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# STUDIES ON THE ALKALINITY OF SOME SILICATE MINERALS

BY

R. E. STEVENS

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Shorter contributions to general geology, 1934-35

(Pages 1-13)



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# SHORTER CONTRIBUTIONS TO GENERAL GEOLOGY, 1934-35

## STUDIES ON THE ALKALINITY OF SOME SILICATE MINERALS

By R. E. STEVENS

### ABSTRACT

By grinding minerals under water it has been found that they yield relative and reproducible measurements of the hydrogen-ion concentration resulting from their hydrolysis. Many silicate minerals and two glasses have been studied in this way by a colorimetric method of determining hydrogen-ion concentration, and some of them have been studied more quantitatively by means of the hydrogen electrode.

The results of these tests are a rough index of the weathering qualities of different silicate minerals. The effect of silicate minerals on underground waters and upon geochemical changes is discussed.

### INTRODUCTION

#### USEFULNESS OF MEASURES OF ALKALINITY IN GEOLOGIC STUDIES

The action of pure and carbonated waters in decomposing silicate minerals has long been observed in the field and confirmed by laboratory experiments. Field observation has told much as to the relative stability of minerals toward water. The micas, especially muscovite, are highly resistant, being present as end products of rock decomposition, and the stability of orthoclase has also been observed. Plagioclase feldspars are somewhat more easily attacked, and the more basic mineral constituents of rocks, such as olivine, pyroxene, and the amphiboles, in comparison, yield readily.<sup>1</sup>

This action of water on rocks has been studied by numerous methods in the laboratory, and in a general way the mechanism of the process is understood. The mineral does not dissolve as a unit but, by hydrolysis, yields colloidal complexes of silica and alumina, or under some conditions intermediate products, such as calcite and magnesite, and free alkali. The solutions are alkaline in reaction.

A measurement of the hydrogen-ion concentration of these solutions, therefore, is an index to the extent of decomposition taking place and to the relative stability of the mineral in water. It also indicates the potential powers of the minerals in neutralizing ground waters containing carbonic, humic, sulphuric, and other acids.

The importance of silicates as a source of alkali in geochemical processes seems to be underestimated. A great part of them are capable of yielding more highly alkaline solutions than the carbonates calcite and dolomite. Furthermore, they are present in great abundance. Clarke<sup>2</sup> says:

In the solid crust of the earth the silicates are by far the most important constituents. They form at least nine-tenths of the entire known mass and practically all the rocks except the sandstones, quartzites, and carbonates.

Numerous geochemical changes take place in an environment of silicate minerals, and their effect on the alkalinity of solutions is of primary importance. Many of the chemical reactions can take place only within a certain range of alkalinity or acidity. Thus Wells<sup>3</sup> has shown that copper is precipitated from cuprous chloride solution by ferrous chloride only in a weakly acid or an alkaline solution. Copper, in the Michigan deposits, is associated with prehnite, a highly basic silicate, but not commonly with laumontite, a mineral that is similar but contains a smaller percentage of calcium. Freeman<sup>4</sup> has shown that sulphide ores might be carried in alkaline solution as double sulphides of alkali metals. In the process of enrichment certain ores near the surface are oxidized and carried downward in acid solutions. The solutions are gradually neutralized or made alkaline by the rocks with which they come into contact, causing precipitation of the ore.

A statement merely that the solutions are alkaline, or even alkaline to a certain indicator, is not sufficiently definite to be useful in many chemical studies. The degree of alkalinity or acidity may be precisely stated in terms of hydrogen-ion concentration, expressed as pH, as explained more fully in the following pages. Suffice it to say at this point that nearly all chemical reactions in solutions are affected by the pH number, and in many of them it is a predominant

<sup>2</sup> Clarke, F. W., The constitution of the natural silicates: U.S. Geol. Survey Bull. 588, p. 5, 1914.

<sup>3</sup> Wells, R. C., Chemistry of deposition of native copper from ascending solutions: U.S. Geol. Survey Bull. 778, p. 65, 1925.

<sup>4</sup> Freeman, Horace, Genesis of sulfide ores: Eng. and Min. Jour., vol. 120, pp. 973-975, 1925. See also Foreman, Fred, Hydrothermal experiments on solubility and oxidation of iron and copper sulphides: Econ. Geology, vol. 24, p. 811, 1929.

<sup>1</sup> Clarke, F. W., The data of geochemistry, 5th ed.: U.S. Geol. Survey Bull. 770, p. 476, 1924. Merrill, G. P., Rocks, rock weathering, and soils, New York, Macmillan Co., 1898.

factor. For this reason the role of hydrogen-ion concentrations in geochemistry is an important one.

Solutions cannot come immediately into equilibrium with the rocks through which they pass. As alkali is dissolved and removed, the action is retarded by a protective film of the colloidal complexes of silica and alumina formed at the same time. Only when the mineral is finely divided and presents a large surface can equilibrium be established. In view of the abundance of silicates, however, there seems little doubt that they affect greatly the pH of underground waters.

#### ACKNOWLEDGMENTS

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#### REVIEW OF THE LITERATURE

The decomposition of minerals by pure and carbonated water has long been known and studied. As early as 1848 W. B. and R. E. Rogers<sup>5</sup> tested many minerals and found them all at least slightly attacked. Daubr e<sup>6</sup> showed that orthoclase is attacked by water, and more actively when carbon dioxide is present. Kenngott<sup>7</sup> found that many silicates give alkaline reactions to moistened test paper. M ller<sup>8</sup> showed the effectiveness of carbonated waters in their attack on minerals and analyzed the dissolved material. His analyses show that the alkaline constituents are predominantly dissolved.

Hoffman<sup>9</sup> determined the relative solubility of silicates by their loss in weight, but the accuracy of this procedure is questionable. The works of Johnstone<sup>10</sup> and of D lter<sup>11</sup> show the action of carbonated water.

<sup>5</sup> Rogers, W. B. and R. E., On the decomposition and partial solution of minerals, rocks, etc., by pure water, and water charged with carbonic acid: *Am. Jour. Sci.*, 2d ser., vol. 5, p. 401, 1848.

<sup>6</sup> Daubr e, Auguste, * tudes synth tiques de g ologie exp rimentale*, pp. 271-275, Paris, Dunod, 1879.

<sup>7</sup> Kenngott, A., * ber einige Erscheinungen beobachtet an Natrololith*: *Neues Jahrb.*, 1867, p. 77.

<sup>8</sup> M ller, Richard, *Untersuchungen  ber die Einwirkung des kohlenst urehaltigen Wassers auf einige Mineralien und Gesteine*: *K.-k. geol. Reichsanstalt, Jahrb.*, vol. 27, *Min. Mitt.*, p. 25, 1877.

<sup>9</sup> Hoffman, E. W., *Untersuchungen  ber den Einfluss von gew hnlichen Wasser auf silicate* [*inang. diss.*], Leipzig, 1882.

<sup>10</sup> Johnstone, Alexander, On the action of pure water and of water saturated with carbonic acid gas on the minerals of the mica family: *Geol. Soc. London Quart. Jour.*, vol. 45, p. 363, 1889.

<sup>11</sup> D lter, C., *Einige Versuche  ber die L slichkeit der Mineralien*: *Min. pet. Mitt.*, vol. 11, p. 319, 1890.

Clarke<sup>12</sup> treated a number of powdered silicate minerals with water containing phenolphthalein, noting the intensity of color produced, and thus determined roughly the extent to which they were attacked. Analyses by Steiger<sup>13</sup> show a discrepancy between the intensity of the color and the quantity of alkali found in solution by titration with methyl orange. No cause for this discrepancy is suggested.

Cushman<sup>14</sup> has investigated the mechanism of the decomposition. He has shown that the alkalies dissolve, liberating colloids of silica and alumina. These colloids retain a portion of the separated alkali but give it up to electrolytic solvents. Thus, when ammonium chloride was present, 10 to 20 times as much alkali was freed as when pure water was used alone. This might have been merely a case of base exchange. Similar results have been obtained by Andr e.<sup>15</sup>

Several papers confirm the investigations thus far mentioned.<sup>16</sup> Thugutt,<sup>17</sup> however, believed that orthoclase was attacked little if any by water.

Bouyoucos<sup>18</sup> determined the solubility of several minerals by the freezing-point method. He used four parts of finely ground mineral (100 mesh) to three parts of water, and the silicates tested were amphibole, apophyllite, chrysolite, epidote, kaolinite, oligoclase, orthoclase, prochlorite, pyroxene, quartz, serpentine, stilbite, talc, and zircon. Solution takes place almost immediately, and very little change shows after 80 days. Bouyoucos found that the extent of solution was somewhat dependent upon the ratio of mineral to water and that the solubility increased with increases in temperature or pressure, and also that leached minerals were less soluble than fresh ones. Similar conclusions have been drawn from tests on the durability of glass by the powder method.<sup>19</sup>

Smyth<sup>20</sup> calculated from the average composition of igneous and sedimentary rocks the relative quantities of the rock constituents carried away by water. He

<sup>12</sup> Clarke, F. W., The alkaline reaction of some natural silicates: *U.S. Geol. Survey Bull.* 167, pp. 156-158, 1900.

<sup>13</sup> Steiger, George, The solubility in water of certain natural silicates: *U.S. Geol. Survey Bull.* 167, pp. 159-160, 1900.

<sup>14</sup> Cushman, A. S., The effect of water on rock powders: *U.S. Dept. Agr. Bur. Chem. and Soils Bull.* 92, 1905.

<sup>15</sup> Andr e, G., Displacement of potassium of certain feldspars by substances used as fertilizers: *Compt. Rend.*, vol. 157, p. 856, 1913.

<sup>16</sup> Levison, W. G., On the origin and sequence of the minerals of the Newark (Triassic) igneous rocks of New Jersey: *New York Min. Club Bull.* 2, 1909. Dumont, J., On the chemical decomposition of rocks: *Compt. Rend.*, vol. 149, p. 1390, 1909. Henrich, F., The action of water bearing carbonic acid on rocks: *Zeitschr. prakt. Geologie*, vol. 18, p. 85, 1910. Sicha, F., *Untersuchungen  ber die Wirkungen des beim hohen Druche mit Kohlenst ure ges ttigten Wassers auf einige Mineralien* [*inang. diss.*], Leipzig, 1891.

<sup>17</sup> Thugutt, S. J., The solubility of certain silicates in water: *Soc. sci. Warsaw Compt. rend.*, vol. 6, p. 629, 1914.

<sup>18</sup> Bouyoucos, G. J., Rate and extent of solubility of minerals and rocks under different treatments and conditions: *Michigan Agr. Exper. Sta. Tech. Bull.* 50, 1921.

<sup>19</sup> Thomas, M., Determination of the durability of glass by the powder method: *Soc. Glass Tech. Jour.*, vol. 12, p. 87, 1929.

<sup>20</sup> Smyth, C. H., The relative solubilities of the chemical constituents of rocks: *Jour. Geology*, vol. 21, pp. 105-120, 1913.

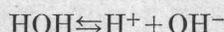
shows that alkalis are dissolved to the greatest extent—sodium and calcium the most completely and potassium the least.

But little work has been done on the hydrogen-ion concentrations of solutions from mineral silicates. The work of Clarke<sup>21</sup> was a rough measurement of their relative alkalinity. More recently Atkins<sup>22</sup> has discussed the application of pH measurements to geology and made several measurements on rocks and minerals. Britton<sup>23</sup> has determined the electrometric precipitation curves of silicic acid, using various alkalis, and gives certain points that are of interest and use in the present article.

#### CHEMICAL THEORY OF pH MEASUREMENTS

Because the discussion of hydrogen-ion concentrations involves principles not yet broadly applied to geology, it seems wise to explain briefly the fundamental ideas involved.

Water ionizes to a moderate extent, yielding hydrogen and hydroxyl ions, thus:



The extent to which this reaction occurs is slight but definite, and in pure water the number of hydrogen ions would be the same as the number of hydroxyl ions. When other substances are present in the water, however, these two numbers are not, in general, equal. Under such circumstances use is made of the fact, based on the law of mass action, that the product of the concentration of  $\text{H}^+$  and  $\text{OH}^-$  is a constant,  $K_w$ . That is,  $K_w = [\text{H}^+][\text{OH}^-]$  where the bracketed quantities represent concentrations or activities. By adding alkali to the water the concentration of  $\text{OH}^-$  is increased. In order to maintain the constancy of  $K_w$  a corresponding quantity of  $\text{H}^+$  must disappear from solution, recombining to form un-ionized water. In a similar manner acid increases the  $\text{H}^+$  concentration and removes  $\text{OH}^-$  from solution.

The value of  $K_w$  has been determined by numerous investigators. At 25° C. it is approximately  $1 \times 10^{-14}$  when concentrations are in gram ion per liter. In pure water or a neutral solution each ion ( $\text{H}^+$  and  $\text{OH}^-$ ) is present in a concentration of  $1 \times 10^{-7}$  gram ion per liter. As these two concentrations are so simply related it is sufficient for most purposes to consider the hydrogen-ion concentration alone. Such concentrations will be expressed as a negative power of 10. The figure following the negative sign is characteristic for each concentration and has been called for short the pH number—for example, 7 is the

pH number for pure water or a neutral solution, as noted above. Expressed mathematically,

$$\log_{10} 10^{-7} = -7 \text{ or } 7 = -\log_{10} 10^{-7} \text{ or } 7 = \log \frac{1}{10^{-7}}$$

and, in general,

$$\text{pH} = \log \frac{1}{[\text{H}^+]}$$

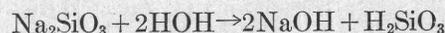
In the same way

$$\text{pOH} = \log \frac{1}{[\text{OH}^-]}$$

At neutrality pH and pOH are both 7. A hydrogen-ion concentration of  $10^{-5}$  is equivalent to pH=5 and to pOH=9;  $[\text{H}^+] = 10^{-11}$  is the same as pH=11 and pOH=3, etc., in each case the sum of pH and pOH being 14. Thus the concentration of either ion in solution is given simply by pH, it being understood that pH=7 signifies neutrality, that alkaline solutions are at pH greater than 7 and acid solutions less than 7, and that an increase in pH signifies a decrease in hydrogen-ion concentration or, in general, in acidity.

It becomes obvious, from what has been said of the ionization of water, that the strength of an acid or a base is dependent on the extent to which it ionizes into H or OH ions in solution. Thus hydrochloric acid, nitric acid, and sulphuric acid ionize readily and are strong acids, whereas acetic acid, silicic acid, and others that ionize feebly are classed among the weak acids. Alkali and alkaline earth hydroxides ionize readily, giving OH ions, whereas ammonium hydroxide is more weakly ionized.

A salt, on hydrolysis, reacts with the ions of water to form an acid and a base. A good example is the hydrolysis of an alkali silicate, thus:



The products are a strongly ionized base, sodium hydroxide (NaOH), and the weak metasilicic acid ( $\text{H}_2\text{SiO}_3$ ). For this reason solutions of sodium silicate are strongly alkaline. Silicate minerals hydrolyze in the same way and give alkaline solutions.

Two methods of measuring hydrogen-ion concentrations are in common use. The direct measurement is with the hydrogen electrode. An electrode of platinum, covered with platinum black, dissolves a small quantity of hydrogen which is capable of ionizing reversibly when an electric current is passed. The potential of the electrode depends on the concentration of hydrogen ions in the solution being measured. This resulting potential is determined against that of a standard calomel half cell. The pH of the solution is then given by the equation

$$\text{pH} = \frac{\text{e.m.f.} + E_{\text{par}} - E_{\text{cal}}}{kT}$$

<sup>21</sup> Clarke, F. W., *op. cit.* (Bull. 167), pp. 156-158.

<sup>22</sup> Atkins, W. R. G., Some geochemical applications of measurements of hydrogen-ion concentration: Roy. Dublin Soc. Sci. Proc., vol. 19, pp. 455-460, 1930.

<sup>23</sup> Britton, H. T. S., Electrometric study of the precipitation of silicates: London Chem. Soc. Jour., 1927, p. 425.

in which e.m.f. is the electromotive force of the cell as measured,  $E_{\text{bar}}$  is a small correction for the vapor pressure of water,  $E_{\text{cal}}$  is the potential of the standard half cell,  $k$  is a constant, and  $T$  the absolute temperature.

The colorimetric method of measuring pH is an indirect method used where the demands of accuracy are not great and as a check upon the hydrogen-electrode measurement. Organic dyestuffs are used as indicators, their color depending upon the pH of the solution. Phenolphthalein, for example, is colorless below pH=8.3, shows increasing depths of red from pH=8.3 to pH=10.0, and develops the full red color above pH=10.0. The determination is made by matching the color of the solution being examined with that of one of a set of standard buffer solutions<sup>24</sup> of known pH containing an equal quantity of indicator. (See also pp. 5, 10, and 11.)

#### COLORIMETRIC DETERMINATION OF pH

##### METHOD OF PREPARING THE MINERAL SOLUTION

In order to obtain results that would be comparable for different minerals it was necessary to get the solution as near equilibrium with the mineral as possible before making measurements. The solution of silicates depends upon the surface exposed. This is probably the result of the protective action of colloids of silica and alumina. The use of high temperature and pressure is to be avoided because alkali liberated under such conditions recombines but slowly on cooling with the colloidal silica and alumina set free at the higher temperature and pressure. Continued churning of the powdered mineral for 15 minutes to 2 hours in a Clark hydrogen-electrode vessel with water, followed by electrometric pH measurements, gave results that were obviously low and that could not be duplicated in successive measurements. Repeated exposure of fresh surfaces to the action of water and the removal of protective films of silica and alumina was necessary.

By grinding continuously in an agate mortar with one drop of water and one of indicator solution many of the minerals caused phenolphthalein to turn full red (at least pH=10.0). With orthoclase the depth of red reached a maximum after about 1½ minutes of grinding. Other minerals incapable of changing phenolphthalein to full red were found to cause a maximum of change in the same period of time. The effect of the agate mortar and pestle on the accuracy of the pH determination was thought negligible, owing to their extreme hardness and the relatively small surface exposed in comparison to that of the mineral. (See also p. 8.)

<sup>24</sup> Buffer solutions "have the ability to resist changes in pH through the addition or loss of acid or alkali." For a more comprehensive treatment see Clark, W. M., *The determination of hydrogen ions*, Williams & Wilkins 1928.

#### NEUTRALIZING ACTION OF MINERAL

Most silicate minerals have a strong neutralizing capacity toward acid solution when there is sufficient surface exposed to solution. Powdered orthoclase was ground in the agate mortar with one drop of phthalate buffer at pH=5.0 and one drop of cresol-red indicator, which is yellow below pH=7.2 and red above, with its full red color at pH=8.8. After 3 minutes of grinding the solution was bright red, showing that the acidity of the buffer had been neutralized by alkali from the mineral. However, when orthoclase was ground with an alkaline buffer solution at pH=10 no change in pH was noted.

#### DETAILS OF COLORIMETRIC METHOD

The colorimetric determinations in table 2 were made by grinding the mineral with the appropriate indicator and matching the color with that of a standard buffer solution of known pH containing an equal quantity of the indicator. The quantity of mineral used had no measurable effect on the results, provided there was sufficient to give a heavy suspension. To the mineral was added one drop of carbon-dioxide-free distilled water and one drop of indicator solution, and grinding was continued for 2 minutes. One drop of indicator was then added to one drop of a standard buffer and the color comparison made.

#### METHOD OF COLOR COMPARISON

The turbidity of the mineral solutions made comparison with the clear buffer solutions difficult. The spot-plate method did not seem to give good results. Comparison in capillary Pyrex tubes, of about 1 millimeter bore, was more satisfactory.

A column of the solution was made to rise in the tube by capillarity, and the tube was held upright for about a minute to allow mineral particles to settle as much as possible. Occasionally nearly clear solutions were obtained thus, but in most tests the solutions remained turbid. Any error due to absorption of dye by the mineral could be noted at the bottom of the tube, but none of the minerals tested seemed to cause such an effect.

The tubes were laid on the edge of a table with tubes of standard buffers, a white background was placed about an inch below the tubes, and the comparison was then made in indirect sunlight. The buffers differed by 0.4 pH in the series, but in all cases interpolation to 0.1 pH was attempted. For certainty, colors were duplicated several times, and whenever possible checks were run with different indicators.

#### SELECTION OF INDICATORS

The indicators used were selected from those described by Clark.<sup>25</sup>

<sup>25</sup> Clark, W. M., *op. cit.*, pp. 92-94.

TABLE 1.—Indicators used in colorimetric determinations of pH

Clark and Lubs				
Indicator	Concentration (per cent)	Range of pH	Color change	
			Acid	Alkaline
Bromphenol-blue	0.02	3.0-4.6	Yellow	Blue.
Bromcresol-purple	.01	5.2-6.8	do	Purple.
Bromthymol-blue	.01	6.0-7.6	do	Blue.
Phenol-red	.01	6.8-8.4	do	Red.
Cresol-red	.01	7.2-8.8	do	Do.
Thymol-blue	.01	{ 1.2-2.8 8.0-9.6	Red Yellow	Yellow. Blue.

Sørensen				
Indicator	Concentration (per cent)	Range of pH	Color change	
			Acid	Alkaline
Methyl-orange	0.01	3.1-4.4	Red	Yellow.
Methyl-red	a. 02	4.2-6.3	do	Do.
Phenolphthalein	b. 05	8.3-10.0	Colorless	Red.
Thymolphthalein	b. 04	9.3-10.5	do	Blue.
Alizarin-yellow R	.01	10.1-12.1	Light yellow.	Deep yellow.
Tropaeolin O	.01	11.1-12.7	Yellow	Orange.

a In 60 percent alcohol.  
b In 50 percent alcohol.  
c Faded quickly; found of little use.

SELECTION OF BUFFERS

Buffer solutions were prepared differing by 0.4 pH unit and ranging from pH=4.2 to pH=12.0, as listed below.<sup>26</sup> Their pH was checked at intervals by means of the Clark hydrogen-electrode vessel.

	Range of pH
Phthalate-NaOH	4.2-5.8
KH <sub>2</sub> PO <sub>4</sub> -NaOH	5.8-7.8
Boric acid, KCl-NaOH	7.8-10.0
Soda-borax	9.4-11.0
Na <sub>2</sub> HPO <sub>4</sub> -NaOH	11.0-12.0

RESULTS OF COLORIMETRIC DETERMINATIONS

The results of these colorimetric measurements are listed in table 2, approximately in order of increasing pH. This grouping of the minerals is in fair agreement with field observations of their stability to water, and a relation can be observed between the alkali content and the pH obtained. This table is discussed more fully on page 9.

TABLE 2.—Results of colorimetric tests

Index no.	Mineral	Source	Composition	pH
1	Beryl	Connecticut	Be <sub>3</sub> Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub>	7.2
2	Genthite		Ni <sub>2</sub> Mg <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> .6H <sub>2</sub> O	7.8
3	Lepidolite		KLi[Al <sub>2</sub> (OH.F)]Al(SiO <sub>3</sub> ) <sub>3</sub>	8.4
4	Phillipsite		(K <sub>2</sub> , Ca)Al <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> .4½H <sub>2</sub> O	8.4
5	Stilbite	Mexico	(Na <sub>2</sub> , Ca)Al <sub>2</sub> Si <sub>6</sub> O <sub>18</sub> .6H <sub>2</sub> O	8.6
6	Muscovite no. 1	Utah	H <sub>2</sub> KAl <sub>3</sub> (SiO <sub>3</sub> ) <sub>3</sub>	8.8
7	Muscovite no. 3		do	8.4
8	Muscovite no. 6		do	8.5
9	Muscovite no. 2		do	8.6
10	Muscovite no. 5		do	8.7
11	Muscovite no. 4		do	9.0
12	Calamine		H <sub>2</sub> (Zn <sub>2</sub> O)SiO <sub>4</sub>	8.8
13	Biotite	Philadelphia	(H,K) <sub>2</sub> (Mg, Fe) <sub>2</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	9.0

a Sericite, fine powdery variety.

<sup>26</sup> See also Clark, W. M., op. cit., pp. 192-220.

TABLE 2.—Results of colorimetric tests—Continued

Index no.	Mineral	Source	Composition	pH
14	Pollucite	Buckfield, Maine	H <sub>2</sub> Cs <sub>2</sub> Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>5</sub>	9.0
15	Anthophyllite	Montana	(Mg, Fe)SiO <sub>3</sub>	9.0
16	Laumontite	Mordon, Nova Scotia	H <sub>4</sub> CaAl <sub>2</sub> Si <sub>4</sub> O <sub>14</sub> .2H <sub>2</sub> O	9.0
17	Orthoclase no. 2	Maine	KAlSi <sub>3</sub> O <sub>8</sub>	8.8
18	Orthoclase no. 1	Deadwood, S.Dak.	do	9.2
19	Spodumene	Maine	LiAl(SiO <sub>3</sub> ) <sub>2</sub>	9.2
20	Clinochlore	Chester County, Pa.	H <sub>3</sub> Mg <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>18</sub>	9.2
21	Albite no. 1		NaAlSi <sub>3</sub> O <sub>8</sub>	9.4
22	Albite no. 2		do	9.8
23	Wyomingite (leucite)	Montana	KAlSi <sub>2</sub> O <sub>6</sub> (?)	9.4
24	Labradorite no. 2		NaAlSi <sub>3</sub> O <sub>8</sub> .3CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub> (?)	9.4
25	Labradorite no. 1		do	9.8
26	Margarite	Chester, Mass.	H <sub>2</sub> CaAl <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	9.8
27	Natrolite		Na <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>16</sub> .2H <sub>2</sub> O	10.0
28	Epidote		Ca <sub>2</sub> (Al.OH)(Al,Fe) <sub>2</sub> (SiO <sub>3</sub> ) <sub>3</sub> Varies.	10.0
29	Actinolite	Roan Mountain, Tenn.	Ca(Mg, Fe) <sub>2</sub> (SiO <sub>3</sub> ) <sub>4</sub>	10.0
30	Phlogopite		H <sub>2</sub> KMg <sub>3</sub> Al(SiO <sub>4</sub> ) <sub>3</sub> (?)	10.1
31	Diopside		CaMg(SiO <sub>3</sub> ) <sub>2</sub>	10.1
32	Hornblende		CaMg <sub>3</sub> (SiO <sub>3</sub> ) <sub>4</sub> with Na <sub>2</sub> Al <sub>2</sub> (SiO <sub>3</sub> ) <sub>4</sub> +Mg <sub>2</sub> Al <sub>4</sub> (SiO <sub>6</sub> ) <sub>2</sub>	10.2
33	Olivine	Willits, N.C.	(Mg, Fe) <sub>2</sub> SiO <sub>4</sub>	10.2
34	Thulite		HCa <sub>2</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>12</sub>	10.2
35	Talc	Edwards, N.Y.	H <sub>2</sub> Mg <sub>3</sub> (SiO <sub>3</sub> ) <sub>4</sub>	10.2
36	Pyroxene		Ca(Mg, Fe)(SiO <sub>3</sub> ) <sub>2</sub>	10.2
37	Tremolite no. 1		H <sub>2</sub> Ca <sub>2</sub> Mg <sub>5</sub> (SiO <sub>3</sub> ) <sub>8</sub>	10.2
38	Tremolite no. 2		do	10.2
39	Pectolite		HNaCa <sub>2</sub> (SiO <sub>2</sub> ) <sub>3</sub>	10.4
40	Prehnite no. 3		H <sub>2</sub> Ca <sub>2</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	10.2
41	Prehnite no. 2	Michigan	do	10.4
42	Prehnite no. 1		do	10.5
43	Apophyllite no. 1		H <sub>7</sub> KCa <sub>4</sub> (SiO <sub>2</sub> ) <sub>8</sub> .4½H <sub>2</sub> O	10.4
44	Apophyllite no. 2		do	10.4
45	Wollastonite		CaSiO <sub>3</sub>	10.8
46	Glass no. 106 <sup>b</sup>		SiO <sub>2</sub> 75.48; Na <sub>2</sub> O 15.26; CaO 9.26.	11.2
47	Glass no. 135 <sup>b</sup>		SiO <sub>2</sub> 78.40; Na <sub>2</sub> O 16.17; CaO 0.21.	11.4

<sup>b</sup> Analyses by F. W. Glaze, Bureau of Standards.

ELECTROMETRIC DETERMINATION OF pH

KIND OF ELECTRODE USED

By means of hydrogen-electrode measurements it was possible to study more quantitatively the pH of many mineral solutions. Solution of the mineral was brought about by grinding in an agate mortar, as in the colorimetric test, with two drops of carbon-dioxide-free distilled water. Increasing the quantity of water and mineral indiscriminately was considered unwise, and with so small a volume of solution the use of some form of microelectrode was necessary.

The electrode described by Bodine and Fink<sup>27</sup> was simplified and found to give good results. Pyrex glass tubing of about 3 millimeters inside diameter was drawn to a 1-millimeter capillary below an opening in the tube for inserting the electrode. The electrode of platinum wire, B. & S. no. 25, sufficiently long to reach well into the capillary, was sealed into a Pyrex glass tube to be filled with mercury for making electrical

<sup>27</sup> Bodine, J. H., and Fink, D. E., A simple microvessel with electrodes for determining the hydrogen-ion concentration of small amounts of fluid: Jour. Gen. Physiology, vol. 7, p. 735, 1925.

contact. It was flattened out at the point to increase the surface and thinly platinized by electrolysis in platinic-chloride solution. The capillary was then filled with water to keep the electrode moist, and the electrode was inserted and sealed in with Kotinsky cement. The seal was then coated with collodion to insure its being airtight. This electrode is shown in figure 1, A.

#### SOURCE AND PURIFICATION OF THE HYDROGEN

Traces of impurities in the hydrogen, especially oxygen, cause gross errors in potentiometric pH determinations of alkaline solutions. For this reason the hydrogen was generated electrolytically in caustic

type K potentiometer, in conjunction with a Weston standard cell (unsaturated), two 2-volt storage batteries in parallel, and a needle-type galvanometer. In the preliminary work a normal calomel electrode was used with a saturated potassium-chloride bridge, but it was later replaced by the tenth normal electrode recommended by Clark.

At the beginning of a series of measurements the apparatus was first thoroughly swept out with a stream of hydrogen from the generator *a* (fig. 1, B), the capillary point of the electrode being kept beneath the surface in a beaker of distilled water. The electrode was then removed from the water and placed in the solution under measurement, and the flow of

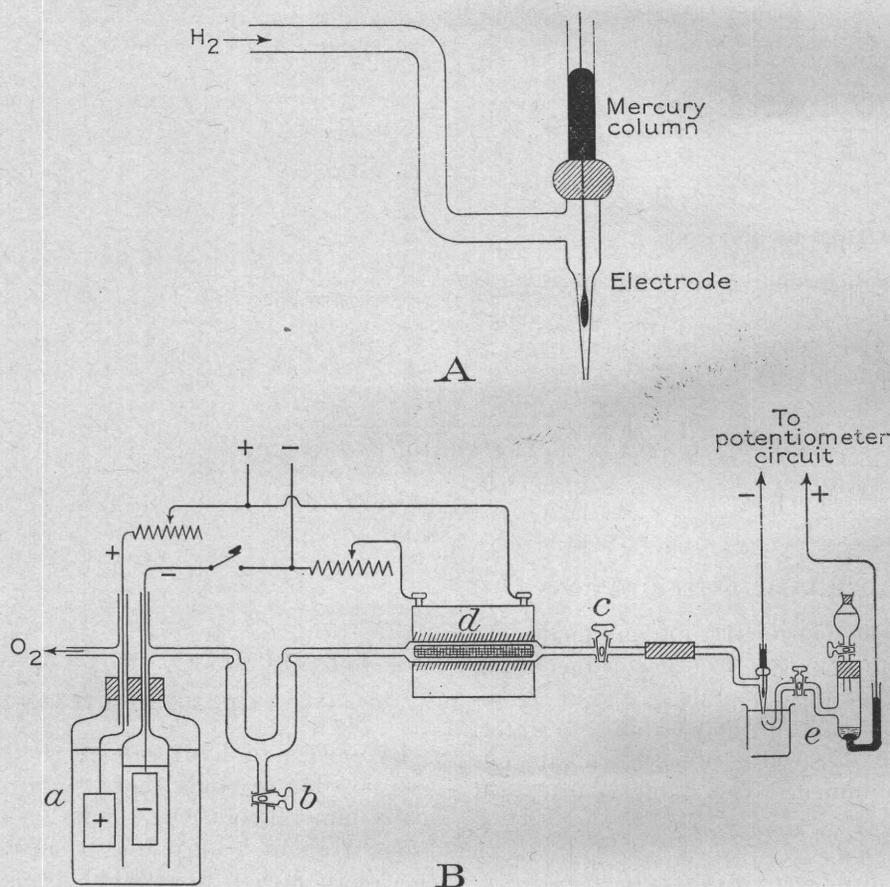


FIGURE 1.—A, Microvessel and electrode. B, Assembly of apparatus for pH determination: *a*, Hydrogen generator; *b*, *c*, stopcocks; *d*, electric furnace at 500° C. with copper gauze; *e*, hydrogen electrode, calomel half cell, and saturated KCl bridge.

soda solution with 110-volt direct current and passed over copper gauze held at 500° C. to remove traces of oxygen. The flow of hydrogen was controlled with a 24.5-ohm rheostat. Between measurements the capillary point was kept below the surface of some distilled water, thus allowing a steady stream of hydrogen to bubble through under a slight pressure.

#### ASSEMBLY AND MANIPULATION OF APPARATUS

In figure 1, B, is shown diagrammatically the assembly of apparatus. The measurements of electromotive force were made with a Leeds & Northrup

hydrogen was continued for a few seconds. By switching off the hydrogen generator and opening stopcock *b* for a second, the hydrogen was reduced to atmospheric pressure, and the solution was drawn into the electrode vessel by capillarity. The capillary point was then placed just below the surface in the saturated potassium-chloride bridge, and readings were begun.

The apparatus was frequently checked with an alkaline buffer solution  $\frac{M}{20}$  borax, described by Kolt-

hoff.<sup>28</sup> These check readings on buffer solutions were consistently a trifle low by 0.02 to 0.05 of a pH number, and rarely, as in the case of a poorly activated electrode, they were low by as much as 0.10 of a pH number. Checks upon an acid buffer (phosphate, pH=6.81) gave results equally low, and the presence of oxygen as an impurity in the hydrogen did not appear to be the source of this small error. In most of the determinations as many checks on  $\frac{M}{20}$  borax

were made as measurements on the mineral solutions, with a view to adding a small correction factor to the results. Further study, however, showed that the mineral solutions came into equilibrium with the electrode much more quickly than the buffer solution, and slightly low buffer readings were attributed to the slowness of the electrode in reaching equilibrium.

In the measuring of all solutions readings were taken at intervals of 1 minute until four check readings were obtained. Initial readings were consistently low, then showed an upward creep in electromotive force until a constant value was obtained. Owing to the low conductivity of the mineral solutions no attempt was made to make readings closer than 0.5 millivolt or in some readings 1 millivolt.

EFFECT OF CARBON DIOXIDE

That atmospheric carbon dioxide affected to some extent, though perhaps slightly, the pH of the mineral solutions prepared for the colorimetric determinations was obvious, and elimination of carbon dioxide was attempted by preparing the mineral solutions in carbon-dioxide-free nitrogen. For this purpose a thin rubber membrane was fitted tightly over the top of the mortar by means of passepartout, with small openings for inserting the pestle and the nitrogen inlet.

The mineral particles were placed in the mortar, after which nitrogen was allowed to flow slowly through, sweeping out all air. Three drops of carbon-dioxide-free distilled water was then added, followed by insertion of the pestle in the opening. The rubber membrane became inflated by the nitrogen, the overflow leaking out around the sides. The flow of nitrogen was continued during the grinding and solution of the mineral and until the solution was drawn into the electrode vessel.

To be sure of the absence of carbon dioxide the nitrogen was tested by bubbling it through baryta solution. After 5 minutes no precipitation was noticed.

To show the effect of carbon dioxide if no special precautions are taken to exclude it, one of the more alkaline materials, glass no. 135, was tested in air and in nitrogen, with the results given in table 3.

TABLE 3.—Effect of carbon dioxide on pH

[Material, glass no. 135, ground 2 minutes; normal calomel electrode used]

Ground in air			Ground in carbon-dioxide-free nitrogen		
Temperature (°C.)	E.m.f.	pH	Temperature (°C.)	E.m.f.	pH
25-----	0.9468	11.21	27-----	0.9660	11.47
25-----	.9555	11.36	27-----	.9675	11.49
26-----	.9491	11.21	27-----	.9650	11.46
28-----	.9340	10.90	28-----	.9680	11.47
28-----	.9490	11.15	28-----	.9710	11.51
Average-----		11.17	Average-----		11.48
Maximum deviation--		.27	Maximum deviation--		.03

The results in the presence of atmospheric carbon dioxide were evidently low by 0.31 pH unit and showed poor agreement. When the effect of carbon dioxide was eliminated, however, the results showed remarkable precision. In all subsequent determinations, therefore, the action of carbon dioxide was eliminated. Its effect is discussed in the comparison of electro-metric with colorimetric determinations (p. 9).

TIME OF GRINDING

In preparing solutions the time of grinding was, of course, limited by evaporation of water in the carbon-dioxide-free nitrogen, but the period could be extended to 3 minutes without the suspension becoming so thick as to make measurements impossible. The comparison of results obtained by grinding for 1, 2, and 3 minutes with glass no. 135 and with spodumene is given in table 4.

TABLE 4.—Time of grinding needed to reach equilibrium

[Normal calomel electrode used]

Glass No. 135

1 minute			2 minutes			3 minutes		
Temperature (°C.)	E.m.f.	pH	Temperature (°C.)	E.m.f.	pH	Temperature (°C.)	E.m.f.	pH
30-----	0.9680	11.40	27-----	0.9660	11.47	30-----	0.9745	11.50
30-----	.9685	11.40	27-----	.9675	11.49	30-----	.9760	11.53
Average-----		11.40	Average-----		11.48	Average-----		11.51

Spodumene

30-----	0.8280	9.08	30-----	0.8410	9.28	31-----	0.8470	9.36
30-----	.8330	9.15	30-----	.8450	9.35	31-----	.8420	9.27
			30-----	.8430	9.32	31-----	.8430	9.29
Average-----		9.11	Average-----		9.32	Average-----		9.31

It appears from these results that equilibrium is almost established by grinding for 1 minute, the results being only 0.08 to 0.20 of a pH unit lower than after

<sup>28</sup> Kolthoff, I. M., pH and electro-titrations, p. 100, New York, John Wiley & Sons, 1931. For temperature corrections see p. 40.

grinding for 2 or 3 minutes. In view of the results of grinding for 2 or 3 minutes, the establishment of equilibrium in 2 minutes seems a logical conclusion, the agreement being remarkably good. With glass no. 135 a small difference, 0.03 of a pH number, was found between the results of grinding for 2 minutes and 3 minutes. It must be remembered, however, that this difference is well within the limits of accuracy of the method and that it may have been caused by the shift of temperature from 27° to 30° C. The test for spodumene, a material less easily attacked by water, was made at nearly constant temperature and showed a better agreement between the results for 2 minutes and for 3 minutes.

#### EFFECT OF AGATE MORTAR

The action of the silica of the agate mortar in neutralizing the alkalinity of the mineral solutions remained a matter of doubt. There are several reasons for thinking that any such action would be slight. Presumably the silica would first have to become hydrated to silicic acid before its acid properties could become manifest, and this reaction occurs but slowly at ordinary temperatures. Moreover, the silication of an alkali reduces the pH number only slightly. The hardness of the agate and the small surface exposed to water in comparison to that of the mineral were other reasons for thinking the action negligible. Under the conditions of experimentation the strong neutralizing action of the minerals was found to develop quickly, as noted for orthoclase in the colorimetric work. (See p. 4.)

The silica of the agate mortar, if effective in neutralizing mineral alkalinity, should have an action on a buffered solution, neutralizing alkali and reducing the pH. The use of an unbuffered alkaline solution in this test was thought undesirable because of possible changes in concentration due to evaporation. A buffer solution was accordingly used, as such solutions are but little affected by dilution.

Measurements of  $\frac{M}{20}$  borax ground in an agate mortar for 2 minutes in carbon-dioxide-free nitrogen gave a reading within 0.02 of a pH number of the correct value, while the untreated buffer gave a reading within 0.03. Later, the effect of grinding the buffer with powdered quartz was determined. The electrode in this test was a little less active. The untreated buffer gave results 0.05 of a pH number lower than the correct value; the buffer ground for 2 minutes with quartz powder gave results 0.07 of a pH number lower than the correct value.

Indicator solutions ground alone in the agate mortar showed no change of color.

These results, although not conclusive enough to show that the agate is completely ineffective, indicate that the resulting error, if present, is very small.

#### EFFECT OF IRON IN MINERAL

Two factors limited the number of minerals that could be used for electrometric pH measurements. Minerals of low alkalinity gave solutions so low in conductivity that measurements of electromotive force could not be made with any certainty; therefore, for the most part, only the more alkaline minerals were tested. The presence of oxidizable materials—chromium, manganese, and most particularly iron—causes gross errors. Minerals containing more than a trace of iron were found unsuitable for test by this method. Substances present in an oxidized condition not only give an oxidation-reduction potential but reduce the pressure of hydrogen at the electrode surface and thus decrease the hydrogen-electrode potential.<sup>29</sup> This effect seems particularly pronounced in the use of the microelectrode.

The action of iron as an impurity upon the measurements on prehnite is shown in table 5. For prehnite no. 1 and no. 2, the results are an average of three tests; for prehnite no. 3, an average of two tests.

TABLE 5.—Effect of iron on electrometric measurements of pH

Mineral	Colorimetric determination of pH	Percent of Fe	Electrometric determination		
			Temperature (°C.)	pH	Maximum deviation from average
Prehnite no. 3	10.5	0.37	28	10.38	0.04
Prehnite no. 2	10.4	3.66	27	10.06	.01
Prehnite no. 1	10.2	5.7	26	8.5	.8

#### EFFECT OF TEMPERATURE

No attempt was made to study the effect of temperature, but in each test the temperature of the electrode was measured with a thermometer dipping beneath the surface of the potassium-chloride bridge. The ionization of water increases rapidly with increase in temperature, and that would have an effect on the hydrolysis of the mineral and the resulting pH. However, there seems no simple method of controlling the temperature in the rather complex operations of grinding and of transferring the solution to the electrode. In many of the determinations it was noted that small fluctuations in the temperature affected the pH readings but little. This is especially apparent in the tests on glass no. 135. During the seven determinations the temperature ranged from 27° to 30° C., but the maximum deviation from the average was only 0.05 of a pH unit.

#### RESULTS OF ELECTROMETRIC DETERMINATIONS

The results of electrometric measurements on a number of minerals are listed in table 6, with the colorimetric results from table 2 for comparison. For

<sup>29</sup> See Clark, W. M., op. cit. p. 371.

minerals giving solutions with pH near 9.0, the two methods of determination gave results in close agreement. For the more alkaline minerals, especially those containing calcium and magnesium, the effect of atmospheric carbon dioxide in the colorimetric method becomes more apparent, and the results of the two methods differ by as much as 0.4 of a pH unit. Solutions of calcium carbonate were found to be especially sensitive to atmospheric carbon dioxide, and as the color of the indicator slowly faded, the colorimetric tests were unsatisfactory in consequence. Atkins<sup>30</sup> determined colorimetrically the pH of calcite solutions made by boiling and cooling to be a little above 9.0. This shows close agreements with the electrometric result listed in table 6, pH=9.03.

Especially worthy of note is the high pH value obtained for wollastonite (pH=11.17). This shows a good comparison to the electrometric titration curve of silicic acid with calcium hydroxide as determined by Britton.<sup>31</sup>

TABLE 6.—Results of electrometric tests

Index no.	Mineral	Colorimetric determination of pH	Electrometric determination			
			Temperature (° C.)	Number of determinations	pH	Maximum deviation from average
	Calcite-----	<sup>a</sup> 9.0	25	2	9.03	0.02
14	Pollucite-----	9.0	26	2	8.96	.02
17	Orthoclase no. 1--	9.2	28	3	9.18	.03
19	Spodumene-----	9.2	30-31	6	9.31	.05
22	Albite no. 2-----	9.8	28	2	9.84	.04
27	Natrolite-----	10.0	28	2	10.05	.03
37	Tremolite no. 1---	10.2	22	3	10.50	.02
38	Tremolite no. 2---	10.2	24	3 <sup>b</sup>	10.17	.06
44	Apophyllite no. 2--	10.4	26	3	10.79	.02
45	Wollastonite-----	10.8	24	3	11.17	.01
47	Glass no. 135-----	11.4	27-30	7	11.49	.05

<sup>a</sup> Determined by Atkins.

<sup>b</sup> Probably too low. Contained a trace of iron and 1.15 percent of manganese.

#### COMPARISON OF COLORIMETRIC AND ELECTROMETRIC METHODS AND FACTORS INVOLVED IN TESTING

In a general way the two methods of determining the hydrogen-ion concentration of mineral solutions described in the preceding pages yield similar results, but each method has certain limitations.

In the colorimetric test as actually used there are two sources of error—the effect of atmospheric carbon dioxide and the great turbidity of the solutions. However, as shown by comparison with electrometric results obtained in the absence of carbon dioxide, the error due to its presence is small where the pH of the solution is under 9.0, although it becomes larger with increasing alkalinity. This error would likewise not be the same for different minerals but

would be more pronounced with minerals containing calcium and magnesium because of the insolubility of the carbonates formed. Elimination of carbon dioxide and compensation for turbidity might yield results of greater precision, such as those determined electrometrically and given in table 6. However, the results obtained colorimetrically are roughly comparable when small differences in pH are not considered, and they are capable of yielding many useful generalizations.

It must be remembered that minerals are seldom pure, and in solutions of the less alkaline minerals the pH may be the result of alkaline impurities such as calcite. This is shown most clearly with calamine, the composition of which is given by the formula  $H_2(ZnO_2)SiO_4$ . Britton<sup>32</sup> has determined the pH precipitation curves of various metallic hydroxides. He found that the precipitation of zinc from zinc sulphate solution began at pH=5.2. Some uncertainty exists as to whether this precipitate was the hydroxide or a basic sulphate. Nevertheless, in view of these results, it does not seem possible to obtain a pH value as high as that observed for calamine, pH=8.8, without the presence of an alkaline impurity.

In the electrometric tests the chief source of difficulty has been the presence of iron and other oxidizable material in the minerals. Errors due to the presence of iron seem to be particularly pronounced with the microelectrode, some form of which was required for the tests. It is true that in numerous reports in the literature fairly accurate determinations of pH were obtained in the presence of ferric iron by use of the Hillebrand electrode or the Clark hydrogen-electrode vessel, but in both of these designs the hydrogen at the platinum electrode surface is constantly renewed. With the microelectrode no means is provided for keeping the hydrogen on the electrode surface at atmospheric pressure, and consequently good results could be obtained only when iron was absent, or nearly so.

There is need for an electrode that is not affected by oxidizable materials. Such an electrode is the glass electrode, described by MacInnes and Dole,<sup>33</sup> but its use in this study would be difficult, owing to the low conductivity of the mineral solutions. Furthermore, tests with the electrode for solutions with pH above 9.0 show a large error, which varies in the presence of different alkali and alkaline earth hydroxides, and, as previously shown, figures as high as pH=11.17 (wollastonite) are obtained for these mineral solutions. The limitations of the quinhydrone electrode and of the oxygen electrode in alkaline solutions are even greater than those of the hydrogen electrode.

<sup>30</sup> Atkins, W. R. G., Some geochemical applications of measurements of hydrogen-ion concentration: Roy. Dublin Soc. Sci. Proc., vol. 19, pp. 455-460, 1930.

<sup>31</sup> Britton, H. T. S., Electrometric study of the precipitation of silicates: Chem. Soc. London Jour., 1927, p. 425.

<sup>32</sup> Britton, H. T. S., Electrometric studies of the precipitation of hydroxides, pt. 2: Chem. Soc. London Jour., vol. 127, pp. 2120-2141, 1925.

<sup>33</sup> MacInnes, D. A., and Dole, Malcolm, The behavior of glass electrodes of different compositions: Am. Chem. Soc. Jour., vol. 52, p. 29, 1930.

It is noteworthy that the results listed in table 6, determined with the hydrogen microelectrode, were obtained with an excellent degree of reproducibility, the maximum deviation from the average being 0.01 to 0.05 pH unit. Three determinations on wollastonite showed a maximum deviation of only 0.01 pH unit from the average. Six tests on spodumene yielded a maximum deviation of 0.05 pH unit from the average, and seven determinations on glass no. 135 showed a maximum deviation of 0.05 pH unit from the average. This reproducibility, together with the study of the grinding period needed to reach equilibrium (see table 4), shows that the true equilibrium is approached sufficiently close to give comparable results for the extent of decomposition possible with different mineral silicates.

The effectiveness of high temperature and pressure in increasing solubility of minerals has been noted by Bouyoucos,<sup>34</sup> and, presumably the resulting pH would thereby also be increased. The ionization of water increases with temperature, as does also the pH of many buffer solutions. No control of these factors has been attempted, but the conditions of the experiments were such as to give comparable results. For the electrometric measurements the approximate temperature of the electrode was noted.

#### GENERAL APPLICATIONS

It is well known that the measurement of hydrogen concentrations has found numerous applications in biology and industrial chemistry, but the subject does not seem to have received as much consideration in geochemical studies as it deserves. The present study has shown that many silicates give intensely alkaline solutions when the mineral is sufficiently exposed to the action of water. Solutions percolating through the earth's crust come into contact with immense quantities of these silicate materials, which may neutralize acidity and maintain a definite pH.

Numerous investigators have shown that the maintenance of a definite and limited range of pH is a condition necessary for certain chemical reactions and for the deposition of many minerals and ores. Wells<sup>35</sup> has noted such limitations in the precipitation of metallic copper by ferrous chloride. Furthermore, the deposition of sulphides and carbonates is affected to a great degree by changes in pH.<sup>36</sup> Many chemical reactions are catalytic in their nature; in such reactions the pH of the solution may determine the speed of the reaction, although it does not, in general, influence the final equilibrium. Related to catalysis are ad-

<sup>34</sup> Bouyoucos, G. J., Rate and extent of solubility of minerals and rocks under different treatments and conditions: Michigan Agr. Exper. Sta. Tech. Bull. 50, 1921.

<sup>35</sup> Wells, R. C., Chemistry of deposition of native copper from ascending solutions: U.S. Geol. Survey Bull. 778, p. 65, 1925.

<sup>36</sup> Stieglitz, Julius, The elements of qualitative chemical analysis, pt. 1, pp. 100-202, New York, Century Co., 1911.

sorption and the precipitation of colloids, phenomena conditioned by the pH of the solution. pH frequently determines the crystal form and the water of hydration of material separating from solution. A great multitude of studies deal with the influence of pH on inorganic equilibria. The many applications of pH are discussed by Clark.<sup>37</sup>

However, the neutralizing power of silicates is subject to certain limitations, which must be remembered in applying the results under geologic conditions. The writer has already mentioned the protective action of colloidal complexes of silica and alumina formed in the decomposition of silicates and the need of exposing a large surface in order to reach an equilibrium between the mineral and the solution. In any case, an equilibrium is established between the surface exposed and the solution, and if complexes containing a smaller amount of base are formed on the mineral surface the equilibrium will be between these complexes and the solution. Only by removal of this colloid or the exposure of fresh material can the true equilibrium of mineral to solution be established.

The principles of buffer action need also to be borne in mind, with the conception of pH as an intensity factor in acidity or alkalinity and not as a quantitative measure of the total acid or alkali in the solution. A brief discussion of buffer action may serve to emphasize the limited neutralizing action of silicate solutions from this viewpoint and to contrast the intensity factor pH with the quantitative relations involved in neutralization.

Buffer solutions are solutions of weak bases and their salts or weak acids and their salts—for example, a solution of acetic acid and sodium acetate. The addition of strong hydrochloric acid, HCl, to this solution would form sodium chloride and acetic acid. The acetic acid thus produced is weakly ionized, and for that reason the pH of the solution is altered but slightly by small additions of the strong acid. Similarly, the addition of small quantities of the strong base sodium hydroxide, NaOH, results in the destruction of acetic acid, which is so weakly ionized that by its removal from solution the pH is but slightly changed. In contrast to this, the titration of a strong alkali with a strong acid results in the destruction of the strong alkali, and the pH is shifted greatly by small additions of the acid.

The silicate minerals under consideration are salts of strong bases and an exceedingly weak acid, and if they were present in solutions in large quantities the solutions would have a strong buffer action. But the solubility of these minerals is very slight, their high alkalinity being the result of nearly complete hydrolysis into a strong base and a very weak acid (silicic acid). Because the quantity of mineral dissolved is so

<sup>37</sup> Clark, W. M., op. cit., p. 549.

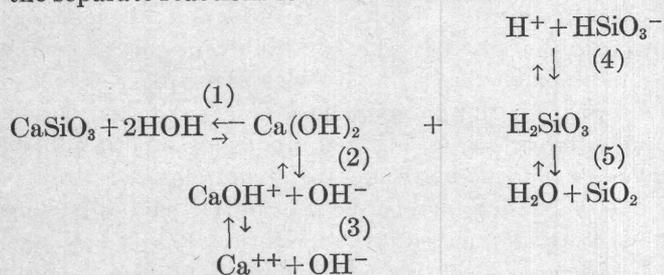
small the neutralizing power of the solution is limited, though this neutralizing power may be replenished by the exposure of fresh surfaces to the solution.

Neutralization with carbonates results only in the evolution of a gas, carbon dioxide, and in the formation of soluble salts, products which under the conditions existing at the surface of the earth are quickly removed and in no way retard the neutralizing action. In contrast to this, silicate decomposition forms colloidal films of silica and alumina and their complexes on the mineral surface, and this retards the neutralizing activity. Therefore it follows logically that under surface conditions the principal neutralizing agents for acid ground waters are the carbonate minerals.

But in deep-seated waters, which are under pressure, there is no means for the removal of the gaseous product, carbon dioxide, and the carbonates become less potent as sources of alkali. It would seem that the great mass of silicate minerals might then cause solutions previously neutralized by carbonates to become extremely alkaline.

The effect of neutral salts on the alkalinity of silicates is another factor that needs brief consideration. These salts are always present in underground waters, being dissolved in the downward flow or formed by the neutralization of ground-water acidity. The effect of salts on the pH of solutions and in increasing the solubility of other salts has been shown in many experiments; their influence on the pH of mineral solutions needs study.

Consider the hydrolysis of calcium metasilicate in its simplest form, the products being calcium hydroxide and silicic acid with the ions and decomposition products formed from them. This is expressed by the equation given below, in which the relative size of the arrows indicates the relative speed of the reaction in each direction and the numbers at the arrows designate the separate reactions for later reference.



According to the law of mass action the extent of reaction 1 is expressed by  $K_1$ :

$$K_1 = \frac{\text{products}}{\text{reactants}} = \frac{[\text{Ca(OH)}_2][\text{H}_2\text{SiO}_3]}{[\text{CaSiO}_3][\text{HOH}]_2}$$

This expression may be simplified, as the reactants are present in excess, so that their concentration in solution is constant. For the same reason the concentration of silicic acid may be neglected, the solution being saturated with it at all times owing to its removal as colloidal

silica according to reaction 5. The extent of reaction 1 is then given by the constant  $S_1 = [\text{Ca(OH)}_2]$ . Thus under conditions where an excess of  $\text{CaSiO}_3$  is present, no matter what the concentration or nature of the dissolved salts, the concentration of  $\text{Ca(OH)}_2$  in the solution is constant.

Reactions 2 and 3 are expressed by the constants  $K_2$  and  $K_3$ , respectively:

$$K_2 = \frac{[\text{CaOH}^+][\text{OH}^-]}{[\text{Ca(OH)}_2]}$$

$$K_3 = \frac{[\text{Ca}^{++}][\text{OH}^-]}{[\text{CaOH}^+]}$$

Reaction 4 may be neglected, as it occurs to so small an extent.

The addition of an acid to the solution results in the formation of water and of the calcium salt of the acid and in the temporary removal of OH ions. However, the removal of OH ions causes further reaction, and equilibrium is again established in accordance with  $S_1$ ,  $K_2$ , and  $K_3$ . Thus the OH-ion concentration would remain essentially constant after small additions of acid, when an excess of  $\text{CaSiO}_3$  is present. The addition of a salt with acid properties but containing no ion in common with  $\text{CaSiO}_3$  would have a like effect. But the presence of calcium salt in the solution, either formed by neutralization or present by direct addition to the solution, would result in a large concentration of the ion  $\text{Ca}^{++}$ , and reactions 2 and 3 might be thus repressed in accordance with the constancy of  $K_2$  and  $K_3$ . In this discussion calcium metasilicate has been used as an example, but the relations apply equally well to other silicates.

However, calculations show that a slight change in ionization of a strong base would affect the pH but slightly. For example, a solution of sodium hydroxide at pH = 10 would be at pOH = 4 and  $[\text{OH}^-]$  would be equal to 0.0001. If half of the hydroxyl ions were removed from solution by a mass-action effect,  $[\text{OH}^-]$  would be 0.00005. As  $\text{pOH} = \log \frac{1}{[\text{OH}^-]}$ , pOH would then be about 4.3 and pH about 9.7. Thus by removing half of the hydroxyl ions the pH of the solution is decreased by only 0.3 of a pH unit. It would seem, therefore, that the pH resulting from the hydrolysis of silicate minerals would be decreased but little by any salts that the solutions may contain.

As a general principle the presence of additional salts would tend to increase the solubility of the relatively insoluble minerals and might cause slight changes in the pH figure, the direction and extent of which would depend on the nature of the salts.

The neutralizing activity of silicates and the effect of salt solutions on their alkalinity were not studied further in the present investigation. Such a study would obviously be preceded by experiments on the

action of pure water, such as are described in this paper.

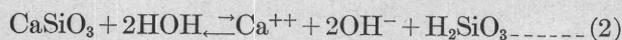
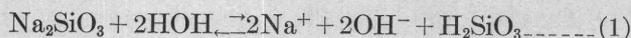
The results presented in table 2 show decided differences between minerals, but too much weight should not be given to small differences in pH, on account of the effect of possible impurities in some of the specimens, incipient alteration, possible varieties in the species, and similar variations inherent in natural products. Such variations with different samples of the same mineral were found for muscovite, orthoclase, albite, labradorite, tremolite, prehnite, and apophyllite.

As the basic constituents are progressively leached from these materials in weathering, their reaction to water would become less alkaline. In this connection several clays and decomposed rocks were tested colorimetrically and were found to give acid or nearly neutral reactions to indicators—for example, a decomposed granite collected near the surface in the District of Columbia gave approximately pH=3. It cannot be definitely stated whether this acidity is due to organic acids or to aluminosilicic acids formed by decomposition. Soil chemists are not in close agreement as to which of these materials causes the acidity of many soils.<sup>38</sup>

In any event, alteration seems a logical explanation for the small difference in pH found for different samples of the same mineral and suggests the need for further study of rocks and minerals regarding this point.

In a broad way, the order of the minerals in table 2 shows their potential alkalinity. A general increase in pH with increase in alkaline content may be observed, and this suggests a correlation between the pH values of silicates and their composition. The content of silica, alumina, and the different bases should have some definite effect on the resulting pH, and with improved methods of testing it might be useful as a rough check on analyses. However, the chemical structure is not known for all silicate minerals, and, as illustrated by organic compounds, properties may be determined more by chemical structure than by percentage composition. But the relation between composition and alkalinity is definitely indicated in table 1 and is evidence that in chemical structure the mineral silicates are relatively simple in contrast to the complexity of organic compounds.

A brief consideration of the measurements in connection with the law of mass action results in a further understanding of weathering. Consider the solution and hydrolysis of sodium silicate and of calcium silicate together in the same solution, thus:



For simplicity the sodium and calcium hydroxides formed are assumed to be completely ionized.

According to the law of mass action the extent to which these reactions may occur is determined by the relative concentrations of the products and reactants and is expressed by the equilibrium constant K. Thus in reaction 1

$$K_1 = \frac{\text{products}}{\text{reactants}} = \frac{[\text{Na}^+]^2 [\text{OH}^-]^2 [\text{H}_2\text{SiO}_3]}{[\text{Na}_2\text{SiO}_3] [\text{HOH}]}$$

and in reaction 2

$$K_2 = \frac{\text{products}}{\text{reactants}} = \frac{[\text{Ca}^{++}] [\text{OH}^-]^2 [\text{H}_2\text{SiO}_3]}{[\text{CaSiO}_3] [\text{HOH}]}$$

The concentrations of the reactants and of the silicic acid may be considered constant, as they are in excess, and the extent of the reaction is given more simply by the product S, where

$$S_1 = [\text{Na}^+]^2 [\text{OH}^-]^2$$

$$S_2 = [\text{Ca}^{++}] [\text{OH}^-]^2$$

On account of solubility and possibly for other reasons reaction 1 occurs to a greater extent than reaction 2, so that  $S_1$  is greater than  $S_2$ . When sodium silicate and calcium silicate are acted upon by water together the sodium silicate hydrolyzes to an extent expressed by  $S_1$ , giving a relatively large concentration of OH ions to the solution. The presence of a large concentration of OH ions obtained by reaction 1 retards reaction 2 to a degree commensurate with the figure for  $S_1$ . In this way the presence of sodium silicate tends to protect the calcium silicate from the action of water. Thus when water acts on mineral silicates together in a rock the alkaline constituents may serve as a protection to those that are less alkaline.

Measurements of the pH of mineral solutions indicate the quantity of alkali removed and thus serve as an index of the decomposition taking place. It also follows from the consequences of mass action shown above that the order of the minerals as listed in table 2 gives an approximate idea of their relative stability. Thus we find minerals such as beryl, lepidolite, and muscovite giving solutions with relatively low pH; it is generally considered that they are less readily attacked in weathering processes. Biotite, laumontite, orthoclase, and spodumene are slightly more attacked, and they are found to give higher pH. The plagioclase feldspars albite and labradorite are next in the list, along with such minerals as leucite, margarite, natrolite, and others. The alkalinity and ease of decomposition of the more basic rock constituents such as prehnite, pyroxene, tremolite, apophyllite, and especially wollastonite are shown by their high pH.

<sup>38</sup> On the pH of soils see Wherry, E. T., Soil acidity, its nature, measurement, and relation to plant distribution: Smithsonian Inst. Ann. Rept. for 1920, p. 247, 1922.

The results are in fair agreement with field observations on the decomposition of rocks and stability of minerals, and it is hoped that further field observations will serve to supplement the conclusions that have been tentatively drawn from the laboratory observations.

In addition to geochemical applications, it may be possible that the method of testing above described could be used practically in determining the weathering qualities of ceramic materials and glass. Tests of two glasses are shown in table 2, and the more accurate electrometric tests of glass no. 135 are given in table 6. Several glasses containing a larger percentage of alkali gave pH numbers above 12. The colorimetric test on some Pyrex glass was about pH=8. This Pyrex glass and the more alkaline glasses tested represent extremes of durability and show a good contrast by the method of test.

The effectiveness of silicate minerals as agents in determining the pH of aqueous solutions in geochemical processes seems to be clearly indicated by the experiments described in this paper, although it should be again pointed out that the abundance of carbonate rocks near the surface leads to their being the source of alkalinity in many natural waters. In deep-seated waters the silicates would have a major influence.

In brief, the results of these tests are a rough index of the weathering qualities of different silicate minerals and show how the silicates in nature may affect the pH of solutions with which they are in contact. The pH of the solutions thus produced by the hydrolysis of these minerals may, in turn, have an influence on the chemical reactions taking place and in determining the materials deposited from the solutions.

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