but noticeable, at this low concentration. The exponent, n, has been assumed provisionally to be unity. It appears then, for this limited amount of data at least, that within the limit of error Equation 6 holds for the potassium ion as well as for the chloride ion. It is hoped to extend this investigation to cover a wide range of strong electrolytes.

Summary

A modification of the moving boundary method of Denison and Steele for determining transference numbers, involving a single boundary, has been developed.

The boundaries move with the theoretical velocities only when the two solutions in contact at a boundary are adjusted, within about 5%, to the relation $C/T = C'/T'$ in which C and C' are the concentrations and T and T' are the transference numbers. The correct value for T can therefore be obtained by a series of experiments approaching more and more closely to this condition. Unless this adjustment is obtained results are not independent of the composition of the indicator solution, or of the current through the apparatus, and may vary widely and erratically from the true values.

Transference numbers at 25°, for potassium chloride and potassium bromide in 0.1 N solutions have been obtained. These numbers show that the conductance of the potassium ion is the same in these two solutions if correction is made for viscosity.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE AMERICAN TELEPHONE AND TELEGRAPH COMPANY, AND THE WESTERN ELECTRIC COMPANY, INC.]

THE WETTING OF GLASSES BY MERCURY[1]

BY EARLE E. SCHUMACHER

RECEIVED JUNE 30, 1923

A number of observers have held that mercury does not wet glass because the latter is always covered by a film of adsorbed gas which prevents the mercury from coming into real contact with the glass. If this view is correct then, as Bancroft[2] has pointed out, mercury should readily wet glass if the adsorbed gas were completely removed. In order to test the accuracy of this hypothesis, a number of experiments were performed in which mercury was placed in glass containers whose walls had been

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[1] The term wetting is used in this paper in the sense that wetting is complete when the angle of contact between liquid and solid is zero and the meniscus concave, and that the liquid does not wet the solid in cases in which the angle of contact is zero and the meniscus is convex. In these experiments wetting was considered to have taken place whenever the meniscus of mercury was less convex at the conclusion of the experiment than it was at the start.

[2] Bancroft, *J. Ind. Eng. Chem.*, **13**, 88 (1921).

freed as far as possible of adsorbed gas. A description of several of these experiments will be given in this paper, together with a discussion of the results obtained and the conclusions reached.

Experimental Part

Fig. 1 illustrates the apparatus used in the first experiment.

The essential parts are the small aspirator, D, the distilling apparatus, B, the liquid air traps, G and F, and the mercury-vapor pump, H. In addition to the apparatus shown in this figure, two motor-driven oil pumps were utilized to maintain a suitably low pressure at the outlet of the mercury-vapor pump, H. All glass parts in the apparatus were made of soda-lime glass and before being used in these experiments, were cleaned with chromic acid and then thoroughly washed with distilled water. Immediately after the last washing the glass apparatus was sealed to the evacuating system and the water that still remained on the glass was pumped off.

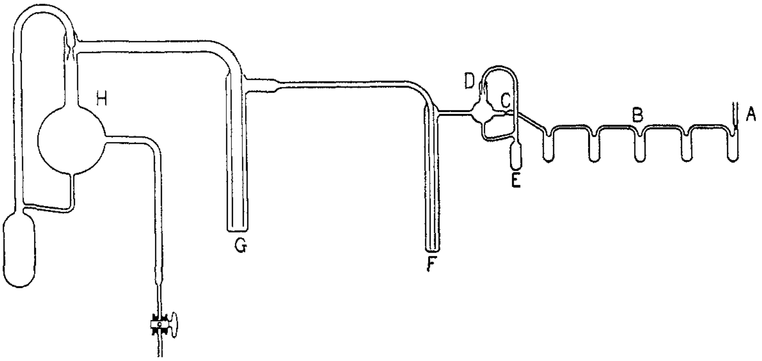

Fig. 1

At the start of the experiment the glass parts B, D and F, were subjected to a temperature of 400° for several hours, the pressure within the apparatus being maintained continuously at approximately 1×10^{-6} mm. of mercury, as measured by the Buckley type of ionization manometer. This treatment undoubtedly reduced the amount of adsorbed gas on these parts to a minimum. After this heat treatment the glass tube leading upward from Bulb A of the distilling train, B, was opened and redistilled mercury, purified according to the method recommended by G. A. Hulett,[3] was introduced into Bulb A, after which the tube was immediately closed and the internal pressure again reduced to at least 1×10^{-6} mm. of mercury. The aspirator, D, was then kept at a temperature of 400° for approximately 50 hours and at the same time, 4 of the 5 bulbs in the distilling train were receiving similar treatment.[4] By distil-

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[3] Hulett, *Phys. Rev.*, **33**, 307 (1911).

[4] In this connection some consideration was given to the possibility of further reducing the amount of adsorbed gas on the glass by heating to higher temperature in a vacuum oven. On account of the physical limitation that would be imposed under this plan it seemed that the preliminary nature of the experiments did not warrant its adoption.

ling the mercury from one bulb to another it was possible to give the glass in the distilling train a good heat treatment, thereby freeing its surface of the adsorbed gas that was taken up when the mercury was introduced. Gases entrapped by the mercury were, of course, released and pumped out during this distillation of the mercury from one bulb to another. All glass parts in the distilling train received higher heat treatment during this heating than they ever received again during the experiment. After terminating the heat treatment to which the glass parts B and D were subjected, about 12 cc. of mercury was distilled over into D and the distilling train then sealed off at C. This amount of mercury was sufficient to cause the small aspirator, D, to function as such very satisfactorily. The distilling of the mercury in D, was continued for 50 hours and this was believed to have removed any gas that was still entrapped by the mercury.

The experiment described above was repeated five times, using different aspirators in each case, all of which, however, were made of soda-lime glass. In all of the experiments the conditions were maintained as near like those cited above as possible. In two of the aspirators, at the termination of the experiments, the mercury seemed to wet the glass slightly, while in the other three the mercury behaved just as it ordinarily does when placed in a glass container which has not been evacuated. In the two cases where a wetting seemed to occur, the surface of the mercury in Bulb E appeared to be perfectly flat. The mercury surface in one of these aspirators when exposed again to air slowly acquired a convex meniscus; the mercury in the other aspirator was not appreciably affected by air even after exposure for several days. In none of these experiments did the mercury ever assume a concave meniscus.

Additional experiments were conducted in a similar apparatus made of 702-EJ Pyrex glass instead of soda-lime glass. The results obtained were about the same as those found when soda-lime glass was used, except that in the cases where there was evidence of wetting it usually took place more quickly. As it seemed possible that a correlation might exist between wetting and the chemical composition of the glass, further work was undertaken to investigate this point. For the small type of aspirator used in the above experiments an apparatus was substituted consisting of 6 bulbs sealed together. The first 4 bulbs, at the entrance of the train were made of soda-lime glass; the fifth bulb was made of Pyrex 702-EJ glass and the sixth bulb was of quartz. In several of these experiments a bulb made of Pyrex 702-P glass was substituted for one of the soda-lime bulbs. The soda-lime glass was sealed to the Pyrex bulb by connecting tubing made of glass varying in composition from that of the soda-lime glass at one end to Pyrex 702-EJ glass at the other. By means of a similar connecting tube, varying in this case from Pyrex at one end to quartz at the other, the Pyrex bulb was sealed to the quartz bulb. The bulbs, after being sealed to the evacuating system, were exhausted and with the pressure[5] being maintained within them at approximately 1 × 10^{-6} mm. of mercury they were heated to a high temperature for about 50 hours, the soda-lime glass being kept at 400° while the Pyrex and quartz bulbs, by means of individual heating units, were kept at temperatures of 550° and 800°, respectively. After this heat treatment, which must have reduced the amount of adsorbed gas held by the glass to a minimum, mercury was distilled into the bulbs from a distilling apparatus such as was used in the experiment described above. After sufficient mercury had distilled into the bulbs to fill any one of them, the distilling apparatus was sealed off from the rest of the system. The mercury was then distilled from one bulb to another until the experiment was concluded; during this process whenever any bulb was empty it was always subjected to a heat treatment before mercury was again distilled into it. In each of these five experiments entirely new soda-lime and Pyrex bulbs were used. On account of the difficulty of obtaining satisfactory quartz bulbs, however, and also because of their high cost, it was necessary to use the same quartz bulb in all five cases.

In these experiments, the behavior of the mercury in the quartz bulb was extremely interesting. Before the curvature of the mercury showed any change in the soda-lime or Pyrex containers, it usually became quite flat in the quartz bulb. In only one experiment did the meniscus of the mercury actually become slightly concave, but in four other experiments the surface of the mercury was absolutely flat. In the previous experiments in which the small aspirators were used, if a wetting did occur there was always the possibility that something from the glass or some other source had contaminated the mercury, but here in the case of the wetting of quartz by mercury no such possibility existed. In every experiment during the early stages of the distillation the mercury that wet the quartz, when distilled again into the soda-lime or Pyrex glass bulbs, failed to show any wetting. The same mercury here wet in one bulb and failed to wet when distilled into another.

In these experiments with the bulbs, as in the experiments with the small aspirators, the behavior of the mercury in the Pyrex and soda-lime containers differed considerably from one experiment to another. In two of the experiments the surface of the mercury became quite flat in the Pyrex containers, but in at least four others it did not. In the two cases, the mercury was distilled from bulb to bulb for at least 30 hours before the flattening became at all pronounced. With the soda-lime glass bulbs, in only one case was there any noticeable change in the mercury surface,

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[5] It should be noted that pressures of this magnitude were maintained in all of these experiments. No degree of wetting was ever obtainable where higher pressures were maintained.

and that took place only after the distillation had continued for 50 hours. In this one case the mercury surface was still slightly convex after the experiment had been run for 75 hours. At the conclusion of this run the train of bulbs while still evacuated was sealed off from the rest of the system, the mercury was then poured from one bulb to another and measurements upon the curvature of the mercury surface in each bulb were taken. By properly mounting the bulbs the vibration of the mercury was reduced to a minimum and this made it possible to take fairly accurate readings. These measurements, which were taken with a cathetometer, are given in Table I and represent the differences in height between the places where the mercury cut the glass of the container and the top portions of the meniscus. For comparative purposes, measurements were also taken upon mercury in a soda-glass container that was evacuated but had never been heat-treated.

Table I

Wetting Measurements

Type of glass:	Soda-lime unheated	Soda lime	702-P	702-EJ	Quartz
Diff. in height, mm.:	1.6	0.6	0.3	0.0	sl. concave

The chemical compositions of the various types of glass used are given in Table II. Glass 702-EJ was a borosilicate glass containing no metal of the magnesium-lime-zinc group nor any heavy metals, and the quartz was of course practically pure silica.

Table II

Chemical Compositions of the Glasses Used

	Soda lime	702-P		Soda lime	702-P
SiO_2	69.93	72.05	K_2O	0.10	1.12
Al_2O_3	1.54	2.21	P_2O_5	0.08	Trace
Fe_2O_3	0.19	0.05	Sb_2O_3	0.05	...
PbO	1.44	6.11	MnO_2	0.09	0.01
CaO	3.17	0.06	F_2	...	Trace
MgO	0.03	0.09	B_2O_3	2.36[a]	14.07[a]
Na_2O	21.02	4.23			

[a] By difference.

These results would indicate that a parallelism exists between wetting and the chemical composition of the glass. It is interesting to note that in a previous paper[6] on "Measurements of the Gases Evolved from Glasses of Known Chemical Composition," a similar parallelism was found to exist between the amount of gas evolved by a glass and its chemical composition.

Fig. 2 shows diagrammatically the last type of apparatus worked with. Here, as can be seen, capillary tubes were inserted in two of the bulbs; one made of soda-lime glass, the other of Pyrex. The small holes seen in the tubes just above the point where they become capillary, were to keep the pressure inside the capillary the same

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[6] Harris and Schumacher, *Ind. Eng. Chem.*, **15**, 174 (1923).

as in the outer bulb when the bottom of the capillary was closed by mercury. For denuding the glass of its adsorbed gas and for introducing the mercury into the apparatus, the methods employed in the preceding experiments were used.

Ten different runs were made with this type of apparatus. In one run a slight rise of the mercury in the capillary made of Pyrex glass was noted. In one other case there was neither a rise nor a depression in the Pyrex capillary. In 8 different runs the mercury was depressed in the Pyrex capillary. In no case was a rise observed in the soda-lime glass capillary.

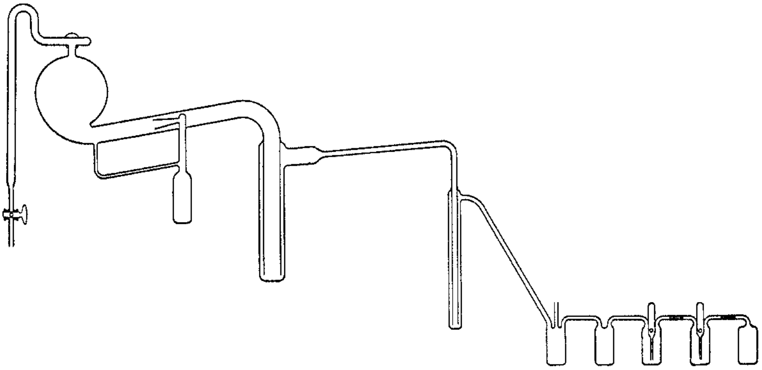

Fig. 2

Discussion

The results of the experiments that have just been described indicate that the chemical composition of the glass either directly or indirectly plays a part in determining whether or not mercury will wet the glass. The tendency of mercury to wet glass seems to decrease as the alkaline content of the glass increases. Similarly, as pointed out previously, the gas evolved from a glass increases as the alkaline content increases. A glass containing a high percentage of soda would be more easily hydrolyzed than one that contained a lower percentage, and the result of such an hydrolysis would be the formation on the surface of the glass of a thin film of sodium hydroxide, together with some amorphous silica. It is reasonable to assume, therefore, that mercury does not ordinarily wet a soda-glass surface because this film prevents it from ever touching the glass. On the other hand, such a film may have only an indirect effect on the wetting of glass by mercury due to the tenacious retention of large quantities of gas. If this alkaline film is either directly or indirectly responsible for the non-wetting of ordinary glass by mercury, then the results obtained in these experiments can be accounted for.

On the quartz surface, where there was no chance for an alkaline film to exist, a degree of wetting was always obtained. On the surface of Pyrex glass the alkaline film would surely be thinner than on the soda lime glass and, as will be recalled, mercury seemed to show a greater tendency to wet Pyrex than it did soda-lime glass. That on two occasions a degree of wetting was noted when a soda glass was used can be accounted for by assuming that the specific conditions of washing and subsequent drying of the soda glass were such as to prevent any appreciable alkaline film formation. In the case of the capillary tubes, on the other hand, no marked wetting ever occurred in the capillaries because a longer period of time was required to remove the water from within these tubes than from surfaces outside, and this was favorable to the formation of alkaline films.

Summary

An attempt has been made to cause mercury to wet glass and quartz after their surfaces have been denuded of gas as far as it is possible with the present means at our command. The difficulty of this task appears to become greater as the alkaline content of the glass increases. Fairly good wetting can generally be obtained on quartz, while on Pyrex and soda-lime glass it is obtained only occasionally.

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LIESEGANG RINGS. III. THE EFFECT OF LIGHT AND HYDROGEN-ION CONCENTRATION ON THE FORMATION OF COLLOIDAL GOLD IN SILICIC ACID GEL. RHYTHMIC BANDS OF PURPLE OF CASSIUS

By Earl C. H. Davies

Received July 2, 1923

Introduction.—In a previous paper[1] the author showed that light has a pronounced influence on the tendency for colored bands of colloidal gold to form in silicic acid gel. It was the purpose of the present work to make a more exhaustive study of this light effect. The following factors were investigated: the effect of light of different wave lengths; the relation between band formation and hydrogen-ion concentration; the variation of band formation with kind of acid used in making the silicic acid gel; the effect of variation of oxalic acid concentration; the result of using different strengths of gold chloride solution; the result of replacing the oxalic acid by other reducing agents.

The Effect of Light of Different Wave Lengths.—For the first series of experiments, glass cylinders, 18 × 5 cm., were fitted with large corks holding 2.5cm. test-tubes, within which were smaller tubes, containing the gel in which diffusion was to take place. Some of the gel was protected by

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[1] Davies, This Journal, **44**, 2700 (1922).