme left and right of the diagram, whilst that for benzenesulphonic acid has been displaced vertically by 10 units in order to prevent overlapping. It will be observed that the points for the three acids lie on parabolas. It is true that a straight line extending to about 0·008$N$ can be drawn for benzenesulphonic acid, but this extends to a region where the complete ionisation hypothesis is not intended to apply and leads to a high value for $\Lambda_0$. The decreasing curvature in these graphs for the three acids corresponds to the decrease in the value of the exponent $n$ in formula (1), thus : hydrochloric acid, $n = 0{\cdot}929$; iodic acid, $n = 0{\cdot}837$; and benzenesulphonic acid, $n = 0{\cdot}740$.

That a straight line can be made to fit closely to the $\Lambda$–$C^{0{\cdot}5}$ curve for benzenesulphonic acid is not altogether surprising in view of the relatively small curvature of the parabola. A similar result is obtained for iodic acid at 18°. It is highly probable that if the measurements were carried out with better conductivity water (say, of $\kappa = 0{\cdot}1$ gemmho), so as to yield trustworthy results over the range 0·0001–0·0005$N$, which has not been utilised in the present calculations, the curvature at low concentrations would be more apparent. This is, indeed, what is found if Kraus and Parker's results for iodic acid ($\kappa = 0{\cdot}1$ gemmho) are plotted on the graph. The following table shows the values of $\Lambda_0$ determined by direct extrapolation of these straight lines together with the observed and calculated slopes [the latter from equations (4) and (5)], and $\Delta$ the percentage deviation of the observed value from the theoretical, *i.e.*, $\Delta = 100(x_{\text{obs.}} - x_{\text{calc.}})/x_{\text{calc.}}$ (see J., 1930, 2497). The large deviation for iodic acid is noteworthy.

| Acid. | $\Lambda_0$. | $x_{\text{obs.}}$. | $x_{\text{calc.}}$. | $\Delta$. |
|---|---|---|---|---|
| $C_6H_5{\cdot}SO_3H$ at 25° ... | 387·1 | 161·4 | 148·1 | + 9·0 |
| $HIO_3$ at 18° ............ | 350·4 | 226·8 | 129·0 | + 75·9 |

Onsager (*Physikal. Z.*, 1927, **28**, 294) had previously shown that the $\Lambda$–$C^{0{\cdot}5}$ curve for iodic acid is a parabola, and by utilising Parker's results for hydrochloric acid at 25° he obtained a straight line, the slope of which agreed well with that computed theoretically from equation (5) (see also Davies, " The Conductivity of Solutions," 1930, p. 83). Parker himself (*loc. cit.*) obtained a straight line by plotting $\Lambda$ against $C$, since he found the Ostwald dilution formula to hold. In the light of the present authors' experimental results, little significance can be attached to the calculations of Onsager (*loc. cit.*) and of Davies (*loc. cit.*). This remark also applies to Murray-Rust, Gatty, MacFarlane, and Hartley's criticism (*Ann. Reports*, 1930, **27**, 346) of the Ferguson and Vogel method for extrapolation to $\Lambda_0$. Further, it must be pointed out that the values of $n$ in equation (1) for potassium chloride are 0·452 at 18° (*Phil. Mag.*, 1925, **50**, 971) and 0·547 at 25° (J., 1931, 1719). The figure 0·374, quoted by Hartley and others for potassium chloride, refers to a temperature of 0° and is based upon the experimental results of Walden and Ulich (*Z. physikal. Chem.*, 1923, **106**, 49).

The $\Lambda$–$C$ curve for sodium benzenesulphonate is expressed by the equation $\Lambda_0 = \Lambda + 240{\cdot}8C^{0{\cdot}711}$, giving a mean value of $\Lambda_0$ of 86·33. Extrapolation for this salt has also been carried out by means of the square-root formula (2); a slightly different straight line is obtained according as one assumes that the formula holds down to 0·0014$N$ or 0·002$N$. In the former case $\Lambda_0 = 86{\cdot}58$, $x_{\text{obs.}} = 60{\cdot}8$, $x_{\text{calc.}} = 79{\cdot}5$, and $\Delta = -23{\cdot}5$, and in the latter case $\Lambda_0 = 86{\cdot}88$, $x_{\text{obs.}} = 73{\cdot}0$, $x_{\text{calc.}} = 79{\cdot}6$, and $\Delta = -8{\cdot}3$, the agreement with the experimental figures being slightly better. This result indicates that the magnitude of $\Delta$ as a test for agreement with the Debye–Hückel–Onsager theory is not so sensitive as seems to be generally supposed. Similar results are obtained for potassium chloride at 18°. For Kohlrausch and Maltby's results * (*op. cit.*, p. 890), the $\Lambda$–$C^{0{\cdot}5}$ plot gives $\Lambda_0 = 129{\cdot}9 = \Lambda + 77{\cdot}8C^{0{\cdot}5}$; $x_{\text{calc.}} = 79{\cdot}8$, and $\Delta = -2{\cdot}3$ (compare Ferguson and Vogel, *Phil. Mag.*, 1925, **50**, 971, who found that these results are expressed by the equation $\Lambda_0 = 130{\cdot}04 = \Lambda + 61{\cdot}26C^{0{\cdot}452}$), whilst a similar plot for Weiland's experimental figures (*J. Amer. Chem. Soc.*, 1918, **40**, 146) gives $\Lambda_0 = 129{\cdot}9 = \Lambda + 83{\cdot}3C^{0{\cdot}5}$; $\Delta = +4{\cdot}7$ (compare Ferguson and Vogel, *Trans. Faraday Soc.*, 1931, **27**, 290, who find, for Weiland's runs 3 and 4, $\Lambda_0 = 129{\cdot}85 = \Lambda + 174{\cdot}6C^{0{\cdot}587}$).

## EXPERIMENTAL.

*Conductivity Water.*—This was prepared as described by Vogel and Jeffery (Part III, J., 1931, 1201).

*Preparation of Materials and Solutions.*—*Iodic acid.* Kahlbaum's iodic acid "for analysis" was purified as described previously (J., 1931, 1723). Sample A consisted of a mixture of specimens (1) and (2) (*loc. cit.*), and sample B was prepared from a new specimen of iodic acid (Found: $0{\cdot}2933_2$ g. Taken: $0{\cdot}2932_2$ g.).

*Hydrogen chloride.* The apparatus for preparing the constant-boiling solution is shown in Fig. 5. Hydrogen chloride was generated by the action of A.R. concentrated sulphuric acid in the tap funnel *A* upon Kahlbaum's "pure for analysis" sodium chloride contained in the 500-c.c. flask *B*, the gas freed from spray by passing through glass wool in the bubbler *C*, and finally absorbed in conductivity water contained in a small Pyrex beaker by means of the inverted thistle-funnel *D*, placed just below the surface of the water. The reaction was stopped when the increase in weight of the water was

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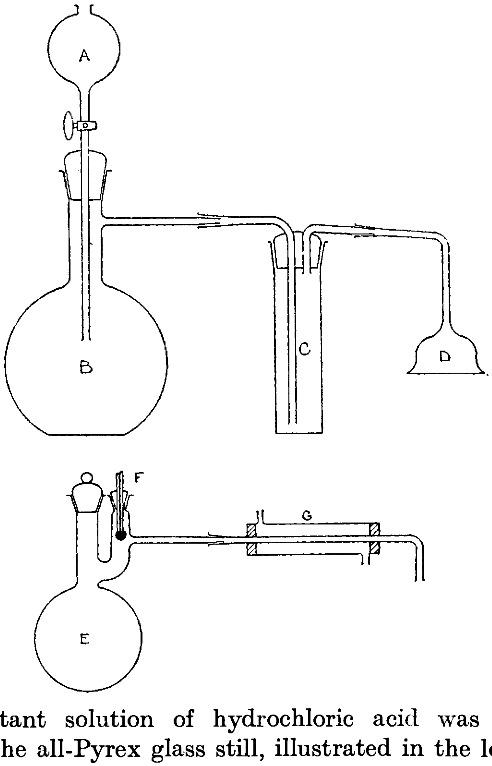
* These have been corrected by the original authors for small variations in temperature from 18°; Frazer and Hartley (*Proc. Roy. Soc.*, 1925, **109**, *A*, 356) have employed the uncorrected figures.

approximately that required for conversion into the constant-boiling acid. The apparatus was constructed entirely of Pyrex glass: no lubricant was employed on the well-ground joints except on the tap, where a thin film of petroleum jelly which had been boiled with conductivity water was used. The glass-wool was boiled three times with aqua regia, well washed with distilled water, finally with conductivity water, and dried at 100°.

FIG. 5.



The resultant solution of hydrochloric acid was fractionally distilled in the all-Pyrex glass still, illustrated in the lower half of the diagram. It consisted of a 75-c.c. Claisen flask *E* with a ground-in glass thermometer of Corning borosilicate glass, manufactured by Messrs. Black to N.P.L. accuracy, which was connected to the condenser *G*, a large Pyrex weighing bottle acting as receiver. The thermometer was graduated over the range 90—160° in 0·1°. The 110° mark was checked with pure boiling toluene. A few pieces of platinum wire were placed in the flask to promote regular ebullition.

The constant-boiling fraction was redistilled from 1—2% of its weight of A.R. barium chloride—to remove traces of sulphuric acid if present—and finally redistilled alone, the exact barometric pressure at the time of the last distillation being observed. No variation in boiling point, which agreed well with that given by Bonner and Wallace (*loc. cit.*), of the collected sample could be detected; a change in temperature of 0·02° was readily discernible. The exact composition was obtained from the pressure by reference to Foulk and Hollingsworth's table (*loc. cit.*). Three independent preparations were employed.

The barometric pressures and the corresponding boiling points of the various specimens used are given below. Specimens 1A and 2A were obtained from specimens 1 and 2 by redistillation.

| Specimen ............ | 1 | 1A | 2 | 2A | 3 |
|---|---|---|---|---|---|
| Pressure (mm.) ...... | 762·70 | 755·00 | 763·55 | 764·85 | 757·05 |
| B. p. .................. | 108·60° | 108·50° | 108·70° | 108·75° | 108·55° |

*Benzenesulphonic acid.* Kahlbaum's purest acid was employed. It was analysed by titration with aqueous baryta, which had been standardised against A.R. potassium hydrogen phthalate, and found to contain 98·52% of the monohydrate (compare Meyer, *Annalen*, 1923, **433**, 328), the remainder being water. Its purity was established by conversion into the sodium salt by the addition of the calculated quantity of pure sodium hydroxide solution, evaporating it to dryness on the water bath, and recrystallising the salt as described below (Found : Na, 12·76. Calc. : 12·78%), and then measuring the conductivity over the range $1 \times 10^{-4}$—$1 \times 10^{-2}N$. (This is referred to as specimen 2 in the tables of experimental results.) The conductivities were in good agreement with those found for the pure sodium salt prepared as described below.

*Sodium benzenesulphonate.* Gattermann's method (Ber., 1898, **21**, 2121; " Die Praxis des organischen Chemikers," 1930, p. 184) of preparation from A.R. benzene was utilised. The salt was recrystallised twice from ordinary absolute alcohol and finally from redistilled absolute alcohol (Found : Na, 12·74%). This is designated as specimen 1.

Pyrex vessels were used throughout, unless otherwise stated, all filtrations being carried out with Jena-glass Buchner funnels provided with sealed-in glass filter discs.

For iodic acid and sodium benzenesulphonate, the solutions were made up by weight as described in Part I (J., 1929, 1480), a small silica weighing bottle being used for the former. The solution of hydrochloric acid was prepared by adding a known weight of the freshly distilled constant-boiling acid contained in a Pyrex weight pipette to a known weight of conductivity water contained in a large weighing bottle. The stock solution of benzenesulphonic acid was prepared by adding a suitable quantity of Kahlbaum's acid as rapidly as possible (this is necessary owing to its extremely hygroscopic character) to a known weight of conductivity water, the increase in weight giving the weight of acid employed. The concentration of the stock solution was calculated from the known purity and the weight employed, and was also determined by direct titration with standard baryta : the results agreed to within 0·1%. All the stock solutions for runs in the silica conductivity cell were made up in a silica weighing bottle, provided with a ground-in silica stopper, of 250 c.c. capacity. For the runs in the Pyrex cells, Pyrex vessels were exclusively employed.

*Conductivity Cells.*—A cell of the Hartley and Barrett type (J., 1913, **103**, 789), constructed entirely of silica, was employed. The two grey platinum plates were held at a constant distance apart by means of four thin silica rods passing through holes in the four corners of the plates. For the runs in Pyrex, cells S and V (Part IV, *loc. cit.*) were used. The conductivity of the water was measured in a small cell of the Kohlrausch type.

*Cell Constants.*—These were determined by measuring the resistance of aqueous solutions of potassium chloride prepared with equilibrium water at 25° over the range 0·0001—$0·008N$ ; the values of the specific conductivity at the concentrations used were calculated from the formula $\Lambda_c = 149·83 - 101·6C^{0·547}$ deduced in Part IV. Two typical sets of results of independent determinations for the silica cell are given below.

| $C \times 10^4$. | Cell constant. | $C \times 10^4$. | Cell constant. |
|---|---|---|---|
| 1·821 | 0·026748 | 1·514 | 0·026754 |
| 6·178 | 0·026752 | 6·606 | 0·026747 |
| 23·79 | 0·026738 | 18·70 | 0·026751 |
| 42·34 | 0·026755 | 48·12 | 0·026756 |
| 64·42 | 0·026737 | 82·31 | 0·026746 |
| Mean | 0·026746 | Mean | 0·026750 |

The mean value employed in the calculations was $0·02674_8$. The cell constants for the two Pyrex cells S and V were $0·03422_8$ and $0·02781_5$ respectively, and for the Kohlrausch cell 0·2390.

*Measurement of Conductivity.*—The technique was similar to that described by Jeffery and Vogel (J., 1931, 1723). Successive additions of weighed amounts of the stock solution were made—for the acids a silica weight pipette was employed—to a known weight of water in the cell, and the resistance was determined after each addition. The cell was immersed during the measurements in an electrically controlled thermostat constant to ± 0·01°, the first readings being taken after two hours' immersion.

*Solvent Correction.*—No correction was applied for the acids. The specific conductivity of the water used was subtracted from the measured specific conductivity for the solutions of sodium benzenesulphonate.

*Calculation of the Concentrations.*—All the concentrations are expressed in g.-mols. per litre of solution at the temperature at which the run was carried out, and were computed as described in Part IV (*loc. cit.*).

*Results.*—The following tables give the experimental values of the equivalent conductivity, $\Lambda_c$ obs., of the substances investigated at various concentrations $C$, expressed in g.-equivs. per litre. Entirely independent stock solutions were used for each series of measurements of the same electrolyte. The letters S and V refer to the Pyrex cell employed. The mean values of $\Lambda_0^n$, evaluated from the equation $\Lambda_0^n = \Lambda + BC^n$, the values of the constants of which are given, are included at the head of the tables. Where the square-root relation $\Lambda_0^s = \Lambda + xC^{0 \cdot 5}$ has been applied, the values of $\Lambda_0^s$ and $x$ deduced from it are also incorporated in the table; $\Lambda_c$, calc. was obtained by the use of these constants and its difference from $\Lambda_c$, obs., is shown in the column headed "Diff."; $\kappa$ is the specific conductivity of the water used, expressed in gemmhos, and $M$ is the molecular weight.

*Iodic acid at* 25° ($M$ = 175·94).

Silica cell.

$\Lambda_0^n = \Lambda_c + 1735C^{0 \cdot 837}$; $\Lambda_0^n = 389 \cdot 99$.

| Series, etc. | $C \times 10^4$. | $\Lambda_c$, obs. | $\Lambda_0^n$.* | Series, etc. | $C \times 10^4$. | $\Lambda_c$, obs. | $\Lambda_0^n$.* |
|---|---|---|---|---|---|---|---|
| 1. | 1·606 | 381·33 | — | 2. | 1·040 | 380·30 | — |
| Sample | 4·058 | 386·21 | — | Sample | 2·236 | 384·35 | — |
| A. | 8·041 | 385·62 | 390·08 | B. | 5·454 | 386·44 | 389·66 |
| $\kappa$=0·751 | 18·21 | 381·07 | 389·91 | $\kappa$=0·766 | 11·57 | 383·05 | 389·69 |
| | 28·59 | 377·42 | 390·32 | | 24·56 | 378·92 | 390·27 |
| | 49·67 | 371·15 | (391·65) | | 33·76 | 375·60 | (391·70) |
| | 81·70 | 363·01 | (394·05) | | 56·06 | 369·14 | (391·79) |
| | 100·6 | 358·30 | (395·25) | | 85·84 | 361·99 | (394·35) |

* The values in parentheses were not employed in the calculations.

*Hydrochloric acid at* 25° ($M$ = 36·47).

Silica cell.

$\Lambda_0^n = \Lambda_c + 1380C^{0 \cdot 929}$; $\Lambda_0^n = 423 \cdot 67$.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. | 1·886 | 420·45 | — | 2. | 1·032 | 419·98 | — |
| Specimen | 8·205 | 421·71 | 423·58 | Specimen | 4·213 | 422·12 | — |
| 1A. | 17·54 | 419·78 | 423·57 | 2A. | 10·14 | 421·19 | 423·47 |
| $\kappa$=0·860 | 28·77 | 417·87 | 423·88 | $\kappa$=0·742 | 20·31 | 419·49 | 423·84 |
| | 43·50 | 415·64 | (424·48) | | 50·91 | 414·85 | (424·86) |
| | 57·89 | 414·05 | (424·55) | | 61·34 | 413·52 | (425·66) |
| | 81·70 | 412·03 | (427·87) | | 76·03 | 412·39 | (427·21) |
| | 99·14 | 410·62 | (429·58) | | 93·39 | 411·01 | (428·94) |
| 3. | 1·039 | 420·30 | — | 3. | 32·64 | 417·22 | 423·97 |
| Specimen 3. | 4·991 | 422·05 | (423·23) | Specimen 3. | 44·68 | 415·55 | (424·59) |
| $\kappa$=0·745 | 8·322 | 421·51 | 423·39 | $\kappa$=0·745 | 65·48 | 413·09 | (425·98) |
| | 19·87 | 419·42 | 423·68 | | 77·17 | 412·19 | (427·21) |

Pyrex cells.

$$\Lambda_0^n = \Lambda_c + 576{\cdot}1C^{0{\cdot}788};\ \ \Lambda_0^n = 423{\cdot}66.$$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 1. (V)<br>Specimen 1.<br>$\kappa = 0{\cdot}830$ | 0·956 | 419·01 | — | 2. (S)<br>Specimen 2.<br>$\kappa = 0{\cdot}755$ | 1·474 | 419·51 | — |
| | 5·892 | 421·53 | — | | 8·229 | 421·55 | 423·70 |
| | 13·30 | 420·33 | 423·46 | | 17·42 | 419·60 | 423·50 |
| | 31·63 | 417·40 | 423·59 | | 34·76 | 416·85 | 423·52 |
| | 50·14 | 414·99 | 423·89 | | 48·42 | 415·22 | 423·98 |
| | 66·63 | 413·05 | (424·14) | | 66·17 | 413·09 | (424·77) |
| | 88·20 | 411·57 | (425·46) | | 77·25 | 412·10 | (424·61) |
| | 99·70 | 411·10 | (426·39) | | 90·71 | 411·35 | (425·55) |

*Benzenesulphonic acid at* 25° ($M = 176{\cdot}12$ as monohydrate).

Silica cell.

$$\Lambda_0^n = \Lambda_c + 527{\cdot}1C^{0{\cdot}740};\ \ \Lambda_0^n = 385{\cdot}26.$$
$$\Lambda_0^s = \Lambda_c + 161{\cdot}4C^{0{\cdot}5};\ \ \Lambda_0^s = 387{\cdot}1.$$

| Series. | $\kappa$. | $C \times 10^4$. | $\Lambda_c$, obs. | $\Lambda_c$, calc. | Diff. | $\Lambda_0^n$. |
|---|---|---|---|---|---|---|
| 1. | 0·717 | 1·472 | 380·87 | — | — | — |
| | | 5·985 | 382·90 | 383·15 | −0·20 | 385·07 |
| | | 11·54 | 381·65 | 381·61 | +0·04 | 385·18 |
| | | 24·93 | 378·88 | 379·04 | −0·16 | 385·12 |
| | | 45·49 | 375·81 | 376·21 | −0·40 | 385·55 |
| | | 64·69 | 373·91 | 374·11 | −0·29 | (386·55) |
| | | 93·16 | 372·48 | — | — | (388·04) |
| | | 104·7 | 371·99 | — | — | (390·07) |
| 2. | 0·704 | 3·198 | 382·10 | — | — | — |
| | | 9·542 | 382·12 | 382·18 | −0·06 | 385·15 |
| | | 18·43 | 380·22 | 380·17 | +0·05 | 385·21 |
| | | 45·43 | 375·80 | 376·22 | −0·42 | 385·53 |
| | | 59·32 | 374·35 | 374·67 | −0·32 | (386·20) |
| | | 68·28 | 373·62 | 374·15 | −0·53 | (386·74) |
| | | 80·14 | 372·91 | 372·64 | +0·27 | (387·72) |
| | | 93·65 | 372·41 | — | — | (389·03) |

*Iodic acid at* 18° ($M = 175{\cdot}94$).

Silica cell.

$$\Lambda_0^n = \Lambda_c + 690{\cdot}5C^{0{\cdot}719};\ \ \Lambda_0^n = 348{\cdot}05.$$
$$\Lambda_0^s = \Lambda_c + 226{\cdot}8C^{0{\cdot}5}\ \ \ \Lambda_0^s = 350{\cdot}4.$$

| | | | | | | |
|---|---|---|---|---|---|---|
| 1. Specimen A. | 0·666 | 1·226 | 343·73 | — | — | — |
| | | 5·533 | 344·85 | 344·95 | −0·10 | 348·00 |
| | | 11·86 | 342·42 | 342·53 | −0·11 | 347·86 |
| | | 20·46 | 340·01 | 340·10 | −0·09 | 348·06 |
| | | 39·50 | 335·15 | 336·10 | −0·95 | 348·06 |
| | | 57·32 | 331·69 | — | — | (348·57) |
| | | 74·75 | 328·10 | — | — | (348·52) |
| | | 94·97 | 324·71 | — | — | (348·78) |
| 2. Specimen B. | 0·595 | 1·990 | 344·21 | — | — | — |
| | | 7·915 | 343·90 | 343·98 | −0·08 | 347·97 |
| | | 16·72 | 341·12 | 341·08 | +0·04 | 348·08 |
| | | 32·78 | 336·71 | 337·37 | −1·38 | 348·00 |
| | | 47·17 | 333·40 | — | — | 348·07 |
| | | 66·91 | 329·52 | — | — | 348·38 |
| | | 80·89 | 326·99 | — | — | (350·87) |
| | | 100·2 | 324·01 | — | — | (353·96) |

*Sodium benzenesulphonate at* 25° ($M$ = 180·10).

$$\Lambda_0^n = \Lambda_c + 240{\cdot}8C^{0{\cdot}711};\quad \Lambda_0^n = 86{\cdot}33$$
$$\Lambda_0^s = \Lambda_c + 60{\cdot}8C^{0{\cdot}5};\quad \Lambda_0^s = 86{\cdot}58 \quad \ldots\ldots (6)$$
$$\Lambda'^s_0 = \Lambda_c' + 73{\cdot}0C^{0{\cdot}5};\quad \Lambda'^s_0 = 86{\cdot}88 \quad \ldots\ldots (7)$$

| Series. | $\kappa$. | $C \times 10^4$. | $\Lambda_c$, obs. | $\Lambda_c$, calc. | Diff. | $\Lambda_c'$, calc.* | Diff. | $\Lambda_0^n$. |
|---|---|---|---|---|---|---|---|---|
| 1. (V) Specimen 1. | 0·742 | 1·814 | 85·87 | 85·76 | +0·11 | 85·90 | −0·03 | 86·40 |
| | | 6·535 | 85·10 | 85·03 | +0·07 | 85·01 | +0·09 | 86·40 |
| | | 13·16 | 84·16 | 84·38 | −0·22 | 84·23 | −0·07 | 86·31 |
| | | 27·80 | 82·50 | — | — | — | — | 86·15 |
| | | 45·67 | 81·10 | — | — | — | — | 86·31 |
| | | 59·99 | 80·30 | — | — | — | — | 86·63 |
| | | 88·70 | 79·40 | — | — | — | — | (87·76) |
| | | 112·9 | 79·11 | — | — | — | — | (89·03) |
| 2. (S) Specimen 1. | 0·717 | 1·348 | 85·99 | 85·87 | +0·12 | 86·03 | −0·04 | 86·42 |
| | | 7·169 | 85·01 | 84·95 | +0·06 | 84·92 | +0·09 | 86·41 |
| | | 17·11 | 83·67 | 84·06 | −0·39 | 83·86 | −0·19 | 86·26 |
| | | 35·10 | 81·86 | — | — | — | — | 86·18 |
| | | 48·98 | 80·79 | — | — | — | — | 86·27 |
| | | 66·74 | 80·04 | — | — | — | — | (87·03) |
| | | 77·76 | 79·59 | — | — | — | — | (87·20) |
| | | 95·39 | 79·19 | — | — | — | — | (87·89) |
| 3. (V) Specimen 2. | 0·832 | 3·460 | 85·55 | 85·45 | +0·10 | 85·52 | −0·03 | 86·38 |
| | | 11·30 | 84·41 | 84·52 | −0·09 | 84·43 | −0·02 | 86·39 |
| | | 26·77 | 82·60 | 83·43 | −0·83 | 83·10 | −0·50 | 86·16 |
| | | 35·46 | 81·86 | — | — | — | — | 86·21 |
| | | 47·43 | 81·04 | — | — | — | — | 86·39 |
| | | 65·07 | 80·13 | — | — | — | — | (86·83) |
| | | 92·43 | 79·38 | — | — | — | — | (87·99) |

* $\Lambda_c$, calc. and $\Lambda_c'$, calc. are computed from equations (6) and (7) respectively.

*$\Lambda_c$ at Round Concentrations.*—The values of the equivalent conductivity at round concentrations are given in Table II. Interpolation was carried out on a $\Lambda$–$C$ graph drawn with a flexible spline.

TABLE II.

| $C \times 10^4$. | $HIO_3$ (25°). | $HIO_3$ (18°). | HCl. | $C_6H_5{\cdot}SO_3H$. | $C_6H_5{\cdot}SO_3Na$. |
|---|---|---|---|---|---|
| 1·0 | — | — | — | — | 86·03 |
| 5·0 | 386·74 | 345·09 | 422·18 | 383·22 | 85·33 |
| 10·0 | 384·38 | 343·28 | 421·12 | 381·95 | 84·57 |
| 20·0 | 380·30 | 340·15 | 419·21 | 379·78 | 83·33 |
| 30·0 | 376·89 | 337·42 | 417·56 | 378·00 | 82·34 |
| 40·0 | 373·67 | 334·97 | 416·13 | 376·52 | 81·48 |
| 50·0 | 370·76 | 332·79 | 414·87 | 375·33 | 80·80 |
| 60·0 | 368·25 | 330·82 | 413·78 | 374·35 | 80·29 |
| 70·0 | 365·78 | 328·98 | 412·81 | 373·53 | 79·87 |
| 80·0 | 363·34 | 327·21 | 411·96 | 372·85 | 79·53 |
| 90·0 | 360·96 | 325·54 | 411·19 | 372·29 | 79·26 |
| 100·0 | 358·64 | 323·92 | 410·53 | 371·32 | 79·07 |

The still for the preparation of equilibrium water and moderate-grade conductivity water described in Part III (J., 1931, 1201) was developed from one employed in the earlier work at the Imperial College, London, which was worked as a Bourdillon still (J., 1913, **103**, 791). The principle of fractional distillation to yield two grades of *conductivity water* was not realised at that time and the action of the early still was erratic, the conductivity of the water produced varying considerably from day to day. My best thanks are tendered to Professor J. C. Philip, F.R.S., for the loan of the still used in the early work (J., 1929, 1476) during 1926—29. (A. I. V.)

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