

Research on the Electrometric determination
of the hydrolysis of salts by means of
the hydrogen electrode and of the
quin-hydroquinone electrode

Morris, N.R.

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RESEARCH ON THE ELECTROMETRIC DETERMI-
INATION OF THE HYDROLYSIS OF SALTS
BY MEANS OF THE HYDROGEN ELECTRODE
AND OF THE QUIN-HYDRONE ELECTRODE,
WITH SPECIAL REFERENCE TO THE ANOMALOUS
BEHAVIOUR OF SOLUTIONS OF ZINC SULPHATE.

INTRODUCTION.

Many methods have been described for the determination of the degree of hydrolysis of salts. The following may be given as examples of the more important of these:-

- I. Measurement of the rate of inversion of sugar, as used by:-

H. Ley (Zeit. Physikal Chem., 1899, 30, 193-257),

L. Bruner (Zeit. physikal Chem. 1900, 32, 133-136),

H. Long (J. Amer. Chem. Soc., 1896, 18, 120 & 693),

Walker and Aston (J. Chem. Soc. 1895, 67, 576-586),

C. Kullgren (Bihang. K. Svenska-Vetensk-Akad, Handl., 1900, 25, ii, NO. 2, 1-34),

Armstrong and Grothers (Proc. Roy. Soc., 1908, 81, A, 102-112).

- II. Measurement of the rate of Saponification of Ethyl, or Methyl Acetate:-

J. Shields (Phil. Mag., (5), 35, 365-388).

G. Carrara and G. B. Vespignani, (Gazzetta, 30, ii, 35-63),

H. Ley (Zeit. Physikal Chem., 1899, 30, 193-257),

Walker, (Zeit. physikal, Chem. 1889, 4, 321),

Armstrong and Grothers (Proc. Roy. Soc. 1908,

81, A, 102-112),

H. H. Beveridge (Proc. Roy. Soc. Edin. 1909, 29,
648-667),

III. Determination of Electrical Conductivity:-

Walker (Zeit. physikal. Chem. 1889, 4, 333),

Bredig (Zeit. physikal. Chem. 1894, 13, 317),

H. Lundén (J. Chim. Phys., 1907, 5, 574-608),

E. G. Hill (J. Chem. Soc., 1906, 89, 1273),

H. H. Beveridge (Proc. Royal Soc. Edin. 1909, 29,
648-667),

Stieglitz and Derby, (Amer. Chem. J., 1904, 31, 449-458),

R. Salvadori (Atti Real Accad. Lincei, 1900 (V), 9,
11, 177-180),

Kowalewsky (Zeit. Anorg. Chem. 1900, 23, 1-24),

F. Kohlrausch (Zeit. physikal. Chem. 1900, 33, 257-279),

Carrara and Vespignani, (Gazzette, 30, 11, 35-63),

H. Ley (Zeit. physikal. Chem. 1899, 30, 193-257),

IV. Electrometric determination of Hydrogen ion concentration by Hydrogen Electrode:-

H. G. Denham (J. Chem. Soc. 1908, 93, 41-63),

V. Determination of Freezing Point:-

Kahlenberg, Davis and Fowler (J. Amer. Chem. Soc.
1899, 21, 1-23),

VI. Distillation of Solutions:-

Naumann and Wicker (J. pr. Chem. 1906 (11), 74,
249-275),

Naumann and Müller (J. pr. Chem. 1906, (11), 74,
218-221).

VII. Dilatometric considerations:-

G. Galeotti, (Zeit. physikal. Chem. 1911, 76, 105-126).

VIII. Solubility of Carbonates in water in atmosphere of Carbon Dioxide:-

Agono and Valla (Atti R. Accad. Lincei, 1911 (V), 20, 11, 706-712).

IX. Partition of base between two immiscible solvents.

X. Measurement of Heats of Neutralisation:-

Valley (Trans. Faraday, Soc., 1908, 4, 19-26).

XI. Measurement of the Motion of Ions:-

Denison and Steele (J. Chem. Soc. 1906, 89, 999).

XII. Decomposition of diazoacetic ester by hydrogen ions

Bredig and Fraenkel, (Zeit. Elektro-Chem., 11, 525, 1907).

A consideration of these various methods shows that, while some show reasonable agreement with others, yet in other methods the results do not agree satisfactorily.

H. H. Beveridge (Proc. Roy. Soc. Edin. 1909, 29, 648-667), has shown that the results obtained by the measurement of the rate of saponification of methyl acetate and by the measurement of electrical conductivity are not in agreement. He found "That those methods of determining the hydrolysis which depend directly on the concentration of the hydrogen ion agree fairly well with one another. Such

methods examined were the catalysis of methyl acetate, and of ethyl diazoacetate, and the difference of potential method. Other methods involving the solubility of the amphoteric base in acid solutions of different concentrations and the partition of the base between two immiscible solvents, lead to the same value. On the other hand, the more indirect methods depending on electrical conductivity and freezing point measurements lead to different values for the degree of hydrolysis."

Naumann and Rucker (J. pr. Chem. 1906 (ii), 74, 209-217), give a résumé of the methods which have been described by various authors for the estimation of the degree of hydrolysis of salts in aqueous solution.

It may therefore be reasonably assumed that the more direct the method of determination of hydrolysis, the more reliable are the results. This is what would naturally be expected.

This thesis is the embodiment of an attempt to determine, by one of the more direct means, the hydrolysis of certain salts.

H. G. Denham (J. Chem. Soc. 1908, 93, 41-63), showed that the hydrogen electrode could be used successfully to determine electrometrically the hydrolysis of salts, even in cases where the hydrogen ion concentration was

very low (0.3×10^{-6}). The results obtained show good agreement with the results obtained by other methods. In the case of some salts, however, it was found that for some reason or another the method was unsuitable.

Concerning the estimation of the degree of hydrolysis of zinc sulphate, he says (loc. cit. page 62), "the time experiment for this salt was, as usual, carried out with every precaution against chance impurities, but, although various solutions were measured daily for four weeks, yet no sign appeared of an equilibrium having been reached, the hydrogen ion concentration varying irregularly from day to day."

These results he also obtained later (Zeit. Anorg. Chem. 57, 378, 1908).

Various suggestions have been put forward to account for such anomalous behaviour,

e.g.: 1. Colloidal formation (Denham, J. Chem. Soc., 93, 41, 1908).

2. Reduction of the zinc to a monovalent state as has been shown to take place with lead salts (H. G. Denham J. Chem. Soc. 93, 424, 1908).

3. Theory of formation of ion hydrates, as developed by Jones (Amer. Chem. Journ. 1905, 34, 291), Washburn (Journ. Amer. Chem. Soc. 1909, 31, 322;

1915, 37, 694), and Washburn and Bruyn (Rec. Trav. Chem. 1903, 22, 430). Ion hydrates are ions in which N molecules of water have attached themselves to the ions, thus:-

4. Formation of complex zinc ions, Kummell (Ann. Phys. Chem., 1898, 11, 64, 655-679).

The peculiar behaviour may be due to the influence of any one of these or to the combined influences of any two or more of them. Also it may be due to one of the many possible causes not suggested here.

With a view to ascertaining if possible, whether this anomalous behaviour, particularly of zinc sulphate solutions, was due to the electrolyte or to the electrode used, it was thought advisable to test the zinc sulphate solutions with an electrode which has been described in recent years viz. the Quin-Hydrone Electrode, Binar Billmann (Ann. Chim. 1921, (IX) 15, 109-157). If this electrode gave results similar to the results given by the hydrogen electrode, then the experiment would either be inconclusive or indicate that the anomalous behaviour was due to the zinc sulphate solutions. On the other hand, if the solutions exhibited normal behaviour in the Quin-Hydrone electrode, it would be strong evidence to show that the

abnormalities were due to the hydrogen electrode.

The hydrogen electrode is also unsuitable for the determination of hydrolysis of those salts which would be in any way reduced by the hydrogen of the electrode. Here again it was possible that the Quin-Hydrone Electrode, with its very small solution pressure of hydrogen of -23.34 10 of an atmosphere would be of service.

From these considerations, coupled with the fact that the degree of hydrolysis of copper sulphate has been correctly determined by the use of the Quin-Hydrone electrode (J. B. O'Sullivan Trans. Faraday Soc. XXI, 1925-26, 319-325) this thesis developed.

The Quin-Hydrone Electrode.

A resume of investigations that have involved the Quin-Hydrone Electrode, would not be out of place here. The accuracy, reproductability, convenience, reliability, and general trustworthiness of this electrode are amply proved by the researches of the following investigators:-

Einar Billmann (Ann. Chim., 1921 (IX), 15, 109-157;
Trans. Faraday Soc., 19, 1924, 676-690).

W. Ackermann (Collegium, 1926, 208-211).

A. Hock, (Z. Angew Chem., 1926, 36, 647).

I. M. Kalthoff, (Z. Physial Chem., 1925, 144, 259-271
Rec. trav. Chim. 42, 186-198, 1923).

La Mer and Parsons (J. Biol. Chem. 57, 613-631, 1923
Proc. Soc. Exptl. Biol. Med. 20, 239-243, 1923).

A. Pelling, (J. Chem. Met. Soc. S. Afr., 1925,
26, 88-93.)

This electrode has a wide range of uses. The re-
searches of the following indicate some of its uses,
besides giving further evidence to show the accuracy
and trustworthiness of the method.

Granger and Nelson (Journ. Amer. Chem. Soc., 1921,
43, 1401.)

Billmann and Lund, (Ann. Chim, 16, 321, 1921.)

Sørensen and others (Ann. Chim, 16, 283-320).

A. Schreiner, (Z. anorg. Chem. 1922, 122, 201-235)

Stig. Veibel, (Journ. Chem. Soc., 123, 2203-7,
(1923)).

L. J. Harris, (Journ. Chem. Soc. 123, 3294, (1923)

I. M. Kolthoff) Rec. trav. Chim., 1923, 42,
186-198).

Le Mer and Parsons, (J. Biol. Chem., 1923, 57,
613-631).

Schaefer and Schmidt, (Biochem. Z., 1925, 156,
63-79).

H. Mislowitz, (Biochem. Z., 1925, 159, 72-76,
and 77-97).

C. Brioux and J. Pien (Compt. rend., 1925, 181,
141-143).

Cullen and Billmann (J. Biol. Chem. 1925, 64,
727-738).

Niklas and Hook, (Z. anorg. Chem. 1925, 38,
407-409).

L. R. Wagener and W. J. McGill, (J. Amer. Pharm. Assoc., 1925, 14, 288-94).

L. D. Bayer (Soil. Sci., 1926, 21, 167-179).

D. J. Hissink and J. Van Der Spek, (Verhdl. Zevaiten Komm. int. bodenk. Ges. 1926, Sept., 12 P.P; Chem. Zentr. 1926, I, 3099).

J. B. O'Sullivan, (Trans. Faraday Soc., 21, (1925-6), 319-325).

Pring, (Trans. Faraday Soc., 21, (1925-26), 705-717).

Cray and Westrip, (Trans. Far. Soc., 21, 326-337).

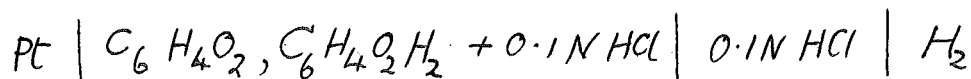
Billmann (Trans. Far. Soc., 19, 1924, 676-690; Bull. Soc. Chim., 41, (1927), 231-286).

In these researches the Quin-Hydrone electrode has been used, among other things, for determination of the hydrogen ion concentration, or PH value, of solutions of salts, soils, blood, serum, alkaloids, milk and milk products, gastric sugars, etc.

The following is a brief account of the Quin-Hydrone Electrode (Einar Billmann; J. Soc. Leather Trades' Chemists, 5, 27-31, 1921).

By dipping a piece of Platinum foil in an acid solution of Quin-Hydrone, which is largely dissociated in aqueous solution into quinone, $(C_6H_4O_2)$, and hydroquinone, $(C_6H_4O_2H_2)$, an electrode is formed which may

be combined with an ordinary hydrogen electrode to form an element:-



In the reactions of this element 2 hydrogen ions disappear in the Quin-Hydrone electrode, and one molecule of quinone is hydrogenated to hydroquinone. The hydrogen ion concentration of the electrode is proportional to the concentration of hydroquinone and inversely proportional to the concentration of quinone, and the potential of the element is independent of the absolute concentrations. The potential of such an element with an equal hydrogen ion concentration at both electrodes is at 25° C, 0.6990 volts, and the hydrogen pressure of the Quin-Hydrone electrode is at 25° C., $10^{-23.34}$ atmosphere.

AIMS OF WORK.

The direct aims of the work are therefore the following:-

I. To determine, if possible, by means of the Quin-Hydrone Electrode, the degree of hydrolysis of the salts:-

Zinc Sulphate, $ZnSO_4$,

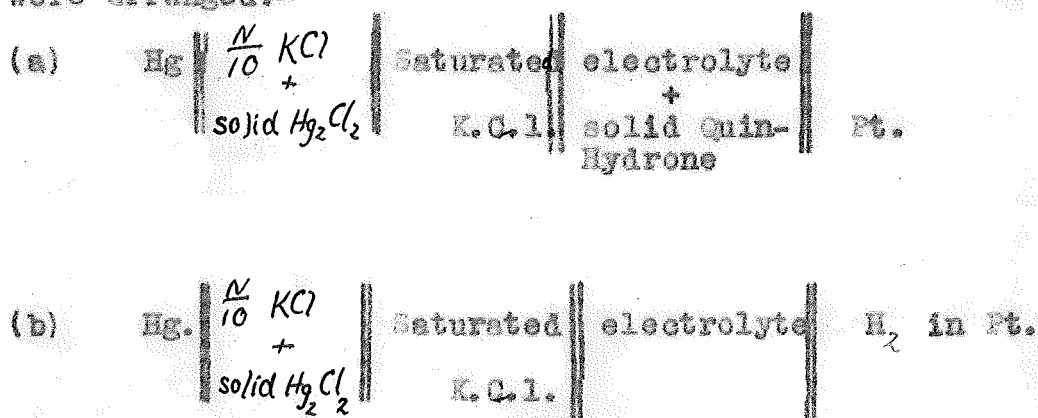
Cadmium Sulphate, $CdSO_4$,
 Lead Chloride, $PbCl_2$,
 Lead Nitrate, $Pb(NO_3)_2$,
 Thallous Sulphate, Tl_2SO_4 ,
 Silver Nitrate, $AgNO_3$,
 Potassium Chromate, K_2CrO_4 ,

II. To show that the hydrogen electrode is unsuitable for such determinations with solutions of:-
 Zinc Sulphate,
 Cadmium Sulphate.

III. To investigate the anomalous behaviour of zinc sulphate solutions in the hydrogen electrode.

METHOD.

In finding the degree of hydrolysis of salts, composite, "unknown" cells of the following types were arranged:-



Type (a) employing the Quin-Hydrone electrode and type (b), the hydrogen electrode. The electromotive force (E.M.F), of the cells were determined, and from the values found, the hydrogen ion concentrations, and hence the degrees of hydrolysis were calculated.

APPARATUS.

Figure I, page 13, shows the general arrangement of the apparatus (c.f., Spencer, "Physical Chemistry", Vol. II, p. 106). The method employed is that due to Poggendorf and generally known as the "Compensation" method.

The circle B represents a thermostat which is maintained at 25° C. by a gas flame, which is controlled by a toluene-mercury regulator, shown at R. The temperature did not vary more than $\pm 0.1^\circ$ C., and usually did not vary more than $\pm .01^\circ$ C. during a series of measurements. H represents the hydrogen or the Quin-Hydrone electrode which constitutes the unknown half element of the cell; E represents the "middle" vessel for the annulling of liquid contact potential, difference between the two half elements; C is the $\frac{N}{10}$

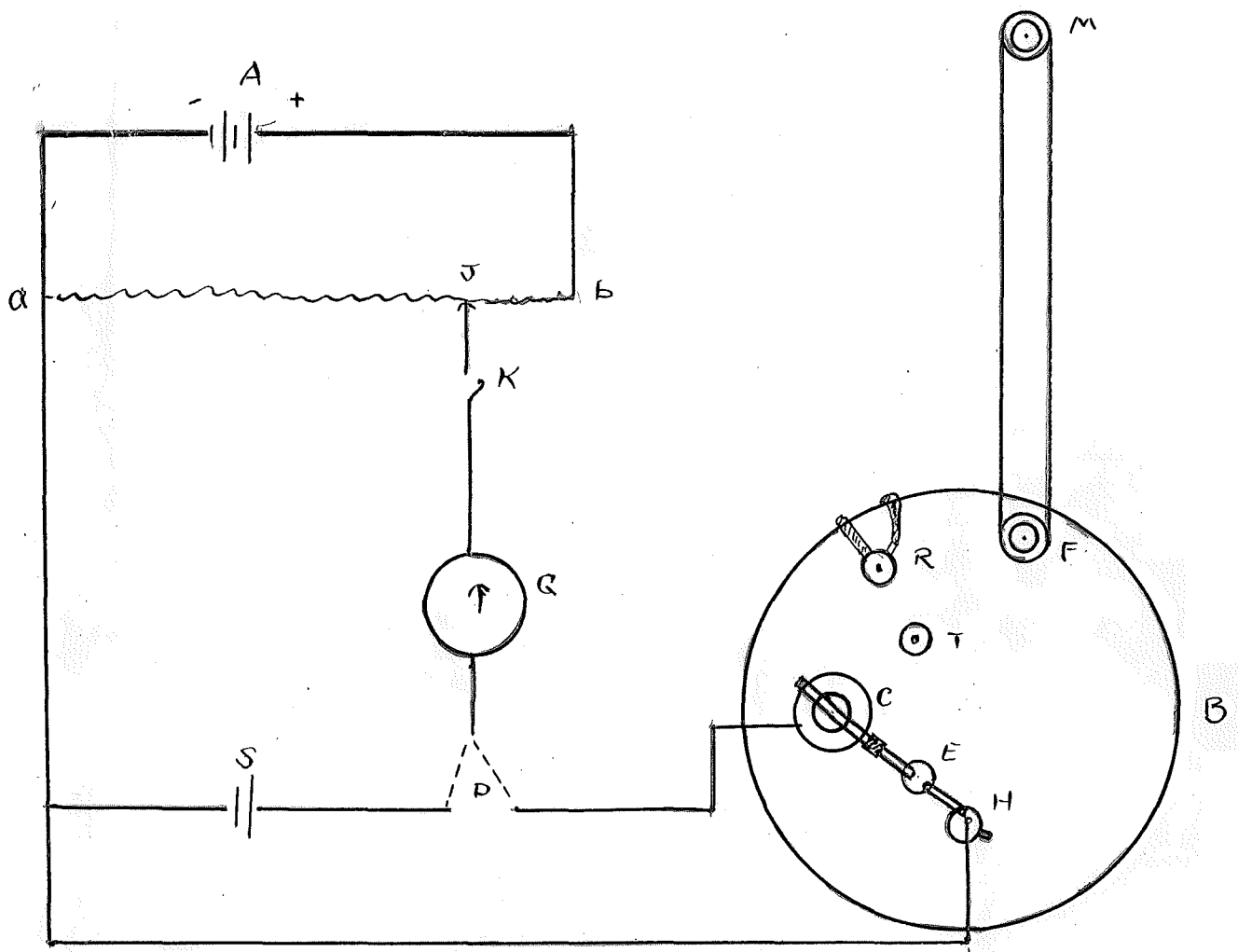


FIGURE. I.

Calomel electrode. Thus the whole of the composite cell was kept in the thermostat. The temperature of the thermostat was shown by the thermometer T. A stirrer, F, driven by a motor, M, ensured even temperature throughout the thermostat. For the ultimate standard of E.M.F. a standard Cadmium (Weston) cell was used, shown at S. A two-volt accumulator, A, was connected to the two ends of a 100 cm. bridge wire, ab, to give a constant potential gradient along it. Contact is made with ab, by ^{the} sliding bridge contact J; G is a Leeds and Northrup galvanometer with a moving coil, and sensitive to 0.05 millivolt. K is a tapping key, and D is a two way switch for throwing either the standard cell or the composite cell into circuit.

DETAILS OF APPARATUS.

Calomel Electrode: A decinormal calomel electrode of the type shown in Figure II, p. 15, was used throughout. This electrode was prepared as described in Spencer, "Physical Chemistry" Volume II, p. 122. This form of calomel electrode is less likely to give inaccurate results than the usual types, for it is

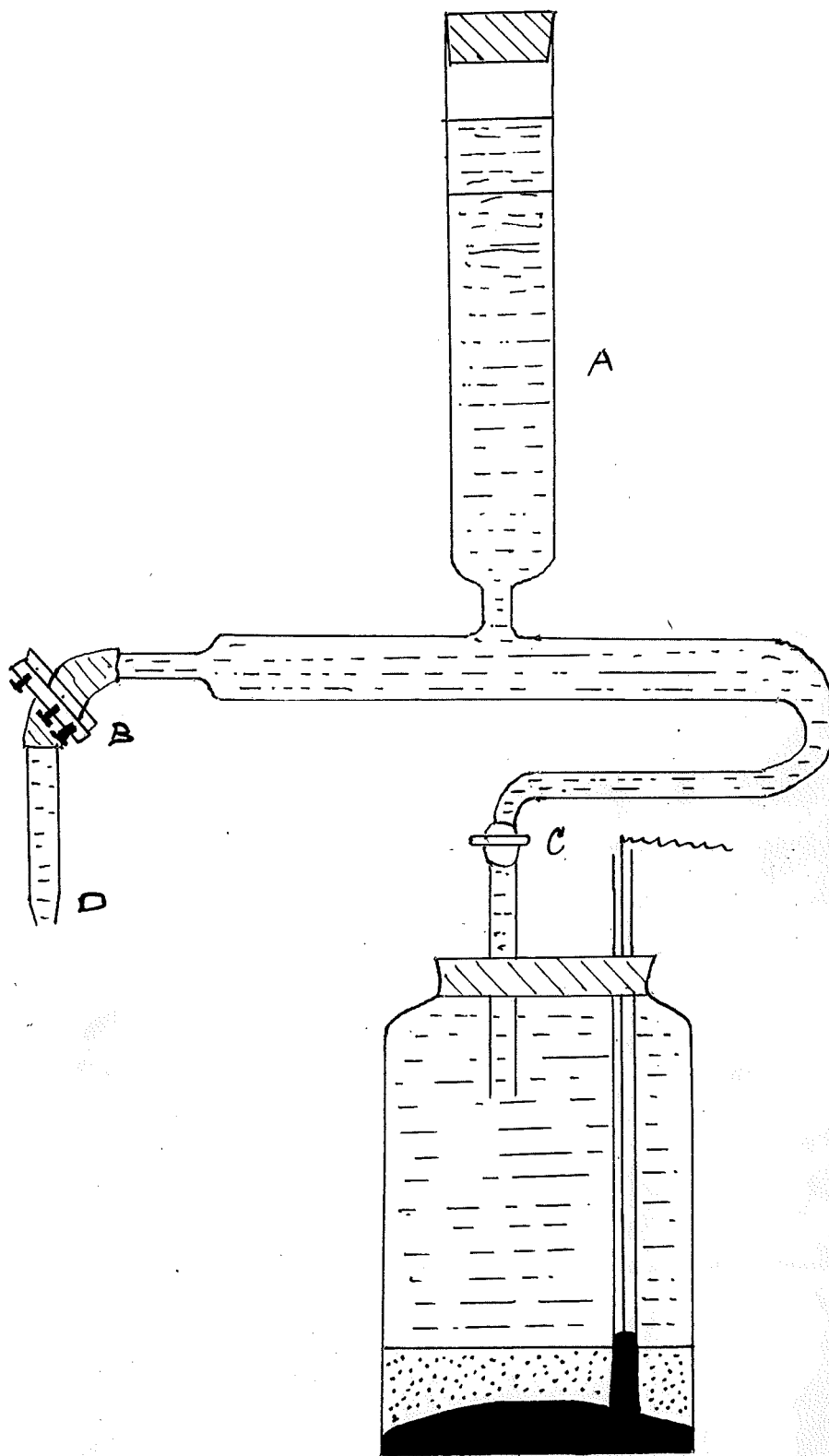


FIGURE II

nearly impossible for the liquid in the cell to become contaminated with other liquids which may diffuse back from the contact vessel. The connecting tube can also be readily washed out by pouring potassium chloride through the vestical tube A. The screw cock at B was kept closed except during an actual measurement, while the stop cock at C was always kept closed, but before a measurement was taken, it was well moistened and lubricated with the potassium chloride solution. D is the nozzle to middle vessel.

The value assigned to the N/10 calomel was that obtained from one of the more recent standard text books, viz. Clark "Determination of Hydrogen Ions", 1925, p.285. At 25° C. the value of the tenth normal calomel measured against the normal hydrogen electrode is 0.3376 volts. This value, referred to normal hydrogen electrode, was the one generally used. If the value of N. hydrogen electrode is taken as +0.277 volts (Lewis, Physical Chemistry, Vol. II, p. 189), then 'absolute' value of calomel would be 0.6146 volts. This electrode was used only at the temperature 25° C.

It was checked against other calomel electrodes in the laboratory, and the agreement was satisfactory.

Standard Cell. This was a Leeds and Northrup Standard Cadmium Cell, and the values assigned it were taken again from the same authority, Clark, (ibid p. 223).

"As a result of co-operative measurements by the National Laboratories of England, France, Germany, and the United States, the value 1.01830 international volts at 20° C. was assigned to the "normal" Weston Cell. Values for other temperatures are taken from the same publication (loc. cit. p. 223).

Accumulator: A quarter of an hour before readings were taken, the accumulator was put in circuit to enable it to attain a fairly constant potential.

"Middle" Vessel. According to the electrolyte used the middle vessel was filled, either with saturated potassium chloride solution or with saturated ammonium nitrate solution, in each case to annul liquid contact potential; the first on the authority of Spencer (Physical Chemistry Vol. II, Chap. VI), O'Sullivan, (Trans. Faraday Soc., 21, 1925-26, 319) and Pring (Trans Faraday Soc., 19, 1924, 712), the second on the authority of Abegg and Cumming (Zeitschr. Electrochem,

1907, 13, 17). To minimise leakage of potential from the middle vessel to the thermostat, the vessel was smeared at the top, inside and outside, with vaseline.

Hydrogen Electrode: Figure III a, p. 19 shows the type of hydrogen electrode used, and known as the Luther-Brislee type. It can be prepared as described by Spencer (Physical Chemistry, Vol. II, p. 140 et seq.) The diagram shows the actual size. Tube A was for incoming hydrogen, tube B conducted the hydrogen away, tube C was for connection with the middle vessel. The stopcock D was kept closed, but during readings was well lubricated with the electrolyte. A platinum wire, E, coated with platinum black, served for the electrode. External connection was made by means of a copper wire dipping into a mercury cup at F. The hydrogen gas used was obtained from the action of pure zinc on pure dilute sulphuric acid. It was purified by bubbling successively through potassium wash bottles (refilled as used), containing respectively, alkaline potassium permanganate, saturated mercuric chloride, silver nitrate and then through a solution of the electrolyte being examined. This last wash bottle was placed in

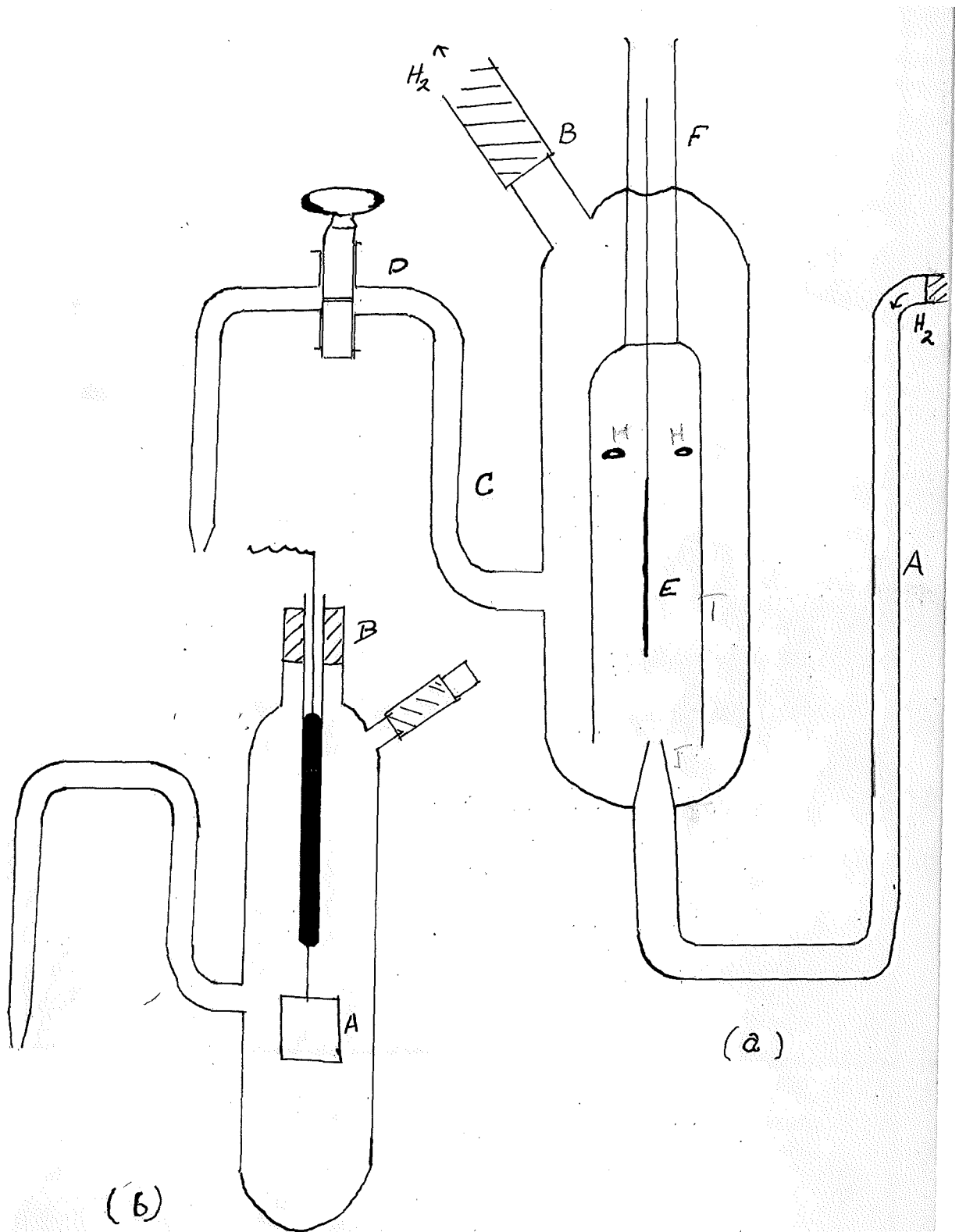


FIGURE III

in the thermostat to prevent cooling etc. of the solution in the electrode, a variable effect depending on the rate of gas. When the gas was led away from the electrode it was bubbled through a water trap to prevent diffusion of air into the electrode vessel.

The platinum wire was coated with platinum black according to the method of Spencer (ibid p. 55). Before readings were taken the gas was allowed to bubble through for about fifteen minutes to ensure stable potential, where possible. In that time also the electrode had taken on the temperature of the thermostat.

Quin-Hydrone Electrode: For this electrode the type of vessel usually employed for measuring single potential differences was used. In figure III b, the general appearance and actual size of the vessel and electrode are shown.

The electrode was of platinum blank. Reference to the literature shows that the actual size appears to be immaterial, and various sizes have been used. Biilman (Bull. Soc. Chim, 41, 1927, 213-286) used a piece of platinum 7 mm x 30 mm, O'Sullivan (Trans. Far. Soc., 21, 1925-26, 319) used 7 mm x 6 mm, and Pring,

(Trans. Far. Soc., 19, 1924, 712) used a piece "about 1 cm x 2 cm". For the purposes of convenience, and of having a standard size the electrodes used in this work were of size, one square cm. This electrode (A in the figure) was welded to a piece of platinum wire, which wire was fused into a piece of glass rod. A rubber stopper, B, held the glass rod (c.f. Pring, loc. cit.). Electrical connection was made by means of a mercury contact. To set the electrode for a measurement about 15 c.c. of the solution to be examined was introduced into the potential vessel, and about 0.05 gms. of solid Quin-Hydrone was added from a scoop; the electrode was placed in the vessel, and the whole was shaken for half a minute, (c.f. O'Sullivan loc. cit.). The concentration of Quin-Hydrone used is about the same as that recommended in the literature, Billmann (J.A.C.S., 1921, 15, 2, 2074), and Bayer (Soil, Sci. 1926, 21, 167-179). Electrical connection was made with the middle vessel and the potential vessel was lowered into the thermostat, and left to attain the temperature of the bath. Stable potentials were usually established in two or three minutes. It was assumed that diffusion did

not take place from the middle vessel, but even if such was the case it must necessarily have been slight for constant potentials were obtained for several hours with each electrolyte. As a check on the work two complete Quin-Hydrone electrodes, designated A and B, were fitted up, and all measurements taken in duplicate. The agreement in practically every case was satisfactory, and in some cases the two values were identical.

Various experimenters have shown that the Quin-Hydrone electrode as described above has limitations. Biilmann (Bull. Soc. Chim. 41, 1927, 213-286), L. J. Harris (J. Chem. Soc., 1923, 123, 3294), and others have shown that it can not be used for solutions having a PH value greater than 8 to 8.5, i.e., in alkaline solutions. Similarly, Biilmann and Lund¹ (J.C.S., 122, 2, 192¹, 111), Sørensen and others (Ann. Chim., 16, 1921, 283-320) and other workers have shown that concordant results are not obtained and that there is a "salt" error if the concentration of the electrolyte is greater than 0.1 N to 0.5 N. The pH values of all solutions used were on the acid side of PH = 8, and the concentrations of all solutions

were not greater than 1/16 molar normal.

The information in the two following sections came to hand, in the form of Abstracts, (British Chemical Abstracts, A) too late to be of use in this work, and for the possibility mentioned, if present, to be avoided.

(a) Kolthoff and Bosch, (Biochem. Z., 1927, 183, 434-443), "When Quin-Hydrone, prepared by oxidation of quinol with ferric ammonium alum and washing, is stored, acid oxidation products arise, the preparation then giving, with solutions poor in buffer, a much too acid reaction. Such preparations give good results if carefully washed. Quin-Hydrone prepared by Valeur's methods gives readily reproducible results."

Directly opposed to this is the following section:- (b) E. Biilmann and Jensen (Bull. Soc. Chim. 1927, IV, 41, 151-166). The mode of preparation and the age of the Quin-Hydrone have no essential influence on the electrode potential. Slight impurities in the Quin-Hydrone have only a very small influence

on the E.M.F. Reproducible values for the E.M.F. of the cell composed of Quin-Hydrone and Hydrogen Electrodes are obtained when the Quin-Hydrone is 0.00016 M, and above.

The evidence is thus conflicting. In this work the sample of Quin-Hydrone used was provided by the British Drug House; but no indication was given as to ^{mode of} its preparation. A brief experiment seemed to show that the change in E.M.F., due to washing the Quin-Hydrone, was within the experimental error. Another check on the sample used was that the results obtained by the Quin-Hydrone electrode and by the hydrogen electrode, where both were used, were in satisfactory agreement.

After a measurement the vessel and electrode were thoroughly washed with distilled water. The potential vessel was dried by warming carefully and drying with an air pump. The electrode was dried with filter paper, as recommended by Cray and Westrip. (Trans. Faraday Soc., 21, 1925-26, 326). Before using again, the vessels and electrodes were rinsed twice with the new solution.

METHOD OF MAKING MEASUREMENTS.

The experimental potential vessel was filled as described above. In the case of the hydrogen electrode the vessel was filled till the solution came about two-thirds the way up the platinum black section of the wire electrode. Connection was made with the middle vessel, and the electrode was lowered into the thermostat and left to attain the temperature of the bath. The calomel electrode, which was also in the thermostat, was placed in the circuit by introducing the nozzle D (Figure II) into the middle vessel, care being taken that no bubbles of air obstructed the passage of the current. Figure I shows the remainder of the electrical connections. Care was taken to ensure good contacts by having clean tight connections.

When the accumulator had been in circuit for 15 minutes, and time had been allowed for the electrodes to obtain the temperature of the thermostat, and to attain constant potentials, where possible, the standard cell was put in circuit and its temperature noted by a nearby thermometer. The sliding contact

on the bridge wire was then moved until the galvanometer showed no deflection. This position of the sliding contact was noted. A reading was then taken with the composite cell, Quin-Hydrone (A) + Calomel, in circuit, then a similar reading for Quin-Hydrone (B) + Calomel. Finally, another reading was taken with the standard cell in circuit to ensure that the voltage of the accumulator had not varied during the series of readings. In practically every case it was found that the accumulator had remained constant. Readings with the hydrogen electrode were conducted in a similar manner. As the value of each reading was noted, the time at which it was taken was also recorded. The intervals at which readings were taken are recorded later. When the series of readings was completed, the experimental electrodes were removed, washed, dried, and refilled with the next solution as described above, and replaced in the thermostat.

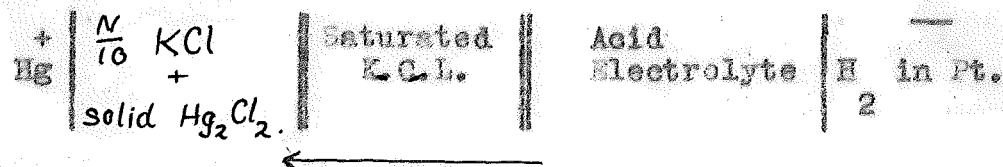
CALCULATION OF RESULTS.

Spencer, "Physical Chemistry" Vol. II, P.106, shows that the E.M.F's of the composite cell, and

the standard cell are proportional to the corresponding readings of the bridge contact at the points of no deflection. Assuming the above values for the standard cell the E.M.F. of any unknown cell is readily calculated. From this value, the calculation of the hydrogen ion concentration, and hence the degree of hydrolysis, can be considered under two heads.

I. HYDROGEN ELECTRODE.

It is assumed that liquid contact potential was annulled, and hence, that the E.M.F. of the cell was the algebraic sum of the potential differences of the two component half elements. As the potential difference (P.D.) of the calomel half element was known, that of the unknown half element was easily calculated. In this work the cells employing hydrogen electrodes were of the type:-



The calomel electrode was in practically every case positive, the current passing inside the cell from right to left. The formula used was the one commonly given, e.g. Lewis, "System of Physical Chemistry".

Vol. II, P. 188.

$$\pi_H = \pi_0 + \frac{RT}{(N)F} \log_e C_{H^+}$$

π_H = measured single electrode potential of hydrogen electrode.

π_0 = potential of hydrogen electrode immersed in a solution, normal with respect to the hydrogen ions, under one atmosphere partial pressure of hydrogen. Its value is + 0.277 volts (Lewis, loc. cit. P.189).

R = gas constant = 8.3129446 units.

F = Faraday = 96496 coulombs.

N = valency of hydrogen ion = 1.

T = temperature on absolute scale = 298° Abs. at 25° C.

C_{H^+} = required hydrogen ion concentration, in gram ions of hydrogen ion per litre. (also $[H^+]$).

$\frac{RT}{nF}$ = 0.05911 at 25° C. (with correction from base e to base 10), from Clark, (The Determination of Hydrogen Ions, P.457).

Therefore, equation reduces to:-

$$\pi_H = 0.277 + 0.05911 \log_{10} C_{H^+}$$

Therefore equation reduces to:-

$$\pi_H = 0.277 + 0.05911 \log_{10} C_H^+$$

The two examples following are given to show the actual method of working results:-

Example I.

M ZnSO₄, 1st day.
16

E.M.F. of standard = 1.0184 Volts

Reading with Standard 53.20

Reading with Hydrogen + Cal. 35.20

∴ E.M.F. of Hydrogen + Cal. = 0.6735 volts.

Measured E.M.F. = 0.6735 Volts

N Calomel at 25°C = 0.6146 "

10

∴ Value of π_H = -0.0589 "

∴ -0.0589 = +0.277 + 0.05911 log. C_H^+

∴ $\frac{-0.3358}{0.05911} = \log C_H^+$

∴ Log C_H^+ = $\frac{-5.6809}{6.3191}$

∴ C_H^+ = 2.09×10^{-6}

Example II.

$\frac{M}{32}$ $ZnSO_4$, 8th day.

E.M.F. of Standard = 1.0184 Volts

Reading with Standard = 52.03

Reading with Hydrogen + Cal. = 33.43

∴ E.M.F. of Hydrogen + Cal = 0.6539 volts

measured E.M.F. = 0.6539 "

$\frac{N}{10}$ Calomel at 25° C = 0.6146 "

∴ Value of π_H = -0.0393 "

∴ -0.0393 = +0.277 + 0.05911 $\log C_H^+$

∴ $\frac{-0.3163}{0.05911}$ = $\log C_H^+$

∴ $\log C_H^+$ = -5.3510

= 5.6490

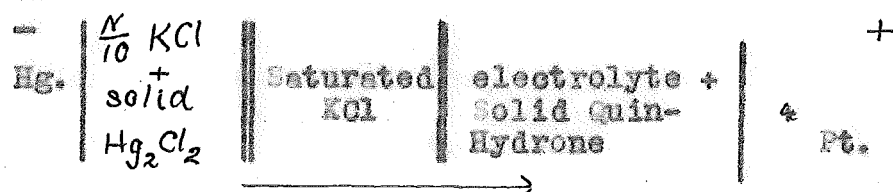
∴ C_H^+ = 4.46×10^{-6}

The value of π_H is negative from a consideration of the signs of the single electrode potentials.

II. Quin-Hydrone Electrode.

Here again it is assumed that liquid contact

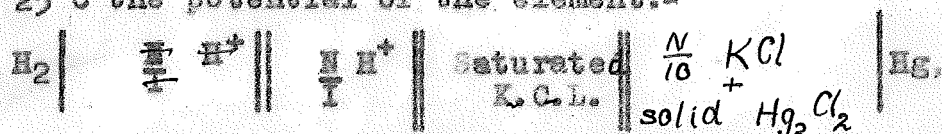
potential was annulled. The cells used were of the type:-



It was found in every case that the Quin-Hydrone half element was positive, the current passing inside the cell from left to right. As the Quin-Hydrone is positive from metal to solution, and also the calomel is positive from metal to solution, these two oppose each other, and the required single electrode potential difference of the Quin-Hydrone half element, is the numerical sum of total E.M.F. and of calomel half element (the calomel having the value as measured against the normal hydrogen electrode, i.e. 0.3376 volts)

O'Sullivan, (loc cit.) has calculated the hydrogen ion concentration of solutions by this method, from the following considerations:-

At 25°C the potential of the element:-



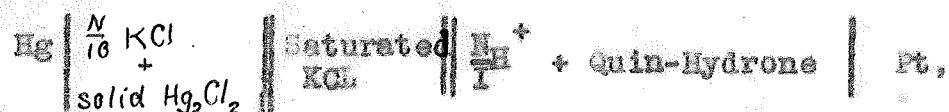
is 0.3376 volts. (Clerk, "Determination of Hydrogen Ions").

At 25° C the potential of element:-



(Biilmann, Ann. Chim., 1921, (IX), 15, 109-157).

Therefore, the potentials of the element:-



is 0.3614 volts. (Not obtainable in practice because of diffusion potential and salt error.)

Now, if the potential of the element:-



is a volts then:-

$$0.3614 - a = 0.0595 \log_{10} x$$

$$\therefore \log_{10} x = \frac{0.3614 - a}{0.0595} = \text{pH} \dots\dots\dots \text{I}$$

Further, if the initial concentration of the solution is C equivalents per litre, and the degree of hydrolysis is X then concentration of acid is XC equivalents per litre. Assuming complete dissociation of the acid (sulphuric acid) the pH of the solution is $\log_{10} \frac{I}{CX}$

$$\text{pH} = \log_{10} \frac{I}{CX} \dots\dots\dots \text{II}$$

Substituting the value of pH in equation I, in equation II, the value of \underline{X} can be calculated.

Clark (ibid p.291) gives the following equation for calculating the result:-

$$E_H = E_K - 0.00019837 T. pH.$$

E_K is a constant, and its value at 25° C is given as 0.699 (p. 292); $0.00019837.T.$, at 25° C is given as 0.05911. (p.457). E_H is observed single electrode P.D of Quin-Hydrone electrode referred to normal hydrogen electrode as zero. The value of pH, and hence the degree of hydrolysis, can be calculated.

Both methods, of course, give identical results. Two examples are given of actual calculations using zinc sulphate solutions. A 1.M Zinc Sulphate solution on complete hydrolysis produces 2N (equivalent normal) Sulphuric Acid.

Example I.

$\frac{M}{16}$ ZnSO_4 , 6th day.

E.M.F. of Standard = 1.0184 volts

Reading with standard = 51.30

Reading with Cal. + Q.H. (A)
+ Standard (in series) = 51.85

∴ E.M.F. of Cal. + Q-Hydrone = 0.0109 v.

∴ $\frac{0.3614 - 0.0109}{0.05911}$ = pH.

∴ pH = 5.9296.

∴ $\text{C}_\text{H}^+ = 1.176 \times 10^{-6}$ gram ions of H^+ per litre

Complete hydrolysis would give $\frac{1}{8}$ equivalent of
acid per litre, from 1 litre $\frac{M}{16}$ ZnSO_4 .

∴ Percentage hydrolysis = $\frac{1.176 \times 10^{-6}}{\frac{1}{8}} \times 100$
= 0.00094 %

Example II.

$\frac{M}{32}$ ZnSO_4 , 9th day.

E.M.F. of Standard = 1.0185 volts.

Reading with Standard = 52.30

Reading with Cal. + Q.H.
+ Standard (in series) = 53.28

∴ E.M.F. of Cal. + Q.Hydrone
= 0.0191v.

∴ $\frac{0.3614 - 0.0191}{0.05911}$ = pH

∴ pH = 5.7909

∴ C_H^+ = 1.618×10^{-6} gram ions of H^+ per litre.

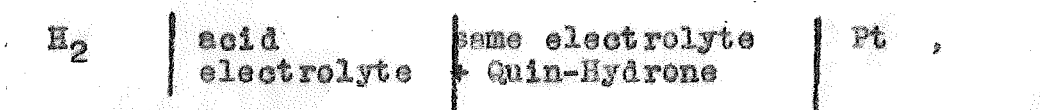
Complete hydrolysis would give 1/16 equivalent of
acid per litre, from 1 litre $\frac{M}{32}$ ZnSO_4 .

∴ Percentage hydrolysis = $\frac{1.618 \times 10^{-6}}{\frac{1}{16}} \times 100$

= 0.00259 %

EXPERIMENTAL SECTION.

Preliminary Experiment. O'Sullivan (loc. cit) points out that Billmann and others have shown that the E.M.F. of the cell:-

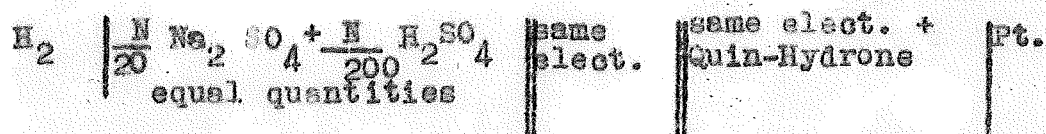


is constant, and at 18 C has the value = 0.7044 volts.

Clark gives the value at 25 C as 0.6990 volts.

O'Sullivan verified this by using as electrolyte a mixture of $\frac{N}{20}$ Sodium Sulphate and $\frac{N}{200}$ Sulphuric acid.

With the object of testing the reliability of all the apparatus that was to be used, especially the Quin-Hydrone electrode, the Quin-Hydrone and the Hydrogen electrode, the following cell was fitted up and measured:-



The sulphuric acid used was of A.R. quality, it was diluted to approximate strength with distilled water and accurately standardised by means of anhydrous sodium carbonate (in triplicate), according to the method in Cumming and Kay "Quantitative Chemical Analysis," (p.56-57). Also of A.R. quality was the

sodium sulphate, ($\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$); 16.1109 gms. were carefully weighed out, and the volume was made up to a litre of solution, in a calibrated standard flask. As this solution was used as a buffer no further standardisation other than the above weighing was carried out. These solutions were stored, for future checking of the electrodes, in Winchester bottles which had been carefully washed and steamed out.

The apparatus was fitted up and measurements taken of the above cell, as described previously.

Results.

| Time | Reading with Standard. | Reading with Unknown | E.M.F. of Unknown. |
|--------|------------------------|----------------------|--------------------|
| 0 min. | 51.95 cms. | 35.60 cms. | 0.6981 volts. |
| 10 " | 51.92 " | 35.60 " | 0.6985 " |
| 15 " | 51.89 " | 35.60 " | 0.6990 " |
| 40 " | 51.96 " | 35.60 " | 0.6981 " |
| 50 " | 51.96 " | 35.60 " | 0.6989 " |
| 60 " | 51.99 " | 35.67 " | 0.6990 " |

Here the value is seen to vary a little, and although in some cases the value is identical with that obtained by O'Sullivan and others, yet in others, e.g.

the 40 minute reading, it is low. In that particular case it was observed that the hydrogen bubbling had temporarily ceased, and although theoretically, if saturation has taken place, the value should be constant, yet some disturbing influence has caused a drop of 0.9 millivolt. The value rose again on restoring the hydrogen stream.

A fresh sample of electrolyte was now prepared from the stock bottles, both electrode vessels were refilled and another measurement taken of the cell. The hydrogen stream was maintained at a more even rate.

Results.

| Time | Reading with Standard | Reading with Unknown | E.M.F. of Unknown |
|---------|-----------------------|----------------------|-------------------|
| 0 mins. | 51.99 cms. | 35.66 cms. | 0.6987 volt. |
| 15 " | 51.99 " | 35.67 " | 0.6990 " |
| 30 " | 52.00 " | 35.67 " | 0.6990 " |

Within the experimental error, these three values are the same as those obtained for the same cell by O'Sullivan and others. This shows that the apparatus, and in particular the electrodes and the Quin-Hydronc, are functioning correctly.

Using this apparatus, experiments were now carried out with Zinc Sulphate, and other salt solutions.

ZINC SULPHATE.

Purification and Standardisation.

The salt used was British Drug House variety. About 200 grams of the crystals ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$), were dissolved in water to give rise to a saturated solution. This solution was filtered through a Büchner funnel. Absolute alcohol was added to the filtrate when about 90% of the salt was precipitated; this was filtered again through a Büchner funnel. The crystals were heated in a water bath to drive off alcohol and moisture. An analysis for sulphate was next carried out to determine which hydrate of zinc was present. For analysis, the method used was that of Cumming and Kay, "Quantitative Chemical Analysis", P.156-158); the analysis was carried out in duplicate. This revealed that the crystals were of the approximate order $\text{Zn SO}_4 \cdot 1.5\text{H}_2\text{O}$. With this established, $2\frac{1}{2}$ litres

of a solution of approximate strength $\frac{M}{16}$, (sixteenth molecular normal), were made up, but the solution was made up over strength. Distilled water was used for making up the solution. A second analysis for sulphate similar to the first, was then carried out in duplicate, and this showed that the strength of the solution was:-

(a) 0.0656 M.

(b) 0.0660 M.

Taking the average of these as the correct strength, the solution was diluted with distilled water, from a calibrated burette, to the exact strength 0.0625 M ($\frac{M}{16}$). More than a litre each of solutions of strengths, $\frac{M}{32}$, $\frac{M}{64}$, and $\frac{M}{128}$, were prepared, in each case from the $\frac{M}{16}$ solution. Calibrated flasks were used in the dilution to these strengths. All these solutions were stored in steamed out Winchester bottled fitted with siphons and carbon dioxide guard tubes.

The four strengths were measured each day for about a fortnight, measurements being taken with the hydrogen electrode, (to show that it gives a variable value), and with the two Quin-Hydrone electrodes, (to discover if a constant value can be obtained). With

each concentration the above measurements were taken concurrently. In the individual measurements the Quia-Hydrone electrodes readily gave constant values, but the hydrogen electrode took longer before an approximately constant value was reached. Before taking readings the electrode vessels were left in the bath sufficiently long to acquire the temperature of the thermostat, and with the hydrogen electrode, time was allowed for saturation of the solution with gas. In all cases, the time that elapsed between the setting up of the electrodes and the taking of readings was the same approximately. As an example of the daily readings the tabulated results for $\frac{M}{15}$ zinc sulphate follow; S represents the bridge reading with the standard cell in circuit, H the same for the cell with the hydrogen electrode, and A and B for the two cells containing the Quia-Hydrone electrodes plus the standard cell in series. In first column is recorded also E.M.F. of Standard cell.

RESULTS:-

$\frac{M}{16}$ ZnSO₄.

| Day | Time | S. | H. | A. | B |
|------------------|---------|-------|-------|-------|-------|
| 1st 1.0184 v. | 0 mins. | 53.20 | 35.20 | 53.80 | 53.80 |
| | 10 " | 53.20 | 35.20 | 53.80 | 53.80 |
| | 20 " | 53.20 | 35.20 | 53.80 | 53.80 |
| | 30 " | 53.20 | 35.20 | 53.80 | 53.80 |
| 2nd 1.0184 v. | 0 " | 53.18 | 35.58 | 53.62 | 53.63 |
| | 10 " | 53.19 | 35.58 | 53.62 | 53.63 |
| | 20 " | 53.19 | 35.60 | 53.62 | 53.63 |
| | 30 " | 53.20 | 35.60 | 53.63 | 53.65 |
| 3rd 1.0184 v. | 0 " | 49.99 | 33.47 | 50.46 | 50.53 |
| | 10 " | 49.99 | 33.48 | 50.46 | 50.53 |
| | 20 " | 49.99 | 33.48 | 50.46 | 50.53 |
| | 30 " | 50.00 | 33.50 | 50.48 | 50.55 |
| 5th 1.0184 v. | 0 " | 50.80 | 34.07 | 51.40 | 51.37 |
| | 10 " | 50.80 | 34.08 | 51.40 | 51.37 |
| | 20 " | 50.80 | 34.10 | 51.40 | 51.37 |
| | 30 " | 50.80 | 34.10 | 51.40 | 51.37 |
| 6th 1.0184 v. | 0 " | 51.29 | 34.10 | 51.84 | 51.81 |
| | 10 " | 51.30 | 34.11 | 51.85 | 51.83 |
| | 20 " | 51.30 | 34.13 | 51.85 | 51.83 |
| | 30 " | 51.30 | 34.13 | 51.85 | 51.83 |
| 7th 1.0184 v. | 0 " | 51.88 | 34.76 | 52.75 | 52.76 |
| | 10 " | 51.89 | 34.78 | 52.75 | 52.76 |
| | 20 " | 51.90 | 34.80 | 52.77 | 52.78 |
| | 30 " | 51.90 | 34.80 | 52.77 | 52.78 |
| 8th 1.0184 v. | 0 " | 52.10 | 33.63 | 52.79 | 52.80 |
| | 10 " | 52.10 | 33.64 | 52.79 | 52.81 |
| | 20 " | 52.11 | 33.66 | 52.80 | 52.82 |
| | 30 " | 52.12 | 33.68 | 52.81 | 52.83 |

M
16 ZnSO_4 (continued).

| Day | Time | S | H | A | B |
|-------------------|---------|-------|-------|-------|-------|
| 9th 1.0185 v. | 0 mins. | 52.33 | 34.93 | 53.10 | 53.10 |
| | 10 " | 52.33 | 34.93 | 53.10 | 53.10 |
| | 20 " | 52.33 | 34.95 | 53.10 | 53.10 |
| | 30 " | 52.33 | 34.95 | 53.10 | 53.10 |
| 10th 1.0184 v. | 0 " | 52.46 | 35.14 | 53.35 | 53.35 |
| | 10 " | 52.46 | 35.15 | 53.35 | 53.35 |
| | 20 " | 52.46 | 35.15 | 53.35 | 53.35 |
| | 30 " | 52.46 | 35.15 | 53.35 | 53.35 |
| 12th 1.0184 v. | 0 " | 52.70 | 32.86 | 53.58 | 53.60 |
| | 10 " | 52.72 | 32.88 | 53.60 | 53.62 |
| | 20 " | 52.72 | 32.90 | 53.60 | 53.62 |
| | 30 " | 52.72 | 32.90 | 53.60 | 53.62 |
| 13th 1.0184 v. | 0 " | 52.97 | 35.07 | 53.89 | 53.89 |
| | 10 " | 52.97 | 35.07 | 53.89 | 53.89 |
| | 20 " | 52.97 | 35.09 | 53.89 | 53.89 |
| | 30 " | 52.97 | 35.09 | 53.89 | 53.89 |

The values for the other dilutions were recorded similarly. From these values the E.M.F. of each cell was found, and the hydrogen ion concentration and the degree of hydrolysis (in the case of Quin-Hydrone electrodes), was calculated as explained previously. In the case of the hydrogen electrode the hydrogen ion concentration only was worked out. The tabulated results follow; in the

hydrogen electrode results the recorded E.M.F. is the total E.M.F. of the cell, calomel electrode plus hydrogen electrode; with the Quin-Hydrone electrode the value recorded is the "absolute" P.D. of the single electrode (Abs. P.D.).

The symbol $[H^+]$ represents hydrogen ion concentration.

Results using Hydrogen Electrode.

| $\frac{M}{16} \text{ ZnSO}_4$ | | | $\frac{M}{32} \text{ ZnSO}_4$ | | |
|-------------------------------|--------------|---------------------|-------------------------------|---------------------|---------------------|
| Day | E.M.F. (vts) | $[H^+] \times 10^6$ | Day | E.M.F. vts. | $[H^+] \times 10^6$ |
| 1st | 0.6735 | 2.085 | 1st | 0.6904 | 1.075 |
| 2nd | 0.6821 | 1.485 | 2nd | 0.6626 | 3.150 |
| 3rd | 0.6819 | 1.500 | 3rd | 0.6834 | 1.412 |
| 5th | 0.6831 | 1.430 | 5th | 0.6939 | 0.938 |
| 6th | 0.6774 | 1.785 | 6th | 0.6539 | 4.560 |
| 7th | 0.6825 | 1.460 | 7th | 0.6899 | 1.095 |
| 8th | 0.6582 | 3.770 | 8th | 0.6539 | 4.460 |
| 9th | 0.6798 | 1.625 | 9th | 0.6671 | 2.665 |
| 10th | 0.6821 | 1.480 | 10th | 0.6591 | 3.640 |
| 12th | 0.6352 | 9.230 | 12th | 0.6880 | 1.180 |
| 13th | 0.6742 | 2.020 | 13th | 0.6705 | 2.335 |
| 14th | no solution | - | 14th | 0.6592 ^u | 3.625 |

Results using Hydrogen Electrode (continued).

| $\frac{M}{64} \text{ ZnSO}_4$ | | | $\frac{M}{128} \text{ ZnSO}_4$ | | |
|-------------------------------|---------------|--|--------------------------------|-------------|--|
| Day | E.M.F. (vts.) | $\left[\frac{H^+}{H}\right] \times 10^6$ | Day | E.M.F. vts. | $\left[\frac{H^+}{H}\right] \times 10^6$ |
| 1st | 0.6982 | 0.794 | 1st | 0.7125 | 0.4545 |
| 2nd | 0.6685 | 2.525 | 2nd | 0.6167 | 18.98 |
| 3rd | 0.6697 | 2.410 | 3rd | 0.6896 | 1.110 |
| 5th | 0.6648 | 2.915 | 5th | 0.6653 | 2.860 |
| 6th | 0.6668 | 2.695 | 6th | 0.6634 | 2.850 |
| 7th | 0.6940 | 0.935 | 7th | 0.6847 | 2.345 |
| 8th | 0.6841 | 1.375 | 8th | 0.6634 | 2.850 |
| 9th | 0.6857 | 1.290 | 9th | 0.7087 | 0.166 |
| 10th | 0.6637 | 3.040 | 10th | 0.6940 | 0.935 |
| 12th | 0.6705 | 2.335 | 12th | 0.6955 | 0.882 |
| 13th | 0.6691 | 2.465 | 13th | 0.6861 | 1.270 |
| 14th | 0.6518 | 4.835 | 14th | 0.6857 | 1.290 |

Results using Quin-Hydrone Electrode.

| Day | Abs. P.D. | Average $\frac{M}{H^+} \times 10^6$ | Per cent. Hydrolysis | Day | Abs. P.D. | Average $\frac{M}{H^+} \times 10^6$ | Per cent. Hydrolysis. |
|------------|------------------|--|-------------------------|------------|------------------|--|--------------------------|
| | | $\frac{M}{16} ZnSO_4$ | | | | $\frac{M}{32} ZnSO_4$ | |
| 1st A B | 0.6259 0.6259 | 1.195 | 0.0010 | 1st A B | 0.6307 0.6299 | 1.418 | 0.0023 |
| 2nd A B | 0.6228 0.6232 | 1.063 | 0.0009 | 2nd A B | 0.6352 0.6356 | 1.730 | 0.0028 ⁴⁵ |
| 3rd A B | 0.6242 0.6246 | 1.126 | 0.0009 | 3rd A B | 0.6327 0.6321 | 1.521 | 0.0024 ¹ |
| 5th A B | 0.6266 0.6260 | 1.213 | 0.0010 | 5th A B | 0.6297 0.6297 | 1.407 | 0.0023 |
| 6th A B | 0.6255 0.6251 | 1.167 | 0.0009 | 6th A B | 0.6314 0.6306 | 1.456 | 0.0023 |
| 7th A B | 0.6316 0.6319 | 1.500 | 0.0012 | 7th A B | 0.6333 0.6323 | 1.569 | 0.0025 |

Results using Quin-Hydrone Electrode (Cont.)

| Day | Abs. P.D. | Average $\frac{M}{H^+} \times 10^6$ | Per cent. Hydrolysis | Day | Abs. P.D. | Average $\frac{M}{H^+} \times 10^6$ | Per cent. Hydrolysis |
|-------------|-------------------------------|--|-------------------------|-------------|-------------------------------|--|-------------------------|
| | $\frac{M}{16} \text{ ZnSO}_4$ | | | | $\frac{M}{32} \text{ ZnSO}_4$ | | |
| 8th A B | 0.6280 0.6296 | 1.338 | 0.0011 | 8th A B | 0.6326 0.6320 | 1.532 | 0.0025 |
| 9th A B | 0.6295 0.6295 | 1.374 | 0.0011 | 9th A B | 0.6337 0.6337 | 1.618 | 0.0026 |
| 10th A B | 0.6319 0.6319 | 1.509 | 0.0012 | 10th A B | 0.6334 0.6334 | 1.600 | 0.0026 |
| 12th A B | 0.6316 0.6319 | 1.500 | 0.0012 | 12th A B | 0.6333 0.6335 | 1.600 | 0.0026 |
| 13th A B | 0.6323 0.6323 | 1.532 | 0.0013 | 13th A B | 0.6352 0.6352 | 1.716 | 0.0027 |
| 14th A B | -- -- | | | 14th A B | 0.6415 0.6411 | 2.180 | (0.0035) |
| | | Average = | 0.0011 | | | Average = | 0.0025 |

Results using Quin-Hydrone Electrode (cont.)

| Day | Abs. P.D. | Average [H ⁺] x 10 ⁶ | Per cent Hydrolysis | Day | Abs. P.D. | Average [H ⁺] x 10 ⁶ | Per cent. Hydrolysis. |
|------------|-------------------------------|--|------------------------|------------|--------------------------------|--|--------------------------|
| | $\frac{M}{64} \text{ ZnSO}_4$ | | | | $\frac{M}{128} \text{ ZnSO}_4$ | | |
| 1st A B | 0.6375 0.6375 | 1.877 | 0.006 | 1st A B | 0.6404 0.6392 | 2.052 | 0.013 |
| 2nd A B | 0.6440 0.6442 | 2.427 | 0.008 | 2nd A B | 0.6397 0.6407 | 2.084 | 0.014 |
| 3rd A B | 0.6409 0.6389 | 2.061 | 0.007 | 3rd A B | 0.6409 0.6399 | 2.101 | 0.014 |
| 5th A B | 0.6426 0.6426 | 2.290 | 0.008 | 5th A B | 0.6367 0.6367 | 1.820 | 0.012 |
| 6th A B | 0.6442 0.6442 | 2.436 | 0.008 | 6th A B | 0.6432 0.6436 | 2.361 | 0.015 |
| 7th A B | 0.6417 0.6421 | 2.227 | 0.007 | 7th A B | 0.6429 0.6421 | 2.280 | 0.014 |
| 8th A B | 0.6441 0.6441 | 2.427 | 0.008 | 8th A B | 0.6384 0.6384 | 1.936 | 0.013 |

Results using Quin-Hydrone Electrode (Continued).

| Day | Abs. P.D. | Average $[H^+] \times 10^6$ | Per cent. Hydrolysis | Day | Abs. P.D. | Average $[H^+] \times 10^6$ | Per cent Hydrolysis. |
|-------------|---------------------------|--------------------------------|-------------------------|-------------|----------------------------|--------------------------------|-------------------------|
| | M ZnSO ₄ 54 | | | | M ZnSO ₄ 128 | | |
| 9th A B | 0.6441 0.6441 | 2.427 | 0.008 | 9th A B | 0.6437 0.6437 | 2.390 | 0.015 |
| 10th A B | 0.6447 0.6443 | 2.465 | 0.008 | 10th A B | 0.6398 0.6398 | 2.052 | 0.013 |
| 12th A B | 0.6446 0.6446 | 2.475 | 0.008 | 12th A B | 0.6436 0.6436 | 2.371 | 0.014 |
| 13th A B | 0.6470 0.6466 | 2.675 | 0.009 | 13th A B | 0.6439 0.6439 | 2.407 | 0.014 |
| 14th A B | 0.6452 0.6452 | 2.533 | 0.016 0.008 | 14th A B | 0.6534 0.6530 | 3.459 | (0.022) |
| | | Average = 0.008 | | | | Average = | 0.014 |

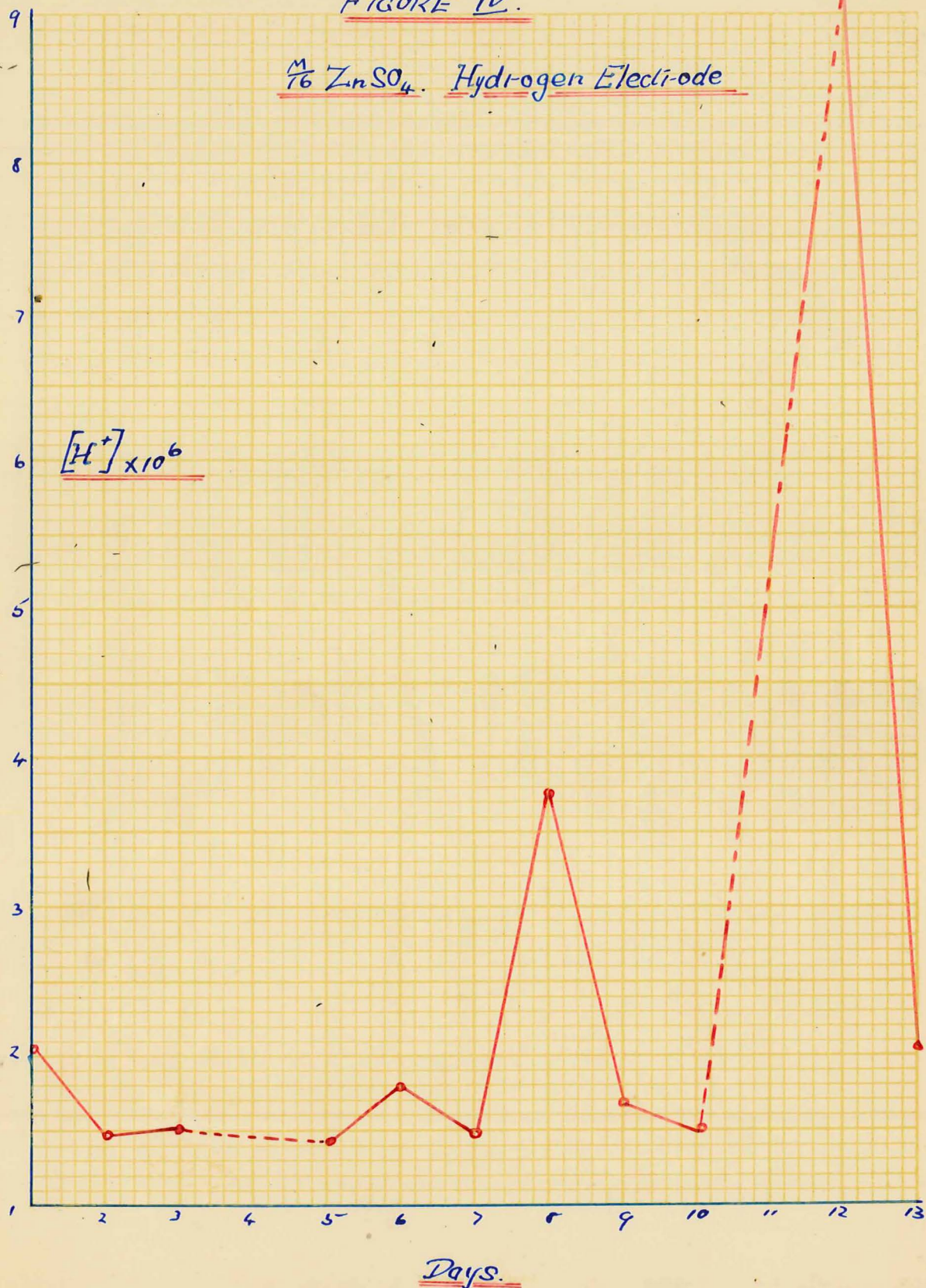
Consideration of Results.

In figures 4, 5, 6, and 7, which follow, the values obtained by the hydrogen electrode, for the hydrogen ion concentrations, (ordinates), have been plotted against the time in days (abscissae). Thus, it is found that, with the four concentrations experimented with in the hydrogen electrode, the hydrogen ion concentration varies irregularly from day to day. As pointed out earlier, Denham (Journ. Chem. Soc., 1908, 93, 41-63, and Zeit. Anorg. Chem. 1908, 57, 381), had previously observed this anomalous behaviour, not only with Zinc Sulphate and Chloride, but also with Magnesium Sulphate, Thorium Sulphate, Caesium Chloride, Cobalt Chloride, and Nickel Sulphate. Possible explanations of this were suggested on page 5, and at the end of this work, experiments were conducted in an attempt to throw light on the problem. Sufficient evidence has been brought forward to show that the hydrogen electrode is unsuitable for the determination of the degree of hydrolysis of zinc sulphate in aqueous solution.

In figures 8, 9, 10 and 11, which follow, the values obtained by the Quin-Hydrone electrode for the

FIGURE IV.

$\frac{M}{16}$ $ZnSO_4$ Hydrogen Electrode



Curves showing irregular $[H^+]$ from day to day. FIGURES IV, V, VI, VII.

FIGURE V $\frac{M}{32} \text{ZnSO}_4$ Hydrogen Electrode. $[\text{H}^+] \times 10^6$ 

Figure. VI.

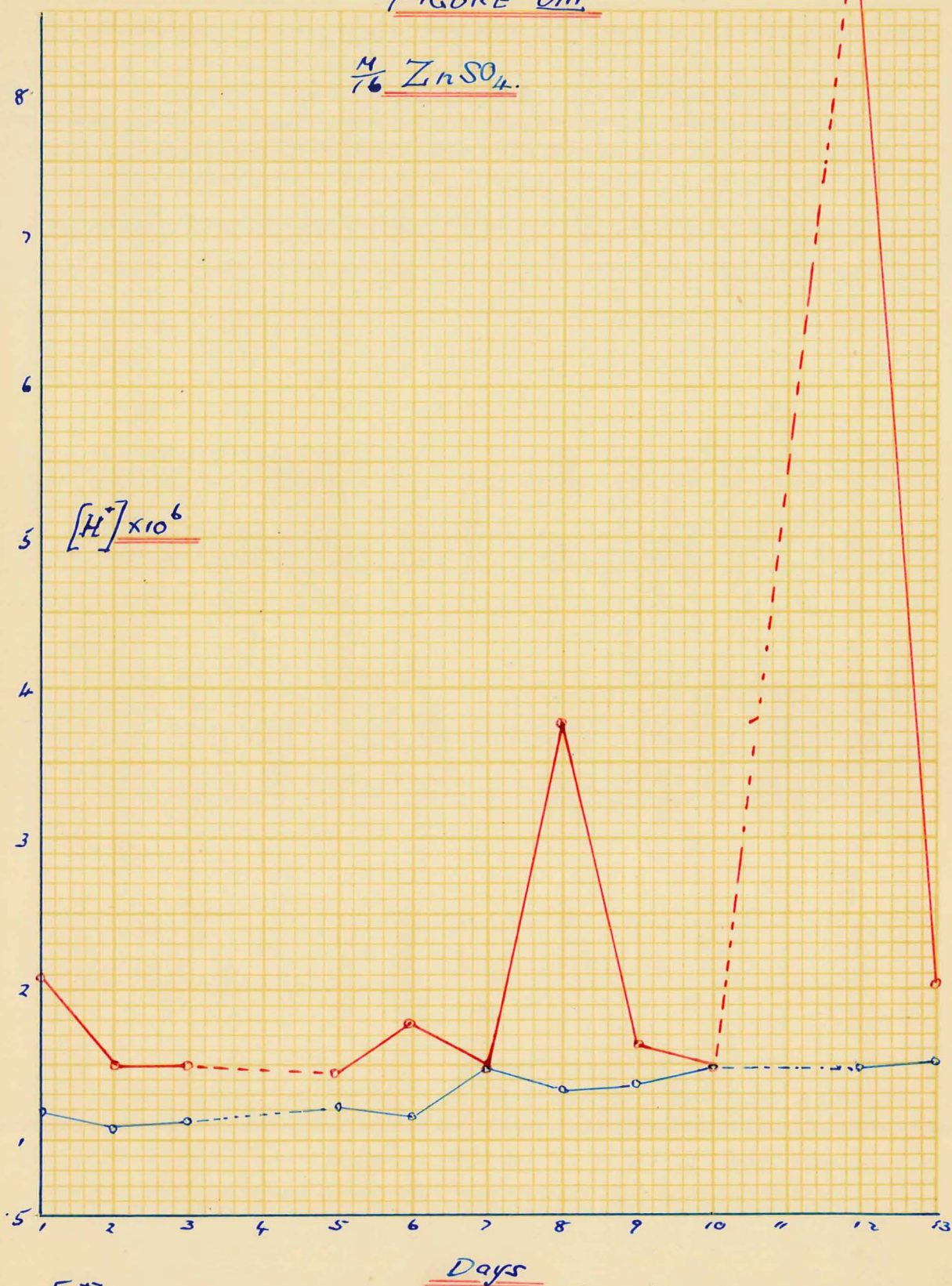
$\frac{M}{64}$ $ZnSO_4$

Hydrogen Electrode.



FIGURE VII.



FIGURE VIII $\frac{M}{76} \text{ZnSO}_4$ 

$[\text{H}^+]$ by A-H electrode compared with $[\text{H}^+]$ by Hydrogen electrode

FIGURES VIII, IX, X, XI.

FIGURE IX.

$\frac{M}{32} \text{ZnSO}_4$

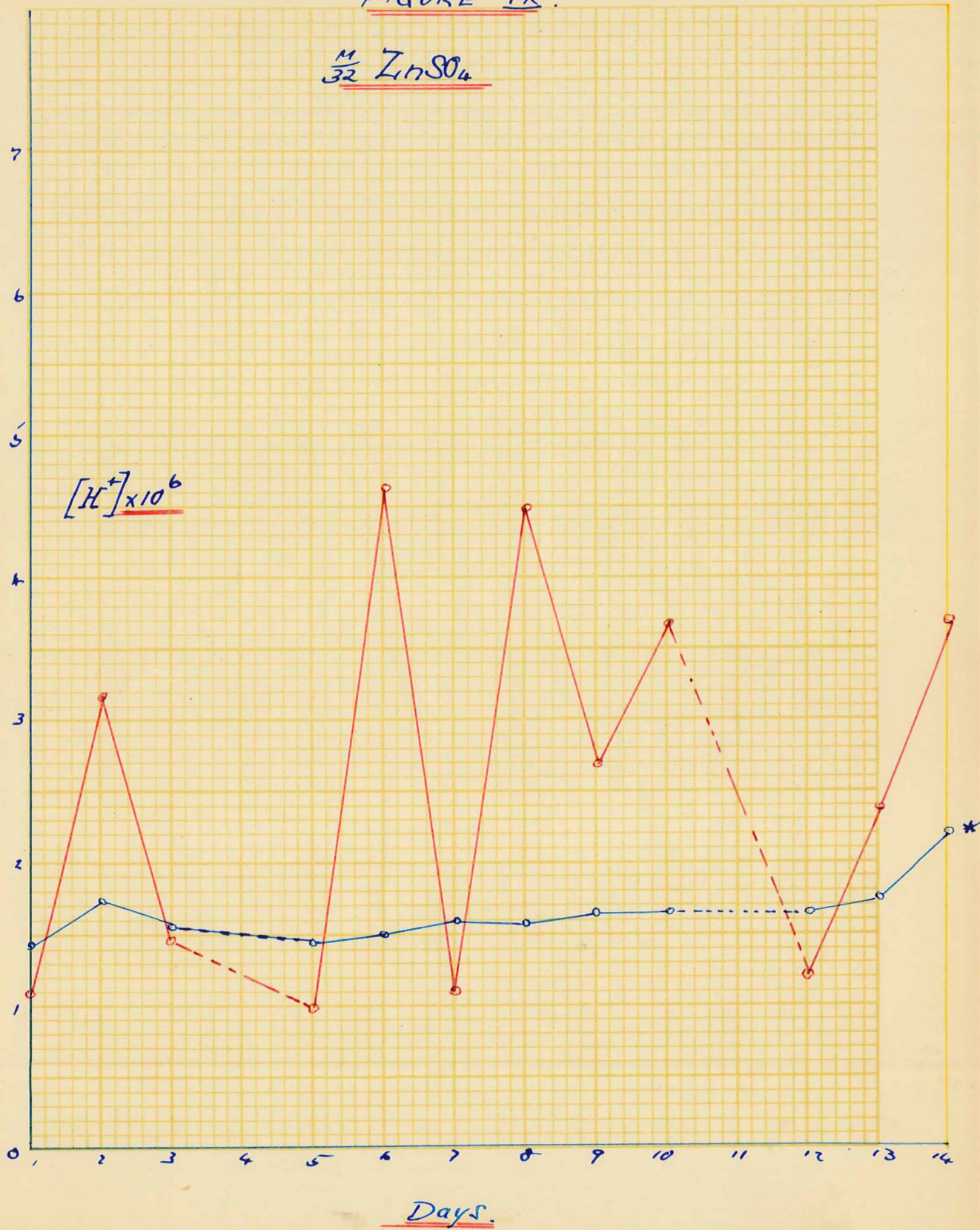


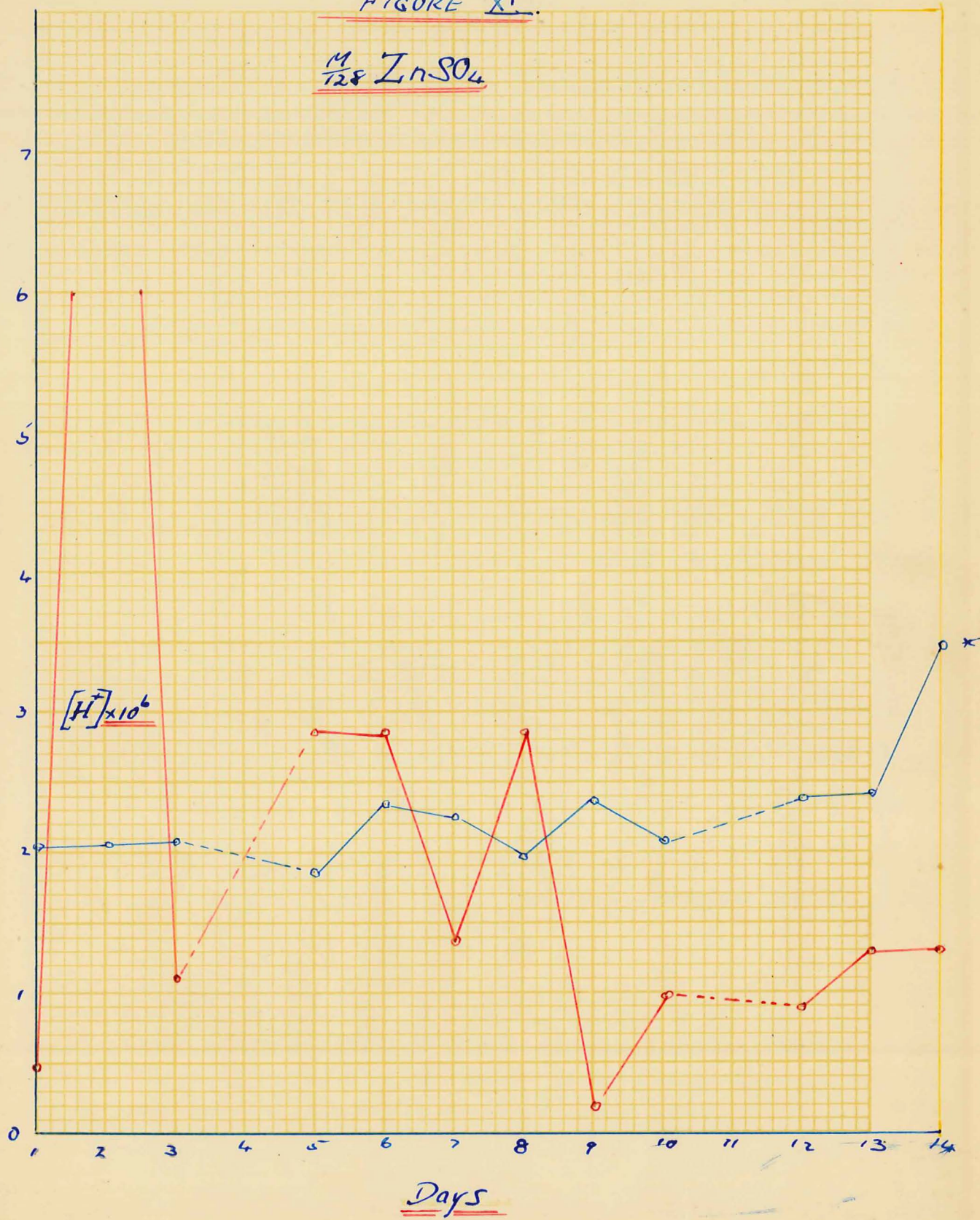
FIGURE X.

$\frac{M}{64} \text{ZnSO}_4$



FIGURE XI.

$\frac{M}{128} \text{ZnSO}_4$



hydrogen ion concentrations have been plotted against the time in days. On the same graphs, for purposes of comparison, are placed the corresponding values obtained by the hydrogen electrode. It is seen from reference to the graphs or to the values on the four previous pages, that for each dilution tried with the Quin-Hydroxide electrode, approximately constant values are obtained for the hydrogen ion concentrations, and for the degree of hydrolysis. This goes to show the following:-

- (a) That the Quin-Hydroxide electrode is satisfactory for the determination of the hydrogen ion concentration, (and degree of hydrolysis), of solutions of zinc sulphate.
- (b). That the irregular values obtained with the hydrogen electrode are due, not to phenomena inherent in the stock bottle solution, such as colloidal formation, but to influences brought about by the hydrogen electrode on the solutions placed in it.

The high values marked with an asterisk are attributed to the fact that the corks had to be removed, and the solutions poured out, and basic salts, etc., which had

settled to the bottom, may have been included.

The average values obtained for the degrees of hydrolysis are:-

| | | | | |
|---------------------|-----------------|---|---------|-----------|
| ZnSO ₄ . | $\frac{M}{16}$ | = | 0.0011% | at 25° C. |
| " | $\frac{M}{32}$ | = | 0.0025% | " " |
| " | $\frac{M}{64}$ | = | 0.008% | " " |
| " | $\frac{M}{128}$ | = | 0.014% | " " |

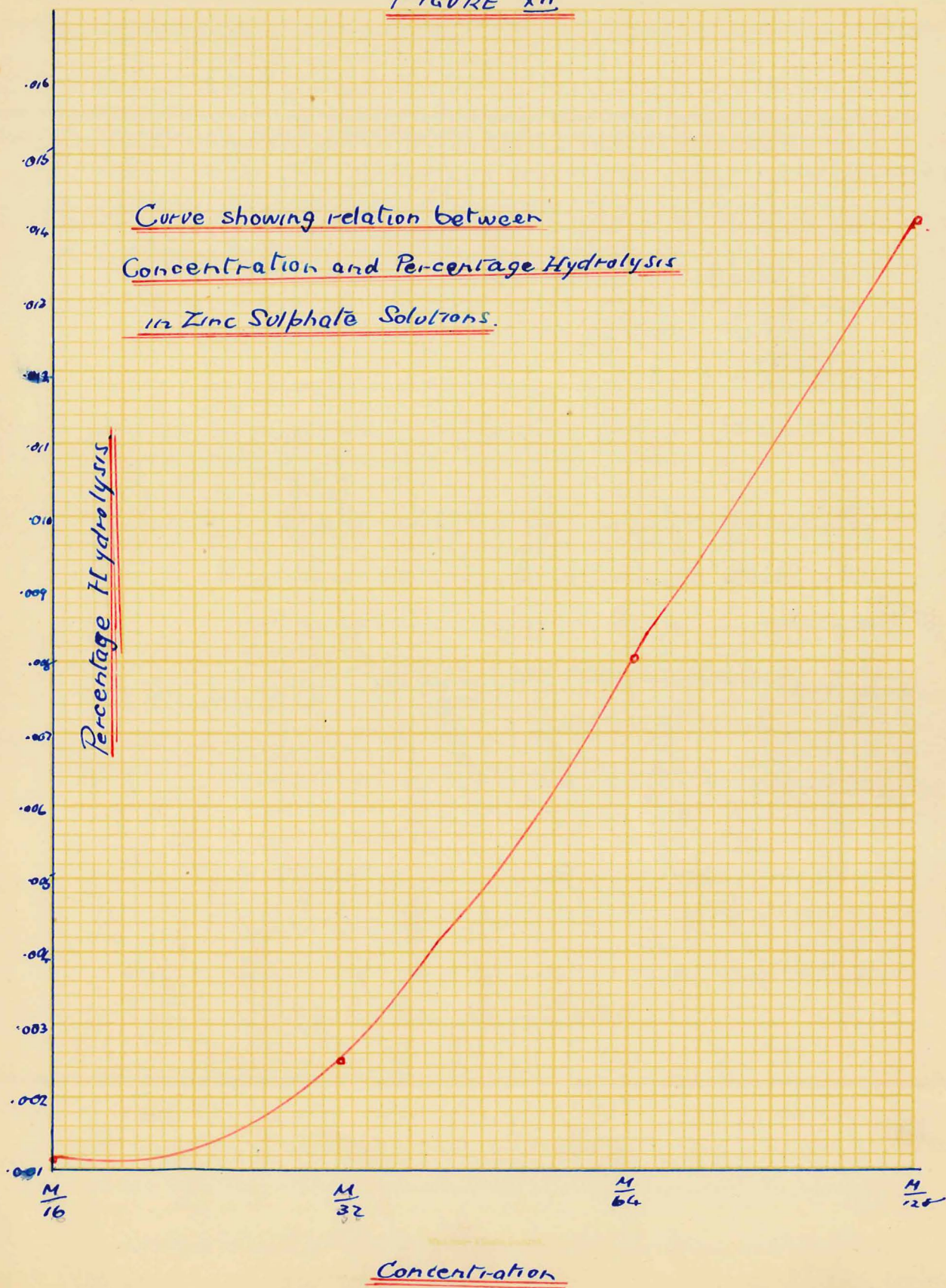
These values are shown in the graph on page 60

(Figure 12). Values obtained by other methods are inserted for comparison.

- 1896: H. Long (Journ. Amer. Chem. Soc., 18, 1896, 693-717).
measured the value by sugar inversion. At 20° C
the value for $\frac{M}{2}$ Zinc Sulphate was 0.016% hydrolysis.
- 1897: H. Ley, (Sitzber. Akad. Berlin, 2194, 1897).
calculated the hydrolysis of a 1/16 molar solution
to be 0.03.
- 1900: G. Carrara and G. B. Vespignani, (Gazz. Chim. Ital.,
30, 11, 35-63), measured the value by the saponi-
fication of Acetate. They obtained the value
0.0075% for a half molar solution.

FIGURE XII

Curve showing relation between
Concentration and Percentage Hydrolysis
in Zinc Sulphate Solutions.



Concerning his experiment H. Long says (loc. cit. P. 703), "The experiment was closed when the sugar was about half inverted, and, as the coefficient is not regular, it is not possible to estimate accurately the mean rate for the whole period." Also the neutral salts have probably a catalytic effect on the rate of inversion of the sugar. (Lewis, "Physical Chemistry", Vol. I, P.248).

Reference to the Graphs, Figures 8, 9, 10 and 11, show that in this experiment, in general, the values for hydrogen ion concentrations, as determined by the Quin-Hydrone electrode, are intermediate between the various values, (at the same dilution), obtained by the hydrogen electrode.

Finally an experiment with $\frac{M}{128}$ zinc sulphate solution in the Quin-Hydrone electrode was carried out, (in duplicate), and it was found that the E.M.F. of the cell, calomel plus Quin-Hydrone, was constant over a period of five hours.

CADMIUM SULPHATE.

Purification and Standardisations:

The sample of salt used was of A. R. quality. For estimation of purity the Cadmium and the Sulphate were determined separately, and the ratio of one to the other compared with the theoretical ratio.

In the estimation of Cadmium the following method was used: An accurately weighed sample (in duplicate) was moistened with a drop of dilute sulphuric acid, and ignited cautiously in an air bath, so that flame was not in direct contact with the crucible. The crucible was cooled in a desiccator and the salt weighed as CdSO_4 . This method is from Treadwell and Hall "Analytical Chemistry", Vol. II, P.151.

For the estimation of Sulphate the method was of Cumming and Kay "Quantitative Chemical Analysis", P.156-158, the sulphate being precipitated as Barium sulphate, and weighed as such. This was also carried out in duplicate.

Using International Atomic weights (1925), the theoretical ratio of Cadmium to Sulphate

is 1.169

Experiment gave (A 1.173
(B 1.170

This agreement was taken as satisfactory, and the A.R. Cadmium Sulphate provided was used directly for making up standard solutions, without further purification.

As an undetermined amount of water of crystallisation was probably present in the original sample, the ratio of pure CdSO_4 to sample was taken as that found in the estimation of Cadmium. On this assumption a litre of solution, apparently $\frac{M}{16}$ was made up by weighing, and dilution in a calibrated standard flask. A further analysis was now carried out, (in triplicate), to find the actual strength, by precipitation of sulphate as Barium Sulphate, (as before). It was found that to give a $\frac{M}{16}$ solution 3.6 c.c. of water had to be added to the remainder of the solution.

From this solution, as in the case of zinc sulphate solutions of strengths $\frac{M}{32}$, $\frac{M}{64}$, $\frac{M}{128}$, $\frac{M}{256}$, were made up by careful dilution, using calibrated flasks.

Previous investigators, (Denham; J.C.S., 1908, Vol. 93, p.834), have shown that when the hydrogen ion concentrations of Cadmium Sulphate solutions are

measured by means of the hydrogen electrode, an increasing value was obtained. That result was repeated in this work with $\frac{M}{16}$ solution, and also with $\frac{M}{128}$ solution to show that the behaviour was not a peculiarity of one solution.

Experiments were then made over an extended period, using Cadmium Sulphate in the Quin-Hydrone electrode to see if a constant value could be obtained. The hydrogen ion concentrations of each of the five solutions were then measured by means of the Quin-Hydrone electrode, and the degrees of hydrolysis determined.

Results:- Cell: Calomel electrode | Saturated K. C. L. | Cad. Sulphate | H_2

Using Hydrogen electrode for several hours.

The E.M.F. is the total: Calomel plus Hydrogen electrode

$\frac{M}{15} \text{ CdSO}_4$

$\frac{M}{128} \text{ CdSO}_4$

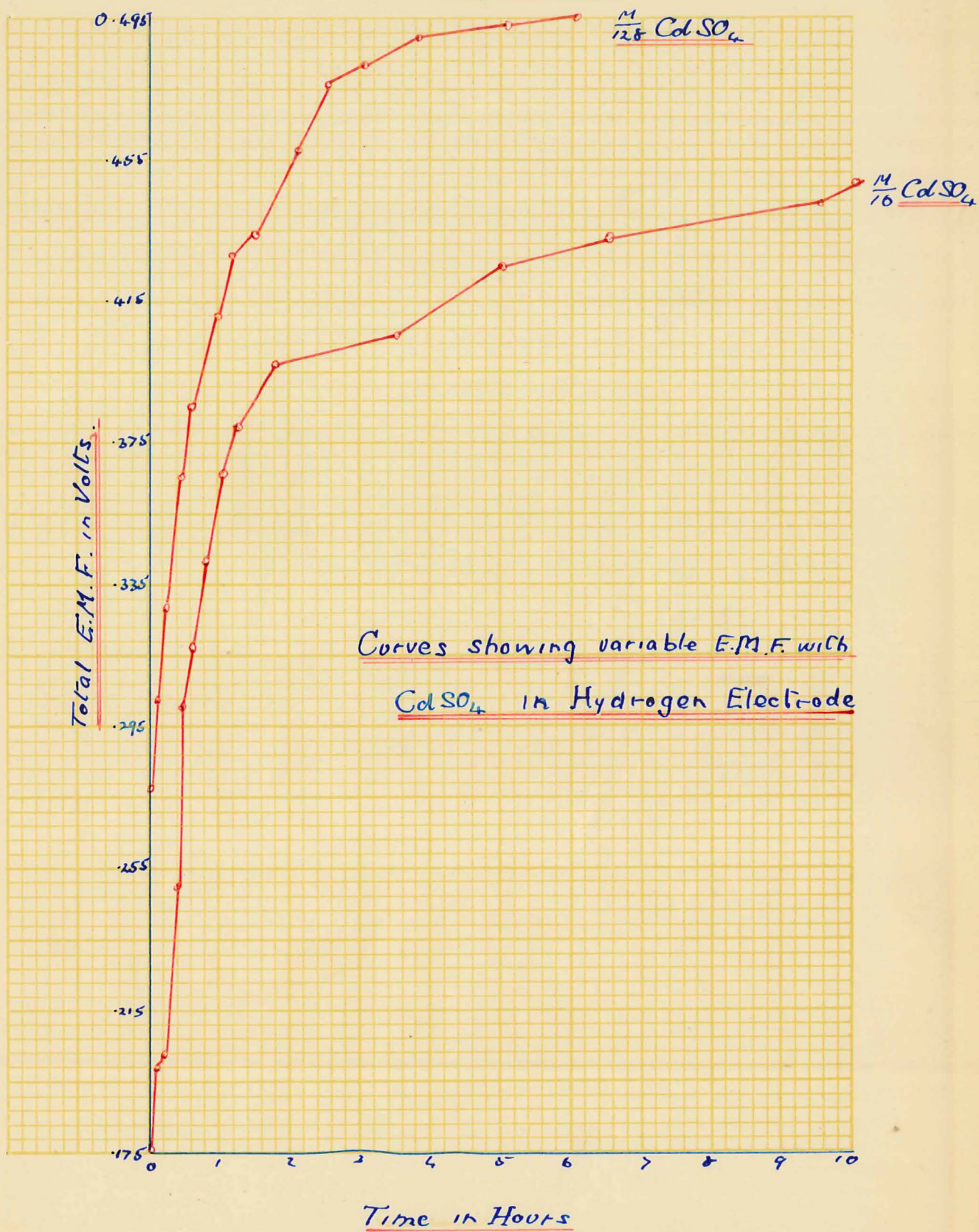
| Time | Standard | "Hydrogen" Cell | Total E.M.F. | Time | Standard | "Hydrogen" Cell | Total E.M.F. |
|-------------------|-----------|--------------------|-----------------|-------------------|------------|--------------------|-----------------|
| 0 mins | 52.73 cms | 9.05 cms. | 0.1743 v. | 0 mins. | 53.29 cms. | 11.55 cms | 0.2780 v. |
| 9 " | 52.82 " | 10.35 " | 0.1995 " | 9 " | 53.29 " | 15.90 " | 0.3021 v. |
| 13 " | 52.84 " | 10.53 " | 0.2030 v. | 15 " | 53.29 " | 17.15 " | 0.3278 v. |
| 23 " | 52.83 " | 12.95 " | 0.2498 v. | 28 " | 53.29 " | 19.05 " | 0.3651 v. |
| 29 " | 52.82 " | 15.55 " | 0.2998 v. | 35 " | 53.29 " | 20.10 " | 0.3844 v. |
| 34 " | 52.82 " | 16.47 " | 0.3170 v. | 1 hour | 53.30 " | 21.45 " | 0.4100 v. |
| 46 " | 52.80 " | 17.70 " | 0.3415 v. | 1 $\frac{1}{8}$ " | 53.32 " | 22.40 " | 0.4279 v. |
| 1 hour | 52.80 " | 18.95 " | 0.3657 v. | 1 $\frac{1}{2}$ " | 53.37 " | 22.75 " | 0.4342 v. |
| 1 $\frac{1}{4}$ " | 52.80 " | 19.65 " | 0.3791 v. | 2 " | 53.39 " | 23.95 " | 0.4569 v. |
| 1 $\frac{3}{4}$ " | 52.80 " | 20.53 " | 0.3962 v. | 2 $\frac{1}{2}$ " | 53.40 " | 24.90 " | 0.4750 v. |
| 3 $\frac{1}{4}$ " | 52.80 " | 21.00 " | 0.4052 v. | 3 " | 53.40 " | 25.20 " | 0.4807 v. |
| 5 " | 52.87 " | 22.03 " | 0.4243 v. | 3 $\frac{1}{2}$ " | 53.43 " | 25.50 " | 0.4862 v. |
| 6 $\frac{1}{2}$ " | 52.89 " | 22.45 " | 0.4324 v. | 5 " | 53.50 " | 25.90 " | 0.4930 v. |
| 9 $\frac{1}{4}$ " | 53.00 " | 23.00 " | 0.4420 v. | 6 " | 53.51 " | 26.00 " | 0.4949 v. |
| 10 " | 53.00 " | 23.30 " | 0.4478 v. | | | | |

In the graph on the following page, the total E.M.F. of the composite cell, has been plotted against the time in hours (Figure 13), for the two dilutions $\frac{M}{16}$ and $\frac{M}{128}$. Irregularities in the curves are attributed to the irregular hydrogen stream. This variable value for the E.M.F. is due to reduction of the Cadmium Sulphate, by the hydrogen, at a solution pressure of one atmosphere, the reduction proceeding probably according to the equation:-



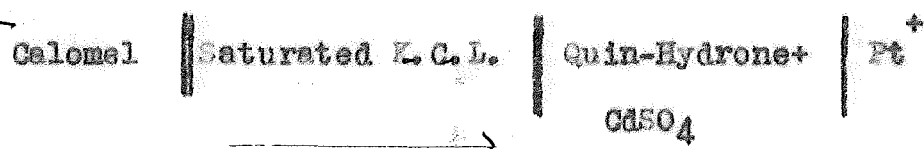
which leads to an abnormal and variable value of the hydrogen ion.

The experiment thus clearly indicates that the hydrogen electrode is unsuitable, for the determination of the degree of hydrolysis of solutions of Cadmium Sulphate.

FIGURE XIII

Experiments were now conducted with the Quin-Hydrone electrode to find if a constant value could be obtained for the hydrogen ion concentration. Each dilution was measured in duplicate.

In the following results the total E.M.F. is the total value of the composite cell:-



Results: $\overset{M}{16} \overset{+5}{\text{CdSO}_4}$ in Quin-Hydrone Electrode.

| Time | | E.M.F. v. | $\frac{[H^+]}{[H]} \times 10^5$ | % Hydrolysis | Time | | E.M.F. | $\frac{[H^+]}{[H]} \times 10^5$ | % Hydrolysis |
|--------|---|-----------|---------------------------------|--------------|----------|---|--------|---------------------------------|--------------|
| 0 mins | A | 0.0770 | 1.544 | 0.0124 | 120 mins | A | 0.0770 | 1.544 | 0.0124 |
| | B | 0.0770 | 1.544 | 0.0124 | | B | 0.0770 | 1.544 | 0.0124 |
| 5 " | A | 0.0770 | 1.544 | 0.0124 | 165 " | A | 0.0770 | 1.544 | 0.0123 |
| | B | 0.0770 | 1.544 | 0.0124 | | B | 0.0772 | 1.556 | 0.0125 |
| 15 " | A | 0.0769 | 1.538 | 0.0123 | 180 " | A | 0.0770 | 1.544 | 0.0124 |
| | B | 0.0769 | 1.538 | 0.0123 | | B | 0.0770 | 1.544 | 0.0124 |
| 20 " | A | 0.0769 | 1.538 | 0.0123 | 210 " | A | 0.0771 | 1.554 | 0.0125 |
| | B | 0.0769 | 1.538 | 0.0123 | | B | 0.0771 | 1.554 | 0.0125 |
| 30 " | A | 0.0769 | 1.538 | 0.0123 | 240 " | A | 0.0771 | 1.554 | 0.0125 |
| | B | 0.0769 | 1.538 | 0.0123 | | B | 0.0771 | 1.554 | 0.0125 |
| 60 " | A | 0.0770 | 1.544 | 0.0124 | 270 " | A | 0.0771 | 1.554 | 0.0125 |
| | B | 0.0770 | 1.544 | 0.0124 | | B | 0.0771 | 1.554 | 0.0125 |
| 70 " | A | 0.0770 | 1.544 | 0.0124 | 285 " | A | 0.0771 | 1.554 | 0.0125 |
| | B | 0.0770 | 1.544 | 0.0124 | | B | 0.0771 | 1.554 | 0.0125 |
| 90 " | A | 0.0770 | 1.544 | 0.0124 | 300 " | A | 0.0771 | 1.554 | 0.0125 |
| | B | 0.0770 | 1.544 | 0.0124 | | B | 0.0771 | 1.554 | 0.0125 |

AVERAGE = 0.0124%

Thus a solution of $1\overline{6}^M$ Cadmium Sulphate in the Quin-Hydrone electrode gives a constant value for the hydrogen ion concentration for a period of at least five hours. The Quin-Hydrone electrode, therefore, is suitable for the determination of the degree of hydrolysis of Cadmium Sulphate solutions. The constancy of the electrode having been established, measurements with the four remaining dilutions were taken for shorter periods. Tabulated below are the results, showing total E.M.F. of composite cell, hydrogen ion concentration and percentage hydrolysis.

Results: Cadmium Sulphate in Quin-Hydrone Electrode.

| Time | | E.M.F. (volts) | $[H^+] \times 10^5$ | % Hydrolysis | Time | | E.M.F. volts | $[H^+] \times 10^5$ | % Hydrolysis |
|-------------------------|--------|-------------------|---------------------|------------------|--------------------------|--------|------------------|---------------------|------------------|
| $\frac{M}{32}$ 0 min | A B | 0.0650 0.0663 | 0.9674 1.017 | 0.0155 0.0163 | $\frac{M}{128}$ 0 min | A B | 0.0557 0.0562 | 0.674 0.686 | 0.0431 0.0440 |
| 10 " | A B | 0.0650 0.0663 | 0.967 1.017 | 0.0155 0.0163 | 10 " | A B | 0.0557 0.0562 | 0.674 0.686 | 0.0431 0.0440 |
| 20 " | A B | 0.0650 0.0663 | 0.967 1.017 | 0.0155 0.0163 | 20 " | A B | 0.0557 0.0562 | 0.674 0.686 | 0.0431 0.0440 |
| 30 " | A B | 0.0650 0.0663 | 0.967 1.017 | 0.0155 0.0163 | 30 " | A B | 0.0557 0.0562 | 0.674 0.686 | 0.0431 0.0440 |
| 40 " | A B | 0.0650 0.0663 | 0.967 1.017 | 0.0155 0.0163 | 40 " | A B | 0.0557 0.0562 | 0.674 0.686 | 0.0431 0.0440 |
| 50 " | A B | 0.0648 0.0661 | 0.960 1.009 | 0.0154 0.0162 | | | | | |
| 60 " | A B | 0.0650 0.0661 | 0.967 1.009 | 0.0155 0.0162 | | | | | |
| 90 " | A B | 0.0649 0.0661 | 0.964 1.009 | 0.0154 0.0162 | | | | | |

Results: Cadmium Sulphate in Quin-Hydrone Electrode (Cont.)

Time E.M.F. $[H^+] \times 10^5$ % Hydrolysis Time E.M.F. $[H^+] \times 10^5$ % Hydrolysis
(volts)

| | | | | | | | |
|------------------------------|------------------|------------------|------------------|-------------------------------|------------------|------------------|----------------|
| $\frac{M}{64}$ A 0 min. B | 0.0578 0.0573 | 0.7307 0.7167 | 0.0234 0.0230 | $\frac{M}{256}$ A 0 min. B | 0.0482 0.0489 | 0.5028 0.5166 | 0.064 0.066 |
| 10 " A B | 0.0578 0.0573 | 0.7307 0.7167 | 0.0234 0.0230 | 10 " A B | 0.0482 0.0489 | 0.5028 0.5166 | 0.064 0.066 |
| 20 " A B | 0.0578 0.0573 | 0.7307 0.7167 | 0.0234 0.0230 | 20 " A B | 0.0482 0.0489 | 0.5028 0.5166 | 0.064 0.066 |
| 30 " A B | 0.0578 0.0573 | 0.7307 0.7167 | 0.0234 0.0230 | 30 " A B | 0.0482 0.0489 | 0.5028 0.5166 | 0.064 0.066 |
| 40 " A B | 0.0578 0.0573 | 0.7307 0.7167 | 0.0234 0.0230 | 40 " A B | 0.0482 0.0489 | 0.5028 0.5166 | 0.064 0.066 |
| | | | | 60 " A B | 0.0482 0.0489 | 0.5028 0.5166 | 0.064 0.066 |

CONSIDERATION OF RESULTS.

With each dilution taken, constant values were obtained. If the hydrolysis is a first stage hydrolysis, e.g.



then the hydrolysis constant, K , equals

$$\frac{x^2}{(1-x) v} \quad (\text{Denham J.C.S., } \underline{93}, 1908, 42).$$

(Where x is the fraction hydrolysed and v is the number of litres containing one gram mole).

SUMMARY OF RESULTS.

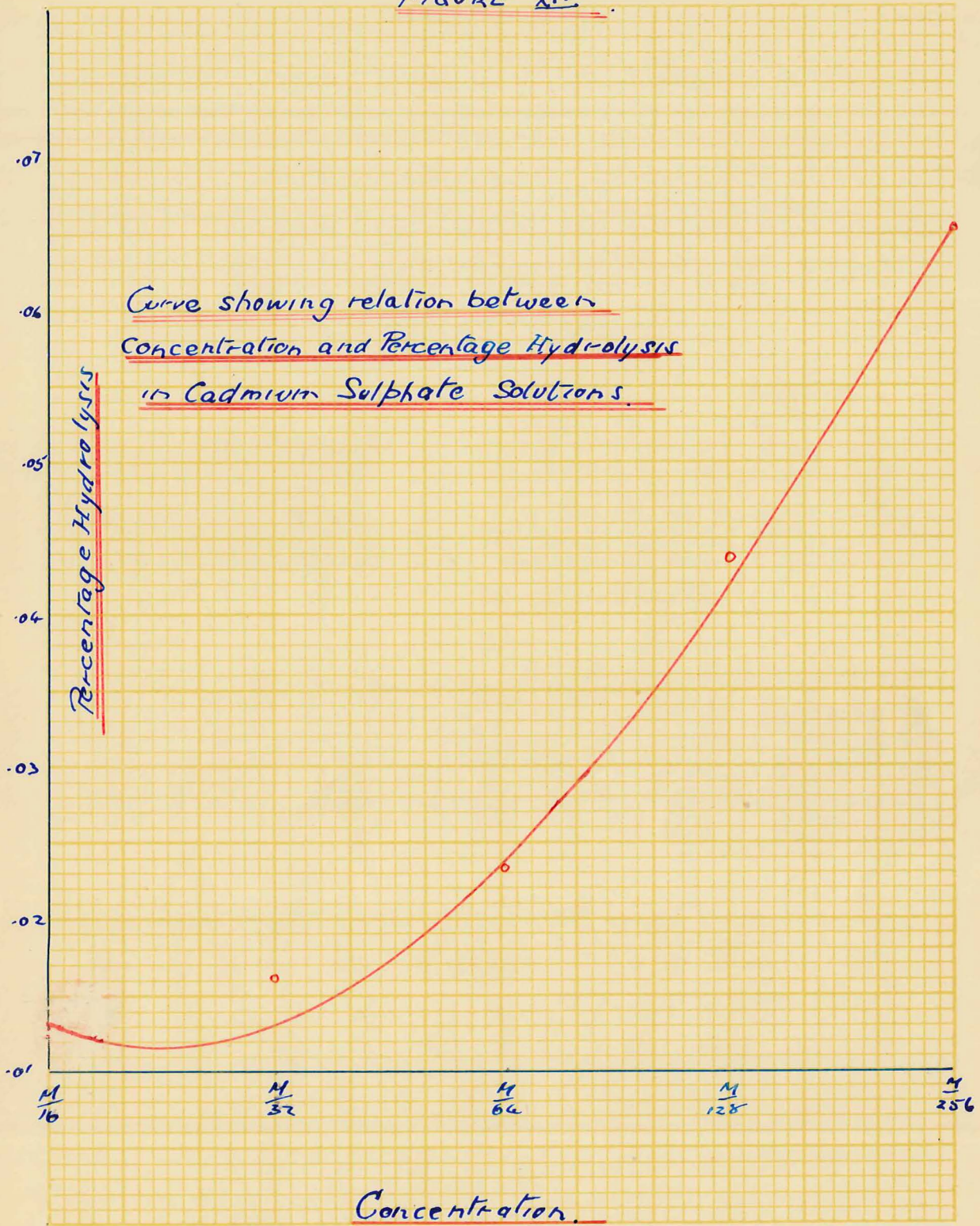
| Concentration | % Hydrolysis | Hydrolysis constant K |
|-------------------------------|--------------|-----------------------|
| $\frac{M}{16} \text{ CdSO}_4$ | 0.0124 | 0.96×10^{-9} |
| $\frac{M}{32}$ " | 0.0159 | 0.79×10^{-9} |
| $\frac{M}{64}$ " | 0.0232 | 0.84×10^{-9} |
| $\frac{M}{128}$ " | 0.0436 | 1.5×10^{-9} |
| $\frac{M}{256}$ " | 0.065 | 1.6×10^{-9} |

$$\text{Average} = \underline{1.14 \times 10^{-9}}$$

The constancy of the value of K shows that over the range investigated the hydrolysis is essentially first stage.

Carrara and Vespignani, (Gazz. Chim. Ital. 30, ii, 35, 1900), found 0.017% for a tenth normal solution of

FIGURE XIV



Cadmium Sulphate.

O'Sullivan, (Far. Soc. XXI, 1925-26, 319-325) determined the hydrogen ion concentration of acidified cadmium sulphate solutions, and found an increasing value (in the Quin-Hydrone electrode.) Apparently he did not make any determinations with neutral solutions of the salt.

LEAD CHLORIDE.

Preparation, Purification and Standardisation.

The lead chloride was prepared as follows:- About 60 grams of "Merck's pure" Lead Nitrate were dissolved in boiling water to give rise to a saturated solution. To this was added a saturated solution containing an equivalent quantity of Ammonium Chloride (A.R. quality). Lead Chloride was precipitated and readily settled. The precipitate was washed ten times by decantation, and the washings were tested till free of Ammonia, Nitrate and Chlorine. The crystals were filtered through a Blichner funnel and dried by leaving in a vacuum dessicator with

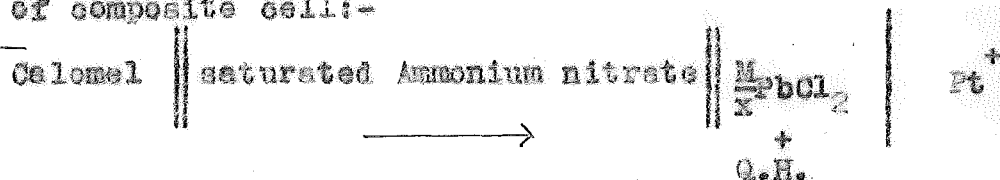
calcium chloride. It was found that when a solution was made with this sample a distinct turbidity was produced. This turbidity permanently disappeared on warming and cooling, but a difference of 0.1% in the hydrolysis was found between a solution so treated and the turbid solution. The turbidity was attributed to the presence of oxychlorides brought about by the drying of the crystals. A fresh sample of lead chloride was therefore prepared. The method of preparation was the same as before, but no attempt was made to dry the crystals. After washing free of Ammonia, etc., the crystals were further purified by recrystallisation. A saturated solution was then prepared, and from its volume and the solubility of the salt the approximate concentration was found. This solution was then diluted to give a solution of strength $\frac{M}{50}$ approximately. An analysis was next carried out by a determination (in triplicate), of the amount of Chloride as Silver Chloride, Cumming and Key "Quantitative Chemical Analysis" P. 150-153. From this result the amount of added water required to give a $\frac{M}{50}$ solution was calculated, and the solution was made up.

Solutions of strengths $\frac{M}{100}$, $\frac{M}{200}$, $\frac{M}{400}$ and $\frac{M}{800}$ were then made up by careful dilution, as before, of the first prepared solution ($\frac{M}{50}$).

Measurements were now taken of these solutions in the Quin-Hydrogen electrode, in duplicate, and the degree of hydrolysis of each solution calculated.

Readings were taken with one solution over an extended period to determine the constancy of the electrode with this salt.

In the following results, E.M.F. is total E.M.F. of composite cell:-



RESULTS:

Lead Chloride in Quin-Hydrone Electrode.

| Time | | E.M.F. (volts) | $[H^+] \times 10^5$ | % Hydrolysis |
|-----------------|---|----------------|---------------------|--------------|
| $\frac{M}{50}$ | | | | |
| 0 min. | A | 0.1155 | 6.918 | 0.173 |
| | B | 0.1150 | 6.784 | 0.170 |
| 10 " | A | 0.1155 | 6.918 | 0.173 |
| | B | 0.1150 | 6.784 | 0.170 |
| 20 " | A | 0.1155 | 6.918 | 0.173 |
| | B | 0.1150 | 6.784 | 0.170 |
| 30 " | A | 0.1155 | 6.918 | 0.173 |
| | B | 0.1150 | 6.784 | 0.170 |
| 40 " | A | 0.1155 | 6.918 | 0.173 |
| | B | 0.1150 | 6.784 | 0.170 |
| $\frac{M}{100}$ | | | | |
| 0 " | A | 0.1031 | 4.628 | 0.232 |
| | B | 0.1027 | 4.202 | 0.210 |
| 10 " | A | 0.1031 | 4.628 | 0.232 |
| | B | 0.1027 | 4.202 | 0.210 |
| 20 " | A | 0.1031 | 4.628 | 0.232 |
| | B | 0.1027 | 4.202 | 0.210 |
| 30 " | A | 0.1031 | 4.628 | 0.232 |
| | B | 0.1027 | 4.202 | 0.210 |

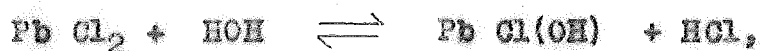
Lead Chloride in Quin Hydronc Electrode (Continued).

| Time | | | E.M.F. (volts) | $\sqrt{H} \times 10^5$ | % Hydrolysis |
|-----------------|--------|---|----------------|------------------------|--------------|
| $\frac{M}{200}$ | 0 min. | A | 0.0925 | 2.824 | 0.283 |
| | | B | 0.0925 | 2.824 | 0.283 |
| 10 " | | A | 0.0925 | 2.824 | 0.283 |
| | | B | 0.0925 | 2.824 | 0.283 |
| 20 " | | A | 0.0925 | 2.824 | 0.283 |
| | | B | 0.0925 | 2.824 | 0.283 |
| 30 " | | A | 0.0925 | 2.824 | 0.283 |
| | | B | 0.0925 | 2.824 | 0.283 |
| $\frac{M}{400}$ | 0 " | A | 0.0849 | 2.100 | 0.420 |
| | | B | 0.0846 | 2.076 | 0.415 |
| 10 " | | A | 0.0849 | 2.100 | 0.420 |
| | | B | 0.0846 | 2.076 | 0.415 |
| 20 " | | A | 0.0849 | 2.100 | 0.420 |
| | | B | 0.0846 | 2.076 | 0.415 |
| 30 " | | A | 0.0849 | 2.100 | 0.420 |
| | | B | 0.0846 | 2.076 | 0.415 |
| $\frac{M}{800}$ | 0 " | A | 0.0810 | 1.804 | 0.722 |
| | | B | 0.0810 | 1.804 | 0.722 |
| 10 " | | A | 0.0810 | 1.804 | 0.722 |
| | | B | 0.0810 | 1.804 | 0.722 |
| 20 " | | A | 0.0810 | 1.804 | 0.722 |
| | | B | 0.0810 | 1.804 | 0.722 |
| 30 " | | A | 0.0810 | 1.804 | 0.722 |
| | | B | 0.0810 | 1.804 | 0.722 |

Further measurements with $\frac{M}{100}$ dilution showed that an approximately constant E.M.F. was maintained for nine hours.

CONSIDERATION OF RESULTS.

Here, again, with each dilution measured, constant values were obtained. If this hydrolysis is a first stage hydrolysis, e.g.



then the hydrolytic constant K again equals $\frac{x^2}{(1-x) v}$.

RESULTS.

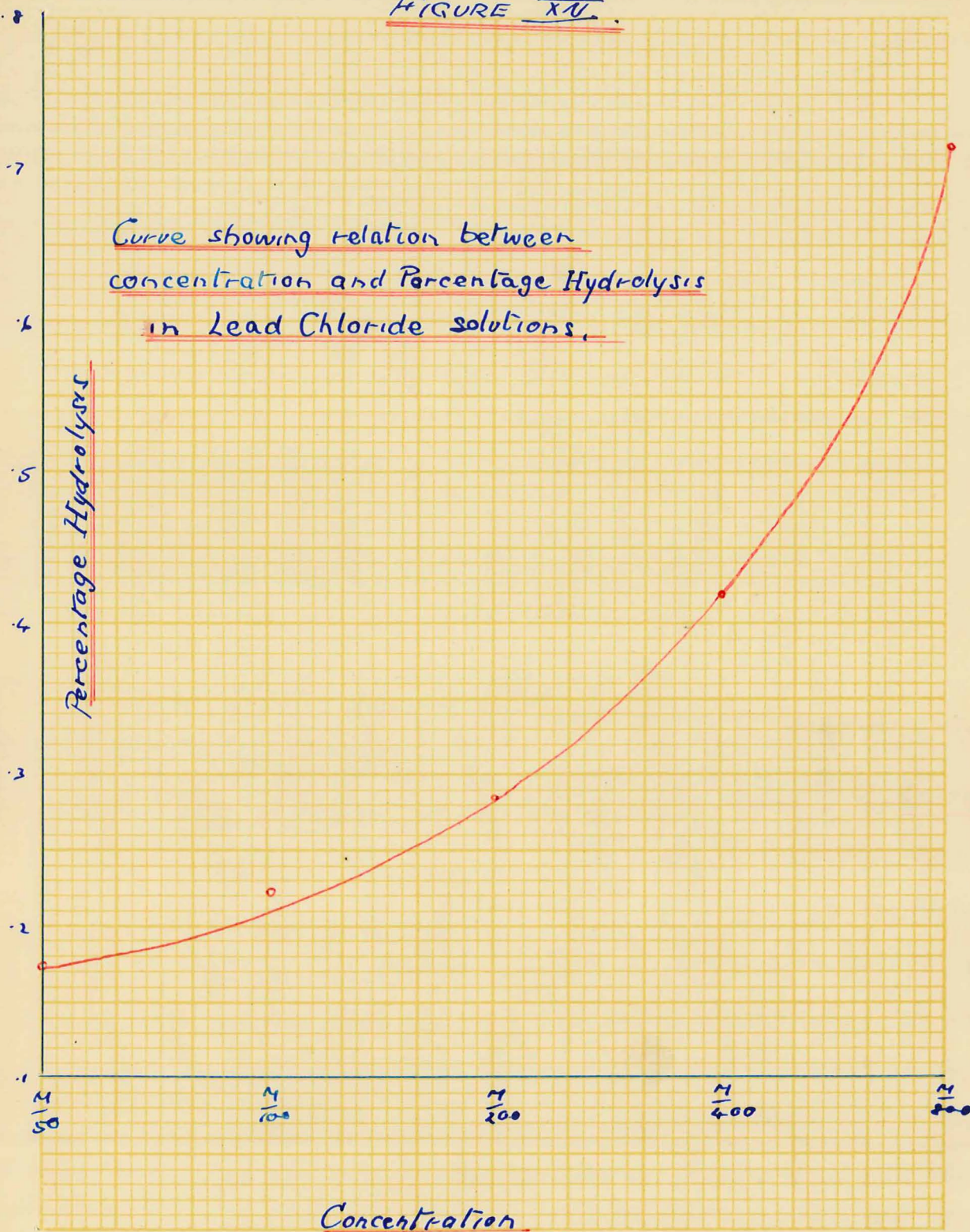
| Concentration | % Hydrolysis | Hydrolysis constant K |
|--------------------------------|--------------|-----------------------|
| $\frac{M}{50}$ PbCl_2 | 0.172 | 0.60×10^{-7} |
| $\frac{M}{100}$ " | 0.221 | 0.50×10^{-7} |
| $\frac{M}{200}$ " | 0.283 | 0.40×10^{-7} |
| $\frac{M}{400}$ " | 0.418 | 0.44×10^{-7} |
| $\frac{M}{600}$ " | 0.722 | 0.66×10^{-7} |

$$\text{Average} = 0.52 \times 10^{-7}$$

The constancy of the value of K shows that over the range investigated, the hydrolysis is essentially first stage.

FIGURE XIV.

Curve showing relation between
concentration and Percentage Hydrolysis
in Lead Chloride solutions.



J. K. Ward (Journ. Chem. Soc. 1910, 97, 878) found the value 0.2% hydrolysis for a tenth normal solution of lead chloride at 25°C.

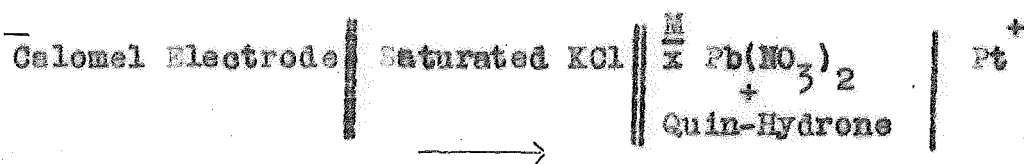
H. Ley (Zeit. Phys. Chem. 1899, 30, 193-257) obtained the value 0.6% for a $\frac{M}{100}$ solution at 99.7°C.

J. W. Mellor "Comprehensive Treatise on Inorganic Chemistry" quotes for $\frac{M}{128}$ $PbCl_2$:- 85.5°C - 0.50%;
100°C -- 0.77%.

LEAD NITRATE.

Standardisation.

The sample of salt used was "Merck's Pure" Lead Nitrate. This was taken as sufficiently pure, and no further purification, and no analysis, was carried out. Using International Atomic Weights (1925) it was calculated that 20.7010 grams of lead nitrate $Pb(NO_3)_2$ were required per litre to give a $\frac{M}{16}$ solution. That quantity was therefore weighed out accurately to the tenth of a milligram, and the volume was made up to a litre in a calibrated standard flask. From this solution, solutions of strength $\frac{M}{32}$, $\frac{M}{64}$, $\frac{M}{128}$, $\frac{M}{256}$ were made up by careful dilution.

$$\text{Calomel Electrode} \parallel \text{Saturated KCl} \parallel \frac{M}{x} \text{Pb(NO}_3)_2 \parallel \text{Pt}^+ \\ \text{Quin-Hydrone}$$


RESULTS: LEAD NITRATE IN QUIN)HYDRONE ELECTRODE.

| Time | | E.M.F. (volts) | $[H^+] \times 10^5$ | % Hydrolysis |
|---------------------------------|---|----------------|---------------------|--------------|
| <u>M</u> <u>16</u> 0 min. | A | 0.1208 | 8.504 | 0.068 |
| | B | 0.1214 | 8.706 | 0.070 |
| 10 " | A | 0.1206 | 8.437 | 0.068 |
| | B | 0.1214 | 8.706 | 0.070 |
| 20 " | A | 0.1206 | 8.437 | 0.068 |
| | B | 0.1214 | 8.706 | 0.070 |
| 30 " | A | 0.1206 | 8.437 | 0.068 |
| | B | 0.1214 | 8.706 | 0.070 |
| 40 " | A | 0.1206 | 8.437 | 0.068 |
| | B | 0.1214 | 8.706 | 0.070 |
| <u>M</u> <u>32</u> 0 Min. | A | 0.1085 | 5.266 | 0.085 |
| | B | 0.1080 | 5.165 | 0.083 |
| 10 " | A | 0.1085 | 5.266 | 0.085 |
| | B | 0.1080 | 5.165 | 0.083 |
| 20 " | A | 0.1085 | 5.266 | 0.085 |
| | B | 0.1080 | 5.165 | 0.083 |
| 30 " | A | 0.1085 | 5.266 | 0.085 |
| | B | 0.1080 | 5.165 | 0.083 |

RESULTS: LEAD NITRATE IN QUIN-HYDRONE ELECTRODE (Cont.)

| Time | E.M.F. volts $[H^+] \times 10^5$ | | % Hydrolysis. | |
|-----------------------|----------------------------------|--------|---------------|-------|
| <u>M</u> 54 0 min. | A | 0.0954 | 3.161 | 0.102 |
| | B | 0.0954 | 3.161 | 0.102 |
| 10 " | A | 0.0954 | 3.161 | 0.102 |
| | B | 0.0954 | 3.161 | 0.102 |
| 20 " | A | 0.0954 | 3.161 | 0.102 |
| | B | 0.0954 | 3.161 | 0.102 |
| 30 " | A | 0.0954 | 3.161 | 0.102 |
| | B | 0.0954 | 3.161 | 0.102 |
| <u>M</u> 128 0 " | A | 0.0829 | 1.943 | 0.125 |
| | B | 0.0833 | 1.973 | 0.127 |
| 10 " | A | 0.0829 | 1.943 | 0.125 |
| | B | 0.0833 | 1.973 | 0.127 |
| 20 " | A | 0.0829 | 1.943 | 0.125 |
| | B | 0.0833 | 1.973 | 0.127 |
| 30 " | A | 0.0829 | 1.943 | 0.125 |
| | B | 0.0833 | 1.973 | 0.127 |
| <u>M</u> 256 0 " | A | 0.0743 | 1.390 | 0.178 |
| | B | 0.0737 | 1.358 | 0.174 |
| 10 " | A | 0.0743 | 1.390 | 0.177 |
| | B | 0.0737 | 1.358 | 0.174 |
| 20 " | A | 0.0743 | 1.390 | 0.177 |
| | B | 0.0737 | 1.358 | 0.174 |
| 30 " | A " | 0.0743 | 1.390 | 0.177 |
| | B | 0.0737 | 1.358 | 0.174 |

The $\frac{M}{32}$ solution was later measured for nine hours and practically constant E.M.F. was maintained during that period.

CONSIDERATION OF RESULTS.

As in the previous cases, constant E.M.Fs. were maintained in each dilution measured. The average values for degree of hydrolysis in each solution, and the hydrolysis constant are as follows:-

| | | Average % Hydrolysis | Hydrolytic constant K |
|-----------------|------------------------------------|----------------------|--------------------------|
| $\frac{M}{16}$ | Pb (NO ₃) ₂ | 0.069 | 0.298×10^{-7} |
| $\frac{M}{32}$ | " | 0.084 | 0.221×10^{-7} |
| $\frac{M}{64}$ | " | 0.102 | 0.163×10^{-7} |
| $\frac{M}{128}$ | " | 0.126 | 0.124×10^{-7} |
| $\frac{M}{256}$ | " | 0.176 | 0.121×10^{-7} |

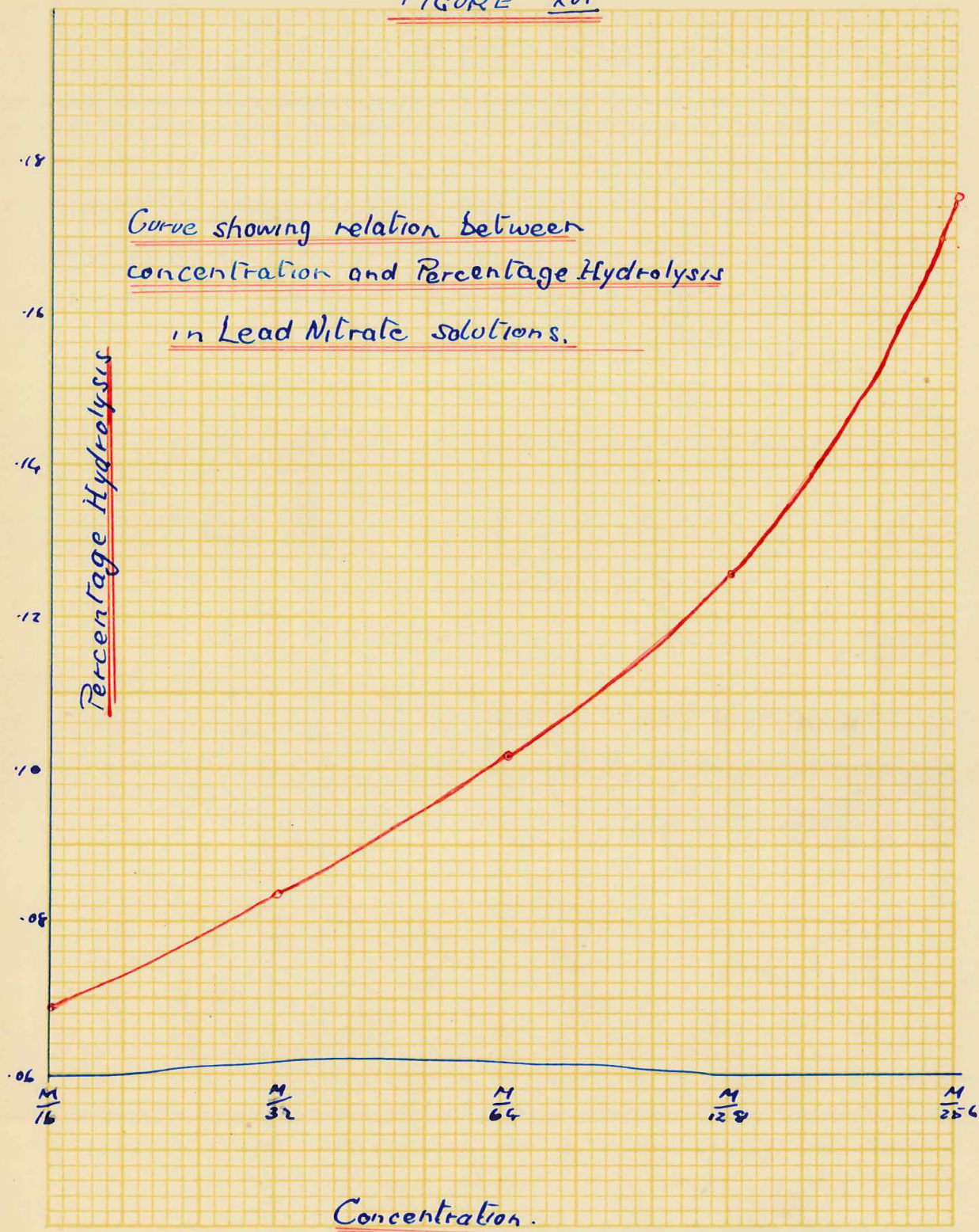
$$\text{Average} = 0.185 \times 10^{-7}$$

The values are shown in the graph on page 87, figure 16.

H. J. Long, (Journ. Amer. Chem. Soc., 1896, 18, 693-717) obtained the value 0.096% hydrolysis for a semi-normal solution of lead nitrate at 20° C.

Walker and Aston, (Journ. Chem. Soc., 1895, 67, 576-586) found 0.15% at 80° C. for a semi-normal solution

FIGURE XVI



of the salt.

J. W. Meller, (ibid Vol. VII, P.861) quotes the following:-

| | 85.5 C | 100 C. |
|-------------------------------|--------|--------|
| $\frac{M}{32}$, $Pb(NO_3)_2$ | 0.253% | 0.482% |
| $\frac{M}{128}$ " | 0.400% | 0.742% |

THALLOUS SULPHATE.

Preparation, Purification and Standardisation.

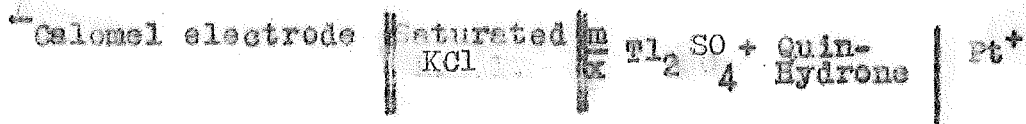
This salt had to be prepared from the pure metal. The metal was washed free of glycerine, (in which it had been stored), and dilute sulphuric acid (A.R.), was added. Slow evolution of hydrogen set in, but became brisker with time. When practically all the Thallium was dissolved the solution became brownish in colour; finally a trace of a dark deposit remained. This was due to the formation of Thallous Sulphate which hydrolysed, giving Thallous Oxide, (dark deposit), which oxide gave the solution its brown colour. Filtration of the solution was carried out

and the filtrate was evaporated to about a quarter of its bulk.

Pure absolute alcohol was added in excess and the Thallous Sulphate was precipitated, this precipitate being washed twice by decantation with alcohol. These crystals were redissolved in boiling water to give a saturated solution. Reprecipitation with alcohol was next carried out, and the precipitate washed by decantation with alcohol three times. The solution at this stage gave no acid test to litmus. Drying of the crystals was brought about by evaporation on the water bath and heating in the air oven at 120°C for one hour. Finally, the crystals were heated in the electric furnace to 500°C, and allowed to cool, partly in the furnace and then in a desiccator. A good white sample of crystals resulted.

The weight of salt required to give a $\frac{M}{25}$ solution was calculated, and an amount of salt was accurately weighed out to give a solution slightly over strength. A determination of the exact strength of this solution was then made by a determination of the sulphate as barium sulphate, (Cumming and Kay), in

duplicate. The calculated amount of water was added to the remainder of the solution to give exactly a $\frac{M}{25}$ solution of Thallous Sulphate. Measurements were taken with six different concentrations of the salt (in duplicate). In the results, the 'E.M.F.' is the total E.M.F. of the cell.



Most of the solutions were measured for half an hour, but two were measured for longer periods.

RESULTS: THALLOUS SULPHATE IN QUIN-HYDRONE ELECTRODE.

| Time | | R.M.F. | $\sqrt{H^+} \times 10^5$ | % Hydrolysis. |
|----------------|----------|--------|--------------------------|---------------|
| <u>M</u> 25 | 0 min. A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 10 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 20 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 30 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 40 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 60 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 80 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 100 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |
| 120 " | A | 0.0613 | 0.838 | 0.0105 |
| | B | 0.0613 | 0.838 | 0.0105 |

RESULTS: THALLOUS SULPHATE in QUIN-HYDRONE ELECTRODE

(Continued).

| Time | | E.M.F. | $[H^+] \times 10^5$ | % Hydrolysis. |
|-----------------------|--------|------------------|---------------------|------------------|
| $\frac{M}{10}$ 0 min. | A B | 0.0689 0.0680 | 1.127 1.087 | 0.0282 0.0273 |
| 10 " | A B | 0.0689 0.0680 | 1.127 1.087 | 0.0282 0.0272 |
| 20 " | A B | 0.0689 0.0680 | 1.127 1.087 | 0.0282 0.0273 |
| 30 " | A B | 0.0689 0.0680 | 1.127 1.087 | 0.0282 0.0273 |
| 40 " | A B | 0.0689 0.0680 | 1.127 1.087 | 0.0282 0.0273 |
| $\frac{M}{100}$ 0 " | A B | 0.0705 0.0713 | 1.199 1.237 | 0.060 0.062 |
| 10 " | A B | 0.0705 0.0713 | 1.199 1.237 | 0.060 0.062 |
| 20 " | A B | 0.0705 0.0713 | 1.199 1.237 | 0.060 0.062 |
| 30 " | A B | 0.0705 0.0713 | 1.199 1.237 | 0.060 0.062 |

RESULTS: THALLOUS SULPHATE in QUIN-HYDRONE ELECTRODE.
(Continued)

| Time | | E.M.F. | $[H^+] \times 10^5$ | % Hydrolysis. |
|-----------------|---|--------|---------------------|---------------|
| $\frac{M}{200}$ | | | | |
| 0 min. | A | 0.0578 | 0.7308 | 0.073 |
| | B | 0.0577 | 0.7280 | 0.073 |
| 10 " | A | 0.0578 | 0.7308 | 0.073 |
| | B | 0.0577 | 0.7280 | 0.073 |
| 20 " | A | 0.0578 | 0.7308 | 0.073 |
| | B | 0.0577 | 0.7280 | 0.073 |
| 30 " | A | 0.0578 | 0.7308 | 0.073 |
| | B | 0.0575 | 0.7224 | 0.072 |
| 40 " | A | 0.0578 | 0.7308 | 0.072 |
| | B | 0.0575 | 0.7224 | 0.072 |
| 50 " | A | 0.0580 | 0.7365 | 0.074 |
| | B | 0.0576 | 0.7251 | 0.073 |
| 60 " | A | 0.0580 | 0.7365 | 0.074 |
| | B | 0.0576 | 0.7251 | 0.073 |
| 80 " | A | 0.0580 | 0.7365 | 0.074 |
| | B | 0.0576 | 0.7251 | 0.073 |
| 100 " | A | 0.0580 | 0.7365 | 0.074 |
| | B | 0.0576 | 0.7251 | 0.073 |

RESULTS: THALLOUS SULPHATE in QUIN-HYDRONE ELECTRODE.

(Continued).

| Time | | E.M.F. | $[H^+] \times 10^5$ | % Hydrolysis. |
|---------------------------|---|--------|---------------------|---------------|
| $\frac{M}{400}$ 0 Min. | A | 0.0630 | 0.8550 | 0.171 |
| | B | 0.0630 | 0.8550 | 0.171 |
| 10 " | A | 0.0630 | 0.8550 | 0.171 |
| | B | 0.0630 | 0.8550 | 0.171 |
| 20 " | A | 0.0630 | 0.8550 | 0.171 |
| | B | 0.0630 | 0.8550 | 0.171 |
| 30 " | A | 0.0630 | 0.8550 | 0.171 |
| | B | 0.0630 | 0.8550 | 0.171 |
| $\frac{M}{800}$ 0 " | A | 0.0615 | 0.8441 | 0.338 |
| | B | 0.0615 | 0.8441 | 0.338 |
| 10 " | A | 0.0615 | 0.8441 | 0.338 |
| | B | 0.0615 | 0.8441 | 0.338 |
| 20 " | A | 0.0615 | 0.8441 | 0.338 |
| | B | 0.0615 | 0.8441 | 0.338 |
| 30 " | A | 0.0615 | 0.8441 | 0.338 |
| | B | 0.0615 | 0.8441 | 0.338 |

CONSIDERATION OF RESULTS.

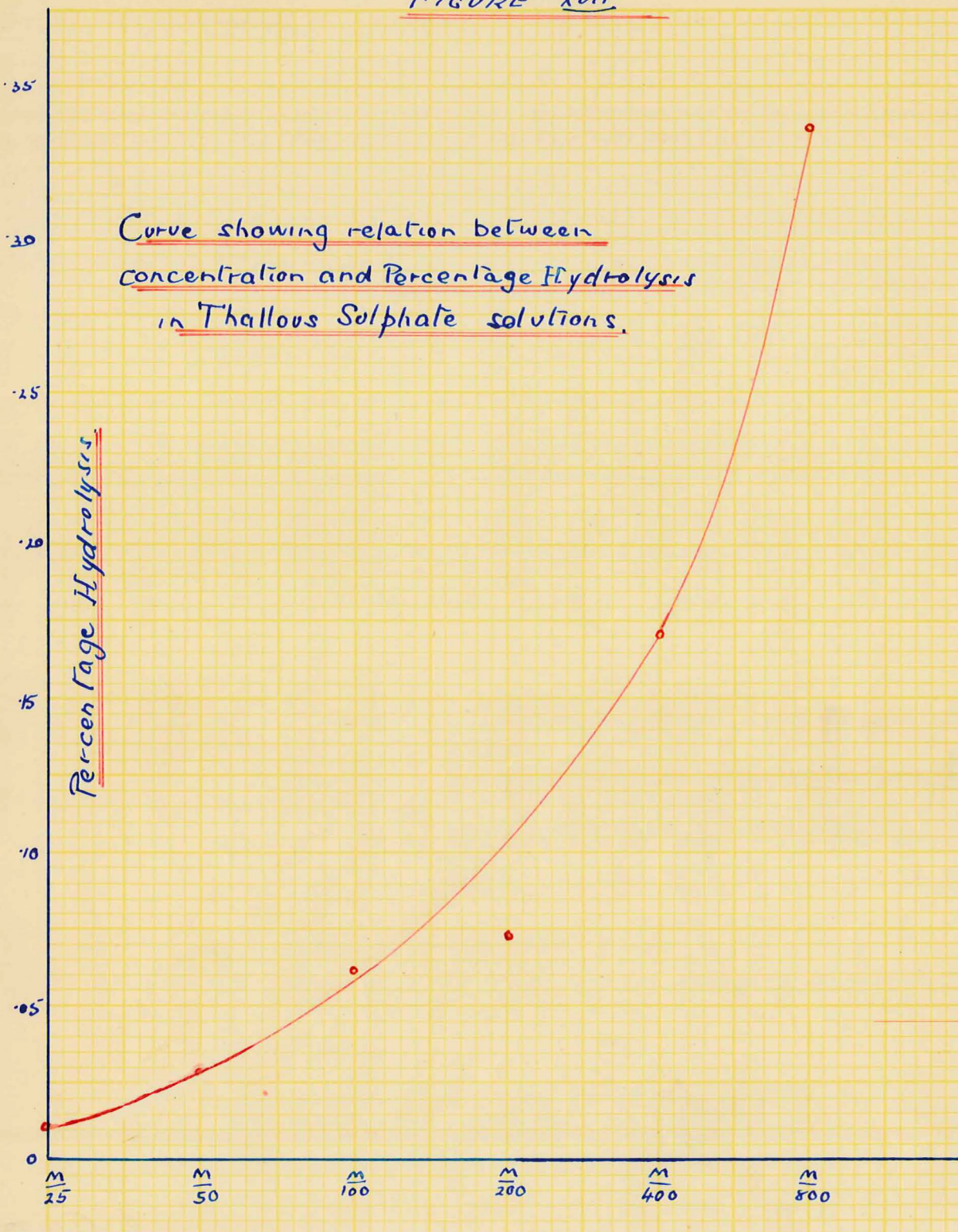
In each case practically constant values were maintained; two solutions which were measured for $1\frac{1}{2}$ and 2 hours respectively still showed constant E.M.Fs. An experiment was conducted using saturated ammonium nitrate in the middle vessel, and $\frac{M}{100}$ Thallous Sulphate as electrolyte. The experiment was done in duplicate, and in both cases the E.M.F. was found to vary in a very irregular manner. Later the experiment was repeated with a more dilute solution, $\frac{M}{200}$, and constant values were obtained, the E.M.F. being the same as was found for the same dilution using saturated potassium chloride in the middle vessel. Shaking the electrode after it had been in commission for half an hour had the effect of slightly increasing the E.M.F. by about 0.8 to 1.0 of a millivolt. As the type of electrode used (Figure III, b) had no stop-cock to minimise diffusion, it is possible that diffused potassium chloride was, by the shaking, mixed with the bulk electrolyte. Hence no great significance can be placed on the increased value. ^{The more} determination of the balance on the bridge wire was difficult with the dilute solutions $\frac{M}{400}$ and $\frac{M}{800}$.—

The average values for the degree of hydrolysis of the different solutions at 25° C are as follows:-

| | |
|---------------------------|---------|
| $\frac{M}{25}$ Tl_2SO_4 | 0.0105% |
| $\frac{M}{50}$ | 0.0278% |
| $\frac{M}{100}$ | 0.061% |
| $\frac{M}{200}$ | 0.073% |
| $\frac{M}{400}$ | 0.171% |
| $\frac{M}{800}$ | 0.338% |

Figure 17, P.96, shows the graph obtained from these values. The only value by other methods ^{that} could be found was that obtained by H. G. Denham (Journ. Chem. Soc. 1908, 93, 41-63), using the hydrogen electrode. He found the value of 4.9% hydrolysis in a $\frac{M}{16}$ solution of Thallous Sulphate at 25° C. The salt used in that experiment was Kahlbaum's crystals and may not have been of exceptional purity. Also, it was shown subsequently (Denham, J.C.S., Vol. 93, p.635) that reduction takes place on the surface of the hydrogen electrode,



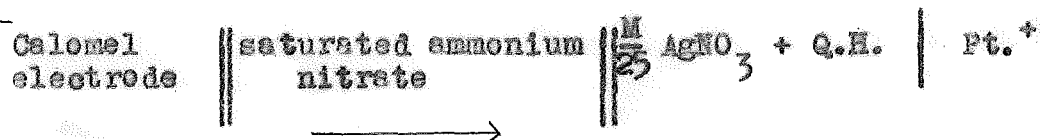
FIGURE XVII

The above results obtained by the Quin-Hydrone electrode, are in accordance with the fact that Thallous compounds are comparable with silver, and the alkali and alkaline earth metals which form strong bases and therefore give sulphates which are very little hydrolysed. Caven and Lander, "Systematic Inorganic Chemistry" (1924), P.164~~m~~ state that "Thallous sulphate closely resembles the alkali sulphates."

SILVER NITRATE.

The salt used was Merck's 'pro analysi'. It was taken as sufficiently pure and a $\frac{M}{25}$ solution was prepared by weighing accurately the calculated amount of salt and diluting to the required volume.

Measurements were taken of the following cell, in duplicate:-



As usual, a few minutes were allowed for the cell to take on the temperature of the thermostat.

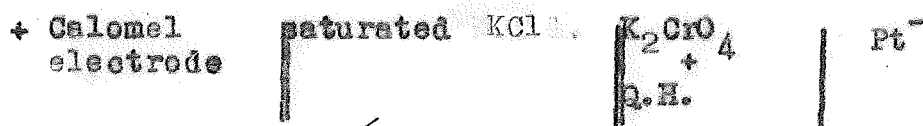
RESULTS.

Although constant E.M.F. was maintained for two hours, yet an inspection of the solution revealed that reduction to metallic silver had taken place. An experiment showed that at 25° C. the electrode vessel became coated with a silvery deposit in five to ten minutes. The bridge readings indicated an apparent hydrolysis of 2500 per cent. The experiment was repeated using silver nitrate at 0° C., Quin-Hydrone was added, the solution was shaken for a few seconds and the potential vessel placed in ice water. Readings were then immediately taken, but practically the same value as before was obtained. An inspection of the electrode did not reveal any sign of a silver deposit or reduction for at least half an hour, when small silvery specks were observed. It is probable that the reduced silver was present in colloidal form, and became apparent as coagulation advanced. (This latter experiment is an example of how rapidly chemical changes may take place, and yet no change be visible for a considerable time)

The degree of hydrolysis of silver nitrate can therefore not be determined by means of the Quin-Hydrone electrode, the reduction being so rapid that even its rate could not be found.

POTASSIUM CHROMATE.

The sample of salt used was of A.R. quality, and was used direct without further purification. It was calculated that 2.4275 gms. of potassium chromate were required in 200 c.c. to give a $\frac{M}{16}$ solution. This solution was therefore made up and the E.M.F. of the following cell (in duplicate) was measured:-

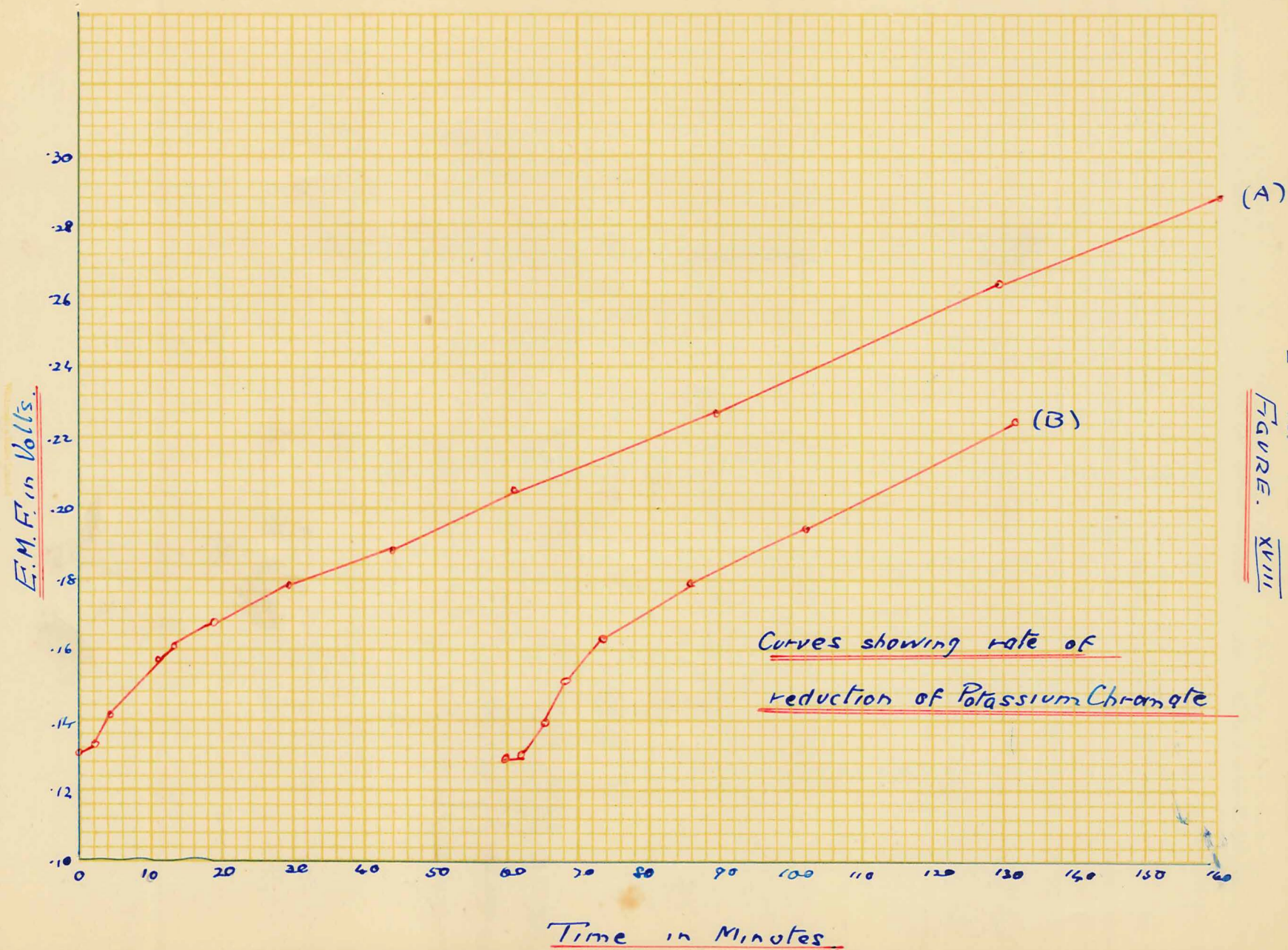


In the following results the total E.M.F. of the above cell is recorded with the time. Constant E.M.Fs. were not obtained, but a slow measurable rate of reduction took place. From the values obtained, curves were drawn, (Figure 18) showing the rate of reduction of potassium chromate in the Quin-Hydrone electrode at 25° C. The lowest value obtained for the E.M.F. was in both cases 0.127 volts. This corresponds to a hydrogen ion concentration of 1.08×10^{-4} and a degree of hydrolysis of 0.17%. Since this value can be obtained it indicates that the degree of hydrolysis of $\frac{M}{16}$ potassium chromate solution is not greater than 0.17%. No values could be found in the literature. This experiment, therefore, gives the above maximum value

for hydrolysis, the reduction curves, and shows that this electrode is unsuitable for measuring the degree of hydrolysis of potassium chromate solutions:

RESULTS: USING POTASSIUM CHROMATE IN QUIN-HYDRONE ELECTRODE

| Time in Mins. | | E.M.F. (A) | Time in Mins. | | E.M.F. (B) |
|---------------|-------|-------------|---------------|-------|------------|
| mins. | secs. | | mins. | secs. | |
| 0 | 0 | 0.127 volts | 0 | 0 | 0.127 volt |
| 2 | 0 | 0.132 " | 1 | 45 | 0.128 " |
| 4 | 10 | 0.140 " | 4 | 30 | 0.137 " |
| 11 | 0 | 0.155 " | 7 | 40 | 0.151 " |
| 13 | 15 | 0.159 " | 13 | 0 | 0.161 " |
| 18 | 30 | 0.166 " | 25 | 50 | 0.177 " |
| 29 | 0 | 0.177 " | 42 | 0 | 0.192 " |
| 44 | 0 | 0.187 " | 71 | 0 | 0.224 " |
| 60 | 5 | 0.204 " | | | |
| 89 | 0 | 0.226 " | | | |
| 129 | 0 | 0.262 " | | | |
| 160 | 0 | 0.286 " | | | |



POTASSIUM DI-HYDROGEN PHOSPHATE (KH_2PO_4).

A solution of this salt of strength $\frac{M}{32}$ was used in a subsequent experiment, and in passing a determination of its hydrogen ion concentration was made, using the Quin-Hydronc electrode. The salt used was of A.R. quality, and was not further purified.

RESULTS. KH_2PO_4 in Quin-Hydronc Electrode.

| Time | Total E.M.F. | $[\text{H}^+] \times 10^5$ | Electrode. |
|--------|--------------|----------------------------|------------|
| 0 mins | 0.1230 | 9.264 | <u>A</u> |
| 15 " | 0.1230 | 9.264 | |
| 50 " | 0.1230 | 9.264 | |
| 75 " | 0.1230 | 9.264 | |
| 0 " | 0.1238 | 9.559 | <u>B</u> |
| 15 " | 0.1238 | 9.559 | |
| 45 " | 0.1238 | 9.559 | |
| 60 " | 0.1238 | 9.559 | |

Hence, average value for hydrogen ion concentration of $\frac{M}{32}$ potassium di-hydrogen phosphate at 25°C . is 9.412×10^{-5} gram ions of hydrogen ion per litre.

E. Salm. (Zeit. Phys. Chem., 57, 471, 1906) obtained the value 3.3×10^{-5} for the hydrogen ion concentration of a tenth normal solution.

AN INVESTIGATION INTO THE ANOMALOUS BEHAVIOUR
OF SOLUTIONS OF ZINC SULPHATE IN THE HYDROGEN
ELECTRODE.

This investigation can conveniently be divided into two sections:-

SECTION A.

A type of hydrogen electrode was fitted up in which were two platinum black electrodes, differently situated as regards the incoming hydrogen gas stream. This was known as the 'double electrode'. The object of this apparatus was to determine if the two electrodes in the same solution would give the same or different values for the potential difference, and hence, the same or different, hydrogen ion concentrations around the electrodes. A diagram of the apparatus appears in Figure 19, on the next page. Both vessels I and II were filled with the same electrolyte. Vessel II was swept out with hydrogen for five minutes from below, through the tube A saturating the solution, (the tube B was closed meanwhile). The electrode in II, previously out of the solution, was then carefully lowered into the electrolyte. Hydrogen was now passed through vessel I by way of the inlet tube C, and was led

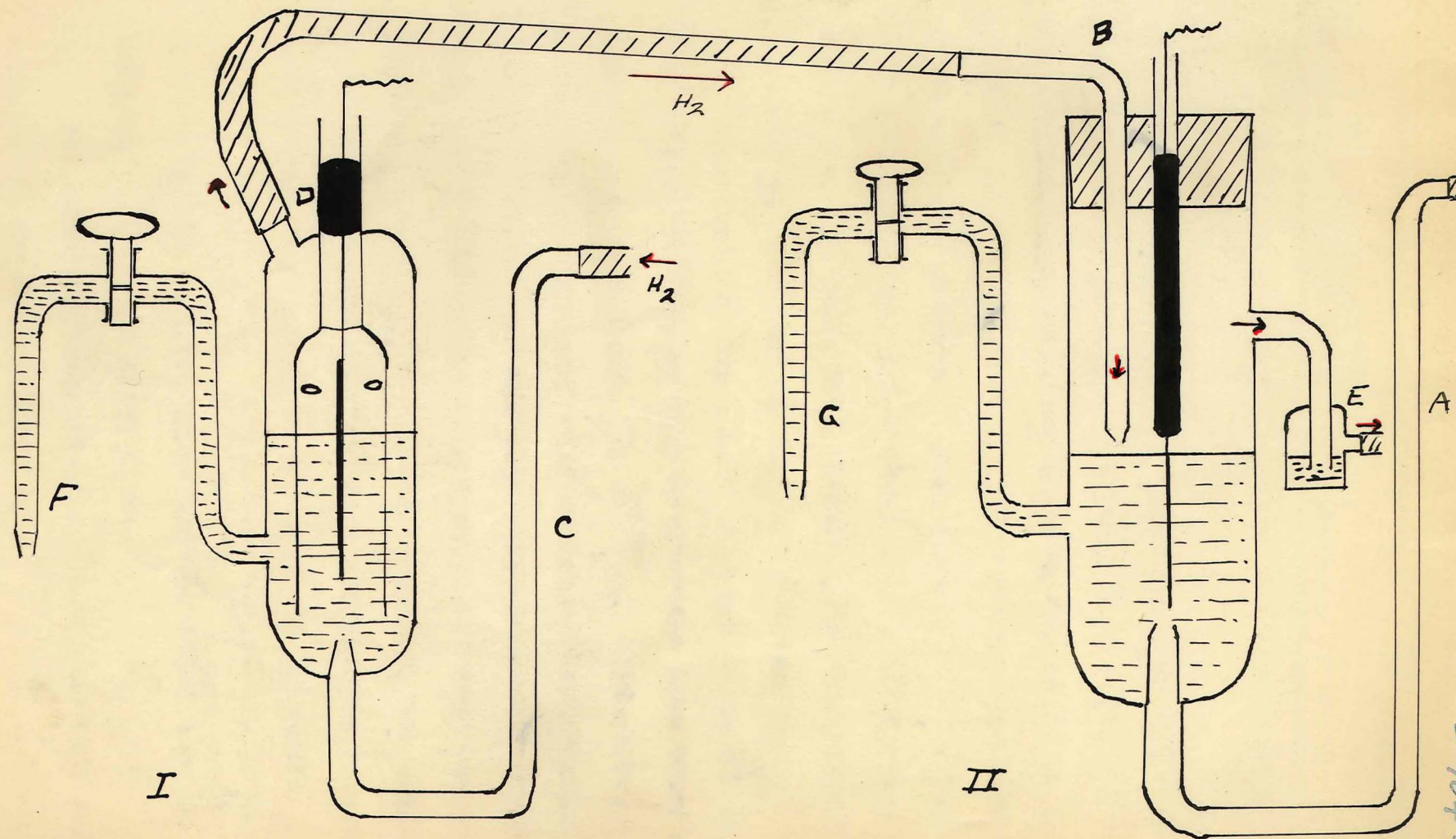


FIGURE XIX

- 401 -

out through the tube D. This gas then passed through tube B, and out through the bubbler E. Vessel I was thus the ordinary type of hydrogen electrode, while in II the solution was saturated from above with hydrogen without disturbing the solution. Both vessels made contact with the middle vessel by the tubes F and G. A $\frac{N}{10}$ Calomel electrode was used as the other half element. The remainder of the apparatus was the same as was used previously.

A preliminary experiment was made using $\frac{N}{200}$ Sulphuric Acid as electrolyte, to test whether the same value was given by each electrode. It was found that although the values were not the same half an hour after starting, yet they gradually approached each other until, at the end of three hours, the values were identical. They remained identical for 15 hours when the experiment was concluded.

Zinc Sulphate crystals were purified as before and a $\frac{N}{32}$ solution prepared by analysis and dilution. The 'double' electrode was washed out, dried, rinsed with the above solution, and set up as before, using the $\frac{N}{32}$ zinc sulphate solution as electrolyte.

Two complete determinations were then made with this solution in the double electrode.

In the following tabulated results, the total E.M.F. of the electrodes I and II, (plus in each case the calomel electrode), are recorded with the times at which the measurements were taken.

RESULTS: ZINC SULPHATE IN 'DOUBLE' HYDROGEN ELECTRODE.

| Time | | E.M.F. I | E.M.F. II | Time | | E.M.F. I | E.M.F. II |
|------|------|----------------|-----------|------|-------|----------------|-----------|
| | | <u>CASE A.</u> | | | | <u>CASE B.</u> | |
| Hrs. | Mins | | | Hrs. | mins. | | |
| 2 | 0 | 0.6237 | 0.6369 | 0 | 20 | 0.6442 | 0.6843 |
| 2 | 30 | 0.6443 | 0.6489 | 0 | 45 | 0.6557 | 0.6880 |
| 3 | 30 | 0.6777 | 0.6614 | 0 | 75 | 0.6576 | 0.6954 |
| 4 | 0 | 0.6800 | 0.6678 | 1 | 30 | 0.6585 | 0.6972 |
| | | | | 2 | 0 | 0.6581 | 0.6975 |
| | | | | 2 | 30 | 0.6701 | 0.6974 |
| | | | | 3 | 0 | 0.6677 | 0.6964 |
| | | | | 3 | 30 | 0.6717 | 0.6974 |
| | | | | 4 | 0 | 0.6791 | 0.6979 |
| | | | | 7 | 0 | 0.6830 | 0.6952 |

The corresponding hydrogen ion concentrations for the last values in Case B, are

$$\begin{array}{lll} \text{I} & [\text{H}^+] & = 1.434 \times 10^{-6} \\ \text{II} & [\text{H}^+] & = 0.892 \times 10^{-6} \end{array}$$

A solution of a salt which could not be reduced was now used as electrolyte. The salt taken was A.R., potassium di-hydrogen phosphate. A $\frac{M}{32}$ solution of the salt was prepared and measurements taken with this as the electrolyte in the double hydrogen electrode. The tabulated results show the E.M.F. of the cells containing each electrode, and the time of measurement.

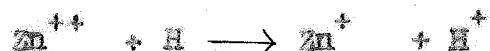
RESULTS: USING $\frac{M}{32}$ $K H_2 PO_4$ IN 'DOUBLE' HYDROGEN ELECTRODE.

| Time | | E.M.F. I | E.M.F. II | Time | | E.M.F. I | E.M.F. II |
|------|-------|----------|-----------|------|-------|----------|-----------|
| hrs. | mins. | | | hrs. | mins. | | |
| 1 | 15 | 0.5779 | 0.5779 | 4 | 15 | 0.5777 | 0.5777 |
| 1 | 50 | 0.5780 | 0.5780 | 4 | 45 | 0.5777 | 0.5777 |
| 2 | 15 | 0.5780 | 0.5780 | 5 | 15 | 0.5777 | 0.5777 |
| 2 | 45 | 0.5780 | 0.5780 | 5 | 45 | 0.5777 | 0.5777 |
| 3 | 15 | 0.5779 | 0.5779 | 6 | 15 | 0.5777 | 0.5777 |

Thus, when equilibrium was established, this electrolyte and the sulphuric acid electrolyte gave constant values and equal values in electrodes I and II. This would show that in the case of zinc sulphate solutions, the variable values and the different values for electrodes I and II are due, not to the apparatus, but to the zinc sulphate electrolyte. A third experiment with zinc sulphate in the double electrode produced similar results to those obtained

in cases A and B previously.

From a consideration of the results it is suggested that reduction by the hydrogen of the hydrogen electrode may be the cause of this anomalous behaviour of zinc sulphate solutions. Such reduction may proceed according to the equation, e.g.



This reaction would lead to an increased hydrogen ion concentration in the surface layer, and recorded value would depend:

- (a) Upon rate of reduction.
- (b) Rate of diffusion from surface into bulk solution.

Variable results would thus occur from day to day, according to the amount of stirring the surface layer receives through increased or decreased rate of hydrogen.

SECTION B.

This experiment was carried out to ascertain if hydrogen, in the presence of platinum black or of a platinum electrode, had any permanent effect on solutions of zinc sulphate, (such as would be brought about if reduction took place.)

METHOD.

A solution of $\frac{M}{32}$ zinc sulphate was placed in the ordinary hydrogen electrode, and pure hydrogen bubbled through slowly for about 24 hours. Platinum black was added to give a greater surface. The E.M.F. of the cell was measured before completion. At the end of the time, the solution was filtered and its hydrogen ion concentration determined by means of the Quin-Hydroxide electrode. This value was compared with that obtained by the Quin-Hydroxide electrode with zinc sulphate solution not so treated.

The platinum black was shaken with distilled water for an hour, washed with water and ammonia, and then washed free of ammonia. The washings were then neutral. It was finally partly dried and washed several times with zinc sulphate solution. This platinum black was shaken in the electrode with zinc sulphate solution. A portion of this solution was filtered off and its hydrogen ion concentration determined by means of the Quin-Hydroxide electrode.

Hydrogen gas from A.R. zinc (+ a drop of CuSO_4) and pure dilute sulphuric acid, was bubbled through the remaining solution for about 24 hours. The hydrogen passed through the freshly filled wash bottled for purification.

RESULTS:-

(a) $\frac{M}{32}$ Zinc Sulphate in Quin-Hydrone Electrode.

(This solution was obtained from the stock bottle.)

| Time | Total E.M.F. | $H^+ \times 10^6$ |
|---------|--------------|-------------------|
| 0 mins. | 0.0203 volts | 1.695 |
| 15 " | 0.0203 " | 1.695 |
| 30 " | 0.0203 " | 1.695 |

(b) $\frac{M}{32}$ Zinc Sulphate in Quin-Hydrone Electrode.

(This solution was the filtrate of a portion of the solution, shaken with platinum black in the hydrogen electrode, prior to treatment with hydrogen.)

| Time | Total E.M.F. | $H^+ \times 10^6$ |
|--------|--------------|-------------------|
| 0 min. | 0.0532 | 6.109 |
| 10 " | 0.0532 | 6.109 |
| 20 " | 0.0532 | 6.109 |

The difference between values (a) and (b) of 0.033 volt is attributed to disturbance of the hydrolytic equilibrium through adsorption by the platinum black.

(c). A reading of the hydrogen electrode, (plus platinum black), was taken shortly before the hydrogen stream was interrupted. This reading showed a total E.M.F. of 0.1251

volts, which corresponds in this electrode to a hydrogen ion concentration of 2.69×10^{-3} .

(d). $\frac{M}{32}$ Zinc Sulphate in Quin-Hydrone Electrode.

(Filtrate of zinc sulphate solution, from hydrogen electrode, after hydrogen had bubbled 24 hours.)

| <u>A</u> | | | <u>B</u> | | |
|----------|--------------|---------------------|----------|--------------|---------------------|
| Time | Total E.M.F. | $[H^+] \times 10^3$ | Time | Total E.M.F. | $[H^+] \times 10^3$ |
| 0 min. | 0.1950 | 1.53 | 0 min. | 0.1943 | 1.23 |
| 15 " | 0.1950 | 1.53 | 15 " | 0.1943 | 1.23 |
| 30 " | 0.1950 | 1.53 | 30 " | 0.1943 | 1.23 |

The difference between the value in (c) and in (d) to that obtained in an earlier experiment (P. 45), is attributed to the longer time of the experiment and to the larger surface presented by the added platinum black. If, as suggested previously, reduction takes place according to the equation:



then both these circumstances would contribute to the increased hydrogen ion concentration due to:-

- The longer time during which reduction can take place
- The increased surface area in which reduction is brought about.

The fact that such a big difference could be obtained between the values in (a), (and in (b)), before experiment, and in (d) after experiment, a difference of 0.14 volt, and 1000 times the hydrogen ion concentration, is strong evidence in favour of the theory that reduction of the divalent zinc ion has taken place.

SUMMARY.

- I. Measurements of the hydrogen ion concentrations of various solutions have been made, using the hydrogen electrode and the Quin-Hydrone Electrode.
- II. Solutions of Zinc Sulphate have again been shown in the hydrogen electrode, to give irregular values for the hydrogen ion concentrations from day to day.
- III. The Quin-Hydrone electrode was found to give constant values for the hydrogen ion concentrations of zinc sulphate solutions, enabling the degree of hydrolysis to be calculated.
- IV. Cadmium Sulphate solutions showed increasing values for the total E.M.F. of the cell: hydrogen electrode plus calomel electrode.
- V. With the Quin-Hydrone electrode Cadmium Sulphate solutions showed again constant values, enabling the degree of hydrolysis to be calculated.
- VI. The Quin-Hydrone electrode has also been used successfully to determine the degree of hydrolysis of solutions of the salts: Lead Chloride, Lead Nitrate, Thallous Sulphate and Potassium di-hydrogen Phosphate.

VII. Owing to a too rapid rate of reduction, the Quin-Hydrone electrode could not be used, to determine the degree of hydrolysis of solutions of silver nitrate and of Potassium Chromate.

VIII. In those cases where the Quin-Hydrone electrode could be used to determine hydrolysis, the results obtained show satisfactory agreement with the results obtained by other methods.

IX. Experiments were carried out with Zinc Sulphate solutions, and from the results, the theory was advanced that reduction may be the cause of the anomalous behaviour of this salt in the hydrogen electrode.
