2. Similarity of the resulting curve, of heat of adsorption against gas concentration on the surface, to that obtained in previous investigations emphasizes the specific nature of the adsorption and the constancy of the charcoal surface.

3. A distribution curve is obtained showing the apparent distribution of activities of the elementary spaces on the carbon surface. Several possible explanations are advanced for the shape of this curve.

4. From a comparison of the shapes of the initial portions of various Q–c curves certain regularities are noted and it is concluded that there is a possibility of obtaining a mathematical expression for the distribution of the more active elementary spaces on the surface.

5. The conclusion is reached that the results support best that form of the multimolecular layer theory previously suggested by Keyes and Marshall.

6. The specific surface of the charcoal is estimated to lie between 2.8×10^4 and 6.1×10^4 sq. cm. per gram.

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[CONTRIBUTION FROM THE HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

GERMANATE GELS OF THE ALKALINE EARTHS

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RECEIVED MARCH 5, 1929 PUBLISHED JULY 5, 1929

The soluble salts of the alkaline earths cause no precipitation in neutral or acid solution of germanium dioxide but when such solutions are made alkaline with ammonium hydroxide most of the germanium is thrown down as a bulky gelatinous mass. Under such circumstances, however, it is not easy to form homogeneous or firmly set gels owing to the flocculating influence of the ammonium salt simultaneously produced. If calcium hydroxide solution be substituted for the salt of the same base the reaction with aqueous germanic acid takes on a surprisingly different character, for the precipitate then assumes the form of a firm, transparent gel even in highly dilute solutions. The direct formation of calcium, strontium and barium germanates by neutralization of aqueous germanic acid results in the formation of insoluble or difficultly soluble salts under conditions most favorable to colloid formation, as water is the only by-product in the reaction. At the same time this reaction is peculiarly characteristic for germanium, for all of the other semi-metallic dioxides in the fourth periodic group are quite insoluble in water.

It is the purpose of this paper to describe the alkaline earth germanates when prepared in the form of highly dispersed systems with particular attention to the calcium salt, which appears to give permanent gels of extraordinary water content.

Preparation of Reagents

Germanic Oxide.—The pure dioxide was obtained by hydrolysis of the redistilled tetrachloride and subsequent ignition of the product in superheated steam. The nearly pure oxide so obtained was frequently moistened, dried and ignited to 900–950° to effect the complete removal of traces of chlorine and finally fused to a glassy mass at 1100–1150° in a platinum crucible. (This can be carried out in an electric resistance furnace with careful exclusion of any reducing gases, but any direct flame touching the crucible results in quick reduction and destruction of the platinum crucible.) The glassy mass of oxide was dissolved in boiling water, using approximately one liter of water for each 5 g. of oxide. After determination of the GeO_2 content of aliquot portions of this solution the bulk was diluted to definite molarity.

Calcium Hydroxide.—Selected crystals of Iceland Spar were ignited in platinum and the residual lime was dissolved in freshly distilled water. The saturated solution of lime water was siphoned off into paraffin-lined flasks and sufficient carbon dioxide-free water was added to dilute beyond the saturation point at room temperature. The exact content of calcium oxide was determined in aliquot portions gravimetrically as calcium sulfate.

Strontium Hydroxide.—Baker's Analyzed $Sr(OH)_2 \cdot 8H_2O$ was dissolved in redistilled water and preserved in paraffin-lined flasks.

Barium Hydroxide.—Baker's Analyzed $Ba(OH)_2 \cdot 8H_2O$ was dissolved in redistilled water. The nearly saturated solution was siphoned off into paraffin-lined flasks and subsequently diluted to solutions of definite concentration.

Water.—The distilled water of the laboratory was redistilled in fresh portions as required, rejecting first and last fractions, collecting middle fractions in paraffin-lined flasks.

Alcohol.—Alcohol was distilled first from lime and then from shavings of metallic calcium.

Ether and benzene were redistilled and dehydrated over metallic sodium.

Flasks, pipets and burets were calibrated at 22–25°.

Calcium Germanate Gels

Preliminary experiments were made with 0.0279 *N* calcium hydroxide and solutions of germanic acid of gradually decreasing concentration, as indicated in Table I. It was immediately observed that calcium germanate formed translucent or transparent gels throughout wide ranges of dilution of acid and base but also that homogeneous gels could only be obtained when the reacting base and acid were rapidly and thoroughly mixed. The following procedure gave most satisfactory results: base and acid were separately drawn off from burets into paraffin-lined beakers and simultaneously poured into a third beaker in which gelation took place. If kept free from dust particles the fresh surface of paraffin allows complete transference of the measured volumes in the few seconds between initial mixing and subsequent gelation.

In the first series of experiments calcium hydroxide and germanic acid were mixed in the calculated ratio for the formation of the salt of hypothetical ortho-germanic acid, ($2CaO:GeO_2$), carrying out the gel formation at 25°. At this temperature, if the mixture is quickly made, the combining acid and base stiffens to an opalescent gel in three to five seconds and during the next minute or two the somewhat uneven cloudiness in the gel mass disappears, leaving an almost clear and colorless permanent gel.

A firm gel was obtained by mixing 108.4 cc. of calcium hydroxide solution containing 0.1122 g. of CaO with the same volume of aqueous germanic acid containing 0.1045 g. of GeO_2. These quantities correspond to $2CaO:GeO_2$ (molar weights expressed in mg.). The volume of the gel was then 216.8 cc. and must have contained 0.2167 g. of total anhydrous solids ($CaO + GeO_2$). The gel appeared perfectly dry and was firm enough to allow inversion of the containing beaker (250 cc.) without loss. The extraordinary dispersion of the calcium salt is evident, for the gel contained 99.90% of water bound or trapped by as little as 0.10% of anhydrous constituents. Otherwise expressed, 0.0184 *M* CaO reacts with 0.00922 *M* GeO_2 with the formation of a solid gel, although the gel contains no more than 1/1000 of its weight of anhydrous oxides.

Properties of Calcium Germanate Gel.—Samples of the solid gel prepared as above were preserved in a large desiccator over dilute sodium hydroxide to prevent drying and contamination by carbon dioxide and after standing for nearly a year showed no sign of syneresis. Exposed to air some drying takes place with slow formation of an opaque white surface as carbon dioxide is taken up. Other samples were broken down by stirring rapidly with a spatula or glass rod and when the mechanically broken gel was thrown on a Büchner funnel it was found that almost all of the trapped liquid could be removed by suction alone, leaving a small residue of the calcium salt on the filter. This residue closely resembles macerated filter paper pulp and after drying at room temperature or at 100° can be almost completely removed from the filter in a single piece. It is almost infusible, but on strong ignition shrinks considerably with the loss of 14–20% of water held by the air-dried salt. The hydrogel is dissolved by 0.2 *M* calcium chloride and by ammonium chloride but is nearly insoluble in the fixed alkali chlorides. Before and after ignition calcium germanate is insoluble in water but is readily soluble in dilute mineral acids. 0.2 *N* hydrochloric acid slowly dissolves the ignited salt and as germanic acid has no effect on methyl orange the CaO content of the salt can be determined by titrating back the excess of acid with standard sodium carbonate. This method gives a rapid check on the composition of the salt.

Microscopically examined the gel itself appears to be amorphous but under highest power (1700–1800 diameters) some indication of crystalline structure appears indistinctly, especially in the ignited salt.

Effect of Temperature.—As calcium germanate gel is so easily broken down by mechanical means, such as violent agitation or suction filtration, it was thought that elevation of temperature would bring about a rapid syneresis, but unexpectedly the gel when once produced resisted temperature changes up to near the boiling point of water. A number of tubes containing the gel were tightly stoppered and immersed in thermostatic baths. The gels all remained unchanged up to 75°. At 100° numerous entrapped bubbles in the gel greatly increased in size, causing separation of a small amount of liquid. Gels which had been heated to 90–95° showed practically no change.

An attempt was made to reproduce the gel by combining hot solutions of both acid and base but under such conditions no gelation occurred. At 60–70° calcium hydroxide and germanic acid gave only well flocculated white precipitates of small volume which settled rapidly and could not be subsequently deflocculated. The solutions of acid and base were then chilled to 0° before mixing and on combining these it was found that gelation did not take place in the cold. The mixtures remained liquid and perfectly clear for some time but on allowing the temperature to rise slowly to 25° almost water-clear solid gels resulted. From these experiments it would appear that the velocity of gelation is greatly cut down by small reduction in temperature and that any appreciable rise above room temperature results in too rapid a precipitation of the salt for any colloidal structure to build up. The latter condition is connected with imperfect mixing of the acid and base, for it was impossible to obtain any homogeneous gel unless an appreciable interval of time was allowed for a fairly good mixture of the two reacting liquids. With the warm acid and base precipitation was instantaneous. The best temperature for gel formation lies between 15 and 25°.

Several gels prepared at 25° were chilled to −17°. The expanding ice crystals increased the volume of the gel, which assumed a rounded or dome-shaped surface. After complete freezing the hard mass was allowed to melt slowly. All signs of gelation had disappeared, leaving a comparatively small precipitate from which the separated liquid could be poured off.

Substitution of the Water of the Hydrogel by Other Liquids

Ethyl Alcohol.—Hydrogels containing 99.90% of water were prepared under conditions favoring firmest set. Conditions are shown in Table III, Expts. 1 and 2, but employing larger volumes. Gel masses of 250 cc. each were used. The hydrogel was immersed in a large excess of 95% alcohol. The gel became much firmer to the touch when so treated and could then be more easily cut up into smaller blocks or cubes. Cubes of about 8 cc. each were selected and again washed with fresh alcohol until most of the water had been removed. Complete extraction was carried out in the Soxhlet apparatus using absolute alcohol. The return alcohol was discarded a number of times, using fresh, dry alcohol and continuing the extraction until the return liquid gave approximately the same density over twenty-four-hour periods. A portion of the gel was selected and the trapped alcohol removed on a dry suction filter. The filtrate protected from moisture gave a density of 0.7949. The original alcohol was d_{16}^{16}, 0.7943, which value corresponds to 99.8 to 99.9% alcohol by volume.

As alcohol substituted the water of the hydrogel there was a corresponding fall in specific gravity of the immersed gel and near the end of the extraction the cubes of gel became light enough to remain suspended in the surrounding liquid for a few moments and at the same time the gel mass, which was easily visible beneath the alcohol as long as water was present, became scarcely visible when nearly all of the water was removed. The changes in both specific gravity and refractive index conveniently show the end-point in the extraction process, making a larger number of density determinations unnecessary.

Methyl Alcohol.—The hydrogel was extracted with pure dry methyl alcohol in the same manner as that described above. In this case the gel volume decreased somewhat more than 50%. The methyl alcohol gel although smaller in volume was softer and less easy to handle than the ethyl alcohol gel. It could, however, be cut into thin slices with a sharp knife without loss of any liquid and was permanent when kept in a well-stoppered flask.

Ethyl Ether.—Half of the alcohol gel prepared as above was extracted for a number of days with dry ether (distilled over sodium), frequently changing the extracting liquid for fresh ether. As in the case of the ethyl alcohol gel formation there was little change in volume of the gel mass and at the end of several days the cubes of ether gel became specifically light enough to remain suspended for some time in the surrounding ether. Extraction with fresh dry ether was continued until the density of the return ether reached the value for the pure extracting liquid (determined by hydrometer). Some of the cubes of gel were removed from the ether and were found to be much firmer to the touch than either the alcohol or water gel from which they had been prepared. Exposed to dry air the ether gel rapidly diminished in volume to a very small irregular fragment which crumbled to a dry powder between the fingers.

Action of Benzene on the Ether Gel.—A part of the ether gel was treated with pure benzene (redistilled over sodium). It immediately contracted to about 40–50% of the original volume, at first becoming milky white and opaque. The opacity was probably due to the formation of some emulsion of benzene and ether, as these two liquids are not miscible in all proportions. After long standing the contracting gel again became transparent, especially on the outer portions of the immersed cubes, but complete extraction of the ether was not possible in several weeks' contact with fresh excess of benzene.

All of the above gels have been preserved in tightly-stoppered vessels and appear to be quite permanent, both in the dry state and when immersed in excess of the same liquids trapped by the gel structure. They are all capable of yielding most of their trapped liquid by strong pressure or suction filtering, especially after the gel has been mechanically broken down by violent stirring. Suction filtering yields a residue of the dry or nearly dry salt which appears absurdly small when compared to the original volume of gel. A whole liter of the hydrogel, for example, can be transferred completely to a 9-cm. filter if a platinum cone and suction be applied. The residue on drying at room temperature or at 100° can then be taken out of the filter in a single piece, leaving almost nothing adhering to the filter paper.

While any conjecture as to the actual nature of the highly dispersed calcium germanate in the above gels would be purely speculative, it seems clear that such gels are entirely structural in character, that is to say, practically all of the liquid present appears to be simply trapped by an enormous number of minute filaments of the dispersed calcium salt. At present it is impossible to say whether these are crystalline or amorphous, for the high power microscope at 1700 diameters fails to show more than a faint suspicion of crystalline structure. Further information in this direction may be obtained by x-ray spectral examination of the gel or its dried residue and an effort to obtain such evidence is being made.

Composition of Calcium **Germanate.**—108.4 cc. of calcium hydroxide containing 0.1122 g. of CaO treated with the same volume of germanic acid containing 0.1045 g. of GeO_2 gave a firm gel of 216.8 cc. After preserving this gel for some hours in a desiccator over dilute caustic alkali, it was broken up by stirring and the whole was transferred to a suction filter. The small mass left on the filter was washed with very little cold water. The residue and filtrate were separately analyzed.

The Residue.—The residue dried at 100° was detached from the filter almost in one piece, leaving scarcely anything on the paper; the latter was separately ashed in a weighed crucible before adding the main bulk of salt. Ignition at bright red heat, weighing before and after, showed that the dried mass had retained about 13.9% of water at 100°. The ignited salt was dissolved in 6 *N* hydrochloric acid and all of the germanium removed by saturation with hydrogen sulfide under pressure. The sulfide was filtered off and converted to dioxide in the usual way, weighing as GeO_2. The filtrate containing all of the calcium and much acid was evaporated nearly to dryness and the residual calcium salt was converted to sulfate by continuing the evaporation with excess sulfuric acid, weighing the residual ignited $CaSO_4$. Results of this analysis were 36.43% of CaO and 63.40% of GeO_2 for composition of the ignited salt.

The Filtrate from the Mechanically Broken Gel.—The combined filtrate and wash water was made 6 *N* with hydrochloric acid and saturated with hydrogen sulfide. Only a very small precipitate of GeS_2 appeared, requiring three or four hours to form. Converted to dioxide this amounted to only 0.0003 g. The filtrate from this small amount of germanic sulfide was examined for calcium by converting the residue obtained by evaporation to calcium sulfate as before. Results showed that the suction filtrate from the original gel was practically pure lime water and that the precipitation of germanium had been about quantitative.

It is also evident that the calcium salt of hypothetical orthogermanic acid cannot be formed by uniting the base and acid in the ratio calculated for this salt, and that the solid produced in the dispersed condition approaches the theoretical composition of calcium metagermanate, $CaGeO_3$ (theoretical values are $CaO = 34.93$, $GeO_2 = 65.07$), about half of the lime water originally added remaining in the free state. An attempt was now made to produce the metagermanate in purer form by combining the base and acid in the calculated ratio for this salt. In this series of gels (some of which are shown in Table II), the expected metagermanate did appear in purer form but a very noticeable change took place in the gelation dilution limit when compared with the gels made in the presence of excess calcium hydroxide. In addition, the second series of gels differed greatly from the first in their lack of clarity, for all of these were milky white or nearly opaque.

Gelation Dilution Limit for Calcium Germanate Gels.—Tables I, II, III and IV show the influence of varying ratios of base and acid upon the gelation dilution limit of calcium germanate gel, the gelation dilution limit being arbitrarily defined as the maximum dilution at which the dispersed salt sets firmly enough to permit the inversion of the container without loss of its contents and without separation of any visible untrapped liquid over a period of several days, gelation being carried out at 22–25° in all experiments.

TABLE I

GELS FORMED BY MIXING CALCIUM HYDROXIDE AND GERMANIC ACID IN THE CALCULATED RATIO FOR THE HYPOTHETICAL ORTHOGERMANATE, $2CaO:GeO_2$

	$Ca(OH)_2$, cc.	CaO, g.	GeO_2, cc.	GeO_2, g.	Gel. vol., cc.	H_2O in gel, %	Remarks
1	30	0.02345	8.85	0.02177	38.8	99.884	Firm gel, sl. cloudy, permanent
2	30	.02345	11.8	.02177	41.8	99.892	Same as 1
3	30	.02345	14.75	.02177	44.7	99.899	Firm gel, clearer than 1 and 2
4	30	.02345	14.75	.02177	44.7	99.899	Same as 3
5	30	.02345	17.7	.02177	47.7	99.905	Firm gel, nearly cl., no water sep.
6	30	.02345	23.6	.02177	53.6	99.915	Stronger gel than 7
7	30	.02345	29.5	.02177	59.5	99.924	Very clear, fairly firm set
8	15	.00782	15.0	.00729	30.0	99.950	Not firm, falls from inv. cont.
9	15	.01172	17.7	.01088	32.7	99.931	Poor gel, some water sep.
10	15	.01172	23.6	.01088	38.6	99.941	Not very firm set gel
11	15	.01172	24.1	.01088	39.1	99.942	About same as 10
12	30	.02345	29.5	.02177	59.5	99.924	Fair gel, not very firm set
13	108.3	.11218	108.3	.10450	216.6	99.900	Quite firm, clear gel, remains in inverted container

The results shown in Table I indicate that the gelation dilution limit for mixtures of calcium hydroxide and germanic acid lies between fairly narrow limits of water content, for those gels containing more than 99.92% of water do not set firmly, while those containing less than 99.88% of water are cloudy and give evidence of too rapid a precipitation of the calcium salt to allow the highest dispersion. All gels in this table are prepared by combining acid and base in the $2CaO:GeO_2$ ratio and inspection of the other tables (II, III and IV) will show that varying the proportions of acid and base results in noticeable change in dilution limit.

The best working conditions for the formation of good gels for this ratio of acid and base appear to be found at dilutions corresponding to 99.90% of gel water, as shown in Table I, Expt. 13.

TABLE II

CALCIUM GERMANATE GELS PRODUCED BY COMBINING ACID AND BASE IN CALCULATED RATIO TO FORM THE CALCIUM SALT OF HYPOTHETICAL METAGERMANIC ACID, $CaGeO_3$, SHOWING GELATION DILUTION LIMIT FOR GELS SO PREPARED

	$Ca(OH)_2$ soln., cc.	CaO, g.	GeO_2 soln., cc.	GeO_2, g.	Vol. of gel	H_2O in gel, %	Remarks
1	30	0.02345	29.5	0.04354	59.5	99.887	Cloudy white, not very firm gel
2	30	.02345	29.5	.04354	59.5	99.887	Cloudy wh., few water drops sep.
3	25	.01954	14.85	.03653	39.85	99.859	Cloudy white, fairly solid
4	25	.01954	18.8	.03653	43.8	99.872	Poor gel, water sep.
5	25	.01954	29.7	.03653	54.7	99.897	Very poor gel, white, not firm
6	30	.01172	8.85	.02177	38.85	99.914	No gel at all, ppt. sep.
7	25	.01954	13.9	.03653	38.9	99.856	Fairly firm, white gel
8	25	.01954	9.9	.03653	34.9	99.839	Like 7 but little firmer
9	80.3	.05609	80.3	.10450	160.6	99.900	Very poor gel with sep. water
10	160.6	.11218	160.6	.20900	321.2	99.900	About same as 9

From the ten experiments shown in Table II it will be seen that the combination of calcium hydroxide and germanic acid in the $CaO:GeO_2$ or 1:1 ratio also brings about gelation at relatively high dilution but the gelation dilution limit in this case is reached when the water content becomes 99.83 to 99.85%; the gels in Table I made in the $2CaO:GeO_2$ ratio of base to acid reached limiting dilution at about 99.90% of water (see No. 7, Table I, and compare with No. 7, Table II, as representing dilution limit in these two systems). In these gels it is seen that No. 7, Table I, offers a gel containing 0.04522 g. of total anhydrous solids per 59.5 cc. of gel and No. 7, Table II, a gel containing 0.05607 g. of anhydrous constituents per 38.9 cc. of gel volume. Calculating these to the same volume of gel in each case, the limiting values for anhydrous oxides in the two become 0.07596 g. per 100 cc. of gel of the ortho, ratio $2CaO:GeO_2$ for Table I, and 0.15138 g. of anhydrous oxides per 100 cc. of gel of the meta, ratio $CaO:GeO_2$ for Table II. These values show the real difference in gelation dilution limit in the two series of gels more clearly than simple expression of their respective water percentages and point out that the content of anhydrous oxides per cc. of gel made as in Table I is only about half that required for a gel of similar consistency made as in Table II.

In addition to variation in dilution limit in the two series of gels it is to be noted that those in Table II are all white and almost opaque and lack the almost water-clear, homogeneous character of those formed under the conditions in Table I.

The previously described analyses of the gels of Table I showed that the composition of the dispersed solid, mechanically freed from trapped water and ignited, approached the theoretical composition of calcium metagermanate and that the trapped water was almost pure lime water which had remained uncombined with germanic acid. These facts together with the poorer gelation obtained under the conditions in Table II indicate that a certain excess of free or uncombined base greatly favors gelation, although the dispersed calcium salt approaches the composition of calcium metagermanate in both cases.

A large quantity of gel was prepared under the conditions shown in Table II, Expt. 7, and the milky white mass was broken up mechanically and sucked as dry as possible on a Büchner funnel; residue and filtrate with wash water now were separately analyzed in the way already described. The residue on the filter after ignition contained 64.12% of GeO_2 and 35.80% of CaO (the theoretical values for $CaGeO_3$ are 65.07 and 34.93). The filtrate drawn from the original gel mass contained germanium which had evidently escaped precipitation in the solid structure of the gel. Complete analysis of this filtrate showed that the total solids present amounted to only about 10% of the total solids present in the original gel and that of this dissolved portion 34.44% was CaO and 65.66% was GeO_2. Evidently germanium is not completely precipitated by mixing calcium hydroxide and germanic acid in the $CaO:GeO_2$ ratio, as in Table II, although $CaGeO_3$ is produced in both this or the former ratio $2CaO:GeO_2$ of Table I. On the other hand, analyses of the gels of Table I showed that the germanium was completely precipitated by the excess lime water and was to be found in the solid gel structure and not in the trapped water.

The fact that the dispersed calcium salt is the same in composition ($CaGeO_3$), whether the base is added in considerable excess as in Table I or in the calculated amount to produce this salt as in Table II, naturally leads to the belief that a certain excess of base is required to favor the formation of homogeneous gels at high dilution as well as to quantitatively precipitate the germanium in the solid or filterable structure of the gel. In the next series of gels, described in Table III, the base and acid were added in a ratio intermediate between those of the former two tables, that is, the $4CaO:3GeO_2$ ratio. Examination of this table will show that by so uniting the base and acid the gelation dilution limit was still further advanced and firm gels of the highest dilution could be so obtained. It was at first thought that the better gelation under these circumstances was connected with the formation of the calcium salt of a hypothetical trigermanic acid but analyses of these gels, seen under Table III, show that again the salt produced was nearly pure calcium metagermanate and that the union of base and acid in the above ratio simply furnished a still more favorable hydroxyl-ion concentration for best gelation.

TABLE III

CALCIUM GERMANATE GELS FORMED BY UNITING BASE AND ACID IN THE CALCULATED RATIO, $4CaO:3GeO_2$, SHOWING GELATION DILUTION LIMIT FOR THIS RATIO

	$Ca(OH)_2$ soln., cc.	CaO, g.	GeO_2 soln., cc.	GeO_2, g.	Gel vol., cc.	Gel comp., % H_2O	$CaO + GeO_2$	Remarks
1	89.64	0.07478	89.64	0.10450	179.28	99.90	0.10	Firm clear gel in 10 sec.
2	26.9	.02243	26.9	.03135	53.8	99.90	.10	Same as 1
3	40.7	.02243	40.7	.03135	81.4	99.935	.065	Firm clear gel in 2 min.
4	45.7	.02243	45.7	.03135	91.4	99.942	.058	Gel in 3 min., not firm set, falls from beaker
5	53.5	.02243	53.5	.03135	107.0	99.947	.053	Bulky mass, will not set
6	78.68	.08971	85.28	.1254	163.96	99.869	.131	Firm, clear gel in 2–3 sec., remains in inv. vessel on shaking

Results indicated in Table III show that the mixture of calcium hydroxide and germanic acid in the $4CaO:3GeO_2$ ratio gives the conditions which favor greatest dispersion of the precipitated calcium salt. Experiments 3 and 4 mark the gelation dilution limit between 99.93 and 99.94% of water. Gel No. 3 is particularly interesting because, as far as the writers can ascertain, no gel of comparable water content has thus far been reported in the literature of colloids either in the organic or inorganic field; the total anhydrous oxides present in this dispersed salt is less than a fifth of the anhydrous components found in previously known colloidal dispersions. A liter of this gel (No. 3) contains 0.27579 g. of CaO and 0.38510 g. of GeO_2 or a total solid content of 0.66089 g. It will keep indefinitely (over a year), without any syneresis and if kept in a tightly-stoppered vessel will resist any change up to near the boiling point of water. Any quantity of this gel can be prepared by quickly combining equal volumes of 0.009837 *M* CaO and 0.00737 *M* GeO_2.

The $4CaO:3GeO_2$ gel prepared as in Expt. 6, Table III, and containing 0.08971 g. of CaO and 0.1254 g. of GeO_2 in the gel volume of 163.96 cc. was broken up by actively stirring and the whole was filtered by suction, using a platinum cone and filter paper. The small residue on the filter after washing with a small amount of cold water was ignited and analyzed by the method before described. The ignited salt contained 36.42% of CaO and 63.48% of GeO_2. The filtrate plus wash water contained less than 0.001 g. of GeO_2 and 0.0087 g. of CaO, nearly all of which was present as free base. Again it is seen that the insoluble structure of the gel is essentially calcium metagermanate. The GeO_2 found in the ignited salt is low by about 2% when compared with the theoretical value for GeO_2 in this salt and the value for calcium is correspondingly high. It is believed that this discrepancy can be explained in two ways—first, the complete washing of the colloidal residue is difficult on account of adsorbed calcium hydroxide and, second, the alkaline filtrate or trapped gel water quickly takes up carbon dioxide if exposed to the air during filtration—both of these effects result in apparent rise in CaO content of the salt and corresponding low values for GeO_2 found in the filtered residue.

TABLE IV

CALCIUM GERMANATE GELS OBTAINED BY COMBINING CALCIUM HYDROXIDE AND GERMANIC ACID IN THE RATIO $3CaO:2GeO_2$, SHOWING GELATION DILUTION LIMIT

	$Ca(OH)_2$ soln., cc.	CaO, g.	GeO_2 soln., cc.	GeO_2, g.	Gel vol., cc.	Gel comp., % H_2O	% solids ($CaO + GeO_2$)	Remarks
1	94.32	0.08414	94.32	0.10450	188.63	99.900	0.100	Firm clear gel, sets in 1 min.
2	25.0	.02140	33.5	.02670	58.5	99.918	.082	Not firm gel, some liq. sep.
3	25.0	.02140	32.2	.02670	57.2	99.916	.084	Fairly firm, some water sep.
4	25.0	.01290	25.0	.01610	50.0	99.942	.058	No geln., ppt. settles to bottom
5	22.5	.01290	22.5	.01610	45.0	99.936	.064	Only partial geln., much liq. sep.
6	26.0	.02140	26.0	.02670	52.0	99.908	.092	Fair gel, sets in 2-min. diln. limit in this series

Table IV shows that the gelation dilution limit for mixtures of calcium hydroxide and germanic acid in the $3CaO:2GeO_2$ ratio is reached at a water content of 99.908 or total solid content of 0.092% but brings out the fact that no gelation will take place at the maximum dilution for gels of the $4CaO:3GeO_2$ ratio in Table III (compare Expts. 3 and 4, Table III, with Expt. 4, Table IV).

Analysis of the gel obtained in Table IV, Expt. 6, showed that the filtrate obtained by mechanical destruction of the gel and suction filtration was essentially free lime water but 0.0023 g. of GeO_2 had escaped precipitation and was also present in the alkaline filtrate. The insoluble portion, which had previously built up the gel structure, on ignition contained 65.40% of GeO_2 and 39.52% of CaO. These results are close to the calculated values for $CaGeO_3$.

Combining all of the results obtained from Tables I to IV, inclusive, it can be safely concluded that more or less pure calcium metagermanate is precipitated by any excess of calcium hydroxide on germanic acid and that this salt alone is responsible for the gelation phenomena observed. Also solid gels are obtained at maximum dilution when acid and base are combined in the $4CaO:3GeO_2$ ratio, Table III, Expt. 3, giving conditions for the most highly dispersed salt obtainable in any known circumstances. This gel contains 99.935% of water and 0.065% of total anhydrous constituents.

Strontium Germanate

Solutions of strontium hydroxide and germanic acid do not form homogeneous gels at dilutions comparable to those used in the formation of the colloidal calcium salt. Strontium germanate gels can be formed, however, if the solutions of acid and base are made up to concentrations of four or five times the molarity of those used under the calcium gels. For this purpose 0.047 *M* SrO (4.9040 g. of SrO per liter) and 0.049 *M* GeO_2 (5.1450 g. of GeO_2 per liter) were used for preliminary experiments.

Strontium germanate gels were prepared under the same general conditions as those described under the calcium salt, combining acid and base in ratios analogous to those already given. All of the strontium gels were opaque or almost opaque in distinction to the transparent or nearly water-clear calcium gels. The strontium gels set much more slowly and under no conditions could be obtained free from enclosed flocculated masses or aggregates of precipitated salt which interfered with the direct passage of light through the solid gel.

Analyses of the strontium gels were made in exactly the same manner as under the calcium gels. The results of these analyses showed that an excess of strontia ($2SrO:GeO_2$) precipitates nearly all of the germanium which appears in the insoluble and filterable solid structure of the gel, the filtrate obtained by suction and violent agitation of the gel being nearly pure strontium hydroxide. On the other hand, in the formation of the strontium germanate under circumstances where the acid and base were combined in any other ratio approaching the 1:1 molecular ratio, there always resulted an incomplete precipitation of the germanium, much of which then passed into the entrapped gel water. The gel residues obtained by suction were all ignited and analyzed and as under the calcium salt it was found that the salt of metagermanic acid in a greater or less degree of purity was always produced, no matter what excess of strontia had been added to the solution of germanic oxide. In mixtures containing the greatest excess of base ($2SrO:GeO_2$), the residual salt after suction filtration contained 56.10% of GeO_2 and 44.01% of SrO. Calculated values for $SrGeO_3$ were 50.21% of GeO_2 and 49.79% of SrO. The gels formed by combining the strontia and germanic acid in the $SrO:GeO_2$ ratio gave 50.66% of GeO_2 and 49.30% of SrO for the composition of the similarly obtained residue.

The gelation dilution limit for strontium germanate is shown in Table V, but as this salt does not show the unusual dispersion of the corresponding calcium compound, only a few typical experiments are shown, combining in one table the limiting dilutions for various mixtures of base and acid.

From the results shown in Table V it may be concluded that strontium germanate gels cannot be obtained with more than 99.75% of water. The gelation dilution limit for these gels is reached at about 0.25% total

TABLE V

STRONTIUM GERMANATE GELS

Showing gelation dilution limit for mixtures of base and acid in several molecular ratios: $2SrO:GeO_2$; $SrO:GeO_2$; $4SrO:3GeO_2$

	$Sr(OH)_2$ soln., cc.	SrO, g.	GeO_2 soln., cc.	GeO_2, g.	Vol. of gel, cc.	Comp. of gel, % H_2O	% solids (GeO_2 + SrO)	Remarks
Gels 1 to 4 made by uniting base and acid in the $2SrO:GeO_2$ ratio								
1	42.1	0.2060	20.3	0.1045	62.4	99.5	0.50	Firm milky white opaque gel
2	31.2	.1030	31.2	.0523	62.4	99.75	.25	Imp. geln. sets in half min., a little water sep.
3	38.8	.0515	38.8	.0261	77.6	99.90	.10	No gel forms, ppt. sep. in 10–15 min.
4	50.4	.2060	50.4	.1045	100.8	99.70	.30	Fairly firm gel, milky translucent
Gels 5, 6 and 7 made by mixing base and acid in the $SrO:GeO_2$ ratio								
5	21.05	.1030	20.3	.1045	41.35	99.51	.49	Firm opaque white, sets in 1 min.
6	41.35	.1030	41.35	.1045	82.7	99.75	.25	Fairly firm gel, sets in 1 min.
7	58.15	.1030	58.15	.1045	116.3	99.83	.17	Very poor gel, sets to semi-solid in 1 min.
Gels 8 and 9 made by mixing base and acid in the $4SrO:3GeO_2$ ratio								
8	72.7	.2072	72.7	.1568	145.4	99.75	.25	Firm opaque gel, sets in 1 min.
9	50.0	.1036	50.0	.0784	100.0	99.82	.18	Poor geln. with sep. of some liq.

solid content (SrO + GeO_2), which is about twice the amount of anhydrous material present in solid gels of the calcium compound. The solid structure of these gels is made up essentially of strontium metagermanate, $SrGeO_3$, although the pure salt is rather difficult to isolate from excess of adsorbed strontia. There appears to be no indication of the formation of any other germanate of strontium no matter what excess of strontia is mixed with germanic acid.

Barium Germanate

Unlike the corresponding calcium and strontium salts, barium germanate is appreciably soluble in water, so that mixtures of baryta and germanic acid at dilutions comparable to those used under the calcium and strontium gels gave nothing more than clear solutions in which only partial precipitation of the barium salt occurred on long standing.

Experiments were carried out with more concentrated solutions, using baryta containing 0.00927 g. of BaO per cc. and germanic acid containing 0.00372 g. of GeO_2 per cc.

Sixty-six and two-tenths cc. of barium hydroxide containing 0.61348 g. and 56.2 cc. of germanic acid containing 0.2090 g. of GeO_2 were combined. A fine crystalline precipitate formed almost immediately and on standing for some time larger crystals were deposited which collected in shining aggregates on the sides and bottom of the beaker. The crystalline mass was filtered off on a suction filter, washed with a small amount of cold water, dried, ignited and weighed. This amounted to 0.2947 g., representing only 35.8% of the total oxides in the original mixture. Analysis of the ignited salt gave 58.68% of BaO and 41.30% of GeO_2 (theoretical values for $BaGeO_3$ are 59.41 and 40.58). The alkaline filtrate from the original precipitation of the crystalline barium salt contained 0.089 g. of GeO_2 which had escaped precipitation, although the base had been added in double the amount required to form the metagermanate. It will be noted that a corresponding excess of either calcium or strontium hydroxide would have quantitatively precipitated the germanium.

A portion of crystalline barium metagermanate was prepared by combining barium hydroxide and germanic acid in the calculated amounts to form pure $BaGeO_3$, warming the solution of acid and base before mixing the two. In this case the solution remained clear for a few moments and on standing for some time partial precipitation took place as before but the crystals were much larger. Analysis of this distinctly crystalline mass gave 59.64% of BaO and 40.46% of GeO_2, values which are fairly close to the calculated composition of $BaGeO_3$. Under the microscope the crystals appeared to be octahedral in habit and further examination under the polarizing prism showed them to be isotropic. The crystals are very fragile and possibly metastable. The isometric habit of barium germanate is in agreement with the crystalline form of the naturally occurring metatitanate perovskite ($CaTiO_3$) of analogous chemical composition.

Solubility of Barium Germanate.—An excess of finely-powdered crystals of the barium salt prepared as above was shaken with water for a number of days. Using a thermostatic bath at 25°, 100 g. of the solution saturated at 25° contained 0.07536 g. of $BaGeO_3$.

Summary and Conclusion

1. The neutralization of dilute germanic acid by calcium hydroxide produces a colloidal calcium germanate of unusually high dispersion. Firmly set gels are obtained in which the total anhydrous constituents may constitute as little as 0.065% of the gel mass. Gelation at maximum dilution occurs when acid and base are combined in the $4CaO:3GeO_2$ ratio.

2. Calcium germanate hydrogels ranging from 99.90 to 99.94% of water content are permanent dispersoids if protected from dry air and carbon dioxide. Gels may be kept at least a year without syneresis.

3. The water present in dispersed calcium germanate appears to be simply trapped water, nearly all of which can be removed by pressure or suction filtration. The solid structure or filterable mass is pure or nearly

pure calcium metagermanate. All of the germanium is present in the insoluble or filterable structure if the proportion of calcium hydroxide reaches or exceeds the amount present in the molecular ratio $2CaO:GeO_2$.

4. The water of the hydrogel may be replaced by a number of other liquids such as methyl and ethyl alcohol or acetone and these non-aqueous liquids may in turn be replaced by ethyl ether or benzene, yielding a series of non-aqueous dispersoids which are permanent if protected from evaporation.

5. Excess of lime water gives a very delicate and characteristic test for germanic oxide. A small fraction of a milligram of GeO_2 in 20 cc. of water may be recognized on account of the extraordinarily bulky nature of the hydrogel.

6. Strontium germanate yields a dispersoid similar to the calcium salt but gels are not obtained at dilutions comparable to those used in the preparation of the calcium salt.

7. Barium germanate is distinctly different from the calcium and strontium salts. This salt is very distinctly crystalline and appreciably soluble in water. Crystalline $BaGeO_3$ is formed in shining aggregates, probably octahedral. Under the polarizing prism it is shown to be isotropic.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE UNIVERSITÉ LIBRE DE BRUXELLES, LABORATOIRE DE CHIMIE PHYSIQUE]

NOTE ON THE VACUUM CONTRACTION OF DENSITY BULBS[1]

BY MARCEL BECKERS[2]

RECEIVED MARCH 6, 1929 PUBLISHED JULY 5, 1929

Having undertaken the systematic study from a physicochemical point of view of the easily liquefied saturated hydrocarbons, we have been led to assemble at the start a considerable body of experimental material, in order to free ourselves from anxiety over apparatus problems during the measurements.

We had already calibrated a series of gas density bulbs for our measurements of the weight of a liter of *n*-butane,[3] but as regards contraction on evacuation, the values obtained differed in general by 25% from those calculated by the formula of E. Moles and R. Miravalles.[4]

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[1] This paper contains the results of an investigation carried out as part of Project No. 32 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund donated by the Universal Oil Products Co. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council. Professor J. Timmermans is Director of Project No. 32.

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[3] Beckers, *Bull. soc. chim. Belg.*, **36**, 559 (1927).

[4] Moles and Miravalles, *J. chim. phys.*, **21**, 1 (1924).