JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 57 APRIL 5, 1935 NUMBER 4

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Structural Changes Taking Place during the Aging of Freshly Formed Precipitates. III. The Mechanism of the Aging of Lead Sulfate Precipitated at Room Temperature

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In previous studies[1] it has been shown that freshly prepared lead sulfate obtained by mixing 0.1 molar lead nitrate and 0.1 molar potassium sulfate at room temperature consists of microscopically visible particles of a highly porous structure. These small particles consist of amicroscopic crystals and are separated by fine capillaries which are filled with mother liquor. On keeping the precipitate in the mother liquor or an aqueous solution of lead sulfate in water, a rapid aging process occurs resulting in a large decrease of the internal surface, whereas the external surface decreases but slightly.

It was of interest to study the mechanism of this aging more in detail. The decrease of the internal surface might be attributed to either one of the two following reactions or to both occurring simultaneously. (a) The amicroscopic crystals are surrounded by the mother liquor contained in the microscopic particles. The former can move freely and may grow together by virtue of the fact that the positive ions of one amicroscopic crystal attract the negative ions of the other one. (b) The internal surface of the imperfect particles contains many active spots. Lead and sulfate ions are easily deposited on these spots and may go into solution from other spots of the surface. The mechanism of the aging is thus explained by a recrystallization process. It will be shown in this paper that the aging at room temperature actually is to be attributed to the latter and that the cementing together of the amicroscopic crystals is of subordinate significance, if of any importance. In a subsequent paper evidence will be given that the recrystallization occurs mainly by way of external solution (mother liquor) and that internal recrystallization within the capillaries is much less pronounced.

Experimental

If the aging process is to be attributed to a recrystallization, it may be expected that the speed of perfection of the particles will decrease when the crystals are kept in a medium in which the solubility of the lead sulfate is less than in water. In order to test this point experiments of the following kind were performed: 98.6 ml. of 0.1 *m* potassium sulfate was added to 103.6 ml. of 0.1 *m* lead nitrate, the precipitate filtered as quickly as possible, washed four times with 10-ml. portions of conductivity water and four times with 10-ml. portions of absolute alcohol. After this treatment the precipitate was made air dry by aspiration of air of a relative humidity of 0.25 to 0.6. By working rapidly the 3 g. of precipitate was only fifteen to twenty minutes old after the washing process with alcohol. The air-dried precipitate was divided among Pyrex flasks containing either the desired aging media or a radioactive lead solution as indicated in Table I. A small portion was saved and permitted to age in the air-dried state. The aging medium in experiment 2 (Table I) had the same composition as the mother liquor after precipitation of the lead sulfate according to the above procedure. After the indicated time of aging the precipitate was filtered on sintered micro glass filter crucibles and most of it, without further washing, transferred to the thorium B solution whose composition is

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[1] (a) THIS JOURNAL, **56**, 1264 (1934); (b) **56**, 1658 (1934).

TABLE I

FRESHLY PRECIPITATED LEAD SULFATE, AIR-DRIED, AGED UNDER VARIOUS CONDITIONS, THEN SHAKEN WITH THORIUM B FOR ONE AND FIFTEEN MINUTES, RESPECTIVELY, AT ROOM TEMPERATURE (ABOUT 27°)

Number		1	2	3	4	5	6	7
Medium in which ppt. was aged		..	0.00162 *M* $Pb(NO_3)_2$ + 0.0652 *M* KNO_3	Satd. $PbSO_4$	...	As 2 in 70% alc.	99.9% alc.	Air
Composition of Th B solution			0.00162 *M* $Pb(NO_3)_2$ + 0.0652 *M* KNO_3		Same in 70% alc.		Same as 1	
Time of aging, minutes		0^b	76	84	0^b	98	107	110
"Pb exchanged"	Mg./1 g. $PbSO_4$ 1 min. shaking with Th B	15.0	2.9	3.6	3.7	4.0	5.0	14.5
	If aged in mother liquor, same conds.[a]	14.3	3.6	3.3	14.3	3.1	3.0	3.0
Time of aging, minutes		0^b	99	130	0	129	...	160
"Pb exchanged"	Mg./1 g., 15 min. shaking with Th B	280	13.8	11.2	4.0	4.3	...	167
	If aged in mother liquor, same conds.[a]	118	14.2	12.3	118	12.3	...	11.0

[a] These figures were taken from results reported in a previous study.[1a]

[b] These values represent the duration of the immersion of the solid in the medium before Th B was added. Actually the total age of the precipitate after it had been sucked air dry was 21 to 22 minutes. Therefore the total ages of these samples are greater by 21–22 minutes than those recorded.

given in Table I and with which it was shaken for one minute and fifteen minutes, respectively. From the amount of thorium B adsorbed the number of mg. of lead (per 1 g. of lead sulfate) having taken part in the kinetic exchange was calculated in the usual way.[1a,b] For the sake of comparison, the amount of lead exchanged, previously found[1a,b] after one and fifteen minutes of shaking with thorium B after the precipitate had first been aged for corresponding times in the mother liquor, is given in columns 6 and 9 of Table I. The amount of lead sulfate used in each experiment was found after the shaking with thorium B by filtering in a Gooch crucible and weighing after heating to 500°. All experiments have been duplicated and gave a satisfactory agreement.

An unexpected result is found in experiment 4. When the fresh precipitate was shaken with thorium B in 70% alcohol (exact composition of solution see under 2, Table I) instead of in water, the amounts of exchanged lead (in mg. per 1 g. of lead sulfate) were 3.7 and 4.0 after one and fifteen minutes of shaking, respectively, whereas the corresponding figures in water were 15.0 and 280, respectively. Still more striking is the fact that the amounts of exchanged lead were nearly the same after one to two hours of aging in 70% alcohol before shaking with thorium B (expt. 5). The peculiar results of experiments 4 and 5 can be explained only when it is assumed that the speed of recrystallization of the amicroscopic particles as well as the speed of kinetic exchange in 70% (and still more in 100%) ethanol is much slower than in water. Therefore a comparison of the amounts of exchanged lead found in these media with those in aqueous solutions of thorium B would yield misleading results regarding the degree of imperfection of the precipitate.

That the above assumptions are correct was shown conclusively by the following experiments. Portions of air-dried lead sulfate, prepared just as were the products used in Table I, were shaken for various times with a thorium B solution in 70% ethanol, containing 0.0016 mole of lead nitrate and 0.065 mole of potassium nitrate per liter.

TABLE II

Time of shaking in hours	0.3	2.5	22.5
Pb exchanged, in mg. per 1 g. $PbSO_4$	4.2	5.1	10.3

In another set of experiments the air-dried lead sulfate was shaken first for two hours in 70% ethanol, filtered and then shaken with the radioactive lead solution in 70% alcohol.

TABLE III

Time of shaking in hours	0.3	2.5	20.5
Pb exchanged, in mg. per 1 g. $PbSO_4$	2.5	3.2	6.1

Evidently the aging is strongly inhibited in a medium of 70% ethanol. This was shown to be true in more drastic experiments in which the air dry lead sulfate was shaken for two days in 70% alcohol. The "age" was then determined by shaking with an aqueous solution of thorium B. After fifteen minutes of shaking the amount of lead exchanged was 5.85 mg., after three and one-fourth hours of shaking 22.5 mg. per gram. The original air-dried and fresh precipitate gave the figures 280 and 700 mg., respectively. The aging in 70% alcohol therefore is distinct but much less pronounced than aging in aqueous medium. Precipitates kept in the aqueous mother liquor for two days gave the following exchanges: 4.1 and 4.8 mg. after fifteen minutes and three and one-fourth hours of shaking, respectively.

From the above one would expect that the aging in absolute ethanol would be much less again than in 70% alcohol, since the solubility of the lead sulfate in the former is very much less than in the latter. However, from the first part of experiment 6 in Table I, one would be inclined to infer that lead sulfate ages as rapidly in ethanol as in water. The peculiar result can be explained by the fact that on aging in alcohol the capillaries of the fresh precipitate become filled with ethanol. The latter is not entirely replaced by water upon subsequent shaking with an aqueous thorium B solution for a very short time (one minute of shaking). Upon longer shaking, however, the thorium B should distribute itself completely if the precipitate has remained in a fresh state. *Actually it could be shown that hardly any aging occurs if the air dry precipitate is kept in absolute alcohol for a shorter or longer time.*

Air dry lead sulfate (Table I) was shaken for one and two-thirds hours at 27° with absolute ethanol, filtered, made air dry and shaken for various times with aqueous thorium B solutions (composition see expt. 1, Table I).

TABLE IV

Time of shaking with Th B in hours	0.25	3	21
Pb exchanged, in mg. per 1 g.	140	700	700
Pb exchanged/Pb in ppt. × 100	20	100	100

Similar experiments were made after aging for one day in absolute alcohol at 27°.

TABLE V

Time of shaking with Th B in hours	0.25	3
Pb exchanged, in mg. per 1 g.	70	700
Pb exchanged/Pb in ppt. × 100	10	100

Aging experiments have also been carried out in pure methanol. It may be expected that the solubility of lead sulfate in this solvent is intermediate between that in water and ethanol, and that, therefore, the speed of aging will be found to be between that in the two other solvents. Air-dried fresh lead sulfate (Table I) was shaken for twenty-three hours in pure methanol at 25°. After filtration it was made air dry, and portions were shaken with aqueous thorium B solutions.

TABLE VI

Time of shaking with Thorium B in hours	0.3	3
Pb exchanged, in mg. per 1 g.	31	105

The aging appears to be less pronounced than was found in 70% ethanol but much more so than in absolute alcohol (Table V).

Discussion

By experiments to be reported in the next paper of this series it was shown that the capillaries of the fresh lead sulfate were filled with ethanol or methanol, when kept in these solvents. From the fact that no, or a greatly inhibited, aging takes place in these solvents, it may be concluded that the drastic aging process in an aqueous medium is not to be attributed to a cementing together of the amicroscopic crystals embedded in the microscopic particles, but to a recrystallization. The speed of this recrystallization and, therefore, of the aging as well, increases with the solubility in the particular medium. It was shown, for example, although not reported in this paper, that the speed of aging in dilute aqueous nitric acid was much faster than in the absence of the acid. The recrystallization does not take place strictly in such a way that the larger of the microcrystals grow at the cost of the smaller ones. The amicroscopic particles are highly imperfect and not well ordered; therefore at certain spots they may go into solution and grow at other active spots, thus leading to the formation of more perfect particles. Eventually these may cement together, yielding microscopic crystals with a more regular mosaic structure. The microscopic particles are subject to still further aging, especially if they are small and heterodisperse, by recrystallization and cementing together. From all the work we have done so far with lead sulfate we are led to the conclusion that the aging of the precipitate in the aqueous mother liquor takes place very rapidly in the beginning when the precipitate is just formed but that the crystals are not in thermodynamic equilibrium with the environment even after long times of aging at room temperature.

Acknowledgment.—We wish to express our sincere appreciation to the Cyrus M. Warren Fund of the American Academy of Arts and Sciences for the allotment of a grant, which enabled us to pursue part of the present study.

Summary

1. Freshly precipitated lead sulfate hardly undergoes any aging when kept in ethanol. In

methanol and in 70% ethanol the aging is much less rapid than in aqueous medium.

2. The rapid aging is to be attributed to a recrystallization of the fresh precipitate. The speed of this recrystallization and, therefore, of the aging, decreases with decreasing solubility of the lead sulfate in the particular medium.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 18, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Effect of the Hydrogen Bond on the Dielectric Constants and Boiling Points of Organic Liquids

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The dielectric constant of liquids is a function of the number of molecules per cc., of the dipole moment, of the electronic and atomic polarizations, of temperature, and of the interaction of the molecules with each other. If all but one of these factors can be made constant for a group of compounds, then the plot of the variable factor against the dielectric constant should be some simple curve.

The factors are eliminated or made constant as follows: temperature by taking all data at the same temperature; electronic polarization by subtracting the refractive index squared n^2 from the dielectric constant ϵ; the atomic polarization contributes so little to the dielectric constant that it may be neglected; the different number of molecules per cc. by correcting $\epsilon - n^2$ to the value it would have when there are the same number of molecules per cc. This is accomplished by use of the equation

$$(\epsilon - n^2) \text{ corrected} = (\epsilon - n^2)Md_0/dM_0$$

where M_0 is the molecular weight of the compound chosen as standard, d_0 its density, M the molecular weight of the compound being corrected and d its density. Acetone at 20° was taken as standard so $(\epsilon - n^2)$ corrected represents the dielectric constant each of these compounds would have if the contribution of the electronic polarization were eliminated and each cc. made to contain the number of molecules that exist in a cc. of acetone at 20°.

In this way the effects of all factors have been eliminated except the dipole moment and the interaction of the molecules. There has been no evidence that indicates clearly whether the interaction of molecules which causes a variation in dielectric constant is essentially of a physical or a chemical nature.[1,2] A physical interaction would be expected to be due mainly to the attractions between polar molecules, and to affect the dielectric constant in a way dependent chiefly on the dipole moments of the molecules. The quantity $\sqrt{(\epsilon - n^2)}$ corrected would be expected to be some simple function of the dipole moments of the free molecules. On the other hand, if the interactions involve the formation of bonds, the values of $\sqrt{(\epsilon - n^2)}$ corrected would vary greatly from this function and there would be no simple relationship between the quantity $\sqrt{(\epsilon - n^2)}$ corrected and the dipole moments of the free molecules. Since it appeared from the equations connecting dielectric constant and dipole moment that the square root of the dielectric constant plotted against the dipole moment should give a more simple curve than the dielectric constant itself, the square root has been used.

Evidence can be obtained on this question by taking first a group of liquids in which the molecules would not be expected to form chemical bonds and plotting the square root of the dielectric constant as corrected above against the dipole moment. If this interaction is of a chemical nature, it is eliminated by the choice of liquids and the plot should be some simple curve (assuming, of course, that compounds were chosen that do not form chemical bonds).

Ten liquids of widely divergent character that would not be expected to form bonds and with dipole moments from zero to 3.91, were taken at random and $\sqrt{(\epsilon - n^2)}$ corrected was plotted against the dipole moment μ. The compounds are benzene, ethyl ether, ethyl acetate, chloroform, ethyl iodide, ethyl bromide, acetaldehyde, acetone, acetonitrile and benzonitrile. It is seen in Fig. 1[3] that all of these ten compounds fall

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[1] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, New York, 1927, p. 134.

[2] Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, 1931, p. 188.

[3] The dipole moment values are from Smyth's book, "Dielectric Constant and Molecular Structure," or from *Trans. Faraday Soc.*, App. I, LXXXVI, Sept. (1934). The dielectric constants and refractive indices are from the "International Critical Tables." The meas