6-1935

Comparison of Hydrogen Ion Concentration Results in Silicic Acid Gel Mixtures by Different Methods

Edward David Luneburg
Union College - Schenectady, NY

COMPARISON

of

HYDROGEN ION CONCENTRATION RESULTS

in

SILICIC ACID GEL MIXTURES

by

DIFFERENT METHODS

E. D. LUNEBURG--1935

COMPARISON

of

HYDROGEN ION CONCENTRATION RESULTS

in

SILICIC ACID GEL MIXTURES

by

DIFFERENT METHODS

A thesis, presented to the Department of Chemistry of Union College, in partial fulfillment of the requirements for the Degree of Bachelor of Science in Chemistry, by

Approved by Charles B Hurd

May 29, 1935

INTRODUCTION

Since a conclusive theory of the structure of gels has not been presented yet, it is still necessary to obtain as much data about gels as possible, in the hope that the assembled data will lead to a theory which which will explain allthe known facts. Thus, the effect of such factors as temperature, concentration of acid and the addition of indicators were studied. Also, the change of the the properties of viscosity and conductivity during the time of set were studied. Recently much attention has been directed toward the studying of the effect of hydrogen ion concentration, which is related to the cocentration of acid and silicate, on the time of set. Until the work of Cooney(1) in 1934 these studies had been carried out quantitatively inth acid range and only qualitatively in the basic range. This study includes the important portion of the pH range, acetic acid furnishing the hydrogen ions. A comparison of pH results of buffers and the quinhydrone potentiometer has been obtained. This study also includes a comparison of readings of used and unused platinum wires in using the quinhydrone potentiometer and an attempt to improve the accuracy in the determination of the pH of silicic acid gels in the basic range by means of buffers.

HISTORICAL

The structure of gels has been a problem ever since they were produced, a problem which has not been definitely solved as yet. The first important theory was the Micellae Theory which postulated that the solid colloidal particles of the solution formed small molicuilar aggregates which interlocked to give a soft spongy structure. Observations of Zsigmondy by means of the ultramicroscope showed that gels could form freely moving ultramicrons which supported the Micellae Theory. However, the more recent theory proposed by Proctor and Robertson in 1914(2) seems to be most generally accepted. This theory, called the fibrillar theory, pictures the gel as being composed of long thread-like chains which lengthen and branch out upon polygmerization, the final structure being an interlocked network resembling a bramble or brush heap. Other theories for the structure of gels are the honeycomb structure, solid frame with interspersed fine capillaries.

Recently work has been done in studying the time of set as a function of temperature. It has been shown that, for acetic acid-sodium silicate gels, the logarithm of time is a linear function of reciprocal temperature, $\frac{d \ln T}{d/T} = Q/R$ where Q is Archenius' heat of activation, which was determined from these results. This study was extended this year(1935) to other acids. This work was confined, however, to weak acids whose pH can be reproduced with reasonable accuracy by using identical mixtures. For strong acids,

it is impossible to reproduce the same pH by measuring the same amounts of constituents because of the nature of the strong acid, ie. a large change of pH occurs with a very small amount of acid. Therefore, it is desirable to obtain an accurate method for determining the pH, not only to obtain time of set as a function of pH but also to obtain heats of activation which may be an important factor in helping to formulate a conclusive theory of the mechanism of gels.

APPARATUS

The quinhydrone electrode metod was used for determing the hydrogen ion concentration. Platinum wire was used as an electrode, altho gold can also be used. The reference electrode was a saturated calomel half cell. The potential was measured by the Leeds and Northrups polentiometer constructed for pH measurements using the quinhydrone electrode.

A water thermostat was used to keep the gels at constant temperature since temperature has an appreciable effect on the time of set. The thermostat was regulated to 25° C and was constant within .05° C. The thermostat consisted of a well insulated water bath and two electric heaters which maintained the bath at the required temperature. The thermal regulation was accomplished by means of a mercury regulator in series with a storage battery and the primary coil of a telephone relay. The heaters were connected in series to the secondary of the relay. In winter at 60 watt bulb was in series with the heaters while in summer only a small pilot bulb was in series with the heaters when contact was made in the mercury regulator. The water was circulated by means of stirrer run by a small motor.

EXPERIMENTAL

The "E" brand sodium silicate furnished by the Philadelphia Quartz Company and acetic acid were used in making the gels. The Na_2O-SiO_2 ratio in the "E" brand is 1/3.25 by weight. The sodium silicate solutions were standardized with standard HCl using Methyl Orange as the indicator. The acetic acid was standardized with standard NaOH using Phenolphathlein as the indicator. Oxalic acid was used as the final standard. All distilled H_2O used was boiled to expel CO_2.

The total volume of the gel mixture was 80 cc., 25 cc. being silicate solution which was measured with the same 25cc. pipette thruout, and the remaining solution consisted of acid and water measured by the same two burettes thruout. The acid-water solutions were kept in separate beakers from the silicate solution until they were ready to be mixed. Upon mixing, the solution was poured back and forth in the two beakers three times. The pyrex beaker containing the solution was set in the thermostat and was covered with a $2\frac{1}{2}$" watch glass after a sample was extracted for the determination of the pH with the standard buffers. The watch glass prevents evaporation which affects the time of set. If the pH of the gel was in the range of the Quinhydrone, double portions were used and 80 cc. was used to determine th pH by means of the Quinhydrone and 80 cc. was used for determining the time of set after a sample had been extracted for determining the pH by means of buffer solutions. The gel was considered set when a rod 3mm. in diameter and 10cms. long was supported at an angle of about 15 to the vertical.

The saturated calomel cell was made up as described in Daniels, Matthews and Williams(3). It is advisable to flush the calomel cell from time to time. Leeds and Northrup(4) claim their apparatus is good up to a pH of 9, but this is not so as will be seen from the results obtained. The calculation of the potential depends on an excess of the solid quinhydrone, therefore in adding the quinhydrone it is essential to add an excess so that some of the solid remains on the bottom of the beaker.

Qinnhydrone is an equimolar mixture of quinhydrone and hydroquinone. The reaction which takes place is:

$$\text{Hydroquinone} = \text{Quinone} + 2H^{+} + 2e$$

The equilibrium constant is:

$$K = \frac{(\text{Quinone})(H^{+})^{2}(e)^{2}}{(\text{Hydroquinone})}$$

The potential is;

$$E = E_{o} - \frac{RT}{2F}\ln(\text{Hydroquinone}) + \frac{RT}{F}\ln(H^{+})$$

For the equilibrium;

$$\text{Quinone} + \text{Hydroquinone} \rightleftharpoons \text{Quinhydrone}$$

we may write;

$$K_{q} = \frac{(\text{Quinone})(\text{Hydro quinone})}{\text{Quinhydrone}}$$

Since (Quinhydrone) is constant:

$$(\text{Quinone})(\text{Hydroquinone}) = K_{qs}$$

However, the solution is also saturated with respect to the hydroquinone in the solid phase. Therefore $K_{fs} = C$ and the equation reduces to :

$$E = E_{o} + \frac{RT}{F}\ln(H^{+})$$

This equation reduces to:

$$pH(25^{\circ}) = \frac{0.4532 - E}{0.0591}$$

where E is the measured potential. The pH values have been calculated and appear in booklet form so the pH values can be read directly by means of E.

Hydrogen ion concentrations from pH 6.8 up were determined by standard buffer buffer solutions as well as by the Quinhydrone method. These standard buffers were those recommende by Clark(5). The indicators Brom Thymol blue and Thymol blue were used for ranges 6.0-8 and 8.0-9.6 respectively. Phenolphthalein was tried in the range 9.6-10.2. It has been found by DiGesro(6) that, altho the alcoholic solution of phenolphthalein affects the time of set, it does not change the pH for gels in the acid range. Thus, it was assumed that phenolphthalein did not change the pH when used as the indicator in the gel. Alizarin Yellow GG was the indicator used in the range from 10.4 up. Previously Alizarin had been tried, but this indicator was found to be unsuitable because the aqueous solution faded rapidly. The aqueous solution is more desirable , altho the alcohol was found not to change the pH in the acid range, the alcohol is just another factor which may complicate the reaction.

After mixing the add and silicate, several drops were removed by means of a clean eye dropper and placed in a small glass cup about 3/8" in diameter and 3/16" high, part of the equipment of the LaMotte apparatus. A drop of the proper indicator was then added.

It makes little difference whether the drop of indicator is in the cup before the gel is added or whether the indicator is added to the gel, altho it seemed that the indicator diffused more rapidly when added to the gel. When determining the pH of a quick setting gel, it is more convenient to have the indicator already in the cup. However, on the few gels which set before the indicator was added, I found that the indicator diffused thru the gel and a reading was obtained which agreed with a check determination. The opacity of the gel did not appreciably affect the color.

The series of buffers has to be freshly prepared from the standard buffers for each run. Evaporation takes place and decreases the volume of the standard and in order to obtain good results, all volumes should be nearly equal, both the volumes of the standards and of the gels. The color of the Alizarin Yellow GG in the standards, as in the case of Alizarin, fades. Thus this alkaline series gave trouble because the yellows and straws are hard to distinguish and also becausw they had to be replaced by a new series after a short time with new solution from the standard buffer solutions, because of the fading.

Buffer action is the resistance to change of pH upon the addition of or loss of alkali of a solution. The explanation of ordinary buffer action is not difficult. If to a solution , containing a weak acid, HA, and one of its salts, MA, there is added a small amount of an acid or base the solution will resist a change in pH by neutralizing the added substance according to

the reactions:

$$A^- + H = HA$$

$$HA + OH^- = H_2O + A^-$$

Thus, if the reserve acidity is equal to the reserve alkalinity, the concentration of A^- must be equal to that of HA. According to the law of mass action:

$$C_{H^+} = \frac{C_{HA}}{C_{A^-}} K_A$$

Therefore since $\frac{C_{HA}}{C_{A^-}} = 1$ $\qquad C_{H^+} = K_A$

The buffer Na HPO , KH PO (6.8-8.0) was chosen in preference to a citrate buffer because citrate buffers have a tendency to mold within a comparatively short time. The buffer cinsisting of H BO , KCl-NaOH was chosen for the range7.8-10.0. The buffer consisting of Na CO , Na B O, was selected for the range 10.0-11.0. Sometimes a constituent of a buffer has a specific effect on an indicator. It has been found that alizarin, in passing from a phosphate to a borate buffer micture, exhibits a sudden transition which appears to be a specific effect of the borate on the indicator.

Altho the indicator method has been fairly successful, there is still chance for improvement, especially in the alkaline range from 10.0 up.

RESULTS

First a trial run was made to determine the pH range for various amounts of acid added. This run aided in getting a rapid reading on the quinhydrone and determined the range of the series of standard buffers and indicator which were prepared. This procedure was followed in both concentrations of acid and silicate. All runs were made in duplicate and only averages are given. Table 1 shows the results obtained.

The results obtained from Table 1 showed the amount of acid that should be added in order to obtain a pH in the desirable range. A run was made comparing the quinhydrone method with the buffer method using Brom Thymol Blue (6.0-7.6), Thymol Blue (7.6-9.6), Phenolphthalein (9.6-10.4) and Alizarin Yellow GG (10.4-) as the indicators. Results are shown in Table 2.

After making the runs mentioned above, the solutions were used up and new solutions were prepared. The range of pH for various amounts of acid was determined as in the previous case. Table 3 shows the results.

The range having been determined, the Quinhydrone method was compared with the buffer method, the indicators this time were Brom Thymol Blue (6.0-7.6), Thymol Blue (7.6-10.0) and Alizarin Yellow GG (10.2-). These results are shown in Table 4.

Table 5 consists of a comparison of readings taken with the Quinhydrone potentiometer using different platinum electrodes as described in the table.

The comparison of Pt electrodes show that the electrodes become unfit for use after they have been used for some time. From these results, it also shows that in order to keep the electrode in as good condition as possible, it is advisable to clean the electrode with hot concentrated NaOh, HCL and distilled H O and then flashed. The hot concentrated NaOh peptizes the gel and removes it from the surface of the electrode, the HCL removes the NaOH forming NaCL which is very soluble. It seems necessary to flash the electrode for best results. The very acid mixture was chosen so that the gel would not set thruout the comparisons. This difference is probably greaterin this region than in the ordinarily used region of about apH of 6. There is a large change in the reading with time. This change appears to be due to a polarization of the Pt electrode rather than a time lag necessary to obtain the true reading. This is probably the effect which Cooney interpreted as a change in pH of the gel in the acid range. The indications however, are that it is a polarization of the PT electrode.

I think that possibly 6" test tubes would be an improvement over using the La Motte cups. Larger volumes could be used and thus differences in volume would not comprise as great a % of the total volume. The small cups are not very uniform. The test tubes could also be stoppered, preventing detrimental effects from the air and evaporation.

Several indicators may be tried in place of Alizarin Yellow GG, and one may prove to be better by far. The indicator Alizarin blue S would be very good if it was satisfactory as it covers a range from 6-14. Then the mixed indicator Thymol violet, if there were no specific effects, should prove to be good since it covers the range 9-13. Thymol violet consists of Tropaeolin O

(1 part) and thymolphathlein (4 parts). The indicator and buffer method of PH determination should prove very successful if a satisfactory indicator above the range 9.6 can be found.

BIBLIOGRAPHY

1. Hurd & Cooney — Thesis, Union College (1934)
2. Proctor and Robertson — Chem. Soc. Trans., 105:313 (1914)
3. Daniels, Mathew and Williams — Experimental Physical Chemistry
4. Leeds and Northrup — Booklet for Operation of Quinhydrone Apparatus
5. Clark — The Determination of Hydrogen Ions
6. Hurd & Digesero — Thesis, Union College (1934)
7. Hurd & Griffeth — Thesis, Union College (1934)
8. Prideaux — The Theory and Use of Indicators Chap. 4,5,6,7,8.

Table 1

Basicity of Silicate Solution 1.15N

Normality of Acetic acid 1.160N

Total volume of acid & water 55cc.

Volume of Silicate 25cc.

(Volumes are for single portions)

cc. of Acid	pH Quinhydrone
55	4.46
50	4.50
40	4.60
30	4.90
20	5.52
15	7.20
10.5	>9.0

Table 2

cc. of acid	pH Quinhydrone	pH Buffer	Time of set Min.	Sec.
16	5.98	6.0	6	34
15.75	6.2	6.25	4	28
15.5	6.34	6.4	2	30
15.25	6.79	6.8	2	8
15.0	7.13	7.20		65
14.5	7.85	7.9		40
14.0	8.01	8.05		33
13.5	8.41	8.55		27
13.0	8.50	8.90		30
12.5	8.63	9.15		32
12.0	8.76	9.25		44
11.5	8.82	9.35		57
11.0	8.87	9.40	1	37
10.5	8.96	9.7	2	47
9.75		10.6	4	32
9.50		10.8	10	17

Table 3

Basicity of Silicate Solution 1.971

Normality of Acetic Acid 1.88

Total Volume of Acid & H_2O 55 cc

Volume of Silicate 25

(Volumes are for single portions)

cc. of acid	pH Quinhydrone	Time of Set Min.	Sec.
55	4.14	360	17
50	4.24	300	2
40	4.38	240	35
35	4.46	180	59
30	4.60	120	16
16	6.20	4	41
15.75	6.30	3	12
12.0	>9.20	1	54

Table 4

cc. of acid	pH Quinhydrone	pH Buffer	Time of Set Min.	Sec.
18	5.4		23	24
17	5.6		13	5
16	6.2		3	58
15.75	6.40		3	7
15.50	6.55	6.6	2	16
15.20	7.0	7.05	1	10
15	7.20	7.15		58
14.75	7.46	7.5		43
14.50	7.68	7.7		38.4
14.25	7.88	8.0		35.4
14.0	8.08	8.3		31.6
13.75	8.4	8.7		32.4
13.25	8.54	8.8		36.6
13.00	8.76	8.85		39.2
12.75	8.83	9.10		40.8
12.50	8.92	9.30		48.8
12.25	8.94	9.60	1	5.4
12.00		9.70	1	19.0
11.75		9.80	1	24
11.50		9.90	1	31
11.25		10.0	2	28

Table 5

(1) Used Electrode that was cleared with NaOH & HCl

E.M.F. - 258.5, - 245.5

(2) Clean Flashed Electrode

E.M.F. - 382, - 384

(3) Clean Unflashed Electrode

E.M.F. -236, - 254, - 258, - 260

(1) Cleaned Electrode cleaned by using NaOH & HCl & H_2O

E.M.F. - 284.0, - 278

(2) Cleaned with H_2O & flashed.

E.M.F. - 364.5, - 332

Washed with H_2O and reflashed

E.M.F. - 378.0 after lapse of about 5 min. - 346

(3) Cleaned Electrode 3 with NaOH & HCl

E.M.F. - 312. After lapse of quite a bit of time - 296

Same electrode after cleaning with NaOH & HCl & flashing

- 396 after lapse of time -387.0

After lapse of 5 min. - 364.0

Cleaned with NaOH & HCl & H_2O & flashed

- 394. after lapse of 4½ min. E.M.F. -374

After lapse of 10 mln. E.M.F. -360

after cleaning with NaOH & HCl & H_2O E.MF. -346

(1) Electrode cleaned & flashed EMF -382

after lapse of 4 min. E.M.F. -358

(3) Electrode flashed E.M.F. -368

rinsed with H_2O & flashed EM.F. -368

after lapse of 2 min. E.M.F. -346

rinsed with H_2O & flashed E.M.F. -365