

A number of observations on the glow phenomenon have been recorded, the most interesting and important fact uncovered being that the glow phenomenon, which invariably results in the crystallization of the chromium oxide, also results in the loss of capacity of the catalyst for activating hydrocarbons. The bearing of these experimental results on current theories of catalysis is discussed.

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THE THEORY OF THE GLASS ELECTRODE. II. THE GLASS AS A WATER ELECTRODE

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Introduction

The inability of the glass electrode to function as a perfect hydrogen electrode in alkaline solutions has recently been explained¹ on the assumption that sodium or other positive ions as well as hydrogen ions may have an appreciable mobility across the aqueous solution glass boundary. This theory, however, fails to account for the interesting errors of the glass electrode in very acid solutions recently discovered by MacInnes and Belcher and by Buchböck² inasmuch as the current carried by the sodium ion across the boundary becomes less and less as the hydrogen-ion concentration increases and the hydrogen ion carries more and more current. Since

¹ Dole, *THIS JOURNAL*, **53**, 4260 (1931). The author wishes to publish the following corrections to this paper. On page 4271 a statement was made concerning the work of Lengyel which is, perhaps, a bit misleading in that Lengyel's experimental procedure was not fully described. Lengyel considered his quartz membranes as condensers, but since he used his electrometer as a null point instrument, the relative capacity of the quartz membrane and of the condenser did not matter; it is only on attempting to measure the potential difference directly by the electrometer deflections that the capacity of the electrometer must be considered in relation to the capacity of the quartz membrane.

The author also wishes to emphasize further concerning his theory of the glass electrode that the experimental equation is highly empirical in that the slope and intercept have to be found from the data; they cannot be calculated. The theoretical significance of the equation rests in the analogy between the empirical equation and one derived on the basis of liquid junction theory (after making several hypothetical assumptions). Hence in reading the author's second paper on the theory of the glass electrode this should be borne in mind.

A misunderstanding has arisen over the mention of the name of Dr. MacInnes in reference 1 of the author's first paper. Dr. MacInnes does not subscribe to the author's theory as given in this paper; Dr. MacInnes' own theory of the glass electrode appeared in a paper previously published with Belcher, *THIS JOURNAL*, **53**, 3315 (1931).

² Buchböck, *Z. physik. Chem.*, [A] **156**, 232-236 (1931); MacInnes and Belcher, *THIS JOURNAL*, **53**, 3315 (1931).

the migration of the sodium ion becomes negligible at a hydrogen-ion concentration of 1×10^{-8} , it can be readily seen that a different explanation is necessary for the acid solution errors. There have been certain theories proposed to account for these results, but they have not proved to be entirely satisfactory. Hence this investigation was undertaken in order to obtain more experimental data and to obtain an explanation for the behavior of the glass electrode in acid solutions which will be thermodynamically sound and which will agree quantitatively with the data.

Experimental

The apparatus and experimental technique were identical with that already described.^{1,3} The glass electrode was carefully compared with the hydrogen electrode in pure solutions of hydrochloric acid and sulfuric acid. A comparison at approximately constant chloride-ion activity was carried out by adding 2 *N* hydrochloric acid to 4.4 *N* lithium chloride. Experiments were performed to find out if varying the positive ion affected the errors; *e. g.*, sodium sulfate, aluminum sulfate, lithium chloride, sodium chloride and aluminum chloride solutions were used in the comparison. These experiments likewise enabled a comparison to be made of the relative effect of the chloride and sulfate ions in causing the acid solution errors. Finally some experiments in ethanol solutions were performed to test any possible effect due to a change in the concentration of the solvent water. These experiments were carried out by adding absolute ethyl alcohol to an aqueous solution of hydrochloric acid at a *P_H* of about one and comparing the glass electrode with the hydrogen electrode as the concentration of the water was changed. The comparison in the approximately 98% ethanol was performed in a separate experiment. A comparison of the glass and hydrogen electrodes was also made in an ethanol solution of sodium iodide over a considerable *P_H* range by adding aqueous sodium hydroxide to the solution.⁴

All the *P_H* values of the tables were calculated neglecting the liquid junction potential between the saturated potassium chloride solution of the salt bridge and the solution under investigation. The data which are

³ Since the first paper was submitted for publication, a paper by MacInnes and Belcher has appeared² in which it is stated that the potentials of the glass electrode in alkaline solution are not reproducible and that different potentials are obtained depending on the direction of the titration, *e. g.*, whether the *P_H* is changed by adding base to acid or acid to base. These results are contrary to those found by the author, who obtained reproducible results in sodium and lithium alkaline solutions and who obtained the same results irrespective of the manner in which the *P_H* was changed. The anomalous results of MacInnes and Belcher may be attributed to the fact that in their titrations the sodium-ion concentration was not held constant, as it was in the author's experiments. On adding sodium hydroxide to hydrochloric or acetic acid, the sodium-ion concentration is continually increasing and is indefinite, and on adding the acid to the base the sodium-ion concentration would decrease continually; hence one would expect to get different results depending on the direction of *P_H* change when the experiments are carried out in this way, since in alkaline solutions the potentials are functions of the sodium-ion concentration.

⁴ The hydrogen-platinum electrodes apparently behaved reversibly in sodium iodide-ethanol solutions although in the neighborhood of the neutralization point they drifted slowly in the direction of higher *P_H* values. No reproducible results were obtained in barium iodide-ethanol solutions; hence these results are not given.

collected in Tables I to IV are not as reliable as the errors in alkaline solutions for they were not so reproducible nor so reversible. A study of the

TABLE I

ERRORS OF THE GLASS ELECTRODE IN HYDROCHLORIC ACID SOLUTIONS AT 25° IN MILLIVOLTS
HCl solutions

Glass electrode no.								
P_H		-0.272	-0.458	-0.543	-0.680	-0.730		-1.67
C-97		-1.1		-2.8		-15.1		
F-17			-1.1					
G-11					-6.5			-18.4
G-14					-6.8			
		2 N NaCl + 2 N HCl						
P_H		1.11	0.884	0.590	0	-0.017	-0.240	-0.621
C-92		-0.4		-0.9		-3.0	-7.4	
C-93		-.4		-.7		-2.1	-5.1	
C-97			-5.6		-6.9			
E-1			-2.1		-2.2			-5.7
		AlCl ₃ + Concn. HCl						
P_H		2.624		1.119		0.069		-0.646
F-44		0		0		-1.1		
F-48								-8.9
		4.4 N LiCl + 2 N HCl						
P_H	C-94	C-97	P_H	C-97	C-98	P_H	D-40	E-7
4.62	-4.6	-6.3	4.60	-5.1	-5.1	4.34	-4.1	-6.7
3.46	-4.0	-8.1	3.47	-7.4	-6.5	1.94	-4.4	-7.4
1.93	-5.1	-10.9	1.31	-9.3	-8.7	0.987	-4.4	-6.9
1.09	-7.3	-11.7	0.795	-7.6	-7.4	.201	-5.7	-6.9
0.57	-8.2	-9.4	.308	-7.2	-6.9	-.458	-8.6	-7.3
.047	-12.0	-7.4	2.68	-7.2	-7.5			
-.477	-18.7	-7.0						
-.345	-20.8	-7.3						
+ .144	-16.9	-7.3						
1.22	-9.8	-6.6						
3.44	-6.4	-6.3						

TABLE II

ERRORS OF THE GLASS ELECTRODE IN SULFURIC ACID SOLUTIONS AT 25° IN MILLIVOLTS
H₂SO₄ solutions

P_H		-0.798		-0.910		-1.354		-1.620
C-92				-7.8		-16.6		
G-10		3.3						36.3
G-13		6.9						33.9
		1 N Na ₂ SO ₄ + Concn. H ₂ SO ₄						
P_H				-0.512				-0.666
F-51				-0.3				-6.1
F-53				-.7				-5.4
		1 N Al ₂ (SO ₄) ₃ + Concn. H ₂ SO ₄						
P_H		0.896		0.210				-0.834
F-17		0		-1.7				-8.5
F-21		0		-1.7				-5.1

TABLE III
 ERRORS OF THE GLASS ELECTRODE IN ETHANOL SOLUTIONS AT 25° (MILLIVOLTS)

% C ₂ H ₅ OH by volume	<i>P_H</i>	Glass electrode no.	Error
33	1.30	F-24	- 1.3
33	0.413	F-35	- 1.3
37	1.86	F-24	- 2.0
55	1.36	F-24	- 4.2
56	1.99	F-24	- 4.6
66	0.712	F-35	- 3.9
98	- .065	F-38	-55.1
98	- .065	F-45	-38.6

TABLE IV
 ERRORS OF THE GLASS ELECTRODE IN ETHANOL SOLUTIONS OF SODIUM IODIDE (1 *N*) AT
 25° (MILLIVOLTS)

<i>P_H</i>	Glass electrode no.	Error	<i>P_H</i>	Glass electrode no.	Error
4.72	F-38	-31.2	7.73	F-45	+2.2
4.72	F-45	-27.2	8.09	F-38	+6.8
6.79	F-38	-18.6	8.09	F-44	1.5
6.79	F-45	-16.2	12.58	F-38	233
6.88	F-38	-12.2	12.58	F-45	226
6.88	F-44	-16.0	12.75	F-38	232
7.21	F-38	-13.0	12.75	F-44	120
7.21	F-45	-12.7	13.16	F-38	255
7.45	F-38	- 4.8	13.16	F-44	244
7.45	F-44	- 8.5	14.09	F-38	296
7.73	F-38	+ 1.7	14.09	F-44	286

data for the 4.4 *N* lithium chloride solution indicates this fact. The errors are plotted against the *P_H* in Figs. 1 and 3 and against the concentration of the alcohol in Fig. 2.

Interpretation of the Results

A possible explanation of the errors of the glass electrode in acid solution may be based on the assumption that negative ions are carrying the current across the glass aqueous solution boundary instead of the positive ions. It will be remembered that the errors of the glass electrode in alkaline solutions depended to a large extent upon the particular positive ions present and not at all upon the negative ions. Since the errors of the glass electrode in acid solutions are of opposite sign to those in the alkaline solutions, it might reasonably be assumed that the acid solution errors are due to the negative ions since these ions are charged oppositely to the positive ions. It would be very difficult to see why positive ions could cause any errors in acid solutions; hence if these errors are to be due to ions, they must be due to negative ions. If this were true, the errors in acid solution should be a function of the concentration and nature of negative ions present just as the alkaline solution errors are functions of the con-

centration and nature of the positive ions. A glance at the data, however, indicates that this is not the case. The difference between the chlorides and sulfates is slight in contrast to the large difference, for example, between the sodium and barium errors in alkaline solutions. Furthermore, a large increase in chloride-ion concentration causes no appreciable increase in the error as the results for 4.4 *N* lithium chloride solutions prove.

It is also interesting to note that the presence of the triply charged aluminum ion has no effect upon the errors, which indicates that the errors are not caused by any adsorption phenomenon. Because of all of these facts we must reject the hypothesis that the acid solution errors are caused by negative ions. Another possible explanation of the errors is that recently advanced by MacInnes and Belcher.² These authors have modified the Horovitzian ionic exchange theory¹ by stipulating that in acid solutions sodium ions in the glass are replaced by hydrogen ions of the solution, thereby diminishing the concentration difference of hydrogen ions between the glass and the outside solution and accordingly

the potential. However, by increasing the hydrogen-ion concentration of the glass the potential difference between the glass and the *inside* solution will be increased and it is easy to show mathematically that the resulting increase will just balance the decrease in potential between the glass and the *outside* solution, and no error will result. In other words, as long as the current through the glass membrane is carried solely by hydrogen ions it does not matter at all what the hydrogen-ion concentration in the glass is. An additional theoretical objection to the theory of MacInnes and Belcher is that ionic exchange should occur at all but one *PH* since there can only be one concentration of hydrogen ions for a given solution where the free energy of transfer of hydrogen ions will just balance the free energy of transfer of sodium ions (the criterion of zero exchange).⁵ A practical objec-

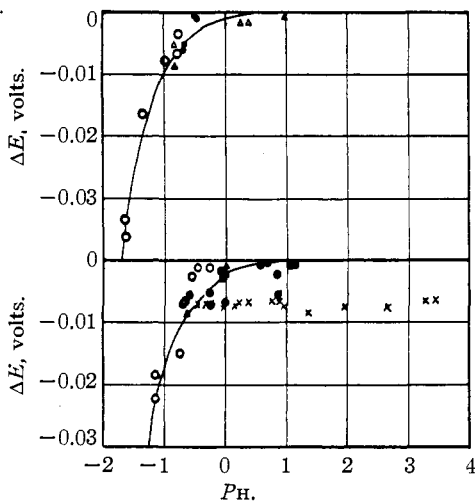


Fig. 1.—Errors of the glass electrode in acid solutions. Top curve: sulfate solutions; circles, H₂SO₄; triangles, Al₂(SO₄)₃ + H₂SO₄; solid circles, Na₂SO₄ + H₂SO₄. Bottom curve: chloride solutions; circles, HCl; triangles, AlCl₃ + HCl; solid circles, NaCl + HCl; crosses, LiCl + HCl; note the constant error in the lithium solutions as the *PH* is changed.

⁵ In a rapid titration complete thermodynamic equilibrium will never be set up unless the concentration of the aqueous solution happens to be at the concentration which

tion to the ionic exchange theory is that the glass electrode error remains constant at -7.0 millivolts in the $4.4 N$ lithium chloride solution over the large P_{H} range $+4$ to -0.5 . Neither of the above theories gives any clue to the explanation of this interesting fact. Nor do they explain why the glass electrode fails to function properly in alcohol solutions.

Since neither the concentration nor the nature of the negative or positive ions had any appreciable influence upon the errors of the glass electrode in acid solutions and since the errors also were not a direct function of the hydrogen-ion concentration, it occurred to the author that possibly the change in activity of the water was causing the error. This idea was strengthened further by a study of the alcohol solutions. Such an error

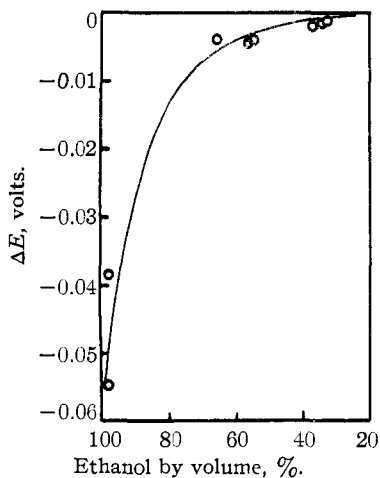


Fig. 2.—Errors of the glass electrode in ethanol-water mixtures.

could be caused by a transfer of water molecules through the glass by the hydrogen ions as they migrated from one solution to the other. A platinum hydrogen electrode transports, of course, no water when it transfers hydrogen ions from one solution to another; hence if water is transferred through an activity difference by the glass electrode, it is obvious that an additional potential will be introduced which will cause the glass electrode potentials to deviate from those given by a perfect hydrogen electrode. This may be easily demonstrated mathematically provided the assumption is made that as the activity of the water is decreased the number of water molecules carried through the glass per hydrogen ion remains unchanged. If S is the number of moles of water carried across the boundary by one equivalent of hydrogen ions, $a_{\text{H}_2\text{O}}$ the activity of the water (taken as unity in the reference solution inside the glass electrode), a_{H} the activity of the hydrogen ion, then the equation for the net potential across the glass membrane is⁶

$$E_1 = \frac{RT}{F} \ln \frac{a'_{\text{H}}}{a_{\text{H}}} + S \frac{RT}{F} \ln a_{\text{H}_2\text{O}} \quad (1)$$

it would have if equilibrium were allowed to take place. With the concentration of the glass at an approximately fixed value, it is obvious that there can be only one concentration of the aqueous solution that will agree with the equilibrium condition. Hence ionic exchange should occur at all but one P_{H} according to the theory of MacInnes and Belcher. But the glass electrode agrees with the hydrogen electrode over a billion-fold change of hydrogen-ion concentration without any apparent error.

⁶ See Taylor, *J. Phys. Chem.*, **31**, 1480 (1927).

If the glass electrode acted as a perfect hydrogen electrode, the equation would be

$$E_2 = \frac{RT}{F} \ln \frac{a_H}{a_H^0} \quad (2)$$

Subtracting E_2 from E_1 an equation for the error of the glass electrode in acid solutions is obtained, namely

$$\Delta E = E_1 - E_2 = S \frac{RT}{F} \ln a_{H_2O} \quad (3)$$

This equation agrees qualitatively with all the facts observed; it shows that the error is independent of the nature and concentration of any ions present including the hydrogen ion and that the error depends only upon the activity difference of the water between the two solutions. If the activity of the water is diminished, the error will be negative in sign as is actually observed. But it is possible to test equation (3) quantitatively. From data given in the "International Critical Tables" and elsewhere the vapor pressure of the water and therefore the activity in the solutions of hydrochloric and sulfuric acids in the alcohol solutions (assuming that the vapor pressure of the water in the alcohol water mixtures is the same as in the acid mixture actually used), and in the 4.4 *N* lithium chloride solution may readily be determined.⁷ If the activity of the water in the reference solution inside the glass be taken as unity, and if a'_{H_2O} is the activity of the water in the solution under investigation, then by plotting $-\log a'_{H_2O}$ against the error of the glass electrode a straight line should be obtained with slope equal to $0.059 S$ and with intercept on the abscissa equal to zero if equation (3) is valid. The data necessary for such a graph are collected in Table V, and are plotted in Fig. 4.

From a study of the data and the graph it is evident that the potentials of the glass electrode agree within the rather large experimental error with the supposition that as the hydrogen ion migrates through the glass it

⁷ The solutions of hydrochloric and sulfuric acids were titrated volumetrically in order to find their normal concentrations at the three lowest P_H values.

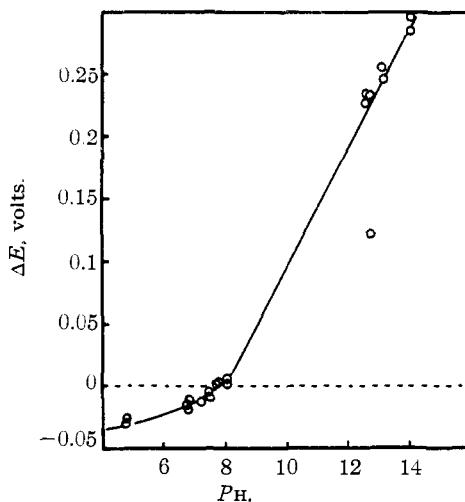


Fig. 3.—Errors of the glass electrode in 1 *N* sodium iodide in ethanol.

TABLE V

THE ERROR OF THE GLASS ELECTRODE IN MILLIVOLTS AS A FUNCTION OF THE ACTIVITY OF THE WATER AT 25°

Solution	P_H	a_{H_2O}	ΔE obs.	ΔE calcd. $0.05915 \log a_{H_2O}$	Dif.
33% ethanol	1.30	0.89	- 1.3	- 3.0	1.7
33% ethanol	0.413	.89	- 1.3	- 3.0	1.7
37% ethanol	1.86	.88	- 2.0	- 3.3	1.3
55% ethanol	1.36	.83	- 4.2	- 4.8	0.6
56% ethanol	1.99	.83	- 4.6	- 4.8	.2
66% ethanol	0.712	.79	- 3.9	- 6.1	2.2
4.4 N LiCl	4 to -0.5	.77	- 7.0	- 6.7	-0.3
H ₂ SO ₄	-0.798	.69	- 6.9	- 9.5	2.6
H ₂ SO ₄	- .798	.69	- 3.3	- 9.5	6.2
HCl	- .680	.65	- 6.5	-11.1	4.6
HCl	- .680	.65	- 6.8	-11.1	4.3
H ₂ SO ₄	- .910	.63	- 7.8	-11.9	4.1
HCl	- .730	.62	-15.1	-12.3	-2.8
HCl	-1.17	.41	-18.4	-22.7	4.3
HCl	-1.17	.41	-22.5	-22.7	0.2
H ₂ SO ₄	-1.35	.40	-16.6	-23.5	6.9
H ₂ SO ₄	-1.62	.27	-33.9	-33.6	-0.3
H ₂ SO ₄	-1.62	.27	-36.3	-33.6	-2.7
98% ethanol	-0.065	.12	-55.1	-54.5	-0.6
98% ethanol	- .065	.12	-38.6	-54.5	15.9

carries just one molecule of water along with it (the slope of the line turns out to be equal to 0.059 and S equal to one). The agreement is best for the 4.4 N lithium chloride solution; this is perhaps because the error in this solution was the most carefully determined error. In the alcohol, hydrochloric acid and sulfuric acid solutions there is the possibility that alcohol or acid molecules might be transported through the glass; this would cause the error to be lower than theoretically calculated. The agreement between the data and the theoretically calculated values, however, indicates that it is water that is carried through the glass in preference to any other neutral molecule. At constant P_H , therefore, the glass electrode would function as a true water electrode. As far as the author is aware this is the only known example of such an interesting phenomenon.

The errors of the glass electrode in alkaline ethanol solutions of sodium iodide are what might be expected from the behavior of the glass electrode in water. An orienting experiment carried out in a solution of barium iodide indicated that quite analogously with aqueous solutions the barium ion causes considerably less error than does the sodium ion in ethanol solutions. The magnitude of the errors, however, is greater than the errors in water, and due to the complex situation, the errors are rather unexplainable on a quantitative basis.

Conclusions

It is now possible to obtain a complete equation for the glass electrode over practically the entire PH range by combining equation 3 with equation 15 of the author's previous¹ paper, and including in the final equation the usual equation for the hydrogen electrode. The equation is

$$E = \frac{RT}{F} \ln \frac{a'_H}{a_H} + \frac{RT}{F} \ln \frac{B/a_H^{(n-1)'} + a'_H}{a'_H} + \frac{RT}{F} \ln a_{H_2O} \quad (4)$$

In equation (4) B and n are constants to be chosen from the data; equation 4 also contains the implication that the reference solution inside the glass electrode will not cause any deviation from the correct hydrogen electrode function on the inside surface of the glass electrode.

The question now arises, can a glass electrode be used to measure the hydrogen-ion activity in non-aqueous solvents? The answer is that it surely will not give the correct potentials if the reference solution inside the glass is an aqueous solution. Furthermore, since MacInnes and Belcher have shown rather conclusively² that glass of the type used in this research contains water, it is exceedingly doubtful if the glass electrode will function at all correctly and reproducibly in any solvent but water.⁸ It is somewhat possible that glasses might be made which would allow waterless hydrogen ions or protons⁹ to migrate; in this case the glass electrode could be used in non-aqueous solutions provided only protons migrated through the glass.

The rôle of the glass electrode as a water electrode reduces the analogy between glass and quartz membranes which was apparent at the time of

⁸ Professor Norris F. Hall has informed me that the glass electrode cannot be used in solutions of glacial acetic acid.

⁹ The theoretical treatment of this paper indicates that the hydrogen ions do not migrate through the glass as protons as suggested by MacInnes and Belcher.²

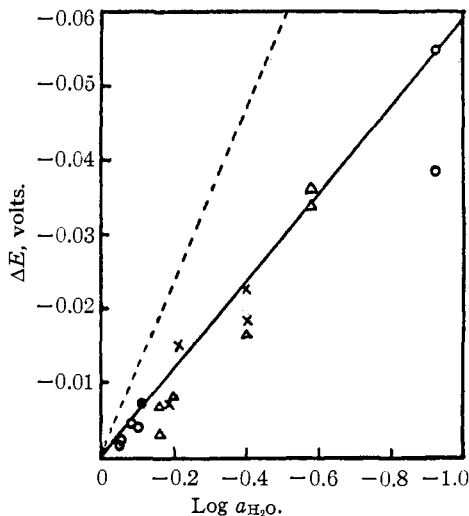


Fig. 4.—The errors of the glass electrode as a function of the activity of the water: circles, ethanol-water mixtures; crosses, HCl solutions; triangles, H_2SO_4 solutions; solid circles, 4.4 N LiCl. The solid line is theoretically calculated on the assumption that the hydrogen ion carries one molecule of water through the glass; the dotted line on the assumption of two water molecules per hydrogen ion. The exact proportionality between the potentials and the logarithm of the water activity shows that the glass may be considered as a water electrode.

writing of the author's last paper. Lengyel¹⁰ conceives of glass electrodes of low electrical resistance as being explainable on purely thermodynamic grounds, but as the resistance of the glass is increased surface effects become more and more pronounced until with quartz membranes surface effects will predominate and a theory of adsorption of ions on the surface will serve to explain the potentials. However, this assumption has not been verified yet in any quantitative fashion. It would be interesting to see whether the quartz membranes will act as a water electrode similarly to the glass membranes. If they should also act as water electrodes, the adsorption theory would have to be abandoned inasmuch as it would be difficult to explain how a neutral molecule on adsorption could affect the potential.

Since the above paper was written, Lengyel has published further work on the quartz electrode¹¹ in which he has discovered errors of the quartz electrode in acid solutions similar to the glass electrode acid solution errors. He tried to explain these results on the basis of a consideration of the negative ions, but finds such an explanation inadequate. The author is unable to explain Lengyel's results quantitatively on the assumption that the quartz electrode acts as a water electrode although qualitatively the theory and the data are not irreconcilable.

Summary

1. The glass electrode is directly compared with the hydrogen electrode in acid solutions of sodium chloride and sulfate, lithium chloride, aluminum chloride and sulfate, hydrochloric acid, sulfuric acid and in acid ethanol water mixtures. A comparison was also made over a wide P_H range in a solution of sodium iodide dissolved in ethanol.

2. The errors of the glass electrode in acid solutions are not a direct function of the nature or concentration of any ion present. This statement includes the hydrogen ion.

3. The errors in alcoholic solutions are similar to the errors in acid solutions.

4. Previous theories to explain these errors are reviewed and rejected.

5. It is found that the acid solution errors are a function of the activity of the water; reduction of the activity of the water makes the error more negative in accordance with the equation

$$\Delta E = \frac{RT}{F} \ln a_{H_2O}$$

Because of this the glass electrode can be shown to act as a perfect *water electrode* at constant P_H (within the experimental uncertainties).

6. The mathematical analysis of the results indicates that as the hydrogen ion migrates through the glass it carries exactly one molecule of water

¹⁰ Béla v. Lengyel, *Z. physik. Chem.*, **A153**, 425 (1931).

¹¹ Lengyel, *ibid.*, **A159**, 145 (1932); Lengyel and Mátrai, *ibid.*, **A159**, 393 (1932).

along with it. In other words, the hydrogen ion or proton is hydrated in the glass.

7. The results indicate that the glass electrode when made of the glass used in this research may not be used to measure the hydrogen ion activity of non-aqueous solutions.

8. By combining the equation for the glass electrode in acid solutions with the equation for the glass electrode in alkaline solutions given in the author's last paper, an equation for the glass electrode over an extensive P_H range is obtained.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE RELATION BETWEEN THE TWO CONSTANTS OF THE ARRHENIUS EQUATION

BY MILTON J. POLISSAR

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Introduction.—The rate constants of both first order and second order reactions can be represented by the following empirical equations

$$K = Se^{-Q/RT}; \log K = B - Q/4.58T \quad (1)$$

The simple collision hypothesis of gaseous bimolecular reactions yields the following equation for the second order rate constant

$$K = Ze^{-Q'/RT}; \log K = \log Z - Q'/4.58T \quad (2)$$

Z is proportional to the square root of the absolute temperature and is equal to the number of collisions between the reacting molecules, in moles per liter per second, when the concentration of each of the two reactants is one mole per liter. Q' is the heat of activation and for reactions measured at or near room temperature it is smaller than Q by about 300 calories. Equation 2 is the mathematical equivalent of the statement that all collisions between two reactant molecules in which the energy of impact is equal to or larger than the heat of activation will result in chemical decomposition.¹

Several investigators tested the applicability of Equation 2 to second order rate constants in liquid solutions. In their calculations of the value of Z they assumed that the gas-kinetic formula may be relied upon to give the right order of magnitude for the number of collisions between the solute molecules. They found that the observed values of the tested rate constants were much smaller than those calculated by means of this formula.²

¹ Cf. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, Oxford, 1929, pp. 100, 105.

² (a) Christiansen, *Z. physik. Chem.*, **113**, 35 (1924). (b) Norrish and Smith, *J. Chem. Soc.*, 129 (1928). (c) Moelwyn-Hughes and Hinshelwood, *ibid.*, 230 (1932).