

LXIV.—*On Haber's Glass Cell.*

By WALTER SCOTT HUGHES.

SEVERAL workers (Hughes, *J. Amer. Chem. Soc.*, 1922, **44**, 2860; Kerridge, *Biochem. J.*, 1925, **19**, 611) have found that the glass cell described by Haber (*Z. physikal. Chem.*, 1909, **67**, 385) can be used to measure hydrogen-ion concentration under conditions which render the hydrogen electrode useless, as in the presence of strong oxidising agents; but difficulties sometimes arise in its use.

The purposes of this paper are (1) to discuss certain factors affecting the behaviour of Haber's cell, and the technique of making and using it; (2) to give experimental data explaining the mechanism by which the cell functions; (3) to show some results obtained by using the cell in various solutions the hydrogen-ion activity of which cannot be readily measured with the hydrogen electrode.

I. *Preparation of Bulbs; Effect of Composition of Glass.*

The chief difficulty in the use of Haber's cell is that it does not readily give reproducible results. There are several reasons for this difficulty. As Mrs. Kerridge (*loc. cit.*) has shown, there is always an asymmetry *E.M.F.* between the two sides of a glass membrane in contact with the same electrolyte which may take several days to become constant. This asymmetry varies even in different cells made from the same glass. It has also been found in almost every case that the change in *E.M.F.* of the glass cell corresponding to a given change in  $p_{\text{H}}$  of the solution in contact with the bulb varies from cell to cell, and from day to day in the same cell.

Mrs. Kerridge recommends checking all  $p_{\text{H}}$  measurements with the glass cell by measuring the *E.M.F.* of the cell when filled with a standard buffer mixture. It is still better to check the measurement of  $p_{\text{H}}$  in the solution under examination by measuring the *E.M.F.* produced by two standard buffer mixtures, one slightly more and the other slightly less acid than the solution; the required  $p_{\text{H}}$  can then be interpolated, and errors due to both the above-mentioned sources will be eliminated.

Mrs. Kerridge also suggests the use of very thin bulbs, which not only conduct better and reach a constant asymmetry  $E.M.F.$  sooner, but give a greater change in  $E.M.F.$  for a given change in  $p_H$ .

In one of our experiments on the effect of bulb thickness, a thin bulb gave a change of 0.514 volt when transferred from  $N/1$ -hydrochloric acid to a  $M/40$ -sodium diborate solution of about  $p_H$  9.2. A thick bulb only changed its  $E.M.F.$  by 0.300 volt under the same conditions. Moreover, it is important to blow the bulbs as rapidly as possible, for prolonged or repeated heating of the bulb, especially if devitrification sets in, may spoil it.\*

The composition of the glass has an important influence on the behaviour of Haber's cell. Most workers recommend "soft soda-lime glass," but different samples of such glass vary enormously in their suitability for this purpose, for which the glass should have a high conductivity; should rapidly reach a constant asymmetry  $E.M.F.$ ; should give as nearly as possible the same change in  $E.M.F.$ ,  $\Delta E_g$ , as the hydrogen cell,  $\Delta E_h$ , for a given change in  $p_H$ ; and should change its  $E.M.F.$  as little as possible on standing in alkaline solutions. These properties were studied in several samples of glass of known composition. The results are in Table I.

Several other samples of ordinary soft glass tubing were found to vary in their suitability for glass electrodes; none was better than 793A, which was furnished by the Department of Glass Technology, Sheffield University. The less alumina a glass contains the better it is for glass-cell work; also a high soda content tends to increase the conductivity of the glass, whereas potash seems to decrease it.

Sample 793A had such a high conductivity that no electrostatic shielding whatever was necessary. In addition to the above-mentioned qualities, this sample had the important property of being almost unaffected by large changes in sodium-ion concentration, provided the hydrogen-ion concentration is not less than  $10^{-9}$  (see Section II). Some of the samples of glass tested by Mrs. Kerridge (*loc. cit.*) were somewhat affected by the sodium-ion concentration.

After the above experiments on the effect of composition were completed, another sample of glass was found which was very nearly as good as 793A as regards conductivity and the closeness with which it followed the hydrogen electrode. It had the additional advantages

\* Rebbeck and Ferguson (*J. Amer. Chem. Soc.*, 1924, **46**, 1991) found that annealing glass reduced its conductivity and drove off the surface layers of absorbed water, both of which effects would be detrimental to its usefulness as a Haber electrode. Further, Dr. E. C. Smith (unpublished communication) found that heating a glass bulb in an autoclave destroyed its hydrogen-electrode function completely.

TABLE I.  
Composition and properties of various glasses.

	No. 1; <i>N</i> -ray.	No. 2; soft German glass.	No. 3; Moucrieff.	No. 793A.	No. 444.
SiO <sub>2</sub> .....	66.88%	70.62%	67.56%	71.83%	72.19%
Al <sub>2</sub> O <sub>3</sub> .....	4.60	3.23	6.53	0.44	8.96
TiO <sub>2</sub> .....	Trace	Trace	Trace	—	—
Fe <sub>2</sub> O <sub>3</sub> .....	0.08	0.11	0.13	0.04	—
MnO .....	Trace	Trace	0.17	—	—
CaO .....	6.76	7.58	6.54	8.36	0.08
MgO .....	0.81	0.25	—	Trace	—
Na <sub>2</sub> O .....	15.48	15.48	15.82	18.83	18.79
K <sub>2</sub> O .....	5.56	2.62	3.34	—	—
SO <sub>3</sub> .....	—	—	—	0.22	—
Total .....	100.17	99.89	100.09	99.72	100.02
Conductivity.	Very low; hence sam- ple useless.	Good.	Poor.	Excellent.	Good.
$\Delta E_p/\Delta E_h$ (over range $p_{11}$ 0—10).	—	0.92	0.88	0.95—0.98	0.24—0.27 (very variable)
Asymmetry.	—	High; slow in attaining constancy.	Very high; slow in at- taining constancy.	Very low; attains con- stancy in a few hours.	Fairly low; attains con- stancy in a few hours.
Decrease in <i>E.M.F.</i> on standing in <i>N</i> - KOH over-night.	—	0.010—0.090	0.077—0.090	0.005—0.079	0.121 [in 0.3 <i>N</i> - Ba(OH) <sub>2</sub> sol.]; <i>E.M.F.</i> variable even in acid solution.

of being more easily workable and of being commercially obtainable, being supplied as "white flint" glass by Wood Bros. Glass Co., Barnsley, Yorks. Analysis: SiO<sub>2</sub>, 69.75; Sb<sub>2</sub>O<sub>3</sub>, 0.22; Fe<sub>2</sub>O<sub>3</sub>, 0.05; Al<sub>2</sub>O<sub>3</sub>, 1.04; MnO, 0.21; CaO, 11.26; MgO, trace; Na<sub>2</sub>O, 16.54; K<sub>2</sub>O, 0.66; SO<sub>3</sub>, 0.34%. Total, 100.07.

The form of glass cell used in the following experiments (see Fig. 1) was a modification of Haber's cell. The bulb was filled with *N*-hydrochloric acid; the inside electrode consisted of a drop of mercury covered with calomel, touching a platinum wire sealed through a glass tube. Above the seal was another drop of mercury with the lead-in wire dipping into it. This electrode could be kept at the temperature of the liquid surrounding it which was contained in a beaker immersed in a paraffin-oil thermostat. The neck of the bulb was held in a paraffin-wax-coated block of wood cut to fit the beaker as a cover, and the rim of the beaker was supported by the paraffin-wax-coated wooden thermostat cover.

The little mercury-calomel-hydrochloric acid electrode could be transferred from the inside of the bulb to the outside when the beaker was filled with *N*-hydrochloric acid in order to measure the asymmetry *E.M.F.* of the bulb.

The external electrode was a saturated potassium chloride-calomel half cell, contained in a tube submerged in the bath as shown in Fig. 2.

The electrometer was of the Compton type, made by the Cambridge Instrument Co., giving a deflexion of about 1.5 mm. at 1 m.

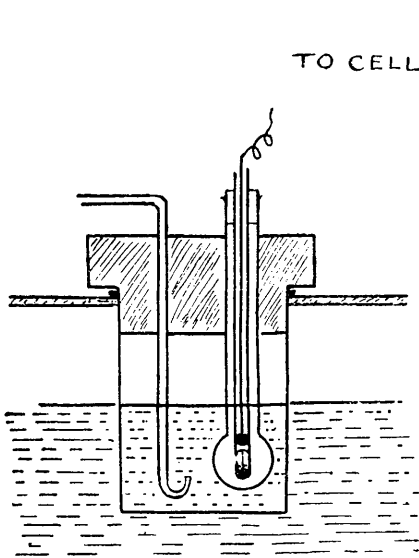


FIG. 1.

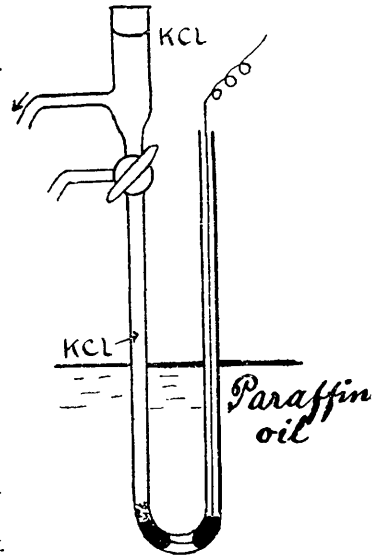


FIG. 2.

per millivolt with the vane charged  $\pm 50$  volts with respect to earth. It was used as a null instrument in the usual way. The wiring

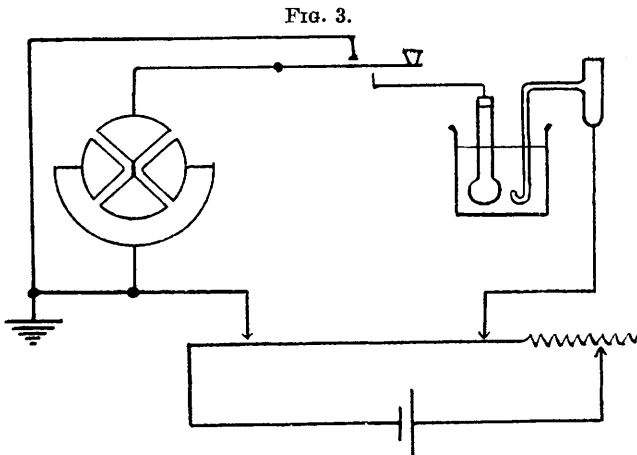


FIG. 3.

diagram is shown in Fig. 3. Connexion was made from the un-earthed quadrants to the inside electrode of the glass cell by means of a two-way tapping key mounted on a vulcanite block. When

the key was released both sets of quadrants were earthed. The key could be dismantled so that the vulcanite base could readily be cleaned to remove conducting surface films of moisture.

## II. *Mechanism of the Hydrogen-electrode Function in Haber's Glass Cell.*

*Influence of Certain Ions other than Hydrogen.*—Horovitz (*Z. Physik*, 1923, **15**, 369) and Schiller (*Ann. Physik*, 1924, **74**, 105) showed that the potential of Haber's glass cell might be a function, not only of hydrogen-ion concentration, but also of other ionic concentrations in the solution in contact with the glass. If the bulb was made of a glass containing much boric oxide, the sodium ion had as much effect as the hydrogen ion on the *E.M.F.* of the cell. They think that glass functions as an electrode by virtue either of (1) its composition as a solid electrolyte, or of (2) an exchange between cations in the surface of the glass and cations from the solution. Thus the sodium-electrode function of the sodium borosilicate glasses is due to their sodium content, whilst the hydrogen-electrode function of soda-lime glass is due to hydrogen ions from the solutions which have replaced other ions in the surface of the glass.

Freundlich and Rona (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, 396) showed that the electrokinetic potential of glass, which was greatly influenced by the surface adsorption of polyvalent ions, had very little connexion with the Haber potential. Schiller must have assumed that ionic exchange may affect the deeper layers of the glass, thus influencing the Haber potential as well as the electrokinetic potential.

This theory does not give an adequate explanation of how the hydrogen-ion concentration in the glass phase is maintained relatively constant when that of the solution changes. The following experiment illustrates the point: A fresh-blown bulb of No. 793A glass was filled with *N*-hydrochloric acid, and allowed to stand a few hours so that the inner surface could come to equilibrium. The electrode within the bulb was mercury and calomel in contact with the acid. The bulb was then dipped in *N*-potassium hydroxide, the outside electrode being a saturated potassium chloride calomel half cell. The *E.M.F.* of the cell, measured immediately at 15°, was 0.624 volt (outside positive), remaining constant for 20 minutes. The bulb was then transferred to a *N*-hydrochloric acid solution, and the *E.M.F.* was then 0.028 volt (outside negative). The change in the *E.M.F.* of the glass cell was thus 0.652 volt. The corresponding change for the hydrogen cell would be about 0.783 volt. This difference of 0.131 volt corresponds to a change

of about 196 to 1 in the hydrogen-ion concentration of the glass (assuming the glass to be functioning only as a hydrogen electrode), *i.e.*, glass in contact with *N*-hydrochloric acid has only 196 times the hydrogen-ion concentration of glass in contact with *N*-potassium hydroxide, although the ratio of the hydrogen-ion concentrations of the solutions is about  $5 \times 10^{13}$ . If the hydrogen ions in the glass phase were derived solely by ionic exchange from the solutions in contact with the glass, one would expect a far greater difference in the hydrogen-ion concentration in the glass.

It is easier to suppose (as Haber did) that the hydrogen ions in the glass phase are derived from water from the solution which dissolves in the glass. Frazer, Patrick, and Smith (*J. Physical Chem.*, 1927, **31**, 897) have recently demonstrated that a considerable amount of water is adsorbed by glass in contact with acids.

Our experimental results are best explained on the view that the hydrogen-ion concentration in the glass phase is held relatively constant by the buffer action of the glass which is a mixture of the salt of a weak acid ( $\text{Na}_2\text{SiO}_3$ ) with the anhydride of that acid (excess  $\text{SiO}_2$ ). This action *prevents* ionic exchange between the glass phase and the solution from altering the hydrogen-ion concentration in the glass, which is thus maintained relatively constant in spite of the exchange of ions with the solution. The effect of ions other than hydrogen on the *E.M.F.* of sample 793A was negligible except in alkaline solutions. In solutions containing sodium or lithium hydroxide the decrease in  $\log [\text{H}^+]$  in the glass becomes greater than its decrease in the solution as the concentration of the base is increased beyond *N*/10. This effect is shown in the following experiments :

Glass : No. 793A ; temp. : 25° ; cell :  $\text{Hg}|\text{HgCl}|\text{KCl}(\text{satd.})|\text{solution}|\text{glass}|\text{N-HCl}|\text{HgCl}|\text{Hg}$ .

Solution.	<i>E.M.F.</i> of cell.	Solution.	<i>E.M.F.</i> of cell.
<i>N</i> /100-NaOH	0.645	<i>N</i> /100-LiOH	0.660
<i>N</i> /10- "	0.681	<i>N</i> /10- "	0.704
<i>N</i> /1- "	0.678	<i>N</i> - "	0.699
10 <i>N</i> - "	0.588	3.3 <i>N</i> - "	0.677 decreasing to 0.662.

The effect of increasing concentrations of caustic soda was explained by Horovitz and Schiller as being due to the sodium-electrode function of the glass ; this might be true in those cells which have a sodium-electrode function even in acid solution, but in the above case the glass showed no indication of such a function in any solution more acid than  $p_{\text{H}}$  9. Furthermore, the lithium ion produces the same effect and the glass (having no lithium ions initially, nor any means of maintaining a constant lithium-ion

concentration within itself if lithium ions penetrate from the solution) could hardly act as a lithium electrode. The reason why  $\log [H^+]$  of the glass phase decreases more rapidly than that of the solution when the concentration of hydroxide exceeds  $N/10$  is that in this region the buffer action of the glass breaks down and its surface is rapidly attacked and dissolved.

The effect of alkaline solutions in increasing the divergence between the *E.M.F.* of the glass and of the  $H_2|Pt$  begins to be noticeable at about  $p_H$  9, *i.e.*, at the point where the buffer action of the sodium hydrogen silicate in the glass would begin to resist the action of alkaline solutions less effectively, since the apparent first dissociation constant of  $H_2SiO_3$  is about  $10^{-9}$  (Hägg, *Z. anorg. Chem.*, 1926, **155**, 21). The rapidly increasing divergence between the two *E.M.F.*'s in the presence of sodium and lithium ions begins at about  $p_H$  13, and the apparent second dissociation constant of  $H_2SiO_3$  is  $10^{-13}$  (Hägg, *loc. cit.*). Beyond this  $p_H$  it is probable that the surface of the glass is attacked with greatly increasing rapidity as the solution becomes more alkaline. The difference in the action of the various hydroxides is probably due to a greater power of penetrating the glass possessed by the lithium ions, and is shown in the following experiments, from which it will be seen that the behaviour of different cells may not be the same.

Glass, 793A.				Another bulb, same glass.			
Solution.	Glass cell <i>E.M.F.</i>	$H_2 Pt$ <i>E.M.F.</i>	Diff.	Solution.	Glass cell <i>E.M.F.</i>	$H_2 Pt$ <i>E.M.F.</i>	Diff.
N-HCl	-0.026	0.248	0.274	N-HCl	-0.024	0.248	0.272
N-KOH	+0.707	1.056	0.349	N-KOH	+0.767	1.055	0.288
N-NaOH	+0.669	1.045	0.376	N-NaOH	+0.675	1.044	0.369
N-LiOH	+0.617	1.041	0.424	N-LiOH	+0.420	1.040	0.620

Another fact indicating that the effect of sodium and lithium ions in strongly alkaline solution is due to a decrease in hydrogen-ion concentration in the glass phase, rather than to a sodium- or lithium-electrode function of the glass, is that the *E.M.F.* of a glass cell falls with time on standing in alkaline solution, *i.e.*, with increasing penetration by sodium or lithium ions. Now if the glass were functioning chiefly as a sodium or lithium electrode, the *E.M.F.* would change in the opposite direction as the ions penetrated the glass.

Yet another indication that the glass is still acting, at least partly, as a hydrogen electrode even in alkaline solution is the slow reversibility of the sodium hydroxide effect, shown as follows: A glass electrode, having an *E.M.F.* of 0.572 volt in 10*N*-sodium hydroxide solution, was transferred to *N*-potassium hydroxide solution, and the *E.M.F.* measured immediately was 0.668 volt, whereas that

measured after 30 mins. was 0.698 volt. The immediate rise after transference might be attributed to the decrease of sodium-ion concentration in the solution, but if the glass had been functioning chiefly as a sodium electrode, the slow drift in *E.M.F.* after the transference would have been in the opposite direction, since the sodium ions would become less concentrated in the glass phase and more concentrated in the solution.

The only real case of an electrode function in glass produced by exchange of ions with the solution seems to be the silver-electrode function observed by Horovitz in glass which had stood over-night in contact with silver nitrate solution. It is possible that, if silver silicate has a low solubility product, the silver-ion concentration in the surface of the glass might remain sufficiently constant to account for Horovitz's results. No silver-electrode function could be produced in the samples now investigated. When a bulb had been left in contact with silver nitrate solution over-night it showed slight changes in *E.M.F.* on varying the silver-ion concentration (the  $p_H$

TABLE II.

Influence of various cations other than  $H^+$  on the *E.M.F.* of Haber's cell.

Temp. 25°. The sign of the *E.M.F.* is + or - according to whether the  $Hg|HgCl$  electrode is + or -.

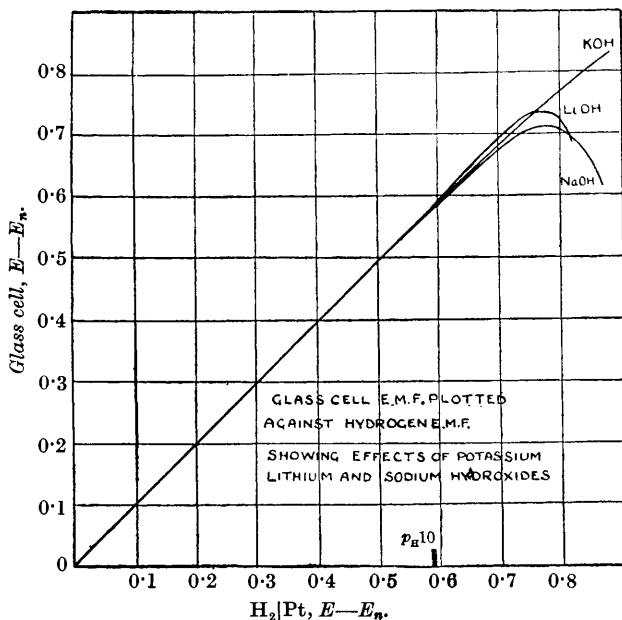
Effect of $K^+$ ions.			
Solution.	$E_g$ .	$E_A$ .	Diff.
<i>N</i> -HCl .....	-0.019	+0.248	0.267
<i>N</i> -HCl satd. with KCl .....	-0.041	+0.223	0.264
KOH (app. 2 <i>N</i> ) .....	+0.660	+1.074	0.414
KOH (app. 2 <i>N</i> ) satd. with KCl .....	+0.673	+1.085	0.412
Effect of $Na^+$ ions.			
<i>N</i> -HCl .....	-0.023	+0.248	0.271
<i>N</i> -HCl satd. with NaCl .....	-0.066	+0.200	0.266
<i>M</i> /22- $K_2HPO_4$ + <i>M</i> /22- $KH_2PO_4$ .....	+0.337	+0.640	0.303
<i>M</i> /22- $K_2HPO_4$ + <i>M</i> /22- $KH_2PO_4$ satd. with NaCl .....	+0.265	+0.568	0.303
<i>M</i> /20- $KH(BO_2)_2$ .....	+0.470	+0.792	0.322
<i>M</i> /22- $KH(BO_2)_2$ satd. with NaCl .....	+0.420	+0.743	0.323
1.3 <i>N</i> -KOH .....	+0.666	+1.061	0.395
1.3 <i>N</i> -KOH satd. with NaCl .....	+0.560	+1.067	0.507
Effect of $Li^+$ ions.			
25 C.c. <i>N</i> -HCl .....	-0.030	+0.247	0.277
25 C.c. <i>N</i> -HCl + 25 g. LiCl .....	-0.121	+0.159	0.280
50 C.c. <i>N</i> -KOH .....	+0.756	+1.056	0.300
50 C.c. <i>N</i> -KOH + 10 g. LiCl .....	+0.692	+1.021	0.329
Same cell after 3 hrs. ....	+0.672	+1.021	0.349
Effect of $Ca^+$ ions.			
<i>N</i> -HCl .....	-0.026	+0.247	0.273
<i>N</i> -HCl + 20% $CaCl_2$ .....	-0.043	+0.226	0.269
13% $CaCl_2$ soln. satd. with $Ca(OH)_2$ .....	+0.540	+0.904	0.364
Dilute $K_2CO_3$ soln. ....	+0.520	+0.883	0.363



being maintained constant by very dilute sodium acetate-acetic acid buffer), but these *E.M.F.*'s varied considerably with time, and rapidly approached the value for an ordinary bulb at the same  $p_{\text{H}}$ .

In order to find to what extent the "mixed electrode functions" described by Horovitz and Schiller might exist in sample 793A, several comparisons were made between the *E.M.F.* of the glass cell and that of the hydrogen electrode before and after the addition of various salts (KCl, NaCl, CaCl<sub>2</sub>, and LiCl): if the difference in *E.M.F.* remains unchanged after addition of a salt, the glass cell

FIG. 4.



must have a hydrogen-electrode function only. It is interesting to note (Table II) that the effect, if any, of adding potassium or sodium chloride on the difference in *E.M.F.* between the glass and hydrogen cells, is in the opposite direction to that which would be expected from Horovitz and Schiller's theory, when the solution is acid. Changes in the potassium-ion concentration affect the *E.M.F.* of the hydrogen electrode in the same way as they affect that of the glass cell; and similarly for sodium and lithium ions except in strongly alkaline solution. The calcium ion, however, has but little influence on the *E.M.F.* of the glass cell, even in alkaline solution.

The curves in Fig. 4 and data in Table III show the behaviour of the glass cell in the presence of potassium, lithium, and sodium

ions. The ordinates represent the difference between the *E.M.F.* of the glass cell filled with the solution which is being studied and that of the same cell filled with *N*-hydrochloric acid. The abscissæ represent the difference in *E.M.F.* of the hydrogen electrode when in the same solution as the glass electrode and when in *N*-hydrochloric acid. The glass was No. 793A; temperature 25°. Lithium and sodium hydroxides both show a maximum glass *E.M.F.* at about  $p_H$  13. The difference between the effects of these ions on the glass cell becomes negligible when the hydrogen-ion activity is greater than  $10^{-10}$ .

The extent to which the glass cell *E.M.F.* departs from the value it would have if the glass had a perfect hydrogen-electrode function is measured by the difference between the abscissæ and ordinates of points on the curves.

TABLE III.

Data for curves (Fig. 4) showing relation between hydrogen and glass cell *E.M.F.* in solutions containing  $K^+$ ,  $Na^+$ , and  $Li^+$  ions.

Solution.	$E_g$ .	$E_g - E_n$ .	$E_h$ .	$E_h - E_n$ .
<i>N</i> -HCl .....	-0.025	0	0.247	0
<i>N</i> /10-HCl .....	+0.032	0.057	0.303	0.056
<i>N</i> /100-HCl .....	+0.088	0.113	0.364	0.117
<i>N</i> /1000-HCl .....	+0.143	0.168	0.418	0.171
<i>N</i> /10,000-HCl .....	+0.196	0.221	0.472	0.225
<i>N</i> /1000-KOH .....	+0.576	0.601	0.860	0.613
<i>N</i> /100-KOH .....	+0.644	0.669	0.933	0.686
<i>N</i> /10-KOH .....	+0.702	0.727	0.997	0.750
<i>N</i> -KOH .....	+0.748	0.773	1.056	0.809
3 <i>N</i> -KOH .....	+0.779	0.804	1.092	0.845
13 <i>N</i> -KOH .....	+0.800	0.829	1.128	0.881
<i>N</i> -HCl .....	-0.026	0	0.247	0
0.1% $Na_2B_4O_7$ .....	+0.484	0.510	0.770	0.523
<i>N</i> /1000-NaOH .....	+0.572	0.598	0.865	0.618
<i>N</i> /100NaOH .....	+0.645	0.670	0.941	0.694
<i>N</i> /10-NaOH .....	+0.681	0.706	0.998	0.751
<i>N</i> -NaOH .....	+0.678	0.703	1.050	0.803
10 <i>N</i> -NaOH .....	+0.588	0.613	1.116	0.869
<i>N</i> -HCl .....	-0.024	0	0.247	0
0.02 <i>M</i> -LiAc + 0.02 <i>M</i> -HAc	+0.242	0.266	0.514	0.267
Li borate (about 0.02 <i>M</i> ) ...	+0.501	0.525	0.778	0.531
<i>N</i> /100-LiOH .....	+0.660	0.684	0.940	0.693
<i>N</i> /10-LiOH .....	+0.704	0.728	0.996	0.749
<i>N</i> -LiOH .....	+0.704—0.699	0.723	1.045	0.798
3.3 <i>N</i> -LiOH .....	+0.677—0.662	0.686	1.066	0.819

### III. Applications of the Cell.

The measurements of  $p_H$  by means of the glass cell (Table IV) show how it can be used in the presence of oxidising agents, of substances such as azoimide and hydrazine which poison a hydrogen electrode, and of a strongly coloured solution such as permanganic acid which precludes the use of indicator methods.

TABLE IV.

Glass, sample 793A. Temp., 25°.

Cell: Hg|HgCl|sat. KCl|solution|glass|N-HCl|HgCl|Hg.

Solution.	$E_p$ .	$p_H$ (apprx.).	Solution.	$E_p$ .	$p_H$ (apprx.).
$M/40. \left\{ \begin{array}{l} \text{KH}_2\text{PO}_4 \\ \text{K}_2\text{HPO}_4 \end{array} \right\}$	... 0.360	6.79*	$M/10. \left\{ \begin{array}{l} \text{KC}_2\text{H}_3\text{O}_2 \\ \text{HC}_2\text{H}_3\text{O}_2 \end{array} \right\}$	0.241	4.63*
$M/40. \left\{ \begin{array}{l} \text{KH}_2\text{AsO}_4 \\ \text{K}_2\text{HAsO}_4 \end{array} \right\}$	... 0.355	6.70	$M/10. \left\{ \begin{array}{l} \text{KN}_3 \\ \text{HN}_3 \end{array} \right\}$ .....	0.233	4.49
$\left\{ \begin{array}{l} M/40. \text{K}_2\text{CrO}_4 \\ + \\ M/80. \text{K}_2\text{Cr}_2\text{O}_7 \end{array} \right\}$	..... 0.350	6.62	$M/10. \text{H}_3\text{PO}_4$ .....	0.062	1.80
$M/40. \left\{ \begin{array}{l} \text{KH}_2\text{BO}_3 \\ \text{H}_3\text{BO}_3 \end{array} \right\}$	... 0.496	9.04*	$M/10. \text{H}_3\text{AsO}_4$ .....	0.065	1.85
$M/40. \left\{ \begin{array}{l} \text{KH}_2\text{AsO}_3 \\ \text{H}_3\text{AsO}_3 \end{array} \right\}$	... 0.498	9.07	$M/10. \text{HCl}$ .....	0.030	
			$M/10. \text{HMnO}_4$ .....	0.030	

\* Denotes determined by hydrogen electrode.

The measurements of  $p_H$  in the buffer mixtures of phosphates, arsenates, and chromates, all half-neutralised with respect to the second hydrogen ion, give an interesting comparison of the strength of these acids. Various values for the second dissociation constant of phosphoric acid\* have been calculated depending on the activities of the phosphates which are assumed (Hodgman and Lange, "Handbook of Chemistry and Physics," 9th edn., p. 422, give  $2 \times 10^{-7}$ ; Cohn, *J. Amer. Chem. Soc.*, 1927, **49**, 192, gives  $6.9 \times 10^{-8}$ ). It seems probable, however, that the salts of all three of these acids would have about the same activity coefficients. If this is the case, the ratios of the hydrogen-ion concentrations of the half-neutralised buffer mixtures would be nearly equal to the ratio of the dissociation constants of the acids. On this assumption the above data indicate that

$$\frac{[\text{H}^+][\text{HPO}_4'']}{[\text{H}_2\text{PO}_4']} : \frac{[\text{H}^+][\text{HAsO}_4'']}{[\text{H}_2\text{AsO}_4']} : \frac{[\text{H}^+][\text{CrO}_4'']}{[\text{HCrO}_4']} = 1 : 1.2 : 1.5;$$

$$\frac{[\text{H}^+][\text{AsO}_2']}{[\text{HAsO}_2']} : \frac{[\text{H}^+][\text{BO}_2']}{[\text{HBO}_2']} = 1 : 1.1;$$

and

$$\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2']}{[\text{HC}_2\text{H}_3\text{O}_2']} : \frac{[\text{H}^+][\text{N}_3']}{[\text{HN}_3]} = 1 : 1.38.$$

If the constant for the second-stage dissociation of phosphoric acid is taken as  $6.9 \times 10^{-8}$ , this would give  $1.03 \times 10^{-7}$  as the constant for the second dissociation constant of chromic acid, a value slightly lower than that obtained by Britton ( $4.4 \times 10^{-7}$ ) using the hydrogen and oxygen electrodes (J., 1924, **125**, 1572). It seems possible that the hydrogen electrode may have been giving slightly low  $p_H$  readings in Britton's measurements.

West (J., 1900, **77**, 705) calculated the dissociation constant of

azoimide from conductivity measurements and stated that it is an acid of "about the same strength as acetic"; the glass-cell results show that it is appreciably stronger.

The only value of the dissociation constant of hydrazine found in the literature was that of Bredig (*Z. physikal. Chem.*, 1894, **13**, 308); this was calculated from conductivity measurements and varied from  $4.4 \times 10^{-6}$  to  $2.1 \times 10^{-6}$  according to the dilution. The  $p_H$  of a solution containing  $M/10\text{-N}_2\text{H}_5\cdot\text{OH} + M/10\text{-N}_2\text{H}_5\text{Cl}$  was found by comparison with phosphate and borate buffers at  $23^\circ$ :

	$p_H$ .	Glass cell <i>E.M.F.</i>
Phosphate buffer .....	6.81	0.389
$M/10\text{-N}_2\text{H}_5\text{Cl} + M/10\text{-N}_2\text{H}_5\cdot\text{OH}$ .....	8.24	0.469
Borate buffer .....	9.24	0.525

The dissociation constant corresponding to this  $p_H$  would be about  $1.7 \times 10^{-6}$  if complete dissociation of hydrazine hydrochloride is assumed; or  $1.4 \times 10^{-6}$  if 80% dissociation (analogous to that of other univalent salts) is assumed.

Hydrochloric and permanganic acids do not differ measurably in strength; this result is in agreement with the comparative strengths of these acids as measured by conductivity.

The dissociation constants thus calculated from hydrogen-ion activities of half-neutralised solutions are summarised below.

Assumed second-stage constant for $\text{H}_3\text{PO}_4$ .....	$6.9 \times 10^{-8}$ *
Second-stage constant for $\text{H}_3\text{AsO}_4$ .....	$8.3 \times 10^{-8}$
"    "    " $\text{H}_2\text{CrO}_4$ .....	$1.0 \times 10^{-7}$
Assumed first-stage constant for $\text{H}_2\text{BO}_3$ .....	$6.5 \times 10^{-10}$ †
Calculated    "    " $\text{H}_3\text{AsO}_3$ .....	$6.0 \times 10^{-10}$
Assumed constant for $\text{HC}_2\text{H}_3\text{O}_2$ .....	$1.86 \times 10^{-5}$ †
Calculated    "    " $\text{HN}_3$ .....	$2.56 \times 10^{-5}$
Dissociation constant for $\text{N}_2\text{H}_5\text{OH}$ .....	$1.4\text{--}1.7 \times 10^{-6}$

\* Cohn, *loc. cit.*

† Landolt-Börnstein, 5te Aufl., p. 1132.

‡ Landolt-Börnstein, 5te Aufl., p. 1141.

*Hydrolysis of Copper Sulphate.*—O'Sullivan (*Trans. Faraday Soc.*, 1925, **21**, 319) measured the hydrogen-ion activity of copper sulphate solutions by means of the quinhydrone electrode. His *E.M.F.* readings changed with time in a direction indicating increasing acidity, and he attributed this to slow oxidation of the quinhydrone. It was found that the hydrogen-ion activity of such solutions as measured by the glass cell changed in a similar manner, indicating that the hydrolysis is probably a slow reaction. The more dilute solutions showed a similar increase after being boiled and cooled. The  $p_H$  of  $M/20$ -copper sulphate measured by the glass cell is 4.24, in fair agreement with O'Sullivan's value, 4.14.

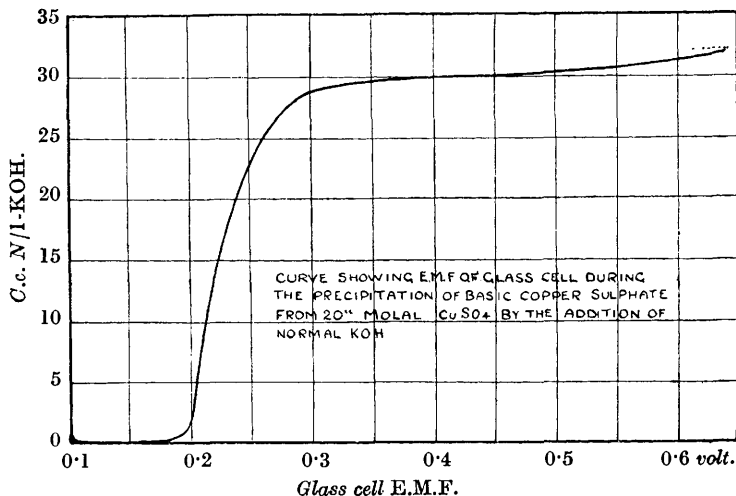
Measurements of various solutions are given in Table V.

TABLE V.

The hydrolysis of  $\text{CuSO}_4$  solutions.

Solution.	$E_p$ .	Diff.	pH.	Temp.
Freshly made $M$ - $\text{CuSO}_4$ .....	0.110	} 0.067	3.43	25°
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ .....	0.177		4.63	"
$M$ - $\text{CuSO}_4$ , next day .....	0.144	} 0.068	3.42	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ , next day .....	0.212		4.63	"
$M$ - $\text{CuSO}_4$ , 2 days later .....	0.138	} 0.074	3.31	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ , 2 days later ...	0.212		4.63	"
25 c.c. $M$ - $\text{CuSO}_4$ + 0.25 c.c. $N$ - $\text{KOH}$ , boiled and cooled .....	0.183	} 0.053	3.71	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ .....	0.236		4.63	"
$M/10$ - $\text{CuSO}_4$ , fresh .....	0.215	} 0.021	4.27	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ .....	0.236		4.63	"
$M/10$ - $\text{CuSO}_4$ , boiled .....	0.204	} 0.032	4.08	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ .....	0.236		—	"
$M/20$ - $\text{CuSO}_4$ , fresh .....	0.231	} 0.006	4.53	18
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ .....	0.237		4.63	"
$M/20$ - $\text{CuSO}_4$ , boiled .....	0.213	} 0.023	4.24	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ .....	0.236		4.63	"
$M/20$ - $\text{CuSO}_4$ , 2 days later .....	0.210	} 0.023	4.24	"
$M/10$ - $\text{KAc}$ + $M/10$ - $\text{HAc}$ , 2 days later ...	0.233		—	"

FIG. 5.



Britton (J., 1925, 127, 2796) measured the *E.M.F.* of a copper electrode dipping into a copper sulphate solution during the precipitation of the basic sulphate by the addition of alkali. He found that a sudden change occurred when three-quarters of the alkali necessary to combine with all the sulphate radical had been added, and concluded that the precipitated basic sulphate had the composition  $4\text{CuO}, \text{SO}_3, x\text{H}_2\text{O}$ . Later Fowles (J., 1926, 1845) claimed to have prepared other basic sulphates of copper.

As the hydrogen-ion activity of a copper sulphate solution must be a function of the copper-ion concentration, there should be a sudden decrease in hydrogen-ion activity as well as copper-ion activity when almost all the copper has been precipitated as basic sulphate. The *E.M.F.* of a glass cell was therefore measured during the precipitation of basic copper sulphate by alkali, and the sudden rise in *E.M.F.* occurred at the stage noted by Britton (see Fig. 5 and Table VI). The initial rapid rise in *E.M.F.* on addition of a small quantity of alkali may be partly due to traces of free sulphuric acid; the remaining rise up to  $E_g$  0.2 may be accounted for on the hypothesis that the reaction  $3\text{Cu}^{++} + 3\text{H}_2\text{O} + \text{CuSO}_4 = \text{CuSO}_4 \cdot 3\text{CuO} + 6\text{H}^+$  is very slow when the hydrogen-ion concentration is greater than  $10^{-4}$ , and then suddenly accelerates, further small additions of alkali being almost without effect on the  $p_{\text{H}}$  of the solution until nearly all the copper has been precipitated (see Table VI).

TABLE VI.

Precipitation of basic copper sulphate at 25°.

Control solution : 20 C.c. of  $N\text{-CH}_3\cdot\text{CO}_2\text{H}$  + 1 c.c. of  $N\text{-KOH}$  + 179 c.c. of water;  $E_g$ , 0.165;  $p_{\text{H}}$  by hydrogen electrode, 3.44. (This buffer mixture was emptied out and replaced by 20 c.c. of  $M\text{-CuSO}_4$  solution.)

<i>N-KOH</i> added, c.c.	$E_g$ .	<i>N-KOH</i> added, c.c.	$E_g$ .	<i>N-KOH</i> added, c.c.	$E_g$ .
0.05	0.164 *	10.0	0.212	28.6	0.292
0.15	0.178	15.0	0.222	29.5	0.361
0.5	0.190	20.0	0.237	30.0	0.464
2.0	0.200 †	25.0	0.261	30.5	0.502
5.0	0.206	27.5	0.281	32.0	0.636 ‡

\*  $p_{\text{H}} = 3.33$ . †  $p_{\text{H}} = \text{app. } 4.06$ . ‡ Changing after 20 mins. to 0.613.

It was thought to be of interest to determine by means of the glass cell what changes in hydrogen-ion concentration take place in the iodide-iodate method for estimating small quantities of strong acids. It was found that, although the  $p_{\text{H}}$  continues to change for 20 mins. after the addition of the acid, this delayed change is so small that the analytical results are not appreciably different from those obtained by immediate titration of the iodine. Moreover, it is seen (Table VII) that the mixture attains neutrality after the addition of two-thirds of the amount of acid necessary to decompose all the iodate.

TABLE VII.

 $p_{\text{H}}$  of iodide-iodate mixture.

Solution.	$E_g$ .	$p_{\text{H}}$ , interpolated.
50 C.c. of (0.1 <i>M</i> - $\text{KIO}_3$ + 0.8 <i>M</i> - $\text{KI}$ ) .....	0.456	8.4
50 C.c. of (0.1 <i>M</i> - $\text{KIO}_3$ + 0.8 <i>M</i> - $\text{KI}$ ) + 20 c.c. of $N\text{-HCl}$	0.378	6.9
Phosphate buffer, $p_{\text{H}}$ 6.81 .....	0.363	—
Borate buffer, $p_{\text{H}}$ 9.19 .....	0.503	—

*Summary.*

1. Glass for use in Haber's cell should be as nearly as possible free from potash, alumina, and borates. A glass containing 72%  $\text{SiO}_2$ , 8%  $\text{CaO}$ , and 20%  $\text{Na}_2\text{O}$  proved very satisfactory. The bulb should be blown as rapidly as possible to avoid devitrification.

2. In acid solutions this glass gave no evidence of the "mixed electrode function" of Horovitz and Schiller. Its behaviour is best explained by the hypothesis that the hydrogen-ion concentration is maintained relatively constant within the glass phase by the buffer action of the sodium acid silicate in the glass. This buffer action begins to become less effective at about  $p_{\text{H}}$  9, which is about the  $p_{\text{H}}$  of a sodium acid silicate buffer mixture half neutralised with respect to the first hydrogen ion of silicic acid (dissociation constant,  $10^{-9}$ ).

3. When the solution in contact with the glass is more alkaline than  $p_{\text{H}}$  13, the glass surface is rapidly attacked. In this  $p_{\text{H}}$  range the second hydrogen ion of silicic acid (dissociation constant,  $10^{-13}$ ) begins to be neutralised, and as the glass surface is attacked the hydrogen-ion concentration within the glass falls rapidly, with a corresponding drop in the *E.M.F.* of the glass cell. Sodium hydroxide shows this effect more than potassium hydroxide; this might be partly due to a sodium-electrode function in the glass, but as lithium hydroxide has a similar effect, it is more reasonable to suppose that glass is more readily penetrated by sodium and lithium hydroxides than by potassium hydroxide, possibly because of smaller dimensions of the ions.

4. The following dissociation constants have been determined by measuring the  $p_{\text{H}}$  of half-neutralised buffer mixtures: the second-stage constants of arsenic and chromic acids ( $8.3 \times 10^{-8}$  and  $1.0 \times 10^{-7}$ , respectively), the first-stage constant of arsenious acid ( $6 \times 10^{-10}$ ), and the constants of azoimide and hydrazine hydrate ( $2.56 \times 10^{-5}$  and  $1.4 \times 10^{-6}$ , respectively).

5. The hydrogen-ion activity of copper sulphate solutions has been measured, and it has been shown that the hydrolysis of copper sulphate is a slow reaction at the ordinary temperature. It has also been shown that the basic sulphate of copper precipitated by alkali must have the composition  $3\text{CuO}, \text{CuSO}_4, x\text{H}_2\text{O}$ , in agreement with the results of Britton.

6. The  $p_{\text{H}}$  of an iodide-iodate mixture has been found to be about 6.9 after two-thirds of the iodate have been decomposed by the addition of hydrochloric acid.

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LABORATORY OF PHYSICAL CHEMISTRY,  
CAMBRIDGE.

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