[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY, THE UNIVERSITY OF MINNESOTA]

Studies on Aging and Coprecipitation. XXXIV. The Aging of Freshly Precipitated Lead Chromate

BY I. M. KOLTHOFF AND F. T. EGGERTSEN[1]

In a previous paper[2] of this series methods for measuring the specific surface of lead chromate have been described. These methods have been used in the present investigation for the purpose of determining the speed of aging of the fresh precipitate under various conditions.

The speed of aging was measured in two ways: (1) by following the rate of penetration of thorium B ions into the precipitate, and (2) by measuring the rate of decrease of specific surface using the wool violet adsorption method[2] to make surface determinations. Some interesting new results were found which gave a more detailed insight into the mechanism of the very involved aging processes.

In addition to the aging study, experiments were performed to determine the effect of certain conditions during precipitation upon the particle size of the product. The results of these latter experiments will be given first.

For details concerning the purity of materials and the manner of performing the wool violet and thorium B experiments the reader is referred to a previous paper.[2] All of the wool violet experiments were performed in at least duplicate, and the deviation from the mean was never more than ± 1 mg. of wool violet per gram of adsorbent.

Particle Size of the Fresh Precipitate: A. Effect of Stirring and of the Order of Addition of Reagents.—Ten ml. of 0.05 *M* lead nitrate was added in fifteen seconds from a pipet to 10 ml. of potassium chromate of the same concentration, the latter solution being contained in a 60-ml. bottle. The precipitation was made in four ways: (1) the lead solution was added down the side of the bottle with no shaking or stirring; (2) the bottle was rotated by hand during precipitation; (3) the solution was mechanically stirred during precipitation; (4) same as (3) except that potassium chromate was added to lead nitrate. Two minutes after the beginning of the precipitation the suspension was in each case centrifuged for two minutes at 2000 r. p. m. The mother liquor was then decanted and the specific surface of the fresh precipitate was determined by the wool violet method, the dye solution being added when the precipitates were exactly eight minutes old. As shown in Table I, the specific surface was found to be greater the more vigorous the agitation during mixing. Also the specific surface was slightly greater when the manner of addition was chromate to lead than when the solutions were mixed in the reverse manner.

TABLE I

EFFECT OF MANNER OF MIXING OF REAGENTS ON PARTICLE SIZE

Method of precipitation		Spec. surf. in mg. W. V. p. g.	Av. particle length, mμ[a]
1. Lead to chromate	(a) No agitation	20.7	151
	(b) Shaking by hand	26.5	118
	(c) Mech. stirring	36.0	87
2. Chromate to lead, mech. stirring		39.3	80

[a] Calculated from the specific surface assuming the particles to be cubical in shape, and the specific gravity to be 6.3. The calculation was possible since it has been established[2] that 0.54 mg. of lead is in the surface for each mg. of W. V. adsorbed.

B. Effect of Concentration of Precipitants.—Equimolar solutions of lead nitrate and potassium chromate were prepared, varying in concentration from 0.05 to 0.005 *M*. Precipitations were made by adding lead to chromate with rapid mechanical stirring, using the same stirring mechanism in all cases. Except when the concentration was 0.005 *M*, 10 ml. of lead was added to 10 ml. of chromate, the latter solution being contained in a 60-ml. wide-mouth bottle. When the concentration was 0.005 *M* the precipitation was made using 100-ml. portions of the solutions and a 250-ml. wide-mouth bottle. Also, in the latter experiments additional potassium nitrate was added in some cases so that its final concentration would be the same as that in the 0.05 *M* experiments. The time for addition of lead nitrate was 15 seconds when the 10-ml. volume was used, and thirty seconds when the volume was 100 ml. Specific surfaces were determined with wool violet in the usual manner when the products were eight minutes old. The results. given in Table II, show that the *particle size de-*

TABLE II

EFFECT OF CONCENTRATION OF PRECIPITANTS ON PARTICLE SIZE

Concn. of precipitants, *M*	Ppt., g.	Concn. of KNO_3 after pptn., *M*	Spec. surf. in mg. W. V. per g.
0.06	0.194	0.06	30
.05	.162	.05	35
.04	.129	.04	36
.03	.097	.03	40
.005	.162	.05[a]	41
		.05[b]	41
		.005[c]	48

[a] Solid potassium nitrate was dissolved in the lead nitrate solution before precipitation. [b] Solid potassium nitrate was dissolved in the chromate solution before precipitation. [c] No potassium nitrate was present other than that formed during the precipitation.

---

[1] From a doctor's thesis submitted by Frank T. Eggertsen to the Graduate School of the University of Minnesota (1939).

[2] I. M. Kolthoff and F. T. Eggertsen, THIS JOURNAL, **62**, 2125 (1940).

creased with decreasing concentration of solutions, which is just the opposite of what would be expected according to von Weimarn's principle. Also there is seen to be an electrolyte effect upon the particle size which was found to increase with increasing potassium nitrate concentration during precipitation according to the data obtained when the concentration of precipitants was 0.005 *M*. A more detailed study is necessary before an interpretation of the reversal of von Weimarn's rule can be given.

C. Effect of Temperature and Acidity of the Solutions.—The precipitations were made by adding in fifteen seconds 10 ml. of 0.05 *M* lead nitrate to 10 ml. of 0.05 *M* potassium chromate with vigorous mechanical stirring. The solutions added together were at a temperature of 20, 25, or 30°. In a fourth experiment the temperature was 25°, but the lead solution contained a small amount of nitric acid so that its *p*H was 3.6 instead of 5.0 (when no acid was added). Specific surface determinations were made in the usual manner when the precipitates were eight minutes old and the results are given in Table III. The conclusions are that smaller particles are obtained at a low temperature and a high *p*H. The pronounced effect of the presence of a *trace* of acid upon the particle size cannot be accounted for quantitatively by an increase of the solubility. Apparently, traces of coprecipitated basic lead chromate, which are neutralized by the acid, greatly affect the rate of growth of the nuclei.

TABLE III

EFFECT OF TEMPERATURE AND ACIDITY DURING PRECIPITATION UPON PARTICLE SIZE

Temp. of pptn., °C.	*p*H of lead nitrate soln.	Spec. surf., mg. W. V. per g.
20	5.0	36.3
25	5.0	34.1
30	5.0	32.4
25	3.6	20.8

D. Effect of Drying upon the Particle Size.—Precipitates were prepared by adding in fifteen seconds with mechanical stirring 10 ml. of 0.05 *M* lead nitrate to 10 ml. of 0.05 *M* potassium chromate. The suspensions were each centrifuged, decanted, and 20 ml. of absolute ethanol was added, the time of addition of the alcohol being six minutes after the precipitation. The suspension was shaken by hand, centrifuged and decanted again, and another 20 ml. of absolute alcohol was added. The precipitate was treated in this manner in order to wash off the mother liquor. Suspensions obtained after adding the second portion of alcohol were treated as follows. In one experiment it was centrifuged and decanted. The stopper was then removed from the bottle and the alcohol was allowed to evaporate from the precipitate at room temperature for four days, when it appeared completely dry. In order to ensure evaporation of the alcohol, one precipitate was dried for an additional twenty-four hours at 90° after the drying period at room temperature had been completed. In another experiment the alcohol was not poured off but the precipitate was allowed to stand for four days under alcohol in the centrifuged state. Specific surfaces of the products prepared in the above manner were measured by the wool violet method, the suspensions in the dye solutions being shaken twelve hours in order to break up the agglomerates. Before surface measurements of the undried products were made, they were washed twice with 20-ml. portions of water by centrifuging and decantation, this process requiring five minutes. The specific surface of the precipitate at the moment the alcohol was added was 38 mg. of wool violet per gram. After the various treatments described above the specific surfaces were:

Undried product	32.9
Dried at room temperature	24.8
After drying at room temp., dried 24 hr. at 90°	25.1

There was a definite decrease in specific surface as measured by wool violet adsorption upon drying from ethanol. Also it is seen that the resulting particle size was the same whether the drying took place at room temperature or at 90°, which indicates that there is no thermal aging of lead chromate at those temperatures.

Two experiments similar to those described above were performed except that after washing once with alcohol one precipitate was washed with benzene and the other with petroleum ether. After drying for four days at room temperature the specific surfaces of these products were found to be 25.0 and 26.1 mg. of wool violet, respectively. These results are in good agreement with those found when the product was dried from alcohol and therefore show that the size of irreversible agglomerates was the same when the drying took place from any one of the three media.

Aging

Aging of Lead Chromate as Indicated by Thorium B Penetration.—In a previous publication[2] it has been shown that when a solution of ThB is shaken with freshly precipitated lead chromate there is a very rapid incorporation of the radioactive ions into the crystals. This process has been investigated more thoroughly and is discussed in the following.

The precipitates were prepared by adding from a pipet 10 ml. of 0.0550 *M* lead nitrate solution to 10 ml. of 0.0500 *M* potassium chromate contained in a 60-ml. bottle. In order to prevent coprecipitation of basic salt, the lead nitrate solution contained a small amount of nitric acid so that its *p*H was 3.6. The time for addition of the lead to the chromate was fifteen seconds and the bottle was not agitated during the precipitation, the lead nitrate solution being run in down the side of the bottle.

After aging the precipitate for the desired period of time on a mechanical shaker, 5 ml. of a radioactive solution having the same composition as the mother liquor was added. (The latter was 0.05 *M* in potassium nitrate and an analysis showed it to be 0.00235 *M* in lead nitrate.) The suspension was shaken with the active lead for a specified time and the per cent. of ThB which had disappeared from the solution was determined in the usual way.

After the various periods of shaking the *apparent* amount of lead exchanged per gram of lead in the precipitate, Pb (exchanged)/Pb (ppt.), was calculated with aid of the equation

$$\frac{\text{Pb(exchanged)}}{\text{Pb(ppt.)}} = \frac{\text{ThB(exchanged)Pb(solution)}}{\text{ThB(solution)Pb(ppt.)}}$$

TABLE IV

SPEED OF PENETRATION OF ThB INTO 10-MINUTE-OLD LEAD CHROMATE

Time of shaking with ThB in hours	0.08	0.17	0.33	0.53	0.75	1	3	5	12
ThB removed in %	55.9	82.6	93.1	95.8	97.4	97.2	96.0	95.1	92.3
Pb(exchanged)/Pb (ppt.)[a]	0.15	0.56	1.6	2.7	4.3	4.1	2.8	2.3	1.4

[a] Equilibrium value is 1.

Under the conditions used in our experiments a removal of 89.5% of the thorium B from the solution corresponds to an apparent amount of Pb exchanged per gram of Pb in the precipitate of one. In other words, if the thorium B were distributed *homogeneously* through the precipitate this value of one corresponds to the state of thermodynamic equilibrium between lead in solution and in the precipitate. A summary of all the results is presented in Fig. 1. For the sake of brevity we omit most of the experimental data, which are given in the thesis of the junior author.[1] For demonstration, one set of results obtained after an aging period of ten minutes is reported in Table IV.

The great speed with which thorium B is incorporated into the crystals indicates that extremely rapid recrystallizations occur. In each case, except with the one-hour-old product, a maximum in the amount of thorium B exchanged was obtained, this maximum corresponding to much more thorium B in the solid than the equilibrium amount. Upon continued shaking after the maximum the distribution approaches the equilibrium value. In the experiments reported in Fig. 1 this equilibrium value was not attained even after twelve hours of shaking. The reason is that the rate of recrystallization becomes much smaller with increasing age of the precipitate. In order to increase the rate of recrystallization and to attain the equilibrium value the following experiments were performed.

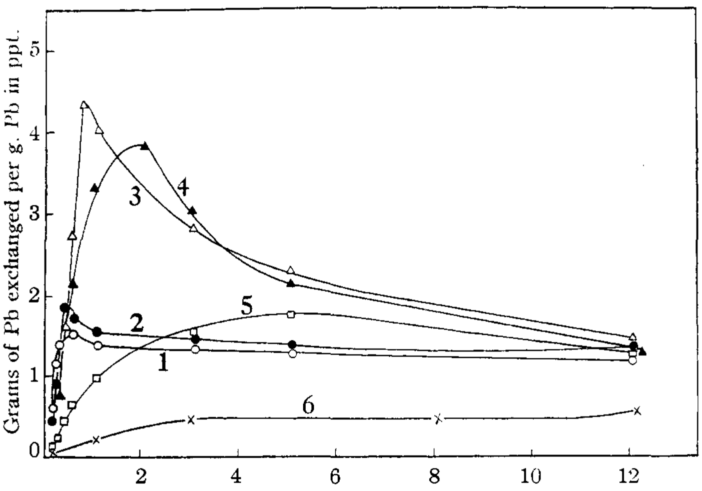

Fig. 1.—Penetration of ThB into lead chromate; age of precipitate: 1, ○, 15 sec.; 2, ●, 1 min.; 3, △, 10 min.; 4, ▲, 20 min.; 5, □, 30 min.; 6, ×, 1 hour.

The experiment of Fig. 1 in which the fifteen-second-old precipitate was shaken for one-half hour was repeated. After this time, when the maximum amount (92.8%) of the ThB had been removed from the solution, 2 ml. of 1 N hydrochloric acid was added, which made the acid concentration 0.08 N. As will be shown later, the rate of recrystallization in 0.1 N hydrochloric acid is much greater than in water. Therefore it was expected that in acid of this concentration a homogeneous distribution (89.5% ThB in the solid) could be attained in a relatively short time. An experiment similar to the one described above was also performed with the ten-minute-old precipitate which had been shaken for forty-five minutes with ThB before the acid was added.

According to the results given in Table V, ThB was returned to the solution from the enriched fractions of the precipitate more rapidly in the presence than in the absence of acid (compare with Table IV). After five hours of shaking with 0.08 N hydrochloric acid homogeneous distribution was very nearly attained.

TABLE V

ThB PENETRATION IN THE PRESENCE OF 0.08 N HCl

Age of ppt.	Time of shaking with ThB —no acid	Time of shaking with ThB in 0.08 N HCl in hours	ThB exch. in %	Pb exch. per g. Pb in ppt.
15 sec.	30 min.	0[a]	92.8	1.52
		.08	92.3	1.42
		.25	92.1	1.36
		1	92.0	1.35
		5	90.7	1.14
10 min.	45 min.	0[a]	97.4	4.33
		.17	94.6	2.06
		.50	93.7	1.76
		1	93.1	1.58
		5	89.5	1.00

[a] No acid was added to the suspension in these experiments.

The following experiments show that the height of the maximum of the thorium B distribution decreases and becomes closer to the equilibrium value when the amount of precipitate is decreased, keeping all other conditions unchanged.

The precipitate was made by adding from a 1-ml.

pipet 0.98 ml. of 0.055 M lead nitrate to an equal volume of 0.05 M potassium chromate. Eighteen ml. of 0.00235 M lead nitrate–0.05 M potassium nitrate was then added from a buret. The total time for precipitation and addition of the lead solution was one minute. Thorium B penetration experiments were performed on a ten-minute-old precipitate with results as shown in Table VI. In these experiments a homogeneous distribution would correspond to 45.5% ThB in the solid. In agreement with the results given in Table IV, it is seen that recrystallization of the ten-minute-old product was very rapid and that an *apparent* but not a true homogeneous distribution was attained after two hours.

TABLE VI

PENETRATION OF ThB INTO 10-MINUTE-OLD LEAD CHROMATE USING A SMALLER QUANTITY OF PRECIPITATE

Time of shaking with ThB, hours	ThB exch. in %	Pb exch. per g. Pb in ppt.
0.17	9.9	0.12
.50	15.5	.22
1	29.0	.49
2	45.7	1.01
3	52.6	1.32
5	54.3	1.42
8	53.6	1.38
12	52.9	1.34

Aging of Lead Chromate as Indicated by Wool Violet Adsorption.—The rapid recrystallization occurring during the early periods of aging (see Fig. 1 and Table IV) is accompanied by a pronounced decrease of the specific surface of the lead chromate particles. This is shown by the results in Table VII in which the amount of wool violet per gram of precipitate is given when the surface of the latter is saturated with the dye.[2]

TABLE VII

RATE OF CHANGE OF PARTICLE SIZE OF FRESH LEAD CHROMATE

(Preparation, see Table IV)

Age of ppt., min.[a]	1	10	20	30	60	120
W. V. adsorbed in mg. p. g.	26	21.1	19.6	19	17.0	14.3

[a] In addition to the age given, six minutes were required for the treatment of the precipitate before addition of the lead nitrate–wool violet solution. With the one-minute-old product this time was reduced to three minutes.

Speed of Aging of Fresh Lead Chromate in Various Media.—The precipitates were prepared by adding from a pipet in fifteen seconds and with rapid mechanical stirring 10 ml. of 0.05 M lead nitrate to 10 ml. of 0.05 M potassium chromate. Immediately after precipitation the mother liquor showed a very slight excess of lead (concentration about 0.0001 M). The resulting suspensions were centrifuged, decanted, and 20-ml. portions of various aging media were added. After shaking on a mechanical shaker for a designated time, the suspensions were centrifuged and specific surface determinations were made using the wool violet method.[2]

The aging medium was added six minutes after the beginning of the precipitation, at which time the specific surface was 38 mg. of wool violet per gram. As a rule, the aging medium was composed of the solution added and approximately 1 ml. of mother liquor (0.05 M potassium nitrate) which remained on the solid after centrifuging and decantation. In some cases it was desirable to wash the precipitate by centrifuging and decantation before the aging medium was added. When the aging had been carried out in acid, potassium or aluminum nitrate solutions, it was necessary to wash the precipitate after aging since these substances interfered with the dye adsorption process. Unless indicated otherwise the precipitates were not washed. In all cases the time for washing is included in the indicated period of aging. In each single washing 20 ml. of distilled water was used and the time required was from two-and-one-half to three minutes.

One set of experiments was performed in which the order of addition of the reagents was reversed, the chromate solution being added to the lead. The rate of aging of the resulting precipitate was followed as in the other experiments. The initial surface of this precipitate was 39 mg. of wool violet per gram (eight-minute-old precipitate) which is of the same order as that of the product prepared by adding lead to chromate.

The results of the above described aging experiments are given in Table VIII.

Discussion

(1) Fresh, imperfect crystalline precipitates are subject to repeated recrystallizations when kept in an aqueous medium. The "unidirectional" recrystallization,[3] the speed of which is proportional to the amount of surface exposed to the solution, results in a very marked enrichment of thorium B and a heterogeneous distribution of the latter in the precipitate during the early periods of shaking with a radioactive lead solution. Consequently, after a certain period of shaking with thorium B a maximum occurs in the distribution curve (Fig. 1). The amount of thorium B in the precipitate at the maximum was found to be much greater than corresponds to the equilibrium value. After reaching the maximum the thorium B content of the precipitate decreases as a result of repeated ("multidirectional") recrystallizations which ultimately lead to a homogeneous distribution of the thorium B between solid and solution. The presence of acid (Table V) promotes these recrystallizations. The location of the maximum is determined by the relative speeds of the unidirectional and multidirectional recrystallizations. At first sight it is surprising that a higher maximum was found

---

(3) *Cf.* I. M. Kolthoff and C. Rosenblum, THIS JOURNAL, **57**, 597, 607 (1935).

TABLE VIII

RATE OF AGING OF LEAD CHROMATE IN VARIOUS MEDIA

(W. V. Method)

Expt.	Aging medium and conditions of aging	Mg. of W. V. adsbd. per g. ppt. after aging for						
		10 min.	0.5 hr.	1 hr.	3 hrs.	1 day	1 wk.	1 mo.
1	Water	27.3	24.5	20.8	17.3	15.3	13.0	11.3
2	Water[a]			21.5	18.7	16.0	13.5	
3	Water[b]		22.0	21.6	17.3	15.2		
4	Water, not shaken during aging			22.0	22.7	21.8	21.4	
5	Water, standing centrifuged			23.4	23.4	20.2	21.1	
6	0.0005 M $Pb(NO_3)_2$		23.9	22.0	22.6	16.1		
7	.0005 M K_2CrO_4		21.6	22.8	17.3	15.3		
8	.001 M K_2CrO_4[a,b]			22.5	27.3	15.6		
9	.01 M $Pb(NO_3)_2$[b]			25.0	23.1	14.8	11.4	
10	.01 M K_2CrO_4[b]			23.0	18.2	15.0	12.2	
11	.5 g./liter $Al(NO_3)_3$[a,b]			19.7	18.0	13.5		
12	Absolute ethanol[b]			27.3	28.8	27.0	28.8	
13	0.01 M HNO_3[b]			17.0	12.3	11.2		
14	.01 M HCl[b]			17.0	10.4	8.1		
15	.1 M HNO_3[b]			10.5	7.9	4.7	1.6	
16	.1 M HNO_3, 0.01 M K_2CrO_4[b]			14.1	7.7	4.5		
17	.1 M HNO_3, 0.01 M $Pb(NO_3)_2$[b]			19.3	13.1	4.6		
18	Mother liquor[c]		22.4	20.5	17.4	13.6	9.6	
19	0.1 M KNO_3[b]			19.2	15.8	12.8	8.4	
20	Water[d]			20.0	16.4			

[a] Washed twice before adding aging medium. [b] Washed twice before dye adsorption (3 times in experiments 11, 15, 16 and 17). [c] Centrifuged before and shaken during aging. [d] Reverse order of addition of reagents: chromate to lead.

with a ten-minute-old precipitate than with a fresher product which had been aged for fifteen seconds or one minute (Fig. 1). This peculiarity is explained by the fact that both types of recrystallization, and especially the multidirectional one, are much faster with the very fresh than with the ten-minute-old products. Keeping the amount of lead in the radioactive solution constant the height of the maximum was found to decrease with decreasing amount of lead chromate in the suspension. The reason is that there is less enrichment of thorium B in the solid as a result of unidirectional recrystallizations when the amount of precipitate is decreased, other conditions being the same.

(2) From the thorium B (Fig. 1) and the wool violet experiments (Table VIII) it is evident that the aging in aqueous medium is very rapid and is most pronounced during the first hour after the preparation of the precipitate. Experiments 6 to 10 in Table VIII reveal the unexpected result that the aging in aqueous solutions containing an excess of lead nitrate or of potassium chromate is of the same order of magnitude as in water. It is quite certain, therefore, that the rate of aging in the absence of acids is not governed by the solubility of the precipitate in the bulk of the solution. If this were the case one would expect a much slower rate of aging in lead nitrate or potassium chromate solutions than in water. In the case of aging of barium sulfate in water, barium chloride and potassium sulfate solutions a similar result has been found in this Laboratory.[4] The above results strongly indicate that the aging process in aqueous medium is not an Ostwald ripening but is primarily a cementing process which occurs as a result of rapid recrystallizations in the aqueous film surrounding the individual particles in an agglomerate. The slight inhibition of the aging, especially in an excess of lead during the early stages, may be attributed to an adsorption.

The reason for the ineffectiveness upon the aging of an excess of lattice ions in the liquid phase is probably that (in the absence of acids) the speed of recrystallization of fresh imperfect precipitates is primarily determined by the rate of exchange between the particles and the thin water film surrounding them. When the active surface is not blocked by adsorbed material, the recrystallization in the aqueous film is little affected by the presence of an excess of lattice ions, and the kinetic exchange (due to hydration energy) is unimpeded as long as the mole fraction of solvent composing the film is practically *unity*. When the aqueous film is replaced by

---

(4) A. H. Bushey, Doctor's Thesis, University of Minnesota, 1940.

ethanol no aging occurs (expt. 12 in Table VIII), undoubtedly because the energy of hydration of lead and chromate ions is much greater than that of alcoholation. The very rapid initial aging in the alcohol experiments is only apparent, being due to washing of the precipitate with water preparatory to specific surface determination. It is evident from Table VIII that electrolytes which have no ion in common with the precipitate promote the aging. Whether this electrolyte effect is due to an increase of the hydration energy (interionic effect) or to a decrease of the distance of approach of the particles in an agglomerate or to both cannot be decided at present.

When the suspensions were not shaken (experiments 4 and 5, Table VIII) the recrystallization process seemed to come to a more or less abrupt halt after one or two hours of aging. The reason for this may be that large agglomerates (necessary for a rapid cementing process) were not formed to the same extent in these experiments as was the case when the suspensions were shaken (the appearance of the suspensions supports this view). Also it is likely that the position of each particle remained quite fixed when there was no agitation and consequently recrystallization (cementing in the liquid films) could occur to a certain extent and no further.

That an increase of solubility by the addition of nitric or hydrochloric acid promotes the aging markedly is evident from experiments 13 to 18 in Table VIII. This aging may be due in part to an Ostwald ripening as indicated by the fact that it was suppressed by addition of lattice ions (solubility effect), according to experiments 15 to 17. In experiments 1 and 20 the rate of aging of lead chromate is shown to be independent of the order of precipitation, *i. e.*, it was found immaterial whether the lead was added to the chromate or the precipitation was carried out in the reverse manner.

TABLE IX

RATE OF PENETRATION OF THORIUM B AFTER AGING OF PRECIPITATES FOR 24 HOURS

(Amount of precipitate 161.6 mg.; Pb (solution) 4.14 mg.)

Aging medium and condition of aging	App. mg. Pb exchanged p. g. $PbCrO_4$ after shaking for 0.33	1	2	4 hr.
Water (shaken)	7.8	9.4	10.2	15.0
Water (not shaken)	8.2	11.5	12.5	24.5
Water (centrifuged, not shaken)	7.8	11.2	16.0	31.0
0.01 *M* lead nitrate (shaken)	8.8	10.1	12	14
0.01 *M* potassium chromate (shaken)	10.4	16	22	36
95% ethanol (shaken)	250	6300	3100	1550

The conclusions drawn from Table VIII could be substantiated by thorium B experiments. Precipitates were prepared and aged in the same way as those described in Table VIII. After twenty-four hours of aging the precipitates were washed and then shaken with radioactive lead solutions. Some of the results are given in Table IX.

Summary

1. The average particle size of lead chromate precipitated at room temperature was found to decrease markedly with more vigorous stirring of the reaction mixture. Practically the same specific surface was found when the chromate was added to an equivalent amount of lead solution as when the precipitation was made in the reverse way.

2. Contrary to the von Weimarn rule the particle size of lead chromate precipitates was found to decrease with decreasing concentration of the precipitants.

3. Upon shaking of relatively fresh imperfect precipitates of lead chromate with a radioactive lead solution there is a rapid penetration of thorium B into the solid. With fresh products a pronounced maximum in the distribution of the thorium B is found, the radioactive lead content of the solid at the maximum being much greater than corresponds to the equilibrium value. Upon further shaking, distribution equilibrium is approached. The results have been interpreted.

4. The rates of recrystallization and of aging of fresh precipitates were found to be of the same order of magnitude in water, 0.01 *M* lead nitrate and 0.01 *M* potassium chromate, although the solubilities of the precipitate in these media are widely different. Apparently, the rate of aging is determined by the rate of exchange of lattice ions between the solid and the water film surrounding the particles. This exchange process seems to be unaffected by the presence of excess lattice ions in the solution.

5. Aging of lead chromate in aqueous medium results in a rapid growth of the individual particles due to the above-mentioned cementing process in the liquid film. No indication of Ostwald ripening has been found in media in which the solubility of the precipitate was small (water, excess of lattice ions, presence of indifferent elec-

trolytes). The aging of lead chromate is greatly enhanced by the addition of acids which increase the solubility. With increasing solubility part of the aging may be attributed to Ostwald ripening.

6. No aging was found in 95% ethanol. The solubility of lead chromate in this medium is extremely small.

MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 3, 1941

[CONTRIBUTION FROM CHEMICAL AND OCEANOGRAPHIC LABORATORIES, UNIVERSITY OF WASHINGTON]

Specific Gravities and Electrical Conductances of Some Calcium Sulfate Solutions and Mixtures of Sodium Chloride and Calcium Sulfate

BY RANDALL E. HAMM WITH THOMAS G. THOMPSON

In previous papers[1,2] were reported specific gravities and electrical conductances of pure salt solutions of sodium chloride, potassium chloride, and magnesium sulfate, and the mixtures, sodium chloride–potassium chloride and sodium chloride–magnesium sulfate. These papers were the beginning of a study of the conductances and specific gravities of salt solutions in concentrations as found in sea water and were made to further the understanding of solutions of mixed electrolytes and the physical chemistry of ocean water. This paper is a continuation of the work and reports specific gravities and electrical conductances of calcium sulfate solutions and mixtures of sodium chloride and calcium sulfate. While previous papers report only the values for mixtures having a constant ionic ratio, this paper also reports electrical conductances of solutions containing varying amounts of calcium sulfate at constant concentrations of sodium chloride.

Experimental Methods

The apparatus used has been described previously.[2,3] The bridge and the thermometers were again calibrated and the cell constants were determined using the data reported by Jones and Bradshaw[4] and Bremner and Thompson.[3]

The sodium chloride used was purified by the method described by Shedlovsky.[5]

The calcium sulfate was prepared and purified by treating the purest Baker Analyzed calcium carbonate with C. P. sulfuric acid slowly until effervescence ceased, bringing to a boil, filtering, and collecting the crystals that formed upon cooling. Successive batches were prepared by treating the original precipitate with boiling dilute sulfuric acid. The crystals were heated to about 200° until all of the sulfuric acid was driven off. Immediately before using, this calcium sulfate was heated to about 500° for eight to twelve hours in a glass-stoppered weighing bottle, the weighing bottle was transferred to a vacuum desiccator, and the desiccator evacuated. Well desiccated air was passed into the desiccator when ready for weighing the calcium sulfate.

The calcium sulfate was weighed using a tare bottle of the same size and shape which had gone through the same previous treatment. All solutions were prepared by weight. Corrections to vacuum conditions were made.

Results

Solutions were prepared which contained quantities of calcium sulfate and of sodium chloride–calcium sulfate comparable to sea water of the chlorinities of 19, 14, 8, and 4 parts per thousand. Table I gives a summary of the weights of the two salts added to one thousand grams of water.

TABLE I

GRAMS OF SALTS ADDED TO ONE THOUSAND GRAMS OF WATER

Approx. chlorinity, ‰	19	14	8	4
	Calcium Sulfate Solutions			
$CaSO_4$, g.	1.5175_4	1.1102_2	0.6290_4	0.3127_5
	Sodium Chloride–Calcium Sulfate Solutions			
NaCl, g.	27.2615_9	19.9443_9	11.3002_0	5.6183_6
$CaSO_4$, g.	1.5175_4	1.1102_2	0.6290_4	0.3127_5

Duplicate or triplicate solutions were prepared in all cases and the specific gravities and electrical conductances were determined at the temperatures 0, 5, 10, 15, 20 and 25°.

The specific gravities of calcium sulfate solutions are listed in Table II. The values calculated from the Root equation are also listed with the difference being given in the last column. The constants of the Root equation were determined by the method of least squares and are given in Table III. The specific gravities of calcium sulfate solutions have been reported by Harkins and Paine[6] and Cameron and Robinson.[7]

---

[1] Bremner, Thompson and Utterback, THIS JOURNAL, **60**, 2616 (1938).

[2] Bremner, Thompson and Utterback, *ibid.*, **61**, 1219 (1939).

[3] Bremner and Thompson, *ibid.*, **59**, 2372 (1937).

[4] Jones and Bradshaw, *ibid.*, **55**, 1780 (1933).

[5] Shedlovsky, *ibid.*, **54**, 1411 (1932).

[6] Harkins and Paine, *ibid.*, **41**, 1155 (1919).

[7] Cameron and Robinson, *J. Phys. Chem.*, **14**, 569 (1910).