mately 160 mg. of copper as $Cu(OH)_2$ and that, therefore, a procedure employing less than this quantity of copper cannot afford quantitative indications for amounts up to 500 mg. of tartrate.

(4) A procedure capable of taking care of 500 mg. tartrate has been suggested and attention has been called to the difficulties which the use of this procedure entails.

(5) Based on the data obtained in this study, a purely qualitative procedure has been devised which is shown to be sensitive to 0.2 mg. tartrate. In consequence, however, of the amount of copper employed, this procedure is capable of supplying quantitative indications only within narrow limits.

(6) Numerous test analyses by this procedure showed that:

(*a*) Rather small amounts of ammonium, arsenite, borate, and phosphate give the test.

(*b*) The colors of chromates, ferrocyanides and ferricyanides mask the test color.

(*c*) Cyanides dissolve the copper hydroxide.

(*d*) One mg. of tartrate gives a negative test in the presence of 500 mg. of any of the following radicals: thiosulfate, arsenate, chromate, fluoride, thiocyanate, nitrite or acetate, or in the presence of 250 mg. of the following radicals: thiosulfate, oxalate, thiocyanate or nitrite.

(7) A great variety of organic substances give the same test.

NEW YORK CITY.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN.]

THE SOLUBILITY OF SILICA.

BY VICTOR LENHER AND HENRY BALDWIN MERRILL.

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While we commonly regard silica as one of our most insoluble substances, yet it has long been realized that silica, even in the form of quartz, is somewhat soluble in water and in dilute acids. The quantitative determination of silica has been known for a long time to be in error, due to the solvent action of dilute hydrochloric acid, and various procedures have been worked out to minimize these losses.[1]

Various workers have given data of widely different character on the solubility of silica. Fuchs[2] digested gelatinous silica with acid cold or hot, filtered the resulting solution through a double filter and determined the silica in 50 g. of the filtrate. He found water at the room temperature to dissolve 0.13 g. SiO_2 per liter, hydrochloric acid (sp. gr. 1.115) to dissolve 0.09 g. SiO_2 at room temperature, and 0.18 g. SiO_2 per liter at the

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[1] Bunsen, *Ann.*, **61**, 265; Ludwig, *Zeit. anal. Chem.*, **9**, 32; Meinike, *Repert. Anal. Chem.*, **7**, 215, 757; Cameron, *Chem. News*, **69**, 171; Hillebrand, THIS JOURNAL, **24**, 362; Lenher and Truog, *Ibid.*, **36**, 1050.

[2] Fuchs, *Ann.*, **82**, 119.

boiling temperature. Such important factors as time of digestion and form of apparatus are not specified. Duplicate determinations vary as much as twenty per cent.

Strückman,[1] working with gelatinous silica, obtained quite different results. He found 0.21 g. SiO_2 to dissolve in a liter of water at room temperature, 0.13 g. SiO_2 to dissolve in water containing dissolved CO_2 and hydrochloric acid (sp. gr. 1.088) to dissolve 1.72 g. SiO_2 in eleven days. Maschke[2] found 0.78 g. amorphous silica to dissolve in CO_2 containing water or about five times the solubility of Strückman. Graham[3] thought that the solubility depends on the hydration, but that the dehydrated gel is insoluble in water. Ludwig[4] found one part of silica to dissolve in twenty four to twenty-seven thousand parts of water. Wunder and Suleiman[5] digested gelatinous silica with various acids in platinum for two-hour periods, filtered the solution and determined the dissolved silica in aliquot portions of the filtrate. Their results are very low, the highest being only 0.14 g. per liter with 1 : 1 boiling hydrochloric acid, while with other strengths of hydrochloric acid and with other acids they reported the solubility very much less. Seeman[6] has also studied the solubility of silca in water and in carbon dioxide containing water as well as in ammonium carbonate and in sodium chloride solutions. Jordis believed that the solubility of silica in water is influenced by the presence of acid or alkali in the water.

On the mineralogical side, Delesse[7] showed qualitatively that quartz is slightly soluble in water at 100°. Calderon[8] states that pure water dissolves silica to the extent of one part in 10,000, and that its solubility is increased by the presence of oxygen, carbon dioxide, nitric acid, small amounts of sulfuric acid, and especially by humus acids. Pfaff[9] found finely powdered quartz at 18° to dissolve in 4700 parts of water, while Spezia[10] found at 25° under 1750–1850 atmospheres pressure no silica to dissolve after five months' contact, but at higher temperatures some silica dissolved. Leitmeier[11] found opal to dissolve in boiling water to a 0.22% solution and chalcedony and quartz to be more difficultly soluble. Leitmeier worked in glass, which may be the cause of the abnormally high

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[1] Strückman, *Ann.*, **94**, 337.

[2] Maschke, *Arch. Pharm.*, **140**, 37.

[3] Graham, *Compt. rend.*, **59**, 174.

[4] Ludwig, *Z. anal. Chem.*, **9**, 32.

[5] Wunder and Suleiman, *Ann. chim. Anal.*, **19**, 45.

[6] Seeman, *Z. anal. Chem.*, **44**, 343; *Z. anorg. allegem. Chem.*, **34**, 445, 45, 367.

[7] Delesse, *Bull. Soc. Geol.*, **1873**, 311.

[8] Calderon, *Assoc. Esp. p. e. Prog. d. l. Liencias*, **1908**.

[9] Pfaff, *Allgem. Geol.*, **1873**, 311.

[10] Spezia, *Atti. accad. Torino*, **31**, 7.

[11] Leitmeier, *Zentr. Min.*, **1908**, 632.

results. Schmidt[1] found quartz to be slightly soluble in sulfurous acid. Weisberg[2] stated that silica is somewhat soluble in sugar solutions, which was contradicted by Petzholdt.[3] Wackenroder[4] found traces of silica in strong brines and Skey[5] noted that silica hydrated in contact with water and passed into solution, but gave no data.

Further studies in one form or another on the solubility of silica in water have been made by Manzella,[6] Davy,[7] Persog,[8] Nicholson,[9] Beyer,[10] Bischoff,[11] Edwards,[12] Wittstein and Pribram,[13] and Souchay.[14]

This investigation of the solubility of silica was undertaken in order to obtain satisfactory observations both from the standpoint of its geological significance, and as well to determine, if possible, the inherent error in the analytical determination of silica.

Experimental.

Apparatus.—A large excess of silica was placed in a platinum bottle together with about 75 cc. of the solvent. This was done in all of our experiments. The bottle was fitted with a cork stopper which in the experiments at higher temperatures was protected from the action of the solvent by being tightly encased in platinum foil. In the experiments conducted at low temperatures it was sufficient to coat the stopper with melted paraffin. The stopper was perforated to allow a fused quartz reflux condenser to pass through. This condenser tube was waterjacketed in order to condense escaping vapors. The platinum flasks were immersed in thermostats which were electrically heated, regulated and stirred. Most of the experiments were carried out at 90°, a few at 25°. The contents of the flasks were continuously churned by means of a platinum ring stirrer, which worked up and down by means of a platinum wire through the quartz condenser and which was driven by an electric eccentric.

Manipulation of Solutions.—After the silica had been in contact with the solvent long enough for equilibrium to be established, the flasks were removed from the thermostats and the contents filtered hot through a No. 589 Schleicher and Schüll filter paper. When working with strong

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[1] Schmidt, *Tsch. Min. Mit.*, 1881, IV, 1.

[2] Weisberg, *Bull. soc. chim.*, 15, 1097.

[3] Petzholdt, *J. prakt. Chem.*, 60, 368.

[4] Wackenroder, *Chem. Chem. Zentr.*, 10, 487.

[5] Skey, *Chem. News*, 22, 236.

[6] Manzella, *Ann. chim. applicata*, 1, 223.

[7] J. Davy, *Edin. New. Phil. Jour.*, 45, 61.

[8] Persog, *Chem. Zentr.*, 32, 79.

[9] Nicholson, *Chem. News*, 25, 171.

[10] Beyer, *Chem. Zentr.*, 40, 945.

[11] Bischoff, *Ibid.*, 5, 597; 8, 886.

[12] Edwards, *Chem. News*, 73, 13.

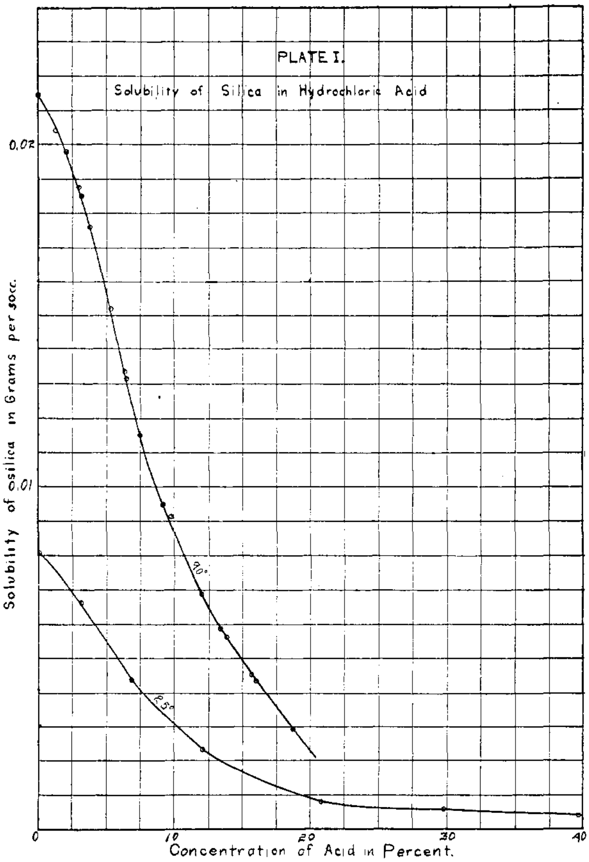
[13] Wittstein and Pribram, *Chem. Zentr.*, 38, 208.

[14] Souchay, *Z. anal. Chem.*, 11, 182.

acids a Munroe platinum crucible was used with suction. Evaporation during filtration was guarded against by covering the filter funnel with a watch glass and setting the funnel directly on the mouth of an Erlenmeyer flask in which the filtrate was received.

The filtrate was cooled to room temperature and 50 cc. were transferred with a pipet to a platinum evaporating dish. The solution was evaporated to dryness with the addition of a few drops of sulfuric acid and the residue ignited to constant weight. The silica was then volatilized with hydrofluoric and sulfuric acids and the dish ignited and weighed. The difference between the two weighings represented the silica dissolved in 50 cc. of solvent. The concentration of the solvent was determined by titrating a second portion of the filtrate with standard alkali.

By this procedure, what was measured was the amount of silica which had changed from an unfilterable to a filterable state of division, without regard as to whether the amount thus dissolved went into true solution or became the colloidal hydrogel of silicic acid.

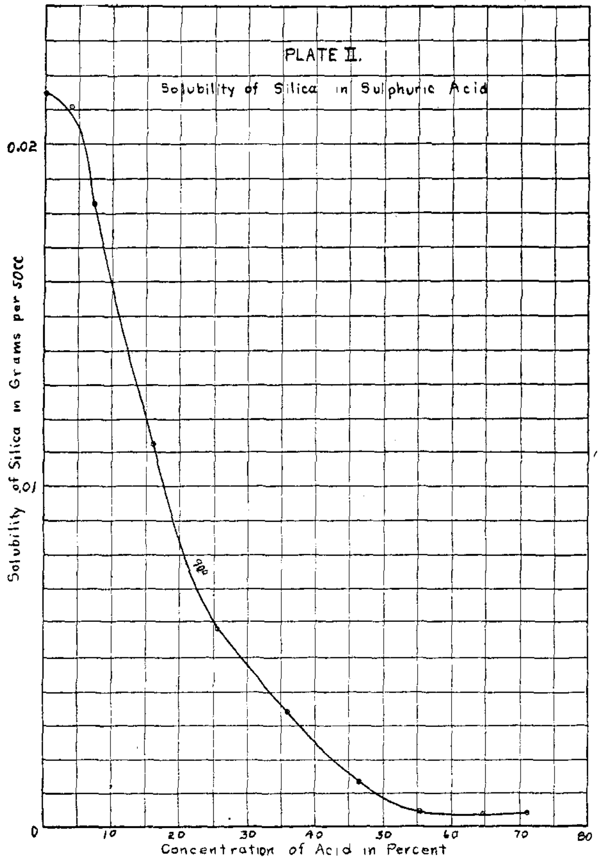


Saturation of the Solvent with Silica.—It was found that with fairly strong acid and gelatinous silica at 90°, saturation is reached in twenty-four hours. With other strengths of acid, a longer period of digestion is required. With ignited silica, equilibrium was not reached in fourteen days.

In general, duplicate determinations were made over different lengths of time for each set of conditions, and equilibrium was assumed to exist when an increase in the time of digestion caused no increase in the amount of silica dissolved.

Solvents Used.—The solvents employed were hydrochloric acid of various strengths, sulfuric acid, conductivity water, and water saturated with carbon dioxide.

Both the hydrochloric and sulfuric acids used were free from residue not volatile with hydrofluoric acid. The hydrofluoric acid used contained a non-volatile residue of from 0.2 to 0.4 mg. per 10 cc. This was determined for each lot and the necessary corrections applied to the results.



The water used was prepared by redistillation of "ammonia free" water from barium hydroxide in an atmosphere free from carbon dioxide and rejecting the first and last portions. Unless the specific conductivity was less than 1.6 × 10^{-6} reciprocal ohms the water was rejected.

Silica Used.—Silica No. 1. The greater part of the experiments were made with gelatinous silica prepared by the addition of silicon tetrachloride to water. The gel thus formed was washed until silver nitrate gave no further reaction for chloride in the filtrate. The product was dried between filter papers and kept in a glass-stoppered bottle until used. This gel when volatilized with hydrofluoric and sulfuric acids left no weighable residue.

Silicas Nos. 2 and 3 were prepared by fusing silica with sodium carbonate. The fusions were dissolved in water to form two solutions containing 1% and 7% of silica, respectively. The solutions were filtered and the silica was precipitated by adding an excess of hydrochloric acid and neutralizing the excess with ammonia. From the more dilute solution the silica separated as a very thin transparent gel. From the stronger solution it separated out as a finely divided slimy precipitate which did not form a coherent gel. Both precipitates were washed chlorine free and when treated with hydrofluoric acid left no weighable residue. These gels Nos. 2 and 3 correspond to Van Bemmelen's preparations A and A_7.

Silica No. 4. By igniting gel No. 1 in a platinum dish with a Méker burner for an hour, amorphous anhydrous silica was obtained. The product was finely ground in an agate mortar.

Cherts.—A weathered chert No. 5, from Albany, Wis., showing SiO_2 93%, $Fe_2O_3 + Al_2O_3$ 3.5%, was used in one experiment, as was also chert No. 6, from Waukesha, Wis., which showed on analysis, SiO_2 98.3%, $Fe_2O_3 + Al_2O_3$ 0.6%, CaO 0.3%, MgO trace. Loss on ignition 0.6. These cherts were very finely ground in an agate mortar.

Solubility Data.

In preliminary experiments made with ignited silica, the solubility figures varied so much that the question was raised whether such silica would ever come to equilibrium with water in any reasonable length of time. Accordingly, experiments were made with gelatinous silica, and in Table I are presented certain typical results showing the agreement of results and the time required to secure equilibrium.

TABLE I.—TIME REQUIRED TO OBTAIN SATURATED SOLUTIONS WITH GELATINOUS SILICA (No. 1) AT 90°.

Time of digestion.	Solvent.	SiO_2 g. per 50 cc.
24 hrs.	Cond. water	0.0214
24 hrs.	Cond. water	0.0212
24 hrs.	Cond. water	0.0215
24 hrs.	Cond. water	0.0216
48 hrs.	Cond. water	0.0212
72 hrs.	Cond. water	0.0214
10 hrs.	HCl 6.3%	0.0128
14 hrs.	HCl 6.3%	0.0134
24 hrs.	HCl 6.3%	0.0133
24 hrs.	HCl 6.3%	0.0132
12 hrs.	HCl 11.8%	0.0070
23 hrs.	HCl 11.8%	0.0069
24 hrs.	H_2SO_4 15.7%	0.0112
24 hrs.	H_2SO_4 15.7%	0.0111
24 hrs.	H_2SO_4 3%	0.0211
24 hrs.	H_2SO_4 3%	0.0211

The figures show that gelatinous silica reaches an equilibrium in water and acids in a comparatively short time.

In Table II is shown the solubility of gelatinous silica in pure water and in hydrochloric acid of various concentrations at 90°.

TABLE II.—SOLUBILITY OF GELATINOUS SILICA NO. 1 IN HYDROCHLORIC ACID AT 90°.

Strength of acid.	Solubility of silica. G. per 50 cc.	Strength of acid.	Solubility of silica. G. per 50 cc.
0.0% (cond. water)	0.0214	6.3% HCl	0.0133
0.0% (cond. water)	0.0212		
0.0% (cond. water)	0.0213	6.4% HCl	0.0132
0.0% (cond. water)	0.0214	7.6% HCl	0.0115
0.0% (cond. water)	0.0215	7.8% HCl	0.0114
0.0% (cond. water)	0.0216	9.3% HCl	0.0095
0.0% (cond. water)	0.0212	9.9% HCl	0.0092
1.2% HCl	0.0204	10.0% HCl	0.0091
2.0% HCl	0.0198	11.8% HCl	0.0069
2.9% HCl	0.0188	11.9% HCl	0.0070
3.0% HCl	0.0186	13.3% HCl	0.0059
3.8% HCl	0.0177	13.6% HCl	0.0056
5.3% HCl	0.0151	15.4% HCl	0.0046
5.4% HCl	0.0152	15.8% HCl	0.0044
6.3% HCl	0.0134	18.7% HCl	0.0028
		18.6% HCl	0.0029

It was not possible to determine the solubility in solutions containing more than 20% hydrochloric acid at 90°.

Entirely similar results were obtained in measuring the solubility of gelatinous silica in sulfuric acid.

TABLE III.—SOLUBILITY OF GELATINOUS SILICA (NO. 1) IN SULFURIC ACID AT 90°.

Concentration of acid.	Solubility. G. per 50 cc.	Concentration of acid.	Solubility. G. per 50 cc.
0.0% (cond. water)	0.0214	25.4% H_2SO_4	0.0058
3.9% H_2SO_4	0.0211	36.0% H_2SO_4	0.0034
4.3% H_2SO_4	0.0211	46.9% H_2SO_4	0.0013
7.3% H_2SO_4	0.0186	55.6% H_2SO_4	0.0005
7.3% H_2SO_4	0.0183	55.7% H_2SO_4	0.0004
11.5% H_2SO_4	0.0144	64.4% H_2SO_4	0.0005
15.6% H_2SO_4	0.0112	71.0% H_2SO_4	0.0004
16.1% H_2SO_4	0.0111		

The influence of carbon dioxide upon the solubility in water was studied. In these experiments the apparatus previously described was modified by passing a second quartz tube through the stopper of the flask and passing a slow current of well-purified carbon dioxide into the space above the liquid. At 90° the effect of carbon dioxide on the solubility of silica in water is *nil.*

A number of measurements of the solubility of gelatinous silica at 25° were made in pure water and in hydrochloric acid.

By comparison of the solubility of silica it is not only noted that at 25° the solubility is much less than at 90°, but also that the solubility curves have the same general trend.

TABLE IV.—SOLUBILITY OF GELATINOUS SILICA (No. 1) IN HYDROCHLORIC ACID AT 25°.

Time of digestion.	Concentration of solvent.	Solubility of silica. G. per 50 cc.	Time of digestion.	Concentration of solvent.	Solubility of silica. G. per 50 cc.
2 days	0.0 (cond. water)	0.0032	2 days	12.0% HCl	0.0023
3 days	0.0 (cond. water)	0.0060	2 days	18.9% HCl	0.0008
8 days	0.0 (cond. water)	0.0080	2 days	19.0% HCl	0.00085
13 days	0.0 (cond. water)	0.0081	2 days	25.1% HCl	0.0006
3 days	3.0% HCl	0.00665	2 days	25.2% HCl	0.0007
3 days	6.3% HCl	0.00465	2 days	34.6% HCl	0.0003
2 days	6.4% HCl	0.0044	2 days	34.9% HCl	0.0004
2 days	11.1% HCl	0.00245			

Physical Character of the Silica.—That the physical form of the silica is a determining factor in its solubility in water and in acids has been repeatedly brought to our attention in our experiments. Ignited silica reaches equilibrium with water very slowly as compared with a silica gel. Table V shows a direct comparison with gel No. 1 and the same silica No. 4 after ignition for one hour in a platinum dish with a Méker burner.

TABLE V.—SOLUBILITY OF IGNITED, AMORPHOUS SILICA AT 90° COMPARED WITH THAT OF GELATINOUS SILICA.

Sample No.	Time.	Solvent.	Solubility SiO_2 g. per 50 cc.
1	1 day	HCl 6.3%	0.0133
4	5 hrs.	HCl 6.3%	0.0123
4	7 hrs.	HCl 6.3%	0.0095
4	10 hrs.	HCl 6.3%	0.0116
4	10 hrs.	HCl 6.3%	0.0108
4	13 hrs.	HCl 6.3%	0.0123
4	1 day	HCl 6.3%	0.0103
4	1 day	HCl 6.3%	0.0109
4	1 day	HCl 6.3%	0.0099
4	2 days	HCl 6.3%	0.0116
4	3 days	HCl 6.3%	0.0108
1	1 day	HCl 6.8%	0.0126
4	5 days	HCl 6.8%	0.0093
1	1 day	H_2O Cond.	0.0214
4	1 day	H_2O Cond.	0.0212
4	1 day	H_2O Cond.	0.0183
1	1 day	HCl 5.0%	0.0156
4	3 days	HCl 5.0%	0.0133
4	7 days	HCl 5.0%	0.0145
4	14 days	HCl 5.0%	0.0124
1	1 day	HCl 2.9%	0.0188
4	8 days	HCl 2.9%	0.0181

TABLE VI.—SOLUBILITY OF SILICA MINERALS IN HYDROCHLORIC ACID AT 90°.

Sample.	Time.	Solvent.	Solubility. SiO_2 g. per 50 cc.
No. 5 (weathered chert)	7 days	HCl 4.6%	0.0165
No. 6 (hard, compact chert)	7 days	HCl 4.6%	0.0100
No. 1 (gel)	1 day	HCl 4.6%	0.0162

Observations.

The solubility of silica has been determined in water and in hydrochloric and sulfuric acids. The solubility is definite and depends on the temperature and concentration.

With gelatinous silica, equilibrium is reached in a few hours, or at most a few days. With ignited silica, equilibrium cannot be attained in days or weeks.

The solubility of gelatinous silica is the same, no matter how the gel is prepared. The true solubility of ignited silica is probably the same as that of gelatinous silica, but as saturation is not reached in any short period of time, the apparent solubility is somewhat less than that of gelatinous silica.

MADISON, WIS.

NOTE.

A Magnetic Gas Circulator.—The accompanying drawing shows a gas circulator which has been successfully used with the Porter and Ralston apparatus for determining the rate of oxidation of coal.[1] This work has been discontinued but the circulator may be used in other situations so is now described.

In studying the oxidation of coal it was desired to measure the volume of gas absorbed by the coal when in oxygen at 0.2 atmospheric pressure and nearly saturated with water vapor. Circulation of the gas was used to prevent condensation of the water vapor on the coal as the oxygen was absorbed.

When in operation, a column of mercury passed down the inclined glass tube, pushing the gas ahead of it and thus causing the circulation. As soon as the mercury had passed the length of the inclined tube, another column of mercury was started. The mercury was moved by the reciprocating iron piston acting in the glass cylinder. Pump-fashion valves were arranged as shown. The piston in turn was reciprocated by the two electromagnets. Current for these was passed alternately through each by a mechanical switch, not shown. The piston was reciprocated 15 to 20 times per minute. Coils were of No. 18 wire; 5 amperes at about 5 volts were required to operate the circulator. The apparatus was used 7 to 8 hours at a time and for a period of several months, without trouble or adjustments of any kind being necessary.

The advantage of this circulator lay in its being hermetically sealed from communication with the outside. The apparatus was thus free from the influence of external pressure changes which might effect the gas measurements. Also the volume of gas in the essential parts of the circulator

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[1] H. C. Porter and O. C. Ralston, Bureau of Mines, *Tech. Paper* **65** (1914).