

SOME CHEMICAL REACTIONS IN SILICA GELS

I. FORMATION OF MERCURIC IODIDE CRYSTALS¹

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ABSTRACT

This investigation was concerned with reactions which form HgI_2 in acidic gels prepared with acetic acid and sodium silicate. The results of this work support the postulation that the yellow crystal frontal zone which advances through the gel as reaction progresses is probably the yellow polymorph of HgI_2 and not a complex alkali metal mercuri-iodide. In addition, the results show that mercuric chloride reacts with iodine in acidic gels to form HgI_2 . A plausible reaction scheme involving enhancement of I_2 hydrolysis and enhancement of the disproportionation of HOI by the presence of Hg^{++} appears to explain this unanticipated behavior.

The suitability of silica gels as a largely aqueous yet nonliquid diffusion-controlling medium for studying chemical reactions and for growing sizable crystals of difficultly soluble materials has been known for at least 50 years. A number of reactions in silica gels including the formation of mercuric iodide crystals (Holmes, 1917, 1934) have been studied in some detail.

A classic experiment for growing mercuric iodide in an acidic silica gel consists of covering a gel containing potassium iodide with a solution of mercuric chloride. As mercuric ions diffuse into the iodide-bearing gel from the supernatant solution, crystals of mercuric iodide form in the gel, sometimes with interesting banding.

The present investigator has repeated earlier work of others (Holmes, 1934; Averett, 1962) and has extended it in an attempt to elucidate certain phenomena observed during the course of the $\text{Hg}^{++}-\text{I}^-$ reaction in silica gels. The results of the present investigations show:

1. That the usual description of the advancing yellow crystal frontal zone as a potassium mercuri-iodide probably is erroneous, and that this frontal zone probably is the yellow polymorph of HgI_2 . (Yellow, rhombic HgI_2 is metastable at room temperature and transforms to stable red, tetragonal HgI_2 in time). Several experiments are described whose results support this postulation.

2. That mercuric chloride reacts readily and controllably with elemental iodine in acidic silica gels to form HgI_2 . A plausible reaction scheme is presented to account for this unanticipated phenomenon.

In the following sections are presented (1) a description of the preparation and composition of silica gels containing various internal reactants including I^- , I_3^- , HgI_4^- , I_2 , and Hg^{++} ; (2) a description of the reaction between Hg^{++} (external) and I^- (internal) and vice versa; and (3) a description of reactions which support the postulation of yellow HgI_2 as the advancing frontal material or which displayed other unexpected phenomena.

EXPERIMENTAL

Formation of Silica Gels

Philadelphia Quartz Company's "N" Sodium Silicate was used in the experimental work. This material is a syrupy, essentially colorless liquid and has a specific gravity of about 1.39 to 1.40. When the silicate is diluted with five volumes of water, the specific gravity of the resultant solution is about 1.066 and its basicity is about 0.6 N. This diluted silicate solution will form stable gels

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when added to an equal volume of acetic ranging in concentration from 0.35 N to 16 N. Gels made with acetic acid weaker than about 0.6 N are slightly basic. Interesting chemical reactions are feasible in acidic gels made with other acids or in basic gels also, and will be described in subsequent papers. The present investigation, however, was concerned with reactions which form HgI_2 in acidic gels prepared with acetic acid and containing the desired internal reactant (I^- or Hg^{++}).

The time required for a gel to set may vary from a few minutes to a day or longer depending on the ultimate pH of the gelling mixture and the nature and concentration of the internal reactant. The more strongly acidic gels (net normality 4 or greater) set slowly, some requiring a day or longer to gel. Gels containing a net normality of KI greater than about 0.3 (after combination of all the

TABLE 1
Composition of typical gels used to study the formation of mercuric iodide crystals

1.066 sp gr N silicate ml used	Acetic acid to form gels		Internal reactant				External reactant				Remarks
	N	ml used	Formula	g	N	ml used	Formula	g	N	ml used	
System I. Hg^{++} (External)— I^- (Internal)											
50	2	25	KI	—	0.01 to 1	25	HgCl_2	—	1 (hot)	25	14 gels
50	4-16	25	KI	—	0.1 to 1	25	HgCl_2	—	1 (hot)	20	6 gels
50	1.2-1.5	25	KI	—	0.5 or 1	25	HgCl_2	2-3.5	—	—	Numerous gels
10-50	1.5	5-25	KI	—	0.5 or 1	5-25	HgCl_2	1-3	—	—	Numerous gels
System II. I^- (External)— Hg^{++} (Internal)											
50-150	0.75-1	50-150	HgCl_2	3.4	—	—	KI	—	1	20-25	Several gels
10	1.5	5	HgCl_2	—	0.4	5	KI	—	0.4	5	1 gel
System III. Hg^{++} (External)— HgI_4^- (Internal)—(With and without excess I^-)											
50	1.5	25	K_2HgI_4	—	1	25	HgCl_2	3.5	—	—	2 gels
50	4	25	K_2HgI_4	—	1	25	HgCl_2	3.5	—	—	1 gel
50	1.5	25	K_2HgI_4	—	0.5	12.5	HgCl_2	3.5	—	—	1 gel
				—	0.25	12.5					
System IV. Hg^{++} (External)—($\text{I}_3^- + \text{I}^-$) (Internal)											
50	1.5	25	KI	—	0.5 or 1	25	HgCl_2	3.5	—	—	Several gels
			I_2	0.2 to 2.1	—	—					
10-20	1.5	5-10	KI	—	1	5-10	HgCl_2	0.7-1.5	—	—	4 gels
			I_2	0.4 to 0.8	—	—					
System V. Hg^{++} (External)— I_2 (Internal)											
50	2	50	KI	2.770	—	—	HgCl_2	3.5	—	—	2 gels
			KIO_3	(0.0167 mol)							
				0.720							
				(0.00334 mol)							

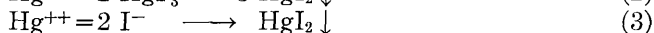
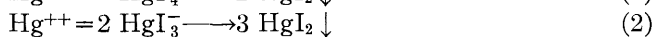
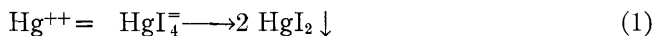
gel components) usually are too soft and weak to use in reliable experiments and produce pseudogeologic effects such as marbling or scalloping when covered with HgCl_2 .

Table 1 presents a summary of the composition of gels pertinent to the present work with a variety of internal reactants and with HgCl_2 or KI as external reactants. The system headings in the table indicate the reaction systems investigated, for example, Hg^{++} (external)— I^- (internal), I^- (external)— Hg^{++} (internal), etc. Results of experiments with each of the five systems designated in table 1 will be described in the following sections.

System I. Hg⁺⁺ (External)-I⁻ (Internal)

A major portion of the present work was done with System I type gels because, at the start of the investigation, experiments described by Holmes (1934) and Averett (1962) were repeated. The external, Hg⁺⁺-furnishing reactants were either hot (near boiling when placed on the gel) or room-temperature aqueous solutions of HgCl₂ or mixtures of HgCl₂ crystals and water which could try to form saturated HgCl₂ solutions in the supernatant liquor before depletion by infusion into the gel as the reaction in the gel to form HgI₂ progressed.

Figure 1 illustrates the progress of a typical System I reaction where HgI₂ is formed by the infusion of 3 meq of HgCl₂ into a gel containing 2.5 meq of KI. As shown in figure 1, the advancing frontal zone is yellow or predominantly so for the first 300 hr of reaction. The front advances into a zone where there are more than enough I⁻ ions to form HgI₂, and conceivably there might be enough I⁻ ions to form KHgI₃=KI·HgI₂ (yellow prisms which decompose in cold water) or K₂HgI₄=2KI·HgI₂ (yellow crystals, very soluble in cold water). HgI₂ (yellow, rhombic) is stable in dilute acids and is only very slightly soluble in water. Comparison of the solubilities and stabilities of HgI₂ (yellow) and the complex potassium mercuri-iodides in cold (room temperature) water suggests, but does not prove unequivocally, that the actual (invisible) reaction front may be a finite, thin layer of the gel where KHgI₃ or K₂HgI₄ form from Hg⁺⁺+(2+n) I⁻, where n=1 or more. At this front Hg⁺⁺ ions enter a virgin I⁻ zone where there are 3, 4 or more I⁻ per Hg⁺⁺. Then, as more Hg⁺⁺ ions enter this zone, they can react with HgI₄⁻, HgI₃⁻, or I⁻, ultimately depleting the zone to and below 2 I⁻ per Hg⁺⁺ as follows:



Accordingly, there is reason to believe that the visible advancing crystal front probably is composed of yellow, metastable HgI₂ which gradually transforms at the rear of the yellow frontal zone (in the presence of excess Hg⁺⁺) to stable, red HgI₂. Support for this postulation is presented in the following sections.

The narrow (about $\frac{1}{16}$ -inch) clear zone which appears at the top of the gel after 20 hr and before 90 hr of reaction time have elapsed is attributed by Holmes (1917) to the formation of a water-soluble xHgCl₂·yHgI₂ complex. Other experiments showed that using less I⁻ in the gel and establishing larger relative excesses of HgCl₂ as the external reactant, the depth of the clear zone can be increased controllably, and that, if desired, all of the HgI₂ formed can be dissolved by using a large excess of HgCl₂.

System II. I⁻ (External)-Hg⁺⁺ (Internal)

A natural sequel to System I type experiments was to reverse the positions of the internal and external reactants as was done in the experiments designated as System II types where I⁻ was permitted to infuse into gels containing HgCl₂.

Figure 2 illustrates the progress of the reaction to form HgI₂ crystals by the infusion of 2 meq of I⁻ from a supernatant KI solution into a gel containing 2 meq of HgCl₂. As shown in figure 2, the advancing front is yellow and the accumulating crystals behind the frontal zone are red. During the first 90 hr of reaction, the rear (top) of the moving red crystal zone was surmounted by an increasingly large clear zone. The clearing of this upper zone is attributed to the solution of HgI₂ crystals in the excess KI infusing into this region from the supernatant liquor. This clearing of the top zone of the gel thus ties up some of the infusing I⁻ ions in mercuri-iodide complexes and thereby limits the amount of I⁻ available for diffusion further downward. Ultimately, as at after 160 hr of

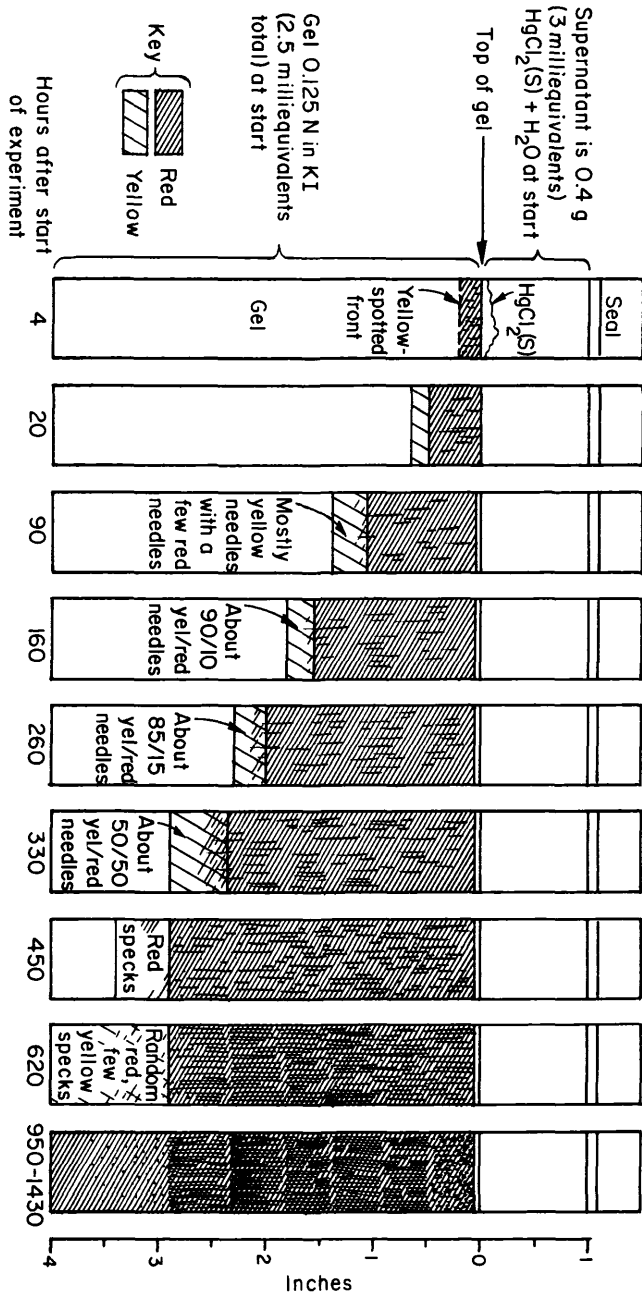


FIGURE 1. Progress of the formation of HgI_2 crystals in silica gels by reaction System I, Hg^{++} (external)— I^- (internal) from start to completion showing advancing yellow front and transformation of yellow HgI_2 (metastable) to red HgI_2 (stable).

reaction, the upward movement of Hg^{++} from the lower portion of the gel has begun to counteract the downward diffusion of I^- ions. The main red crystal zone moves upward slightly, and the original front (which is now the rear of the

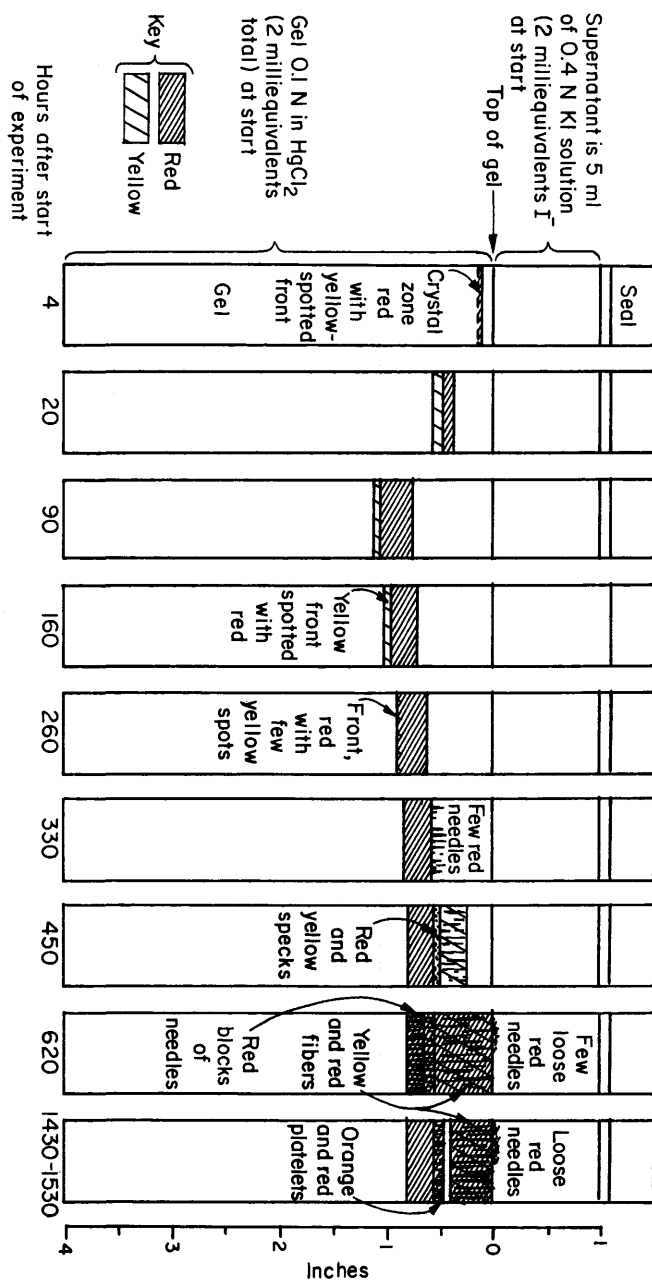


FIGURE 2. Progress of the formation of HgI_2 crystals in silica gels by reaction System II, I^- (external)— Hg^{++} (internal) from start to completion showing advancing yellow front and subsequent counteradvance of excess Hg^{++} through completed red zone.

crystal zone relative to Hg^{++} movement) although still mostly yellow needles is spotted with red needles. After 260 hr of reaction, the main red crystal zone has moved upward still further and the rear surface of this zone (originally the advancing front) is now mostly red needles spotted with a few yellow needles. After 300 hr of reaction, the red crystal zone has moved upward to about its ultimate

location (up to 1530 hr of reaction), and a few red needles appear in the otherwise clear zone at the top of the gel. During the remaining reaction time, up to 1530 hr, yellow needles changing to red needles, or orange or red platelets, grow in the previously clear top zone of the gel, and loose red needles appear in the supernatant liquor above the gel. Results of other similar System II type experiments, where more than a year (8760 hr) has elapsed from the start of the reaction, indicate that all of the orange and yellow needles and platelets still existent at 1530 hr in the experiment detailed above ultimately should turn red in time.

The results obtained from the System II experiment just described are informative. As long as the initial reaction front advances, it is yellow and leaves behind it a contiguous zone of red HgI_2 crystals. At the actual reaction front I^- ions diffuse into a virgin Hg^{++} zone where, under the conditions of the experiment, more than enough Hg^{++} ions are present to react with entering I^- ions to form HgI_2 . The crystals of mercuric iodide which form first are the yellow, metastable form of HgI_2 which transforms to the red form in time. There seems little reason to believe that in System II type reactions the initial yellow front where I^- advances into an excess of Hg^{++} should be composed of crystals of one of the potassium mercuri-iodides which require 3 or 4 I^- per Hg^{++} to form. Accordingly, it is reasonable to assume that the yellow advancing front is HgI_2 . This does not prove that the continuously advancing yellow front observed in System I type reactions (Hg^{++} infusing into an I^- -bearing gel) is yellow HgI_2 , in spite of the essentially identical appearance of the two advancing fronts during a substantial portion of the reaction. However, the very similar appearances of these fronts and other arguments presented earlier strongly suggest chemical as well as visual identity. Results described in a later section will, it is believed, establish this identity.

The disappearance of the rear (top) of the zone of red HgI_2 crystals during the first 90 hr of the System II experiment described above has been accounted for earlier in this section.

Once the countermovement (of Hg^{++} upward from the bottom zone of the gel) has started the originally advancing yellow front retreats upward and becomes, first, spotted with red (160 hr), then, mostly red (260 hr) and, ultimately, entirely red (330 hr and on). The retreat may be caused by (1) augmented growth of red HgI_2 crystals above the immediate frontal zone at the expense of the smaller frontal crystals or, (2) the formation of a water-soluble complex, $x\text{HgCl}_2 \cdot y\text{HgI}_2$ which forms and dissolves as excess HgCl_2 diffuses upward into the zone containing HgI_2 crystals.

As the upward diffusing excess Hg^{++} ions enter into the clear top zone of the gel (cleared by solution in KI of HgI_2 crystals formed earlier in the reaction and simultaneously diminishing the number of I^- ions available for continued downward diffusion), progressively more crystals form in this zone. Finally, excess Hg^{++} ions reach the supernatant liquor and form loose crystals of red HgI_2 which lie on the surface of the gel. The formation of crystals of HgI_2 in the top zone and in the supernatant liquor is attributed to reactions between complex mercuri-iodides and Hg^{++} to form HgI_2 (yellow, transforming more or less slowly to red HgI_2) by reactions (1) or (2) above. The presence of HgI_3^- and/or HgI_4^- in the supernatant liquor is ascribed to the effusion of these ions from the gel into the liquor after I^- ions diffusing downward in excess dissolve HgI_2 crystals at the rear of the originally downward-moving reaction zone.

System III. Hg^{++} (External)- HgI_4^- (Internal)

System III is of interest because (1) it illustrates directly the reaction between Hg^{++} and HgI_4^- , and (2) it provides support for the postulation that the yellow zone which advances in the gel in System I, Hg^{++} (external)- I^- (internal), reac-

tions are composed of crystals of yellow HgI_2 and not of one of the complex potassium mercuri-iodides.

Figure 3 illustrates the progress of a reaction of the System III type. In this System III experiment, 3.5 g (about 26 meq) of HgCl_2 were permitted to infuse into a gel containing 25 meq of K_2HgI_4 . These conditions provide for entrance

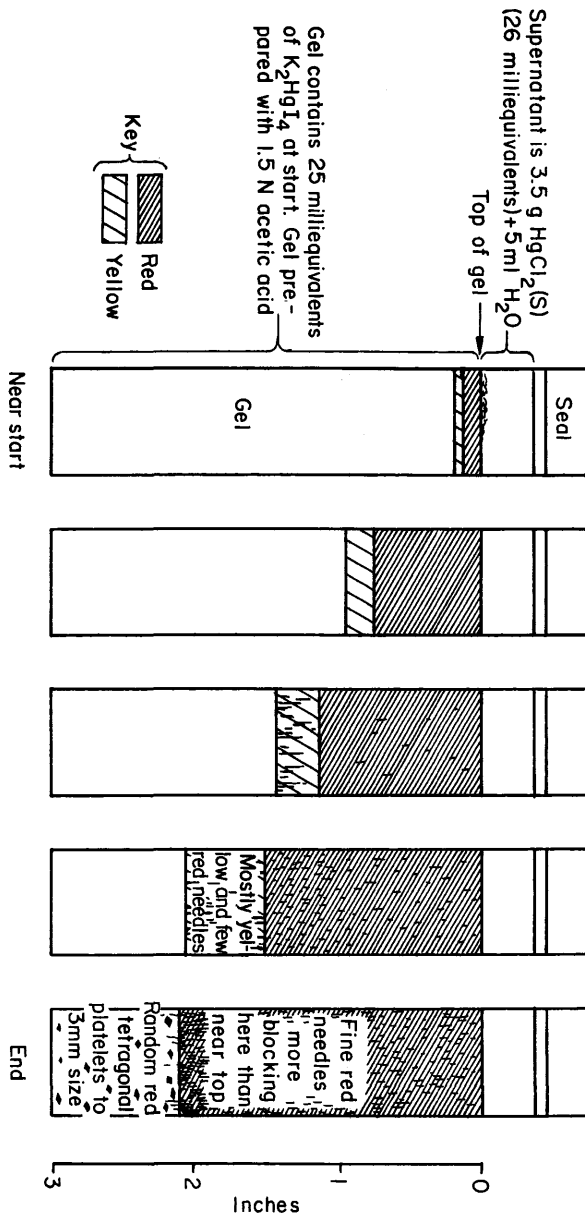
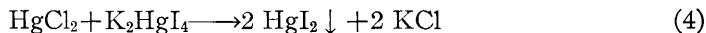
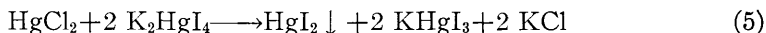


FIGURE 3. Progress of the formation of HgI_2 crystals in silica gels by reaction System III, Hg^{++} (external)— HgI_4^{--} (internal) from start to completion showing advancing yellow front and ultimate transformation of yellow HgI_2 to red HgI_2 .

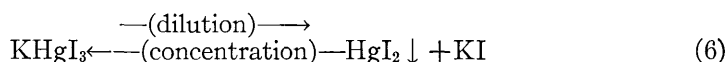
into the gel of an ultimate small excess of Hg^{++} . As figure 3 shows, the advancing front is yellow, and the crystals behind the frontal zone transform from the yellow to the red polymorph of HgI_2 . The reaction which occurs at the front and in the subsequent slow growth of tetragonal plates in the lower third of the gel may be written as follows:



Under the conditions of the experiment, there can be little doubt that the advancing front was composed of crystals of yellow HgI_2 , even if one assumes that the reaction to form KHgI_3 occurs as follows:



KHgI_3 formed under these conditions probably would (1) be soluble in the gel (which is largely water) and produce no crystals, or (2) decompose (because the gel is largely water) into HgI_2 and KI as follows:

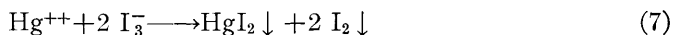


Accordingly, the results of the System III experiment described provide another example where the diffusion of Hg^{++} ions into a gel rich in I^- (although complexed in HgI_4^-) proceeds with the establishment and movement of a yellow crystalline front, just as in System I experiments. Furthermore, the System III results support the postulation that the advancing yellow frontal zone is composed of HgI_2 crystals much more unequivocally than do the System I results which permit speculation and postulation, but provide no indisputable proof that the frontal crystals are yellow HgI_2 .

It is interesting to note that reaction (4) between Hg^{++} and HgI_4^- produces two molecules of yellow HgI_2 per ion of Hg^{++} at the visible front. Also, that reactions (5) and (6), if valid, likewise produce yellow HgI_2 .

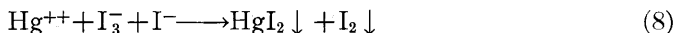
System IV. Hg^{++} (External)–($\text{I}_3^- + \text{I}^-$) (Internal)

System IV was selected as another approach by which the postulate that the advancing yellow crystal front in System I reactions in HgI_2 might be substantiated. It was hoped to produce gels which contained I_3^- only without having excess I^- present. This did not prove feasible with acetic acid as the gelling agent. Excess I^- was required in all instances to dissolve the desired amount of I_2 in a solution of KI in dilute acetic acid. Another acid might permit the stoichiometric formation of KI_3 from $\text{I}_2 + \text{KI}$, but has not been tried yet. The results of experiments with System IV type gels even though carried out with excess I^- (beyond that required to form I_3^-) were gratifying and, as will be shown, opened a new area for investigation concerned with the reaction between I_2 and HgCl_2 . In setting up the System IV experiments it was proposed that Hg^{++} (external) diffusing into ($\text{I}_3^- + \text{I}^-$) (internal) would produce HgI_2 by reaction (3) above and as follows:



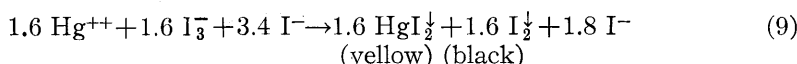
Reactions (3) and (7) proceeded as anticipated as is illustrated in figure 4. However, an additional reaction, which was not expected under acidic conditions, was observed, namely, that between Hg^{++} and I_2 to form HgI_2 . This apparent reversal of the iodide-iodate redox by hydrolysis of I_2 and subsequent disproportionation of OI^- is described and discussed in the next section dealing with System V type gels.

Figure 4 shows the progress of the System IV reaction between Hg^{++} (external) and $(\text{I}_3^- + \text{I}^-)$ (internal) for two concentrations of external reactant. In one instance, just slightly more than enough HgCl_2 was placed on the $(\text{I}_3^- + \text{I}^-)$ -bearing gel to complete the reaction.

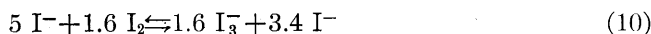


In the other instance, a substantial excess of HgCl_2 above the total I^- [actual (as I^-) and potential (from I_2)] requirements was used.

As shown in figure 4, the left-hand section, the System IV reaction using excess HgCl_2 as the external reactant starts out as expected and forms three crystal layers soon after the reaction is started. The top layer is red HgI_2 resulting from phase transformation of the middle, yellow (advancing front of Hg^{++} into gel) layer of metastable HgI_2 from



based on the $\text{I}_2 - \text{I}^-$ stoichiometry shown in Figure 4, namely,



The bottom layer is black and apparently is I_2 crystals as would be expected in a zone where an excess of Hg^{++} entering the equilibrated $\text{I}_3^- + \text{I}^-$ gel disturbs the equilibrium shown in reaction (10). No crystals of I_2 appear in the red or yellow zones initially and for some time later. As the reaction progresses the zone containing red HgI_2 crystals deepens, the yellow frontal zone advances, and the black crystal zone retreats because excess I^- remains after reaction (9). Accordingly, for a time, no black crystals would be expected to appear or remain above the retreating black crystal zone. Later, increasingly large random crystals of I_2 form below the retreating narrow zone of I_2 "frontal" crystals. Ultimately, the formation of red HgI_2 proceeds, via yellow, metastable HgI_2 needles, to near the bottom of the gel. The random black crystals are engulfed and slowly converted to red HgI_2 , retaining their general original I_2 shape and sprouting hairlike red needles. At the end of the reaction no vestige of the I_2 crystals remain except as the red, needle-sprouting pseudomorphic HgI_2 which has grown essentially in situ on the I_2 and essentially "petrified" the black crystals. This unexpected behavior (HgCl_2 solution (saturated) as prepared with water or with dilute acetic acid does not react at room temperature with elemental I_2) suggested an experiment in which just slightly more than enough HgCl_2 (5.2 meq) was used than the amount required to react with the total available I^- (in I_3^- and in excess I^- , 5 meq) but not enough to react with much of the I_2 . The results of this experiment are illustrated in the right-hand section of figure 4. The reaction starts out and proceeds for a few days essentially the same as the experiment carried out with excess HgCl_2 . Three crystal layers—red, yellow and black—from top to bottom, form. After about 10 days there remain only two major phases, red HgI_2 in the top one-third of the gel and random crystals of I_2 in the lower two-thirds of the gel, with slight vestiges of the original yellow advancing front. This appears to be the furthest advance of the Hg^{++} front into the gel. Thereafter, the red zone retreats slightly as I^- ions diffuse upward and, coincidentally, more random I_2 crystals form lower in the gel and all of the I_2 crystals grow. Ultimately, the completed reaction shows a clear, pale yellow supernatant liquor (saturated aqueous solution of I_2), a red zone with randomly oriented short needles near the top, longer essentially vertically oriented needles below the top layer and four or five tiered bands of short densely packed needles at the bottom of the zone. The random iodine crystals in the lower 70 per cent of the gel are mostly

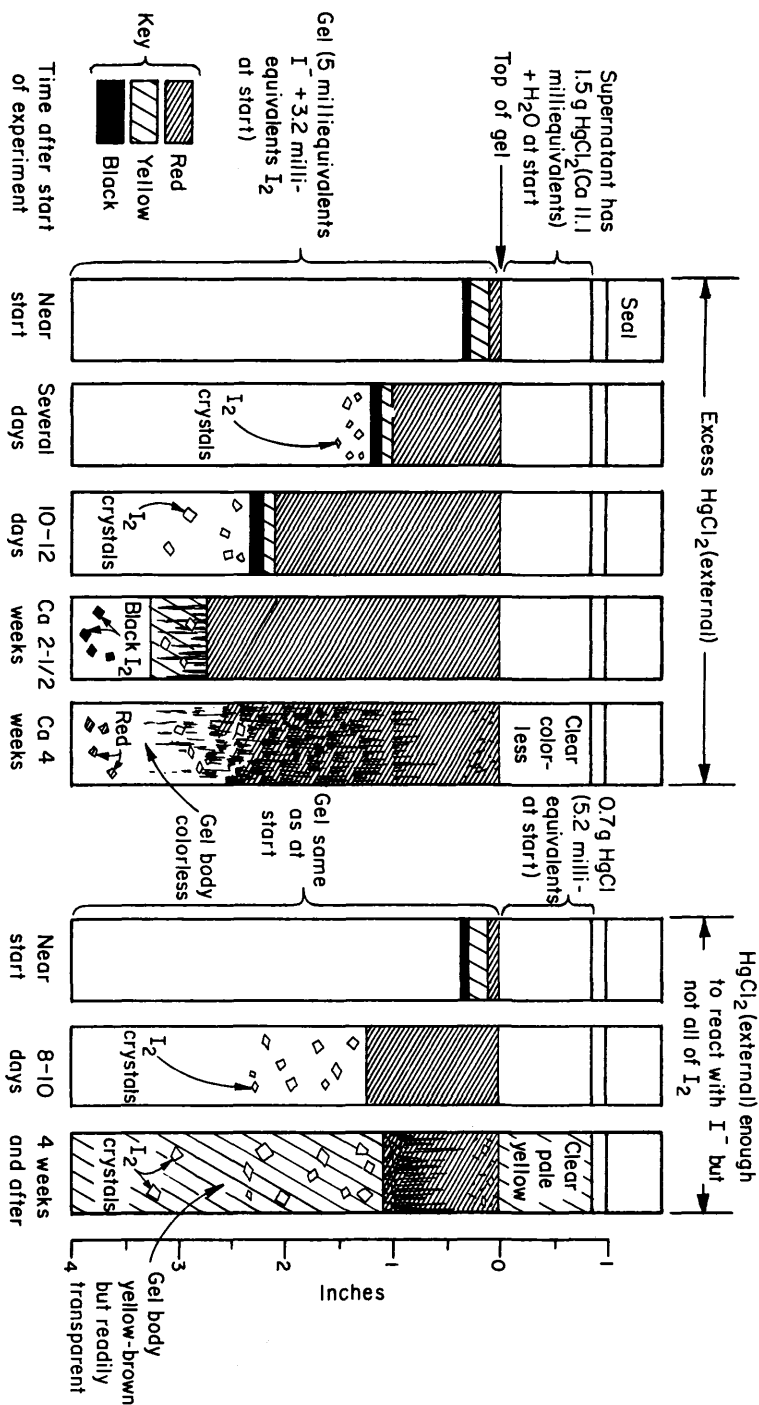


FIGURE 4. Progress of the formation of HgI₂ crystals in silica gels by reaction System IV, Hg⁺⁺ (external) - (I₃⁻ + I⁻) (internal) from start to completion with excess and shortage of HgCl₂ showing advancing yellow front, formation of I₂ crystals and conversion of I₂ to HgI₂ when excess HgCl₂ is used.

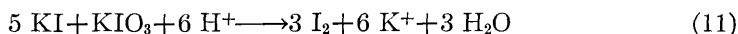
twinned, and some exceed 0.5 cm on a side; all are plate-like. The gel body is light yellow-brown and essentially transparent. When excess HgCl_2 is used as the external reactant, the supernatant liquor and the body of the gel are colorless at the completion of the reaction.

The results of System IV experiments show that as Hg^{++} ions diffuse into a gel containing $\text{I}_3^- + \text{I}^-$ the advancing front is yellow, transforming at the frontal zone to red. The retreating front of black I_2 crystals is absorbed as long as there is sufficient upward diffusion of I^- to dissolve I_2 formed by reaction (9). As depletion of I^- continues random crystals of I_2 form below the retreating front. In the competition for I^- between Hg^{++} and I_2 , Hg^{++} apparently is successful, and as the concentration of I^- is depleted by the formation of HgI_2 , I_2 is forced to crystallize in the gel. The fact that the advancing front of HgI_2 crystals observed when Hg^{++} diffuse into an $(\text{I}_3^- + \text{I}^-)$ -rich gel is yellow provides further support and substantiation for the postulation that the formation of HgI_2 in gels proceeds via yellow HgI_2 (metastable) frontal zones transforming at their rear to red HgI_2 (stable).

The unexpected reaction between HgCl_2 and I_2 in acidic gels described above after its initial encounter in System IV reactions is the subject of the next section.

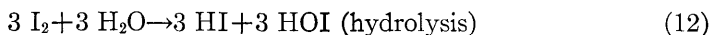
System V. Hg^{++} (External)- I_2 (Internal)

A natural sequel to the System IV experiment where an excess of HgCl_2 was infused into a gel containing $\text{I}_3^- + \text{I}^-$, was an experiment designed to observe the reaction, if any, in an acidic gel between HgCl_2 and elemental iodine in the absence of I^- . An experiment was tried in which I_2 was generated by the iodide-iodate redox using carefully weighed quantities of KI and KIO_3 , 2N acetic acid as the gelling agent, and 1.066 sp gr N silicate solution as the source of silica. It was hoped that the gel would set before the I_2 liberated could crystallize and precipitate out. Such was not the case, however; it made no difference as will be shown. Crystals of iodine resulting from the quantitative reaction,

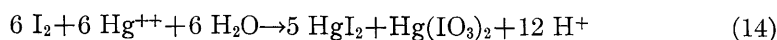


settled to the bottom of the gelling mixture and were permitted to remain there while the gel set. The gel was slightly opalescent, as most gels are, but showed no yellow color, and could be assumed to be free of I^- . The amounts of KI and KIO_3 used were enough to form 0.0100 mol (20 meq) of iodine. The gel was covered with 3.5 g (26 meq) of HgCl_2 crystals and about 20 ml of water. As Hg^{++} diffused into the gel, no evidence of reaction was observed until the external reactant reached the bottom $\frac{3}{8}$ inch of the gel where I_2 crystals formed quantitatively by reaction (11) as described above, had settled before the gel set. Progressively over a period of weeks the I_2 crystal zone turned red with no readily visible change in the shape or size of the originally black crystals. There was no evidence of the appearance of a yellow phase. However, there may have been a yellow "front" as the Hg^{++} ions worked their way into the I_2 crystals in the process of converting them to HgI_2 .

A plausible explanation for this rather unexpected reaction between HgCl_2 and I_2 appears to lie in the displacement of the hydrolysis equilibrium of I_2 by the presence of Hg^{++} and the disproportionation of OI^- to IO_3^- and I^- as follows:



In the presence of Hg^{++} the overall reaction may be written as follows:



The rather slow progress of the reaction is attributed to the formation of H^+ which tends to suppress the reversal of the $I^- - IO_3^-$ redox. Further work concerned with the investigation of this interesting reaction between Hg^{++} and I_2 and between I_2 and other cations is in progress and will be reported in another paper.

Demonstration of the feasibility of direct reaction between Hg^{++} and I_2 in acidic gels in the essential absence of I^- suggests that in the presence of I^- , even in small amounts, the conversion of I_2 to HgI_2 should be enhanced. This was found to be the case as described earlier in the section dealing with System IV.

CONCLUSIONS

It is concluded from the results described that:

(1) The yellow crystal front which advances into a gel as a reaction to form HgI_2 progresses in the gel probably is composed of the yellow form of HgI_2 and not of crystals of one of the (yellow) alkalimetal mercuri-iodides.

(2) The reaction between $HgCl_2$ and I_2 in acidic gels in the essential absence of I^- probably results from enhancement of the hydrolysis of I_2 and enhancement of the subsequent disproportionation of HOI by the presence of excess $HgCl_2$ which removes I^- by formation of HgI_2 .

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