

SOME CHEMICAL REACTIONS IN SILICA GELS II. FORMATION OF CRYSTALS OF A BASIC MERCURIC CHLORIDE, $\text{HgCl}_2 \cdot 2\text{HgO}$ ¹

PHILIP F. KURZ

Battelle Memorial Institute, Columbus, Ohio 43201

ABSTRACT

This investigation was concerned with a study of some factors which control the formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in silica gels. It is possible to control the size, shape, color, rate of growth, and distribution of crystals of this basic salt by varying the initial alkalinity of the gel, the silica content of the gel or the rate of infusion of HgCl_2 into the gel. The level in a gel at which $\text{HgCl}_2 \cdot 2\text{HgO}$ crystal start to grow can be controlled readily by adding H^+ to the HgCl_2 used as external reactant. Evidence is presented to show that the basic salt is $\text{HgCl}_2 \cdot 2\text{HgO}$ and not a more basic or a less basic mercuric chloride.

Holmes (1917, 1934) concluded that the shining, dark red-brown crystalline leaves formed when a saturated solution of mercuric chloride was placed on a moderately basic silica gel were one of the basic mercuric chlorides, $\text{HgCl}_2 \cdot 2\text{HgO}$. In somewhat less basic gels, the crystals were scattered in quite remarkable bands; in more strongly basic gels, the crystals were smaller and more compacted.

I have repeated some of Holmes' work and have extended it. Ways have been found to control (1) the size, shape, and regularity of occurrence of crystals or crystal zones, (2) the location in the gel where the formation of crystals will start, (3) the color of the crystals from dark red-brown to near black, (4) the length of crystal fronds and the degree of branching of the fronds, and (5) the rate of growth of the crystals in gels. Evidence is presented that the particular basic chloride pertinent to the present investigation is indeed $\text{HgCl}_2 \cdot 2\text{HgO}$ and not a less basic or a more basic mercuric chloride.

EXPERIMENTAL WORK

The formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ was studied in gels prepared from Philadelphia Quartz Company's Kasil #1, a potassium silicate, and their C, E, and N sodium silicates. Acetic, chloracetic, sulfuric, nitric, tartaric, citric, oxalic, formic, and hydrochloric acids and sodium bicarbonate were used to cause silicate solutions to gel. Most of the gels used were prepared from N sodium silicate and acetic acid.

Table 1 presents the compositions and relative basicities of the several commercial silicate solutions used in the work. The silicic acids are extremely weak acids. Accordingly, even the acid silicates of alkali metals, which all of these commercial silicates are, produce very strongly alkaline solutions because of extensive hydrolysis. Consequently, all of the Na_2O or K_2O in the commercial solutions may be considered to be available and to require neutralization essentially as hydroxyl ion, OH^- . It is evident from the mol ratios shown in table 1 that all of the silicate solutions used contain excess SiO_2 over the amount required to form the metasilicates, Na_2SiO_3 or K_2SiO_3 . The most basic solution was the C silicate which has an approximate empirical composition of $\text{SiO}_2 \cdot \text{Na}_2\text{SiO}_3$ or $\text{Na}_2\text{Si}_2\text{O}_5$. Kasil #1 is the least basic and has an approximate empirical composition of $2.9 \text{SiO}_2 \cdot \text{K}_2\text{SiO}_3$. Similarly, sodium acetate and potassium acetate, salts of a weak acid and strong bases, produce alkaline media on hydrolysis. Consequently, to achieve the same pH or neutralization of an alkali-metal silicate solution, slightly more acetic acid is required than when a stronger acid, such as HCl , for example, is used. Accordingly, the silicate solutions used were not titrated for

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basicity. However, a limit of "neutralization" was established with acetic acid beyond which the basic mercuric chloride under investigation would not form in or on gels. This was done by using increasingly strong acetic acid with identically diluted portions of N sodium silicate solution. For example, with N sodium silicate (4.0 milliequivalents of OH^- per milliliter commercial solution), it was found that in gels prepared by using 4.5 meq of acetic acid per ml of undiluted silicate, none of the basic salt formed. In gels prepared with 3.9 to 4.25 meq of acetic acid per ml undiluted N silicate, the only formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals was outside the gel and occurred only after a prolonged period of time. In gel systems prepared with less than about 3.9 meq of acetic acid per ml undiluted N silicate, $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals formed in the gel in various manners as will be

TABLE I
Composition of some Philadelphia Quartz Company silicate solutions

Product Name*	Weight, Percent		Mols SiO_2 per mol alkali oxide	Grams alkali oxide per ml undiluted solution	Milli- equivalents alkali oxide per ml undiluted solution	Specific gravity (68F)		Nature
	Alkali oxide*	SiO_2^*				Degrees baume*	Grams per ml	
C Sodium silicate	18.00	36.0	2.06	0.304	9.81	59.3	1.69	Opalescent, very viscous
E. Sodium silicate	8.60	27.7	3.32	0.119	3.84	40.0	1.381	Specially clarified syrupy liquid
N Sodium silicate	8.90	28.7	3.32	0.124	4.00	41.0	1.394	Opalescent syrupy liquid
Kasil #1 (Potassium silicate)	8.30	20.80	3.92	0.105	2.23	29.8	1.259	Clear, slightly syrupy liquid

*From Bulletin 17-1, 1963, Philadelphia Quartz Company, Philadelphia, Pennsylvania.

described in the following sections. The basicities described as milliequivalents OH^- after gelling to form basic salt were calculated by subtracting the milliequivalents of OH^- in the silicate solution, using the values shown in table 1 derived from its alkali oxide content.

PREPARATION OF GEL SYSTEMS

Gels were prepared by adding diluted silicate solutions containing 2 to 17 volumes of water per volume of commercial silicate solution to dilute acetic acid ranging from 0.4 to 1N. In some instances, presumably indifferent additives were dissolved in the acid solution before the silicate solution was added. Concentrations of silicate and acid were selected so that the resultant gels would be slightly to fairly strongly basic.

After mixing the components, the gels formed in time and were allowed to set rigidly. In most instances, gelling occurred within 15 min after mixing. However, some of the gels prepared from the more dilute silicate solutions required one or more days to set.

Tables 2, 4 and 5 summarize the compositions of the 80-odd gels, classified in appropriate systems, which were studied showing:

- (1) The type, dilution, and volume of silicate solution
- (2) The type, concentration, and volume of acidic gelling reagent
- (3) The type and concentration of internal indifferent additive present, if any
- (4) The type, concentration, and mode of addition of the external reagent, HgCl_2 or HgBr_2
- (5) The concentration and volume of dilute acetic acid, if any, as an external additive for establishing the level in the gel where the first basic salt crystals could grow.

Groups I, II, and III in table 2 are concerned with silicate-acetic acid gelling-agent systems which produced basic gels and were reacted with HgCl_2 . Included are N silicate-acetic acid gels which were inverted over HgCl_2 solutions or slurries to permit the reaction to proceed by diffusion of HgCl_2 upward and diffusion of OH^- , if any occurs, downward through the gel. Table 3 describes basic N silicate gels formed with acidic agents other than acetic acid and reacted with HgCl_2 . Table 4 describes basic N silicate-acetic acid gels containing indifferent internal additives and reacted with HgCl_2 or HgBr_2 . Table 5 describes simple basic N silicate-acetic acid gels which were reacted with slightly acidic HgCl_2 solutions.

The growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in gels representing each of the six groups in tables 2 through 5 is described in the following sections and is illustrated with photographs of pertinent examples.

I. N Silicate-Acetic Acid Gels With No Internal or External Additives

Group I in table 2 has been subdivided into six subgroups. Each subgroup represents a related series of experiments designed to study one or more of the parameters which control the size, shape, color, branching, and rate of growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in basic N silicate-acetic acid gels reacted with HgCl_2 .

Influence of basicity of gel on growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals.—Figure 1 shows completed reactions to form $\text{HgCl}_2 \cdot 2\text{HgO}$ in gels prepared from N silicate solutions

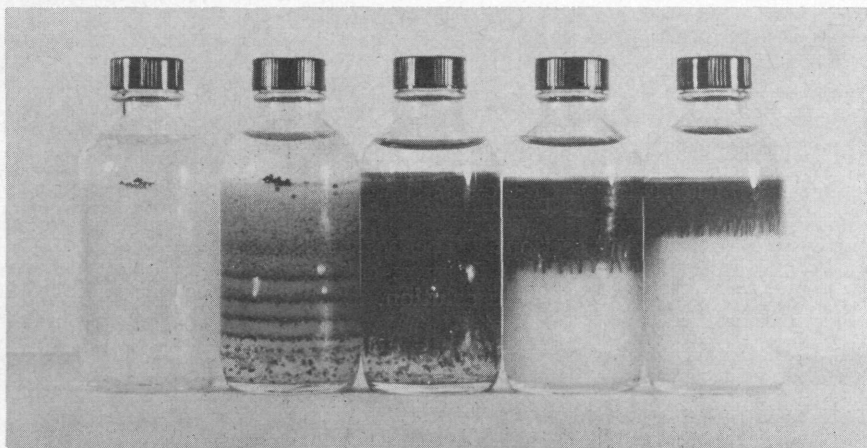


FIGURE 1. Growth of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in gels at five different basicities. All reacted with 3 g of HgCl_2 slurried in water.

	F1-1	F1-2	F1-3	F1-4	F1-5
	F1-1	F1-2	F1-3	F1-4	F1-5
Milliequivalents H^+ per ml undiluted N silicate	4.25	3.5	3	1.75	1.5
Volume H_2O per volume undiluted N silicate	7.5	6	5	2.5	2
Milliequivalents OH^- in silicate	23.5	28.6	33.3	57.2	66.7
0.5 N acetic acid, milliequivalents	25	25	25	25	25
Milliequivalents HgCl_2 in supernatant	22	22	22	22	22
Water in supernatant, milliequivalents	20	20	20	20	20
Milliequivalents OH^- after gelling to form basic salt	-1.5	3.6	8.3	32.2	41.7
Percent of OH^- required by HgCl_2 present	0	12	28	110	142

TABLE 2
Silicate-acetic acid gels used to study the formation and growth of crystals of a basic mercuric chloride

Type	Sodium or potassium silicate solution		Acetic acid to cause gelling		HgCl ₂ used as external reactant, milli-equivalents	Remarks
	Volume ratio water Silicate	Milli-equivalents of OH ⁻	Normality	Milli-equivalents of H ⁺		
<i>Group I—N Silicate-acetic acid gels with no internal or external additives</i>						
N	7.5-2	23.5-66.7	0.5	25	20-22	12 gels at 10 different basicities
N	5	80	0.4-0.6	48-72	37	5 gels at 5 different basicities
N	5	11.3-46.7	0.4-0.6	6.8-42	7.5-15	7 gels at 6 different basicities
N	5	33.3	0.5	25	10	5 gels at same basicity with 5 different rates of HgCl ₂ infusion
N	5-2	16.7-33.3	0.3-0.7	7.5-17.5	0.04-4	10 gels at 7 different basicities used with 4 different rates of HgCl ₂ infusion
N	17-9	16.7-25	0.5	12.5-18.8	7.5-22	3 low silica gels at different basicities and dilutions
<i>Group II—Silicates other than N, gelled with acetic acid</i>						
Kasil #1	3	27.9	0.4-0.5	20-25	22	2 gels at different basicities
C	8.5	58.9	1	43	22	1 gel, basic
E	5	32	0.5	25	4-22	3 gels at same basicity with 3 different rates of HgCl ₂ infusion
E	17	8	0.5	6.3	4-14	3 gels at same basicity with 3 different rates of HgCl ₂ infusion
<i>Group III—N Silicate-acetic acid gels inverted over external reagent</i>						
N	5	11.3	0.5-0.6	8.5-10.2	7.5-11	4 gels, at 3 different basicities
N	5	11.3	0.5	8.5	5	1 gel, basic
N	5-4	12.8-15.4	0.5	10	24	3 gels, at 3 different basicities

TABLE 3
N silicate gels formed with acidic reagents other than acetic acid and used to study the formation and growth of crystals of a basic mercuric chloride

N Sodium-silicate solution		pH lowering agent to cause gelling			HgCl ₂ used as external reactant, milli-equivalents	Remarks
Volume ratio water Silicate	Milli-equivalents of OH ⁻	Agent	Normality	Milli-equivalents of H ⁺		
5	33.3	NaHCO ₃	0.5	25	22	1 gel
5	20-33.3	HCl	0.4 or 0.5	15-25	5-22	3 gels at different basicities. Gels made with 0.5N HCl enhance crystal-band formations
5	33.3	Cl-CH ₂ COOH	0.5	25	22	1 gel
5	20	H ₂ SO ₄	0.5	15	5	1 gel
5	20	HNO ₃	0.5	15	5	1 gel
5	20	H ₂ C ₄ H ₄ O ₆	0.5	15	5	1 gel
5	20	H ₃ C ₆ H ₅ O ₇	0.5	15	5	1 gel
5	16.7	H ₂ C ₂ O ₄	0.5	12.5	5	1 gel Small amount of Hg ₂ Cl ₂ forms on top of gel
5	20	HCOOH	0.5	15	5	2 gels Hg ₂ Cl ₂ forms in and on top of gel

TABLE 4
N silicate-acetic acid gels containing internal indifferent additives and used to study the formation and growth of crystals of a basic mercuric chloride

N Sodium-silicate solution		Acetic acid to cause gelling		Internal indifferent additive			External reagent		Remarks
Volume ratio water	Milli-equivalents of OH ⁻	Normality	Milli-equivalents of H ⁺	Additive	Normality	Milli-equivalents	Reagent	Milli-equivalents	
Silicate									
5	33.3	1	25	Na ₂ SO ₄	2	50	HgCl ₂	50	1 gel, basic
5	33.3	1.25	31.3	KBrO ₃	Saturated	ca. 12	HgCl ₂	26	1 gel, basic
5	33.3	1	25	NaF	1	25	HgCl ₂	26	1 gel, basic
5	33.3	1	25	KCl	1	25	HgBr ₂	17	1 gel, basic
5	16.7 or 66.7	1	12.5 or 50	KCl	1	25	HgCl ₂	4.5 or 50	2 gels, basic; 1 reacted with HgCl ₂ , slurried with water, the other reacted 9 times with 1/10 saturated HgCl ₂
5	16.7	1	12.5	KI	0.001 to 0.1	0.01 to 1.3	HgCl ₂	4 to 15	6 gels, all basic; 2 reacted with HgCl ₂ , slurried with water, 4 reacted with 1/10 saturated HgCl ₂
5	33.3	0.5	25	Sucrose	2 gm	6	HgCl ₂	26	1 gel, basic

of different dilutions and 0.5N acetic acid. Each gel was reacted with 3 g of HgCl₂ slurried in 20 ml of water. The net basicities of the gel-forming mixtures ranged from slightly acidic to fairly strongly basic. As shown in Gel F1-1, the slightly acidic system permits a few glistening black crystals of HgCl₂·2HgO to form in the supernatant liquor. No crystals formed in the gel proper. Gel F1-2 was initially slightly basic and, after reaction with HgCl₂ had a few black crystals of HgCl₂·2HgO in the supernatant liquor; numerous crystals grew within the gel. Randomly dispersed in the upper half of the gel are a few relatively large crystals and a myriad of much smaller ones. In the lower half of this gel are five well-defined bands of crystals, below which is one roughly defined crystal band and a number of moderately sized random crystals near the bottom of the gel.

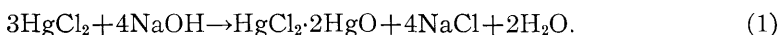
Further increase in initial basicity produced a remarkable change in crystal form and size, as shown in Gel F1-3. No loose crystals formed in the supernatant liquor and the top of the gel is covered with adherent orange-brown microcrystals.

TABLE 5
Basic silicate-acetic acid gels reacted with slightly acidic HgCl₂ in experiments to grow crystals of a basic mercuric chloride

N Sodium-silicate solution		Acetic acid to cause gelling		HgCl ₂ used as external reactant, milli-equivalents	Acetic acid used as external additive		Remarks
Volume ratio water	Milli-equivalents of OH ⁻	Normality	Milli-equivalents of H ⁺		Normality	Milli-equivalents	
Silicate							
5	16.7	0.5	12.5	30	0.1	1	1 gel, basic; supernatant slight acidic
5	16.7	0.5	12.5	4.5	0.5, 1 or 2	0.5, 1.2, or 2	3 gels, all basic; supernatants slightly acidic

In the top $\frac{3}{4}$ inch of the gel are perhaps 10 roughly defined bands of small black crystals. Below these bands are numerous roughly parallel, slightly branched, black, kelp-like fronds, some up to $1\frac{1}{2}$ inches long. In the bottom $\frac{3}{8}$ inch of the gel are a number of random leaf-like black crystals.

Gels, not shown in figure 1, prepared with 3.33 or 2.75 meq of acid per ml undiluted N silicate, produced crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which were quite similar to those formed in Gel F1-3. Still further increase in initial basicity produced the results shown in Gels F1-4 and F1-5. The tops of these gels are covered with light tan microcrystals. Immediately below are three bands of small, dark, red-black crystals and a narrow crystal-free band. Below the clear band are narrow, roughly parallel, increasingly short (with increasing basicity), essentially vertical, black fronds of $\text{HgCl}_2 \cdot 2\text{HgO}$ which extend only part of the way to the bottom of the gel. Gels F1-4 and F1-5 contained substantially more than enough OH^- after gel formation to form $\text{HgCl}_2 \cdot 2\text{HgO}$ with all of the HgCl_2 infused from the supernatant. The reaction to form this basic mercuric chloride may be written as follows:



The crystal zones in Gels F1-4 and F1-5 may be relatively shallow partially because of diffusion of OH^- from the lower to the upper half of the gel. The question of migration of OH^- in gel systems is being studied currently and will be discussed in part later in this paper and in more detail in a subsequent paper when more definitive results are available.

Crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ did not appear in the supernatant of Gel F1-1 until the entire gel-supernatant reactant system was approximately equilibrated. The slight basicity required may have resulted from infusion of H^+ into the gel from the supernatant or from hydrolysis of sodium acetate which was formed when the gel was prepared.

Three grams of HgCl_2 are approximately 22 meq. Equation (1) shows that approximately 29.3 meq of OH^- are required to convert this amount of HgCl_2 to $\text{HgCl}_2 \cdot 2\text{HgO}$. Consequently, in this series, only Gels F1-4 and F1-5 contained an excess of OH^- after gelling to react with all of the HgCl_2 infused from the supernatant slurry. Gels F1-1, F1-2, and F1-3 all contained large excesses of unreacted HgCl_2 after termination of the reaction to form $\text{HgCl}_2 \cdot 2\text{HgO}$. Summarizing the results of the experiments with this related series of gels, it was found that:

- (1) A slightly acidic gel system (F1-1) produced no crystals in the gel and only a few loose crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in the supernatant liquor.
- (2) Slightly basic gels, where about 12 per cent (F1-2) to 20 per cent (not shown in figure 1) of the OH^- theoretically required to form $\text{HgCl}_2 \cdot 2\text{HgO}$ was present after gelling, favored the formation of the crystals in bands. In the more basic of these two systems, the bands consisted of short fronds rather than smaller leaf-like crystals.
- (3) In moderately basic gels where about 24 per cent (not shown in figure 1), 28 per cent (F1-3), or 38 per cent (not shown in figure 1) of the OH^- theoretically required to form the basic salt was present after gelling, the predominant feature of the crystal growth was the formation of long, roughly parallel, frond-like, shining black leaves with only relatively minor branching.
- (4) In more strongly basic gels, where about 50 per cent (not shown in figure 1), 86 per cent (not shown in figure 1), 110 per cent (F1-4), or 142 per cent (F1-5) of the required amount of OH^- was present after gelling, the predominant feature of the crystal growth, as basicity increased, was the formation of successively shorter, more densely packed, narrower, roughly parallel, essentially vertical, glistening black fronds.

as is normal for this type of basic gel. The long fronds in the lower $\frac{2}{3}$ of the gel are branched increasingly from top to bottom. Some are fan-shaped and are iridescent in their lower $\frac{1}{2}$ inch; others give rise to branched needles at their lower extremities. Fan-shaped branching and iridescence were not observed in gels reacted with room-temperature HgCl_2 solutions or slurries.

Gel F2-3 was reacted with 20 ml of a room-temperature saturated solution of HgCl_2 , about 0.5 N. In this system, the 8.3 meq of OH^- presumably available for reaction after gelling were about 62 per cent of the basicity theoretically required to form $\text{HgCl}_2 \cdot 2\text{HgO}$ with the HgCl_2 used. The top of Gel F2-3 is covered with light tan microcrystals. Below is a zone about $\frac{1}{2}$ inch deep containing small black crystals, then a zone about $\frac{3}{4}$ inch deep containing short, narrow black fronds to $\frac{1}{2}$ inch in length. The bottom $1\frac{1}{2}$ inches of gel contain magnificent, random, feathery, black fronds which curve about in various convolutions, some extending almost to the bottom of the gel. The growth of these large fronds in the lower half of the gel was quite slow and occurred after what was thought, at first, to be the approximate termination of crystal growth had been reached.

Gel F2-4 was reacted with 10 successive 20-ml portions of 1/10 saturated HgCl_2 solution, about 0.05 N. Each "spent" portion of external reactant was replaced with a fresh 20-ml portion after being over the gel about 1 week. Gel F2-4, like Gel F2-3, contained about 62 per cent of the OH^- required theoretically to form $\text{HgCl}_2 \cdot 2\text{HgO}$ with the approximately 10 meq of HgCl_2 placed on the gel in ten successive 1-meq portions. Notable in its absence in Gel F2-4 is the tan to red-brown top and the 8 or more bands of tiny black crystals which formed in other gels of this series of four. Instead, in Gel F2-4, there was a tendency to form fronds which are small near the top of the gel, considerably larger about 1 inch below the top, and, in the middle $\frac{1}{3}$ of the gel, to develop needle-like branches and considerable curvature. The lower $\frac{1}{3}$ of the gel contains no crystals.

The four originally identical basic gels in this related series, shown reacted in figure 2, illustrate the remarkable effects on the size, shape, and extent of branching which result from variations in the amount, concentration, and initial temperature of the external reagent, HgCl_2 . It is evident that, by using manifold successive portions of a dilute solution of HgCl_2 , it is possible to eliminate the tan to red-brown, powder-like microcrystalline material which usually forms on gels of the initial basicity pertinent to this series and also to enhance the growth of frond-like, highly-branched, black leaves from the beginning to the termination of crystal growth in the gel.

Modestly basic gels reacted with excess HgCl_2 slurried with water.—The purpose of this portion of the work was to establish more precisely the approximate basicity of gels which favored or which inhibited the formation of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in tiers or bands, and the approximate basicity of gels in which the fronds shortened and the crystal zone did not extend to the bottom of the gel. Table 6 summarizes the compositions of a series of five originally slightly to moderately basic gels, prepared by mixing equal volumes of dilute N silicate solution and acetic acid solutions ranging from 0.6 to 0.4N. All five gel systems were reacted identically with 5 g of HgCl_2 crystals slurried with 5 ml of water. In all five instances, this amount of external reactant was in excess of the HgCl_2 theoretically required by reaction (1) to form $\text{HgCl}_2 \cdot 2\text{HgO}$. The amount of OH^- presumed to be available after gelling, as given in table 6, represents about 17 to 68 per cent of the OH^- required to form the basic salt in question in the five gels in this series.

As was expected from earlier experience, the least basic gel, designated T6-1, fostered the growth of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ primarily in bands below the top $\frac{3}{4}$ inch of the gel, in which zone the numerous crystals are small, randomly distributed. Below, there formed 12 well defined bands of crystals in the lower $3\frac{1}{2}$ inches of the gel. The crystals in each band are successively larger than in the bands above.

In Gel T6-2, the next least basic gel, the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ were increasingly larger from top to bottom, discrete, branched, and black. In the bottom 2 inches of the gel, there was evidence of a vestigial banding tendency, but this was not as well defined as in gels which were less basic.

In Gel T6-3, the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which formed were discrete, not segregated in bands, branched, and black. They increased progressively in size and extent of branching from the top to the bottom of the gel.

Crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which formed in Gels T6-4 and T6-5 were quite similar. Long, roughly parallel, black fronds with short branches formed only in the top $2\frac{1}{2}$ to 3 inches of the gels. Below the zone of long fronds, the formations of basic salt crystals were glistening, black, leaf-like shorter fronds with longer branches, and essentially random in distribution and orientation. As might be

TABLE 6

Summary of pertinent conditions in five different basic N silicate gels, all reacted with an excess of HgCl_2 crystals slurried with water

	T6-1	T6-2	T6-3	T6-4	T6-5
Milliequivalents H^+ per ml undiluted silicate	3.6	3.3	3.0	2.7	2.4
Volume H_2O per volume undiluted N silicate	5	5	5	5	5
Milliequivalents OH^- in silicate	80	80	80	80	80
N acetic acid	0.6	0.55	0.5	0.45	0.4
Milliequivalents H^+	72	66	60	54	48
Milliequivalents HgCl_2 in supernatant	37	37	37	37	37
Water in supernatant, ml	5	5	5	5	5
Milliequivalents OH^- after gelling to form basic salt	8	14	20	26	32
Percent of OH^- required by HgCl_2 present	17	30	42	55	68

expected in these more basic gels, where substantial amounts of OH^- were available to form the basic salt in the presence of an excess of HgCl_2 , there were fewer, though larger, crystals formed near the bottom of the gel. Apparently a definite excess of OH^- is required in the reaction system to cause termination of crystal growth noticeably above the bottom of the gel. These results suggest also that the diffusion of Hg^{++} through the gel is rapid, relative to the diffusion, if any, of OH^- in a basic gel where the equilibrium has been disturbed, as by the consumption of OH^- by HgCl_2 to form a basic salt.

Basic gels reacted with manifold portions of 0.05N HgCl_2 solution.—Figure 3 shows completed reactions to form $\text{HgCl}_2 \cdot 2\text{HgO}$ in a related series of five originally basic gels and one slightly acidic gel, which were reacted with seven successive 10-ml portions of 1/10 saturated HgCl_2 solution. The purpose of this series of experiments was to observe the effect on crystal growth of using a dilute solution of HgCl_2 as the external reactant over gels ranging from slightly to moderately strongly basic. Crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ formed in various ways in the diverse basic gels; as expected, none formed in the one acidic "control" system. In three of the five basic gels, there was present at the beginning of the reaction more than enough OH^- to react with the 3.5 meq of Hg^{++} placed on the gels in seven successive 0.5 meq portions. The least basic gel contained about 36 per cent of the OH^- theoretically required by reaction (1) to react with the total HgCl_2 infused. The acidic "control" gel patently could not support the growth of crystals of the basic salt.

Gel F3-1 contains over four times the OH^- required to form $\text{HgCl}_2 \cdot 2\text{HgO}$ with

3.5 meq of HgCl_2 . Practically all of the crystals of basic salt which form are in the supernatant liquor and in a narrow band at the top of the gel.

Gel F3-2 contains about two times the OH^- required to convert HgCl_2 to $\text{HgCl}_2 \cdot 2\text{HgO}$. In this system only a few crystals of the basic salt formed in the supernatant liquor and the growth in the gel consists of three narrow bands of reddish-brown microcrystals and one underlying band of larger, but still small, shining black crystals.

Gel F3-3 contains about 1.3 times the OH^- required to convert the HgCl_2 to the basic salt. In this system there are no crystals in the supernatant liquor. The top of the gel is reddish-brown mottled with black and the growth of fronds

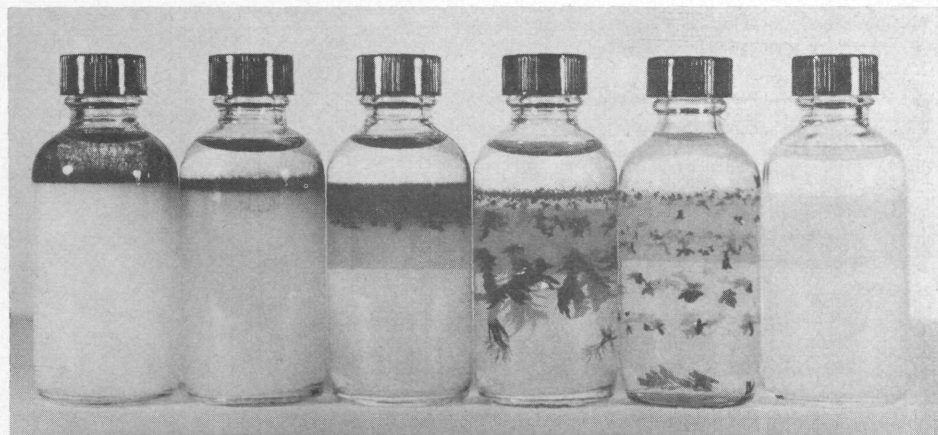


FIGURE 3. Growth of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in five different basic gels using successive portions of 0.05N HgCl_2 solution as the external reactant.

	F3-1	F3-2	F3-3	F3-4	F3-5	F3-6		
			F3-1	F3-2	F3-3	F3-4	F3-5	F3-6
Milliequivalents H^+ per ml undiluted N silicate			1.5	1.8	2.4	3	3.6	4.5
Volume H_2O per volume undiluted N silicate			2	5	5	5	5	5
Milliequivalents of OH^- in silicate			33.3	16.7	16.7	16.7	16.7	16.7
N acetic acid			0.5	0.3	0.4	0.5	0.6	0.75
Milliequivalents of H^+			12.5	7.5	10	12.5	15	18.8
Milliequivalents HgCl_2 in supernatant			3.5	3.5	3.5	3.5	3.5	3.5
Milliequivalents OH^- after gelling to form basic salt			20.8	9.2	6.7	4.2	1.7	-2.1
Percent of OH^- required by HgCl_2 present			435	197	134	90	36	0

of glistening black crystals is confined to the top $\frac{1}{2}$ inch of the gel. The fronds are small at the top and widen with some branching toward their lower extremities.

Gel F3-4 originally contained about 90 per cent of the amount of OH^- theoretically required to convert the HgCl_2 to $\text{HgCl}_2 \cdot 2\text{HgO}$. In this gel, a narrow band of small black crystals grew in the top $\frac{1}{8}$ inch of the gel. Below this was a second band of crystals about $\frac{1}{4}$ inch deep of larger, lustrous, black crystals. Then, extending to within about $\frac{3}{8}$ inch of the bottom, there formed magnificent random, shining black crystals, some of which were kelp-like, others of which were highly branched, and still others from which needle-like tentacles extended laterally and downward.

Gel F3-5, the least basic one in this series, contained only about 36 per cent of the OH^- needed to convert all of the HgCl_2 infused to the basic salt. This gel system promoted the formation of lustrous, black crystals in five distinguishable bands: one band of small crystals at the top of the gel, one of larger crystals near the bottom, and three approximately equally spaced intermediate bands. In Gel F3-5, the crystals in many instances resembled butterflies, other insects, or crustacea in shape.

Influence of silica concentration on growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals.—Table 7 summarizes the experimental conditions for a series of three basic gels prepared to observe the influence of the concentration of silica in the gel on the shape, color, and distribution of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ formed when an excess of HgCl_2 was infused into each of these systems.

Gel T7-1, shown reacted as Gel F1-3 and also as Gel F2-1, illustrates the formation of long, essentially parallel, glistening streamers of black $\text{HgCl}_2 \cdot 2\text{HgO}$, with only minor branching, which occurs in this relatively silica-rich gel.

TABLE 7
Summary of pertinent conditions in three basic N silicate gels containing different amounts of silica and all reacted with an excess of HgCl_2 crystals slurried in water

	T7-1	T7-2	T7-3
Milliequivalents H^+ per ml undiluted N silicate	3	3	3
Volume H_2O per volume undiluted N silicate	5	9	17
Milliequivalents OH^- in silicate	33.3	25	16.7
0.5N acetic acid, milliequivalents	25	18.8	12.5
Milliequivalents HgCl_2 in supernatant	26	22	15
Water in supernatant, ml	20	20	20
Milliequivalents OH^- after gelling to form basic salt	8.3	6.2	4.2
Percent of OH^- required by HgCl_2 present	24	21	21

Gel T7-2 contains about 60 per cent as much silica as does Gel T6-1. The crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which grew in T7-2 are considerably smaller and the streamers are shorter, less parallel, and more randomly disjointed and oriented, but somewhat more branched than those in Gel T7-1. Furthermore, the crystals in Gel T7-2 appear reddish-brown, possibly indicating coexistence of both the red and the black forms of $\text{HgCl}_2 \cdot 2\text{HgO}$ in the microcrystals, whereas those in Gel T7-1 appear black.

Gel T7-3 contains only about $\frac{1}{3}$ as much silica as does Gel T7-1 and just a little more than half as much silica as does Gel T7-2. Gel T7-3 requires several days to set, is only very slightly opalescent, and is quite "jiggly" when first formed. Infusion of HgCl_2 into this basic gel reduced its basicity by forming $\text{HgCl}_2 \cdot 2\text{HgO}$, and the gel became more rigid as the reaction between HgCl_2 and OH^- progressed, and the entire system became relatively more acidic as OH^- was consumed. The crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which grew in Gel T7-3 are reddish brown and highly glistening. The top $\frac{1}{2}$ inch of the gel contains numerous small crystals, which appear to be clusters of branched needles. Below this are highly branched streamers ranging in length from 1 to 2 inches. Some of the streamers show secondary branching from the main branches. At the bottom of the gel are random butterfly-like crystals which are generally not branched.

The results observed in this series suggest that, in these moderately basic gels,

there may be little or, at least, limited migration of OH^- in the gel and that the Hg^{++} ions must seek out the OH^- absorbed, adsorbed, or reacted on the silica skeleton of the gel. Other evidence for this will be presented in a later section of this paper.

II. Influence of Type of Silicate Used to Prepare Gel

In addition to the N sodium silicate, three other silicates, including E and C sodium silicates and Kasil #1, a potassium silicate, were used in preparing basic gels for studying the formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals. It was found that, in basic gels made with each of these silicates, just as has been described for N silicate gels, the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals could be in discrete bands, long fronds, or random large leaves according to the degree of basicity of the gel, the concentration of silica in the gel, or the rate of infusion of HgCl_2 into the gel. Accordingly, it is concluded that the nature of the commercial silicate—sodium or potassium salt, very viscous solution such as C silicate or specially clarified material such as E silicate—essentially has no influence on the size, shape, etc., of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals which grow in basic gels prepared from the various silicates.

Figure 4 illustrates completed reactions to form $\text{HgCl}_2 \cdot 2\text{HgO}$ in five originally

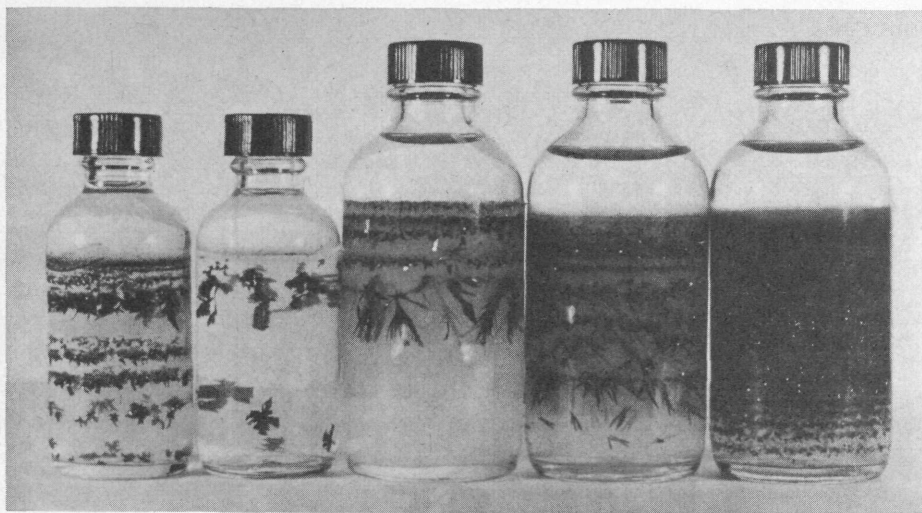


FIGURE 4. Growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in basic E silicate gels at two different silica concentrations and with different rates of infusion of HgCl_2 into the gels.

	F4-1	F4-2	F4-3	F4-4		F4-5	
	F4-1	F4-2	F4-3	F4-4	F4-3	F4-4	F4-5
Milliequivalents H^+ per ml undiluted E silicate	3	3	3	3	3	3	3
Volume H_2O per volume undiluted E silicate	17	17	5	5	5	5	5
Milliequivalents of OH^- in silicate	8	8	32	32	32	32	32
0.5N acetic acid, milliequivalents	6.3	6.3	25	25	25	25	25
Milliequivalents HgCl_2 in supernatant	4(2 x 10 ml ca. 0.2N)	2(4 x 10 ml ca. 0.05N)	4(4 x 20 ml ca. 0.05N)	8(4 x 20 ml ca. 0.1N)	8(4 x 20 ml ca. 0.1N)	22(3 g $\text{HgCl}_2(\text{s})$)	22(3 g $\text{HgCl}_2(\text{s})$)
Water in supernatant, ml	—	—	—	—	—	—	20
Milliequivalents OH^- after gelling to form basic salt	1.7	1.7	7	7	7	7	7
Percent of OH^- required by HgCl_2 present	32	64	130	65	65	65	24

moderately basic gels prepared with E silicate solution and acetic acid. The crystals in the gels in figure 4 show that, by varying silicate concentration and/or the rate of infusion of HgCl_2 into the gels, $\text{HgCl}_2 \cdot 2\text{HgO}$ grows in E silicate gels essentially as it does in similar N silicate gels.

Gels F4-1, F4-2, F4-4, and F4-5 were reacted with excess HgCl_2 , and Gel F4-3 with only about $\frac{3}{4}$ the amount of HgCl_2 required for formation of the basic salt. In Gels F4-1, F4-2, F4-4, and F4-5, the zone of crystal growth ranges from the top to the bottom of the gels. All five gels show banding, which is characteristic of the formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in gels prepared with 3 meq of acetic acid per ml of undiluted E silicate. As with similar reactions in N silicate gels, the gels in figure 4 show that, at relatively high rates of infusion of HgCl_2 into the gel, more and smaller crystals of basic salt form and, vice versa, at relatively low rates of HgCl_2 infusion, fewer and larger crystals form. Compare particularly Gels F4-3 and F4-5, which are relatively silica-rich gels; likewise Gels F4-1 and F4-2, which are relatively silica-poor gels.

Gel F4-1 has three bands of small crystals and one band of much larger, unbranched, dark reddish-black leaves, all resulting from the first two milliequivalent portion HgCl_2 solution used as supernatant reactant. In the bottom half of Gel F4-1 are five bands of crystals, spaced increasingly farther apart from top to bottom, formed by the second 2-meq portion of HgCl_2 solution used. The top band in this series of five consists of small, near-black crystals; the other four bands consist of somewhat larger crystals of approximately uniform size. Many of the crystals in the lower four bands resemble winged larvae, tiny butterflies, starfish, or crustacea.

Gel F4-2 fostered the growth of two bands of large crystals, one in the upper third of the gel resulting from the first two 0.5-meq portions of 0.05 N HgCl_2 solution as supernatant reactant, the other in the bottom third of the gel resulting from the third and fourth 0.5-meq portions of HgCl_2 solutions used. The crystals in the top third of Gel F4-2 are dark reddish-black and resemble miniature lobsters in general configuration. The crystals in the bottom third of the gel are clusters of leaves which somewhat resemble jackstones in general shape.

Gel F4-3 has five bands of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$, all within the top 60 per cent of the gel. The four top bands of this series of five are composed of relatively small crystals of a variety of shapes including leaves, stars, clusters, and non-descript forms. The lowest band of the five is composed of feather-like crystals joined into clusters at their upper ends and ranging from about $\frac{1}{2}$ to nearly 1 inch in length.

Gel F4-4 is a system in which the reactants approximated $\frac{2}{3}$ the stoichiometric quantities required for the formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ in accordance with equation (1). In this gel eight bands of crystals are distinguishable, including one of small crystals at the top of the gel. Directly below this is a band of clustered feather-like crystals in which individual fronds are up to $\frac{1}{4}$ inch long. Next below are two bands of small crystals which resulted from the placement of the second 20-ml portion of 0.1 N HgCl_2 on the gel. Then, below, are four bands of clusters of feathery crystals extending to within $\frac{1}{2}$ inch of the bottom of the gel. Some of the individual feathers in these bands are up to $\frac{1}{2}$ inch in length. Finally, in the bottom $\frac{1}{2}$ inch of the gel, are random H-shaped clusters of smaller, essentially rectangular platelets.

Gel F4-5 was reacted with approximately a threefold excess of HgCl_2 crystals slurried in water as the supernatant external reactant. In this gel, the presence of a large excess of HgCl_2 caused the formation of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals to proceed relatively rapidly. The top of Gel F4-5 contains very small, light reddish-brown crystals, below which are about 10 bands of small black crystals in a zone about $\frac{1}{2}$ inch deep. Then, in the lower 2 inches of the gel are eleven bands of crystals all of which are about the same size, except in the three topmost bands of the

eleven where random clusters of narrow, reddish-brown, feathery crystals up to $\frac{1}{2}$ inch long are found. In general, however, the predominant feature of the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in this moderately basic E silicate gel is the banding.

The crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ grown in the five gels in this series illustrate the marked differences in crystal size, shape, and distribution which can be achieved in E silicate gels of approximately equal initial basicities by (1) varying the silicate content of the gels, and (2) controlling the rate of admission of HgCl_2 into the basic gel by varying the concentration of this reactant in the supernatant solution.

III. *Influence of Type of Acid or Acid Salt Used to Prepare Gel*

As shown in table 3, hydrochloric, sulfuric, nitric, tartaric, citric, oxalic, formic, and chloroacetic acids and sodium bicarbonate, as well as acetic acid, were used to prepare basic gels with N sodium silicate. Work with acids other than acetic and with acid salts as gelling agents has been limited. Results obtained with the acidic materials tried showed unusual effects only with HCl (enhanced banding of crystal formation), HCOOH (substantial reduction of HgCl_2), and $\text{H}_2\text{C}_2\text{O}_4$ (minor amount or HgCl_2 reduced to Hg_2Cl_2). This suggests that, barring hydrochloric acid and strongly reducing acids, such as formic or oxalic, for example, and acid ammonium salts which form white complexes with HgCl_2 , most acidic materials will form basic gels with N sodium silicate, which will promote and sustain the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals very similar to those grown in gels prepared with acetic acid.

IV. *Influence of Internal Indifferent Additives*

As shown in table 4, sucrose and five different anions were incorporated intentionally in separate basic N silicate-acetic acid gels. The presumably indifferent additives, in addition to sucrose, included sodium sulfate, potassium bromate, sodium fluoride, potassium chloride, and potassium iodide. Gels containing I^- as the indifferent anion produced the most remarkable effects. They were studied more in detail and will be discussed separately in the next section.

Table 8 presents pertinent data for seven basic N silicate gel systems containing indifferent internal additives. These gels were reacted with HgCl_2 or HgBr_2 . In all seven systems, an excess of mercuric salt was infused into the gel. Six of the gels had identical moderate initial basicities. Gel T8-5, containing KBrO_3 as the indifferent salt, was only slightly basic. Crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ formed from top to bottom in all seven gels. All of the reacted gels showed some effect of the indifferent additive on the size, shape, or distribution of the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which formed.

Gel T8-1, containing 25 meq of F^- , showed no banding effects, but fostered the growth of a myriad of randomly dispersed, discrete, small black crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$, as compared to the long black streamers with short branches which formed in Gel F1-3, an identically basic gel, containing no F^- .

Gel T8-2, containing 50 meq of Cl^- and reacted with a large excess of HgCl_2 crystals slurried with water, has a thin brown formation of microcrystals on the surface of the gel. Immediately below this is a band about $\frac{1}{4}$ inch deep of very small, discrete black crystals. Then comes a $\frac{3}{8}$ -inch-deep band of larger, but still small, black crystals. Next below are three $\frac{1}{8}$ - to $\frac{1}{4}$ -inch bands of mixed very small and small crystals, then two $\frac{1}{8}$ -inch bands of small crystals, a band of clusters of crystals up to $\frac{1}{4}$ inch in length, and finally, in the bottom $1\frac{1}{2}$ inches of gel, randomly scattered clusters of unbranched, needle-like black crystals, some of which are flat and resemble sea purses, others of which have three dimensional star shapes. Evidently the presence of excess Cl^- in a basic gel in which crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ are growing (1) causes banding, (2) enhances the formation of clusters of needles, (3) prevents the formation of streamers, and (4) suppresses branching.

Gel T8-3 also contained Cl^- as an indifferent additive, but this gel was reacted with 9 successive 10-ml portions of 1/10 saturated HgCl_2 solution. Each portion of external reactant solution was replaced in turn at intervals of 3 to 17 days by a fresh 10-ml portion of HgCl_2 solution. In reacted Gel T8-3, no brown microcrystals formed in the surface of the gel. The top $\frac{1}{4}$ inch of the gel contains two bands of small crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$. Below this in a $\frac{3}{4}$ -inch depth are three bands of clusters of unbranched needles, some up to $\frac{1}{2}$ inch long and a few extending downward and terminating in forked ends. In the bottom $1\frac{1}{2}$ inches of the gel are several randomly distributed clusters of thin needles, some nearly parallel in the cluster, others diverging in three dimensions. Gel T8-3 shows essentially the same effects of the presence of Cl^- on the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ as were summarized under Gel T8-2 above.

TABLE 8
Summary of pertinent conditions in seven basic N silicate gels containing internal indifferent additives and reacted with HgCl_2 or HgBr_2 slurried in water

	T8-1	T8-2	T8-3	T8-4	T8-5	T8-6	T8-7
Indifferent additive	NaF	KCl	KCl	KCl	KBrO_3	Na_2SO_4	Sucrose
Milliequivalents additive in gels	25	50	12.5	25	ca. 12	50	6
Milliequivalents H^+ per ml undiluted N silicate	3	3	3	3	3.75	3	3
Volume H_2O per volume undiluted N silicate	5	5	5	5	5	5	5
Milliequivalents OH^- in silicate	33.3	66.7	16.7	33.3	33.3	33.3	33.3
N acetic acid	1	1	1	1	1.25	1	1
Milliequivalents H^+	25	50	12.5	25	31.5	25	25
External reactant	3.5 g HgCl_2	6.8 g HgCl_2	9 x 10 ml 0.05N HgCl_2	3 g HgBr_2	3.5 g HgCl_2	6.8 g HgCl_2	3.5 g HgCl_2
Milliequivalents of Hg^{++} salt in supernatant	26	50	4.5	16.6	26	50	26
Water in supernatant, ml	20	20	20	20	20	20	20
Milliequivalents of OH^- available after gelling to form basic salt	8.3	16.7	4.2	8.3	2	8.3	8.3
Percent of OH^- required by Hg^{++} salt present	24	25	70	37	6	13	24

Gel T8-4, containing Cl^- as the internal indifferent additive and reacted with a substantial excess of HgBr_2 as the external reactant, produced unusual results. Only 1 band of small black crystals formed, about $\frac{3}{16}$ inch below the top of the gel. A number of random crystals formed near or at the surface of the gel, but none are loose in the supernatant liquor. Numerous small (less than $\frac{1}{16}$ inch) pseudospherulitic aggregates of microcrystals are dispersed randomly through the lower $2\frac{1}{2}$ inches of the gel. All of the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which formed in Gel T8-4 appear to be randomly shaped aggregates, none larger than $\frac{1}{16}$ inch in any dimension, of very small crystals; microscopic examination shows them to be spherulites. The presence of Br^- , in basic gels where $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals are growing, appears to (1) limit banding drastically, (2) prevent streamer, needle, cluster, or leaf formation, and (3) promote the formation of pseudospherulitic aggregates of microcrystals.

Gel T8-5, only slightly basic, containing BrO_3^- internally and reacted with a large excess of HgCl_2 , produced unusual results also. Loose, glistening, crustacea-like, black crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ up to $\frac{1}{4}$ inch in size formed in the supernatant

liquor. Likewise, a few random black crystals identical to those in the supernatant formed in the top $\frac{1}{4}$ inch of the gel. Below this, and extending $2\frac{1}{2}$ inches to the bottom of the gel, are 12 distinguishable bands of random-shaped aggregates of microcrystals. None of the aggregates exceeds $\frac{3}{8}$ inch in size. The formation of loose crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in the supernatant liquor and the formation of bands of crystals in the gel are characteristic of slightly basic gels and are not attributed exclusively to the presence of BrO_3^- in the gel, although some of the banding tendency shown in Gel T8-5 may be charged to the influence of BrO_3^- . It is evident that the inclusion of BrO_3^- in a basic gel which is reacted with an excess of HgCl_2 (1) limits drastically the size of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals which form, (2) prevents the formation of fronds, needles, clusters, etc., and (3) enhances the formation of small pseudospherulitic aggregates of very small crystals.

Gel T8-6, containing SO_4^- and reacted with a large excess of HgCl_2 crystals slurried in water, has a number of loose, very slightly yellow, glistening crystals in the supernatant liquor. These may be crystals of a basic mercuric sulfate or of a less basic mercuric chloride, $2\text{HgCl}_2 \cdot \text{HgO}$ or $\text{HgCl}_2 \cdot \text{HgO}$, for example. No identification by analysis has been made. The surface of the gel has an adherent reddish-brown deposit of microcrystals. The top $\frac{1}{4}$ inch of the gel contains only a few small, random black crystals. Below this and extending to the bottom of the gel are small crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in twelve distinguishable bands, including one band about $\frac{1}{2}$ inch deep at the top of the series, one about $\frac{1}{4}$ inch deep at the bottom, and ten bands each about $\frac{1}{8}$ inch deep in between the extreme bands. The crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in Gel T8-6 are of a variety of shapes including fronds, leaves, clusters, crustacea-like aggregates, and needles. Accordingly, aside from promoting the formation of loose, pale-yellow, crystals in the supernatant liquor, the major influence of SO_4^- on the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals appears to be (1) promote banding and (2) to inhibit the growth of crystals larger than about $\frac{1}{4}$ inch in any dimension.

Gel T8-7, containing sucrose and reacted with a large excess of HgCl_2 , has loose, fine white crystals in the supernatant. These may be mercurous chloride resulting from the reduction of HgCl_2 by reducing sugars present in the sucrose, which could have effused from the gel into the supernatant liquor, or they may be crystals of one of the less basic mercuric chlorides, $2\text{HgCl}_2 \cdot \text{HgO}$ or $\text{HgCl}_2 \cdot \text{HgO}$, for example. The top surface of the gel contains adherent, reddish-brown microcrystals. The gel proper contains about 17 distinguishable bands of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$, including a band about $\frac{1}{4}$ inch deep at the top of the gel which may be considered to consist of ten or so very closely spaced bands of very small crystals. In general, in Gel T8-7, the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ show gradual increases in size in successively lower bands, and some in the lowermost bands approach $\frac{1}{4}$ inch in their largest dimension. Crystals of all previously mentioned shapes are detectable in one band or another, including leaves, fronds, needles, clusters, etc. Accordingly, the major influences of the presence of sucrose on the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ in gels appear to be (1) to promote the formation of crystals in bands and (2) to limit the size of the crystals.

V. *Influence of Iodide as Internal Indifferent Anion on Growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ in Basic Gels*

The addition of I^- to basic gels intended for reaction with HgCl_2 produced most remarkable effects on the size, shape, and distribution of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals growing in such modified gels.

Figure 5 illustrates completed reactions in six initially basic N silicate gels containing from 0.00025 to 0.025 meq of I^- per ml of gel and reacted with HgCl_2 in two different manners.

Gel F5-1 contained only 0.25 microequivalents of I^- per ml of gel and was reacted with nine successive 10-ml portions of $\frac{1}{10}$ saturated HgCl_2 solution. The

presence of even this miniscule amount of I^- in the gel influenced the growth of $HgCl_2 \cdot 2HgO$ in the gel. Compare Gel F5-1, containing a veritable trace of I^- , and Gel F3-4, which contained no I^- and was reacted with successive portions of 0.05N $HgCl_2$ solution. In Gel F5-1 the influence of I^- on the growth of $HgCl_2 \cdot 2HgO$ is (1) to promote banding, (2) to restrict the size of the crystals slightly but definitely, and (3) to enhance the formation of semispherulitic clusters of fronds or needles around a more or less central nucleus in each individual crystal group.

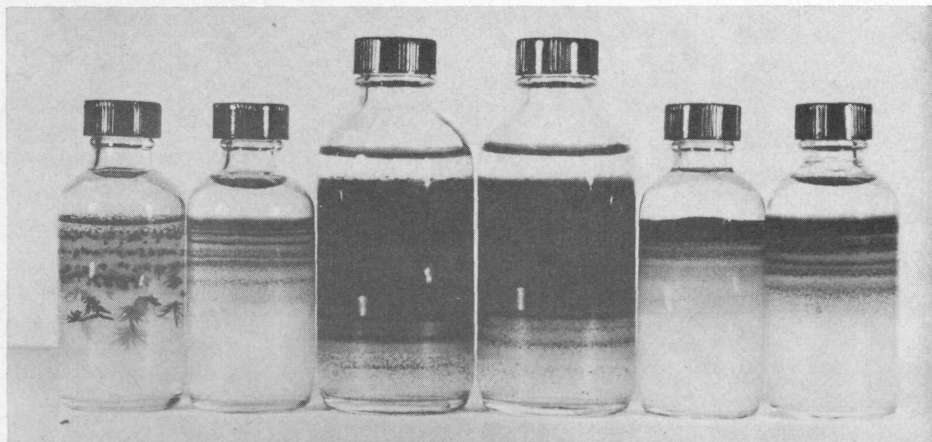


FIGURE 5. Growth of $HgCl_2 \cdot 2HgO$ crystals in six initially identically basic gels containing a range of iodide additive concentrations and reacted with $HgCl_2$ solutions or $HgCl_2$ crystals slurried in water.

F5-1	F5-2	F5-3	F5-4	F5-5	F5-6	
	F5-1	F5-2	F5-3	F5-4	F5-5	F5-6
Milliequivalents I^- in gel	0.0125	0.125	0.625	1.25	0.625	1.25
Milliequivalents I^- per ml gel	0.00025	0.0025	0.00625	0.0125	0.0125	0.025
Milliequivalents H^+ per ml undiluted N silicate	3	3	3	3	3	3
Volume H_2O per volume undiluted N silicate	5	5	5	5	5	5
Milliequivalents OH^- in silicate	16.7	16.7	33.3	33.3	16.7	16.7
1N acetic acid, milliequivalents	12.5	12.5	25	25	12.5	12.5
Milliequivalents $HgCl_2$ in supernatant	$4.5(9 \times 10$ ml ca. 0.05N)	$4(8 \times 10$ ml ca. 0.05N)	15 (2 g)	15 (2 g)	$4(8 \times 10$ ml ca. 0.05N)	$4(8 \times 10$ ml ca. 0.05N)
Water in supernatant, ml			20	20		
Milliequivalents OH^- after gelling to form basic salt	4.2	4.2	8.3	8.3	4.2	4.2
Percent of OH^- required by $HgCl_2$ present	57	79	42	42	79	79

The surface of Gel F5-1 is speckled with numerous small black crystals, which constitute the first of five distinguishable bands. Below are three bands of small to moderately sized (to $\frac{1}{4}$ inch) black crystals, most of which appear to be clusters of fronds. The fifth and lowest band contains the largest crystals, some up to $\frac{1}{2}$ inch in longest dimension, which are mostly clusters of glistening black needles,

some resembling bristling balled-up porcupines or sea-anemones, others resembling exotic insects.

Gel F5-2 contained 10 times as much I^- as did Gel F5-1. The effect on the growth of $HgCl_2 \cdot 2HgO$ of increasing the I^- concentration tenfold, from 0.25 to 2.5 microequivalents per ml of gel is remarkable. No crystals above $\frac{1}{64}$ inch in size are visible in the gel. About 10 bands of crystals, including one in the surface of the gel, are distinguishable, as is also a brown ring around the periphery of the gel surface. The outstanding influence of the presence of 2.5 microequivalents of I^- per ml of gel, as shown in Gel F5-2, is to restrict tremendously the size of the crystals of $HgCl_2 \cdot 2HgO$ which form. Examination of the gel at $7.5\times$ shows that most of the formation of $HgCl_2 \cdot 2HgO$ in Gel F5-2 resembles oblate spheroidal briquets, which have a dull sheen with yellow, blue, or black casts.

Gel F5-3 contained 6.25 microequivalents of I^- per ml and was reacted with an approximately onefold excess of $HgCl_2$ crystals slurried in water. The top of this gel contains reddish-tan microcrystals. The top $\frac{1}{8}$ inch of the gel, examined 2 years after the reaction was started, is clear of crystals except for an irregular band of red crystals, which presumably are HgI_2 and apparently formed very slowly and separated into a crude band over a period of many months. They were not apparent about 1 month after the start of the experiment. Below the clear zone containing the band of red crystals is a zone about $\frac{1}{8}$ inch deep which consists, as observed under a microscope at $7.5\times$, of tiny yellow crystals, which shade into red crystals of similar size giving the zone a reddish-brown appearance. Then, below are a myriad of very small black-appearing crystals arranged in a multitude of bands, some of which, in the bottom half of the gel, are more distinct and appear denser than others. In the bottom $\frac{3}{4}$ inch of the gel there is only one distinguishable band, flanked top and bottom by randomly scattered crystals. None of the crystals of $HgCl_2 \cdot 2HgO$ in this gel exceed $\frac{1}{64}$ inch in size. At $7.5\times$, all of the apparently black crystals in the gel appear to be briquet-like pseudo-spherulitic aggregates of microcrystals, which have dull reddish-brown, yellow, or reddish-black sheens. Thus, the influence of the presence of 6.25 microequivalents of I^- per ml of gel on the formation of $HgCl_2 \cdot 2HgO$ crystals is (1) to inhibit strongly the growth of any sizable crystals, (2) to enhance banding, and (3) to promote the formation of pseudospherulitic aggregates of microcrystals.

Gel F5-4 contained 12.5 microequivalents of I^- per ml of gel and was reacted with an excess of $HgCl_2$ crystals slurried in water. The crystal formations in this gel were quite similar to those described under Gel F5-3 above, with two notable exceptions. These were (1) no red band of HgI_2 crystals formed near the top of the gel and (2) a few random black crystals up to about $\frac{1}{32}$ inch in size formed in the lower $\frac{1}{3}$ of the gel. Also formed in the lower $\frac{1}{3}$ of the gel were three narrow bands containing both red crystals of HgI_2 and black crystals of $HgCl_2 \cdot 2HgO$. Microscopic examination of the gel at $7.5\times$ shows that all of the red and black crystals are discrete and that none are joined or even close neighbors.

Gel F5-5, like Gel F5-4, contained 12.5 microequivalents of I^- per ml of gel, but unlike Gel F5-4, was not overwhelmed with an excess of $HgCl_2$. Instead, Gel F5-5 was reacted with eight successive 10-ml portions of $\frac{1}{10}$ saturated $HgCl_2$ solution which, if all the $HgCl_2$ placed on the gel reacted, was enough to consume the available OH^- in the gel to form $HgCl_2 \cdot 2HgO$. Crystal formations appear only in the upper half of Gel F5-5. The top surface appears reddish-chocolate brown and is immediately underlaid by a very dark band. Below this are eight distinguishable bands of crystals, including two narrow, densely packed bands. The other crystal bands are "hazy", becoming increasingly more so from top to bottom. None of the crystals in this gel even approach $\frac{1}{64}$ inch in size and appear to be aggregates of microcrystals. Examination of the crystals at $7.5\times$ shows the shallow brown layer at the top of the gel to contain many small red crystals and some with golden casts.

Gel F5-6 contained 25 microequivalents of I^- per ml of gel and was reacted with eight successive 0.5-meq portions of 0.05N $HgCl_2$ solution. At the surface of the gel is a reddish-brown band which, under the microscope, is yellow at the top, shading to orange, then red. This is underlaid by a zone about $\frac{3}{8}$ inch deep containing a sharp, dark band of crystals flanked by tiny random near-black crystals. Next below is a reddish-brown band about $\frac{3}{8}$ inch deep, through which passes a narrow black streak. Below this are five fairly well defined bands of near-black crystals and finally, in the lower half of the gel, random crystals diminishing in population density progressively toward the bottom of the gel. In this system, all of the HgI_2 which formed appears to be in the top $\frac{1}{4}$ inch of the gel, mixed with some basic salt crystals. The crystals below the top $\frac{1}{4}$ inch of the gel all appear to be $HgCl_2 \cdot 2HgO$ and none exceed $\frac{1}{64}$ inch in size.

It is concluded from the results obtained with this series of 6 basic gels that the presence of as little as 2.5 microequivalents per ml of gel promotes banding and profoundly limits the size and alters the shape of $HgCl_2 \cdot 2HgO$ crystals which form. Likewise, 0.25 microequivalents of I^- per ml gel produce a noticeable, but not drastic change in crystal size, shape, and segregation into bands.

VI. *Growth of $HgCl_2 \cdot 2HgO$ in Inverted Gels*

One outstanding advantage of using silica gels as reaction media is that they may be oriented at any desired inclination or, being quite rigid, may be inverted over a source of external reactant. Basic gels, prepared for reaction with $HgCl_2$, have been inverted and so reacted to form $HgCl_2 \cdot 2HgO$ with spectacular results.

Figure 6 shows five inverted basic gels of three different initial basicities, which were reacted with $HgCl_2$ crystals or a saturated solution of $HgCl_2$, as shown in the data accompanying the figure. A large excess of $HgCl_2$, above that required to react with the OH^- available after gelling, was used in each instance. The gels fill 18 x 150 mm culture tubes, which are inverted in 22 x 175 mm test tubes or a 50 ml graduate.

Gel F6-1 was only slightly basic and was reacted with about a ninefold excess of $HgCl_2$. As shown in figure 6, only a few random crystals of $HgCl_2 \cdot 2HgO$ form. The crystals are multiply twinned three-dimensional stars or clusters of unbranched flat, roughly rectangular plates. The largest star is about $\frac{1}{4}$ inch across. There are a few small loose black crystals in the supernatant liquor. There is no evidence of banding. Compare with Gel F3-5, also prepared with 3.6 meq of acid per ml undiluted N silicate, which is banded splendidly.

Gel F6-2 was reacted with about a fivefold excess of $HgCl_2$ crystals slurried in water as the supernatant external reactant. Remarkable by their absence are bands which might have been expected from the behavior of an identically basic gel, F3-4, which was upright, i.e., infusion of external reactant was downward. The band-like cloud of mixed small and larger crystals which shows in figure 6 just above the middle of the gel resulted, not as a naturally growing band, but because in this region the gel did not adhere to the tube wall, presumably because the glass surface there was hydrophobic for some reason. No long crystal fronds formed in Gel F6-2 and the crystals in the lower $\frac{1}{3}$ of the gel were $\frac{1}{8}$ inch or less in size. Above this, in the middle $\frac{1}{3}$ of the gel, were star-shaped clusters similar to those in Gel F6-1 and in the top third of the gel were less numerous clusters of fern-like fronds to $\frac{1}{2}$ inch long, some of which were quite highly serrated.

Gels F6-3, -4, and -5 differ only in the amount of $HgCl_2$ used as external reagent and in the state of completeness of the reaction to form $HgCl_2 \cdot HgO$. Gel F6-5, not completely reacted at the time the photograph was taken, has since completed its reaction and now appears essentially identical to Gel F6-4. Gel F6-3 was reacted with about a fivefold excess of $HgCl_2$. The surface of the gel (bottom) is "stained" red-brown with microcrystals. The bottom $\frac{1}{2}$ inch of the gel contains perhaps 8 or 10 rough bands of very small crystals. Above this and

up to about the middle of the gel the crystals are predominantly in the form of fronds up to 2 inches long with short, hair-like branches. The top half of the gel contains mostly shorter fronds and clusters of fronds and/or needles. Some of the frond-needle clusters resemble insects with one or more pairs of single-feather wings.

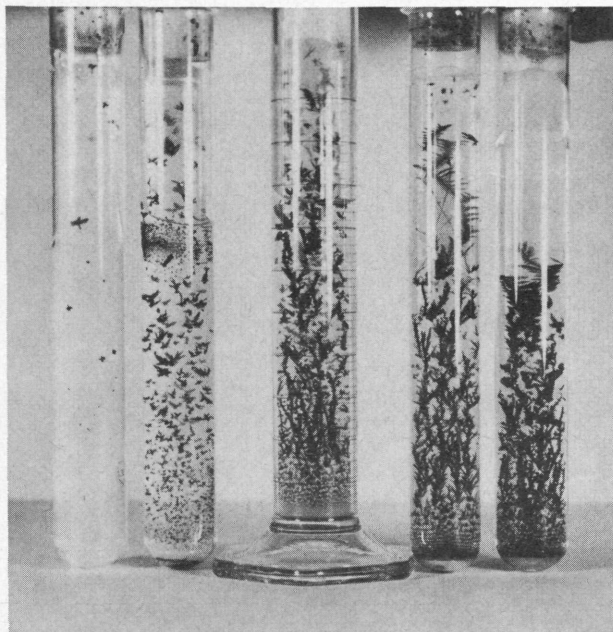


FIGURE 6. Growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in five initially basic inverted N silicate gels each reacted with an excess of HgCl_2 .

	F6-1	F6-2	F6-3	F6-4	F6-5		
			F6-1	F6-2	F6-3	F6-4	F6-5
Milliequivalents H^+ per ml undiluted N silicate			3.6	3.3	3.0	3.0	3.0
Volume H_2O per volume undiluted N silicate			5	5	5	5	5
Milliequivalents of OH^- in silicate			10	10	10	10	10
Milliequivalents of H^+			9	8.3	7.5	7.5	7.5
Milliequivalents HgCl_2 in subnatant			7.4	7.4	11.1	7.4	5
			(1 g)	(1 g)	(1.5 g)	(1 g)	(10 ml 0.5N)
Water in subnatant, ml			10	10	20	10	10
Milliequivalents OH^- after gelling to form basic salt			1	1.7	2.5	2.5	2.5
Percent of OH^- required by HgCl_2 present			10	17	17	25	37.5

Gel F6-4 was reacted with about a threefold excess of HgCl_2 in the form of crystals slurred in water as the subnatant reactant. The lower $\frac{1}{2}$ inch of this reacted gel contains 6 or 8 roughly defined rings of very small discrete crystals. The next higher $2\frac{1}{2}$ inches of gel contain long (up to 2 inches), narrow, highly-branched (short, stubby branches), roughly parallel, slightly twisted crystal fronds. In the next higher 2 inches of gel are three large (up to $1\frac{3}{4}$ inches) and several small magnificent, almost intertwined, highly branched, feather-like black

crystals. Finally, near the top of the gel are a number of small (less than $\frac{1}{4}$ inch) star-like crystals, randomly distributed.

Gel F6-5, which was reacted with about a twofold excess saturated HgCl_2 solution, was incompletely reacted at the time the photograph of this series was made. The now completely reacted gel differs from Gel F6-4 only in that the convoluted feathery crystals start to grow at a lower elevation in Gel F6-5 and the random crystals near the top of the gel are larger and more feathery than those in Gel F6-4. These relatively minor differences are attributed to the somewhat lower "driving pressure" of HgCl_2 in the supernatant of Gel F6-5.

The use of inverted basic gels to grow $\text{HgCl}_2 \cdot 2\text{HgO}$ appears to minimize almost to elimination the segregation of crystals in bands, except for a few bands of very small crystals in the bottom $\frac{1}{2}$ inch of the most basic gels used in this series, and to enhance the growth of spectacularly branched and convoluted feathery fronds in the upper half of the gel.

VII. *Use of Slightly Acidic HgCl_2 Solutions Or Aqueous Slurries As External Reactants*

The frequent formation of light tan to reddish-brown "stains" of microcrystals in the surface of basic gels prepared with about 3 meq or less of acid per ml of undiluted N silicate and reacted with HgCl_2 was annoying, detracted from the esthetic appearance of the reacted gel, and probably is not amenable to a clear-cut, simple explanation. A simple method of preventing microcrystalline formations in the surface of the gel was found when a fairly strongly basic gel was covered with a partially spent originally saturated solution of HgCl_2 which had been used previously as supernatant over an acidic gel system. This solution, while resident over the acidic gel, apparently acquired acidity by effusion of H^+ from the gel into the supernatant liquor. Then, when the partially spent and now acidic HgCl_2 solution was placed over a basic gel, the formation of microcrystals in the surface of the gel was prevented. Furthermore, no crystals of basic salt, $\text{HgCl}_2 \cdot 2\text{HgO}$, appeared in the upper half of the gel. Accordingly, the formation of crystals of basic salt was prevented until the proper pH was established where they could exist, that is, when the acid present in the supernatant liquor had been neutralized by the OH^- present in the basic gel. In this gel, the delineation between the crystal-free top half and the $\text{HgCl}_2 \cdot 2\text{HgO}$ crystal-bearing bottom half is very sharp and well defined.

This finding suggested experiments in which acetic acid was added to the supernatant external reactant over basic gels to prevent formation of surface microcrystals and to observe the influence of the amount of acid added on crystal-zone delineation and crystal formations which grew.

Figure 7 shows four representative basic gels reacted with acidic HgCl_2 solutions or slurries. The initial basicities of all four gels in figure 7 were identical, so each gel theoretically had about 4.2 meq of OH^- available after gelling to form a basic salt with HgCl_2 .

Gel F7-1 was overwhelmed with a tenfold excess of HgCl_2 crystals slurried with an aqueous solution about $\frac{1}{10}$ saturated with HgCl_2 and containing 1 meq of H^+ . As shown in figure 7, the top $\frac{3}{8}$ inch of the gel is crystal free and the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals is in long, slender, roughly parallel, weakly branched, crystal fronds, which extend to within $\frac{1}{4}$ inch of the bottom of the gel. At and near the bottom of the gel are a number of random small star-shaped clusters of crystals. Such relatively rapid growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ in long streamers is typical in gels of this initial basicity which are reacted with large excesses of HgCl_2 .

Gel F7-2 was reacted with a small excess of HgCl_2 used as a saturated solution and containing about 0.5 meq of acetic acid. As shown in figure 7, the top $\frac{1}{4}$ inch of this gel is crystal free. Below this are, first, small star-shaped crystals, then short fronds, and finally, in the lower third of the gel, splendid curved feather-like

fronds $\frac{1}{2}$ inch to 1-inch long. At the bottom of the gel are a few random clusters of platelets. The crystal growths observed in this gel are typical for such basic gels when reacted relatively slowly with only a small excess of HgCl_2 .

Gel F7-3 was reacted with insufficient HgCl_2 to combine with all of the available OH^- in the gel. A $\frac{1}{2}$ -saturated solution of HgCl_2 containing 1.25 meq of acetic acid composed the supernatant liquor. As shown in figure 7, no crystals formed in the upper $\frac{5}{8}$ inch of this gel. Below this, the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals

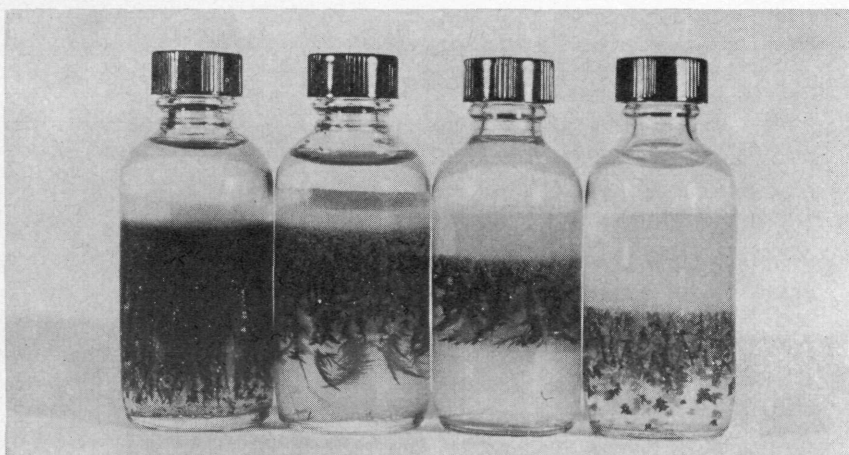


FIGURE 7. Growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in four initially identical basic N silicate gels reacted with different concentrations of HgCl_2 containing different small amounts of acetic acid as supernatant reactant.

	F7-1	F7-2	F7-3	F7-4
Milliequivalents H^+ per ml undiluted N silicate	3	3	3	3
Volume H_2O per volume undiluted N silicate	5	5	5	5
Milliequivalents OH^- in silicate	16.7	16.7	16.7	16.7
0.5N acetic acid, milliequivalents	12.5	12.5	12.5	12.5
Milliequivalents HgCl_2 in supernatant	34(4 g $\text{HgCl}_2(\text{s})$ +9 ml 0.5N HgCl_2)	4.5(9 ml 0.5N)	2.2(8.75 ml 0.25N)	4.5(9 ml 0.5N)
Water in supernatant, ml	10	10	10	10
Milliequivalents H^+ in supernatant	1	0.5	1.25	2
Milliequivalents OH^- after gelling to form basic salt	4.2	4.2	4.2	4.2
Percent of OH^- required by HgCl_2 present	9	70	143	70

was confined to a $\frac{1}{8}$ -inch-deep zone and the bottom $\frac{3}{4}$ inch of the gel contains no crystals. The crystal formations are essentially all fronds, which are short and virtually unbranched near the top of the crystal zone and $\frac{3}{4}$ inch long, highly branched, curved, and feathery in the lower $\frac{2}{3}$ of the crystal zone. The abrupt ending, as well as the abrupt beginning, of crystal growth in this HgCl_2 -deficient gel system are quite remarkable.

Gel F7-4 was reacted with about 30 per cent excess HgCl_2 in the form of a saturated solution to which was added about 2 milliequivalents of acetic acid.

As shown in figure 7, the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals is restricted to the bottom half of the gel. Evidently the inclusion of 2 meq of H^+ in the supernatant liquor prevents the permanent growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ in the upper half of the gel. It is important to note that, during the course of the reaction, crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ formed in the upper half of the gel, but were dissolved as H^+ ions diffused into the gel. Resolution of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals by infusing H^+ releases HgCl_2 for reaction with OH^- at a lower level in the gel. Consequently, as would be expected, the crystal zone extends from the pH-limited upper "barrier" to the bottom of the gel. The crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ formed in Gel F7-4 are either short fronds or clusters of unbranched leaves. No banding is evident and crystal distribution is random.

It is apparent from the reacted gels shown in figure 7 and from the descriptions outlined above that microcrystalline stains in the surface can be prevented and that the location of the upper "barrier" for permanent residence of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in gels can be varied and controlled readily by the addition of H^+ to the supernatant liquor. Additional work with acidified external reactants is in progress, using initially more basic gels and also inverted gels.

VII. Use of Hydroxyl Ions As The External Reactant

A number of experiments were carried out in which OH^- was used as the supernatant external reactant over (1) slightly acidic to essentially neutral gels which contained dissolved HgCl_2 , (2) weakly basic gels which contained uniformly distributed reddish-purple microcrystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ or, (3) slightly basic gels which contained bands of near-black $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals.

The purpose of these experiments was twofold: (1) to grow crystals of a more basic mercuric chloride, $\text{HgCl}_2 \cdot 3\text{HgO}$, for example, and (2) to obtain more evidence that the basic chloride crystals grown by Holmes (1917, 1934) and those described in this paper reasonably may be assumed to be $\text{HgCl}_2 \cdot 2\text{HgO}$. The first purpose has been partially fulfilled and has provided substantiating evidence for the second.

According to Friend (1926), there are five basic mercuric chlorides which have been established as chemical individuals. These are:

$2\text{HgCl}_2 \cdot \text{HgO}$	yellowish-white rhombic prisms
$\text{HgCl}_2 \cdot \text{HgO}$	thin red crystals or yellow powder
$\text{HgCl}_2 \cdot 2\text{HgO}$	alpha form is red, formed from HgCl_2 and HgO under slightly acidic conditions; beta form is black, formed from HgCl_2 and HgO under slightly basic conditions
$\text{HgCl}_2 \cdot 3\text{HgO}$	alpha form is red and amorphous beta form is citron yellow and amorphous gamma form is yellow and crystalline
$\text{HgCl}_2 \cdot 4\text{HgO}$	(1) brown or yellow crystals (2) amorphous brown powder (3) black or very dark brown crystals.

$2\text{HgCl}_2 \cdot 3\text{HgO}$, $4\text{HgCl}_2 \cdot 7\text{HgO}$, $\text{HgCl}_2 \cdot 5\text{HgO}$, $\text{HgCl}_2 \cdot 6\text{HgO}$, and $\text{HgCl}_2 \cdot 6\text{HgO} \cdot \text{H}_2\text{O}$ have been reported in the literature, but both Friend (1926) and Mellor (1929) express doubt that these are single compounds. The inference is that they are mixtures of one of the simpler basic salts and free HgO .

Table 9 describes five HgCl_2 -bearing gels which were reacted with OH^- under various conditions.

Gel T9-1, initially acidic, was reacted on successive days with 15-ml portions of 0.2N NaOH, then, after an interval of 26 days, with four 15-ml portions of 0.1N KOH at intervals of 9, 11, and 22 days. The effect of the 0.2N NaOH supernatant reactant was to cause bright-yellow microcrystals to form on the surface to the gel. Then, the top $\frac{1}{8}$ inch of the gel dissolved slowly and small bright orange-yellow crystals formed in the retreating surface layer. Just below the surface, a band

about $\frac{1}{16}$ inch deep of small reddish-black crystals formed. Infusion of successive portions of 0.1N KOH caused little solution of gel, but increased the number of yellow surface crystals and produced a band, about $\frac{3}{16}$ inch deep, of small reddish-black crystals below the subsurface band and, below this, a band of clusters of near-black needles and feathery fronds, up to $\frac{1}{4}$ inch long. At the surface of this initially acidic gel, contact with OH^- produced two effects, (1) an attack on the silicic acid and acid silicates in the gel and, (2) the formation of orange-yellow crystals in the surface. The surface crystals apparently are not $\text{HgCl}_2 \cdot 2\text{HgO}$, which has no yellow crystal form. Because of the ready mobility of OH^- in the aqueous supernatant and the simultaneous relative immobility of H^+ and HgCl_2 in the rigid gel, more than enough OH^- is available initially at the surface of the gel to form strongly basic salts, e.g., $\text{HgCl}_2 \cdot 3\text{HgO}$. It is an unfortunate coincidence that, in surroundings of such alkalinity, the gel dissolves. As OH^- ions

TABLE 9
Summary of pertinent conditions in five HgCl_2 -bearing gels reacted with OH^- as the external reactant

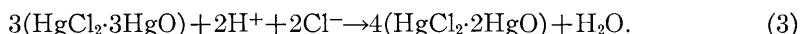
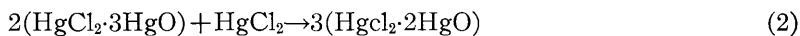
	T9-1	T9-2	T9-3	T9-4	T9-5
Milliequivalents H^+ per ml undiluted silicate	4.5	4.5	4.2	3.6	1.5
Volumes H_2O per volume undiluted silicate	5.0	5.0	5.0	5.0	2.0
Milliequivalents OH^- in silicate	16.7 ^a	16.7 ^a	16.7 ^a	16.7 ^a	18.6 ^b
N acetic acid	1.5	1.5	1.4	1.2	0.5
Milliequivalents H^+	18.8	18.8	17.5	15	12.5
Milliequivalents HgCl_2 in gel at start	6.2	6.2	3.1	6.2	0
Milliequivalents HgCl_2 infused into gel	0	0	0	0	5.0
Crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ present in gel before HgCl_2 infusion	None	None	None	Deep purplish-red microcrystals uniformly dispersed	Band of relatively sizable black crystals
Initial pH of gel	Acidic	Acidic	Acidic	Basic	Basic
Milliequivalents H^+ infused into gel	0	0	0	0	2.5 ^c
Base infused into gel:					
1N NaOH, milliequivalents	0	10	0	0	0
	6	0	0	6	0
0.2N KOH, milliequivalents	(2 x 15 ml)	10	7.5	(2 x 15 ml)	10
	6			9	
0.1N KOH, milliequivalents	(4 x 15 ml)	(2 x 25 ml) (1 x 50 ml)	(5 x 15 ml)	(3 x 20 ml) (1 x 30 ml)	(2 x 15 ml) (2 x 20 ml) (1 x 30 ml)

^aN sodium silicate sp gr 1.066, $\text{Na}_2\text{O}:\text{SiO}_2=1:3.32$ (mol. ratio)

^bKasil #1 (potassium silicate) sp gr 1.086, $\text{K}_2\text{O}:\text{SiO}_2=1:3.92$ (mol. ratio)

^cAcid infused into gel after HgCl_2 infusion to clear top of gel and immediate adjacent gel of red-black crystals before OH^- was used as supernatant

in the supernatant are depleted by reactions which dissolve the gel and form a strongly basic salt or salts, H^+ and HgCl_2 , both of which have been shown in earlier sections of this paper to diffuse readily through silica gels, migrate upward to equilibrate the system. The growth of a band of near-black crystals immediately below the bright orange-yellow surface crystals may result from reaction (1) or from the following reactions:



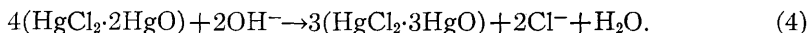
Reactions (2) and (3) are pertinent only to near-surface formations of reddish-black $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals. The formation of the secondary bands of crystals when 0.1N KOH was infused may be attributed to depletion of H^+ by diffusion

to the surface to neutralize OH^- . The pH of the ultimate supernatant liquor four months after the placement of the last 15-ml portion of 0.1N KOH is about 8.0. It is likely, therefore, that the pH of the gel is very nearly the same as that of the supernatant. The depletion of H^+ from the gel and the simultaneous diffusion of HgCl_2 from the HgCl_2 -rich lower regions of the gel to the HgCl_2 -poor zone near the top of the gel (depleted by reaction with OH^-) reasonably can account for the growth of near-black $\text{HgCl}_2 \cdot 2\text{HgO}$ below the top $\frac{1}{16}$ inch of gel. The fact that the gel dissolves, while bright yellow $\text{HgCl}_2 \cdot 3\text{HgO}$ forms at the surfaces, precludes argument that the crystals which form below the surface may be $\text{HgCl}_2 \cdot 4\text{HgO}$, which is more basic than $\text{HgCl}_2 \cdot 3\text{HgO}$ and consequently should require a more basic environment to form and to survive in the presence of encroaching H^+ and HgCl_2 from the lower portions of the gel. This implication that OH^- does not migrate very far, if at all, in silica gels will be treated in detail in a separate paper.

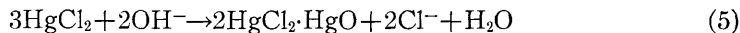
Gel T9-2, initially acidic, was reacted first with 10 ml of 1N NaOH for 35 days, then with two 25-ml portions of 0.1N KOH with a 13-day interval and finally, after 19 days, with one 50-ml portion of 0.1N KOH. The effect of the reaction with 10 meq of NaOH, used as a 1N solution, was (1) to form bright yellow microcrystals in the surface of the gel, (2) to dissolve the gel progressively until only about one-half of the original gel remained, and (3) to cause the growth of three bands of dark reddish-black crystals below the surface, much the same as described under Gel T9-1 above. The first two additions of 0.1N KOH caused (1) further solution of the gel, and (2) the formation of progressively more yellow crystals. The final 5-meq portion of 0.1N KOH completed the solution of the gel. About $\frac{2}{3}$ of the loose crystals in the bottom of the container are bright orange-yellow, the remainder are a deep reddish-black. The ultimate pH of the liquor is approximately 10. As in Gel T9-1, the formation of bright orange-yellow crystals and the dissolution of the gel is a function of the initial concentration of the supernatant OH^- . Solution of the gel proceeds much faster and more extensively with an initial "driving force" of 10 meq of OH^- than with successive uses of two 3-meq portions of OH^- followed by four 1.5-meq portions of OH^- . Significantly, in Gel T9-2 as in Gel T9-1, the orange-yellow crystals formed nearest the source of OH^- , and the red-black crystals formed behind the yellow crystal zone. Accordingly, it is reasonable to believe that the yellow crystals are more basic than the reddish-black ones. Finally, the conversion of a substantial portion of the reddish-black crystals to orange-yellow ones in the ultimate state of the system, at pH 10, provides additional evidence of the greater basicity of the yellow crystals.

Gel T9-3, initially very slightly acidic, was reacted with a total of 7.5 meq of OH^- placed on the gel in five 15-ml portions of 0.1N KOH at 5-, 3-, 7-, and 10-day intervals. The effect of the first two portions of 0.1N KOH was to dissolve the surface of the gel to a depth of between $\frac{1}{16}$ and $\frac{1}{8}$ inch. Simultaneously there formed in the surface of the gel a few orange-yellow randomly distributed crystals. In the top $\frac{1}{8}$ inch of the gel a mixed band of crystals formed. Reddish-black near-surface crystals were scalloped in a remarkably regular pattern into a mixture of vertical, roughly parallel, closely-packed, pale yellow and white needles. The next two 15-ml portions of 0.1N KOH, (1) caused additional minor solution of the gel, (2) converted some of the reddish-black crystals to orange-yellow ones, and (3) produced a band about $\frac{1}{4}$ inch deep of mixed pale-yellow and white vertically oriented needles. The final portion of 0.1N KOH dissolved only a very small depth of gel, but (1) converted more of the reddish-black crystals to bright orange-yellow ones, (2) formed an additional narrow band of mixed yellow and white crystals, and (3) most surprisingly, formed a thin band of reddish-black clusters of needles below the lowest yellow-white band and a few random crystal clusters at the very bottom of the gel. No crystals appeared in the $1\frac{1}{2}$ inches of gel between the reddish-black band and the bottom of the gel. Accordingly,

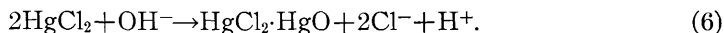
five months after the last portion of 0.1N KOH was placed on the gel, there are orange-yellow crystals and a few reddish-black crystals loose in the supernatant liquor, which has a pH of close to but slightly less than 8. About $\frac{3}{16}$ inch of the original gel has been dissolved, and there are a number of random reddish-black crystals in the surface of the gel. The main crystal feature is a five-tiered band of mixed pale yellow (preponderant) and white (occasional) vertical needle-like crystals, and below this is a thin band of reddish-black crystal clusters. Reactions which involve gel solution and formation of reddish-black $\text{HgCl}_2 \cdot 2\text{HgO}$ have been discussed above. The formation of orange-yellow crystals in the supernatant apparently corresponds to a reaction such as



The formation of the pale yellow and the white crystals are ascribed to depletion of H^+ from the gel by OH^- in the supernatant and by migration and depletion of HgCl_2 in the gel as it strives to equilibrate and as Hg^{++} is consumed at and near the surface of the gel. The pale yellowish-white crystals correspond closely to descriptions of $2\text{HgCl}_2 \cdot \text{HgO}$ (although there is a yellow but powdery form of $\text{HgCl}_2 \cdot \text{HgO}$ known), which can form as H^+ is depleted gently from the gel by weak (0.1N) OH^- . These could form as follows:



or



These apparently are stable also under conditions where $\text{HgCl}_2 \cdot 2\text{HgO}$ can form because the scalloped portion of reddish-black crystals and its directly-adjacent companion band-forming yellow-white crystals coexisted until the third portion of 0.1N OH^- was used as supernatant reactant. Thereafter the reddish-black scallops and their yellow-white companions were converted to bright orange-yellow crystals as the surface of the gel dissolved, but only yellowish-white bands formed below until the fifth and final portion of 0.1N OH^- was reacted as supernatant. This behavior suggests that the rate of extraction of H^+ from the gel is a function of the concentration of OH^- in the supernatant, and that if this rate is slow enough, a less basic chloride, which is transient in more rapid H^+ extractions, can form and coexist in the presence of a more basic one. The implication of the formation of the lowest reddish-black band of crystals is that, by the time these crystals formed, the gel had been so depleted of H^+ that only $\text{HgCl}_2 \cdot 2\text{HgO}$ could nucleate and grow. It is remarkable that the super-resident yellowish white $2\text{HgCl}_2 \cdot \text{HgO}$ was not converted to a more basic salt before the subsident $\text{HgCl}_2 \cdot 2\text{HgO}$ formed. Here again is an implication that OH^- do not migrate far, if at all, in silica gels.

Gel T9-4, initially basic and containing microcrystals of dark reddish-purple $\text{HgCl}_2 \cdot 2\text{HgO}$, was reacted on successive days with 15-ml portions of 0.2N NaOH, then, after an interval of 28 days with three 20-ml portions of 0.1N KOH at 7 and 3-day intervals, and, finally, after an interval of 7 days with one 30-ml portion of 0.1N KOH. The action of the OH^- in this system was twofold, namely, to dissolve the gel and to convert the reddish-purple microcrystals to golden-yellow ones without apparent increase in size. Five months after the placement of the final portion of 0.1N KOH over the gel, about 40 per cent of the original gel remains. The supernatant liquor has a pH of about 10 and contains a multitude of loose golden-yellow microcrystals. The surface of the undissolved gel also contains numerous golden-yellow microcrystals, but the body of the gel has retained its original reddish-purple color. Evidently, aside from the dissolution of the gel, the only other noteworthy reaction has been the coincident conversion of the reddish-purple $\text{HgCl}_2 \cdot 2\text{HgO}$ to golden-yellow $\text{HgCl}_2 \cdot \text{HgO}$ as by reaction (4), for example.

Gel T9-5, originally slightly basic and barren with respect to Hg salts, was

reacted with 5 meq of HgCl_2 for 12 days. This reaction produced a series of bands of small crystals to $\frac{1}{8}$ inch in size extending from the top to the bottom of the gel. Then the gel was reacted with 2.5 meq of H^+ for 13 days. This cleared a zone about $\frac{1}{2}$ inch deep of crystals and was intended to buffer the gel against the initial onslaught of OH^- . Finally, the gel was reacted with two 15-ml portions, two 20-ml portions and one 30-ml portion of 0.1N KOH at intervals of 3, 5, 3, and 19 days. The net result of these successive portions of 0.1N KOH was to dissolve the top $\frac{9}{16}$ inch of the gel and to convert most of the reddish-black crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in the uppermost band to orange-yellow $\text{HgCl}_2 \cdot 3\text{HgO}$. The top band and the surface of the gel were coincident when the reaction ended. A few orange-yellow crystals are loose in the supernatant, which has a pH of about 10. None of the near-black crystals in the subsurface bands were affected by the OH^- in the supernatant liquor. Apparently, the only influence of OH^- on this gel system, aside from dissolving a portion of the gel, was to convert the uppermost band of $\text{HgCl}_2 \cdot 2\text{HgO}$ to $\text{HgCl}_2 \cdot 3\text{HgO}$ as that band and the gel surface became coincident.

The results of these five experiments, in which OH^- was the supernatant external reactant, show that the formation of orange-yellow or golden-yellow crystals of $\text{HgCl}_2 \cdot 3\text{HgO}$ is coincident with destruction of the gel by dissolution in OH^- . Therefore, the near-black crystals which form in unattacked gels under less alkaline conditions cannot be $\text{HgCl}_2 \cdot 4\text{HgO}$ which requires a more alkaline condition to form than does $\text{HgCl}_2 \cdot 3\text{HgO}$. Likewise, $\text{HgCl}_2 \cdot 3\text{HgO}$ is yellow, $\text{HgCl}_2 \cdot \text{HgO}$ is either yellow (amorphous powder) or thin red crystals, and $2\text{HgCl}_2 \cdot \text{HgO}$ is yellowish white. Accordingly, by a process of elimination the near-black crystals which formed in the gels studied are concluded to be $\text{HgCl}_2 \cdot 2\text{HgO}$. This is in agreement with Holmes' (1917) postulation.

CONCLUSIONS

The results of these experiments concerned with the formation of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in silica gels permit the following conclusions:

- (1) The size, shape, and distribution of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in silica gels are controlled mainly by the initial alkalinity of the gel and the rate of infusion of HgCl_2 from the supernatant solution or from the subnatant solution in the instance of inverted gels.
- (2) The level in a basic gel at which the growth of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ will start can be controlled readily by the addition of more or less acid to the HgCl_2 solution or slurry used as external reactant.
- (3) The color of the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which form in a basic silica gel appears to be dependent primarily on the amount of silica in the gel, which appears to control the effective basicity. The rate of infusion of HgCl_2 also can influence the color of these crystals. Likewise, the presence of acid in the supernatant HgCl_2 favors the formation of reddish-brown $\text{HgCl}_2 \cdot 2\text{HgO}$ in the region of the gel where basic salts can form initially.
- (4) The length of crystal fronds of $\text{HgCl}_2 \cdot 2\text{HgO}$ which grow in basic gels appears to be controlled by the initial alkalinity of the gel (the shortest fronds grow in the most basic gel), and by excess HgCl_2 , which favors rapid formation of long fronds with short branches.
- (5) The degree of branching and the length of the branches of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals appears to be controlled by the alkalinity of the gel (more alkaline, less branching), the amount of silica in the gel (less silica, more branching), and the rate of infusion of HgCl_2 into the basic gel (slowest infusion, most feather-like branching).
- (6) The rate of growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ crystals in silica gels appear to be related directly to the concentration of HgCl_2 in the supernatant (or

subnatant) external reactant and to the amount of silica in the gel (less silica, more rapid growth).

- (7) Weakly basic gels and basic gels containing chlorides, bromates, sulfates, iodides, or sugar, as internal indifferent ions or compounds, cause the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ to form in remarkable bands which resemble Liesegang rings.
- (8) Trace amounts of iodide in basic gels cause a noticeable diminution in the size of crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ which form, and induce banding and incipient pseudo-spherulitic formations.
- (9) Small amounts of iodide or substantial amounts of bromide in basic gels limit the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ to small pseudo spherulites.
- (10) The type of silicate used to prepare the gel, including potassium silicate or several varieties of sodium silicate, does not appear to have a noticeable influence on the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ in basic gels.
- (11) The acid or acidic salt used to prepare the gel does not appear to have a noticeable influence on the growth of $\text{HgCl}_2 \cdot 2\text{HgO}$ in basic gels, with the exception of HCl or strongly reducing acids.
- (12) Growing the crystals of $\text{HgCl}_2 \cdot 2\text{HgO}$ in inverted gels appears to minimize almost to elimination the segregation of crystals in bands.
- (13) Orange- to golden-yellow crystals of $\text{HgCl}_2 \cdot 3\text{HgO}$ form under conditions where the gels dissolve when reacted with OH^- as the supernatant external reactant. This precludes $\text{HgCl}_2 \cdot 4\text{HgO}$ as the near-black basic salt which forms in gel unattacked by OH^- and confirms Holmes' postulation that the basic salt in undissolved gels is $\text{HgCl}_2 \cdot 2\text{HgO}$.
- (14) Less basic salts than $\text{HgCl}_2 \cdot 2\text{HgO}$ apparently can be formed in gels by using dilute OH^- as the supernatant external reactant. After formation, such salts as $2\text{HgCl}_2 \cdot \text{HgO}$ or $\text{HgCl}_2 \cdot \text{HgO}$ apparently can coexist with $\text{HgCl}_2 \cdot 2\text{HgO}$ in the gel.

The results of several other phases of work concerned with the formation of basic mercuric chlorides in gels will be reported in separate papers.

REFERENCES

- Friend, J. N.** 1926. Mercuric oxychlorides. A textbook of inorganic chemistry. Charles Griffin & Co. Ltd., London. Vol. III, Part II, 260-1.
- Holmes, H. N.** 1917. The formation of crystals in gels. *J. Phys. Chem.* 21: 709-33.
- . 1934. Reactions in gels. Laboratory manual of colloid chemistry. John Wiley & Sons, Inc., New York. p. 153-9.
- Mellor, J. W.** 1929. Mercuric oxychlorides—Basic mercuric chlorides. A comprehensive treatise on inorganic and theoretical chemistry. Longmans, Green and Co., Ltd., London. Vol. 4: 839-44.
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