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

Studies on Aging of Fresh Precipitates. XVI. The Distribution Coefficient of Chromate Ions between Barium Sulfate and Aqueous Solutions[1]

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Barium sulfate and barium chromate crystallize in the orthorhombic system, the lattice constants of the former being $a = 8.85 \times 10^{-8}$ cm., $b = 5.43 \times 10^{-8}$, and $c = 7.14 \times 10^{-8}$, and of the latter being $a = 9.14 \times 10^{-8}$ cm., $b = 5.54 \times 10^{-8}$, $c = 7.35 \times 10^{-8}$.[2] From the close agreement in lattice constants one would expect that barium sulfate and barium chromate can form a complete series of mixed crystals. In the present study the distribution coefficient of the chromate ion between an aqueous solution and barium sulfate has been determined under conditions of homogeneous distribution of the chromate through the solid phase. Upon shaking barium sulfate with a solution containing sulfate and chromate ions the following exchange occurs

$$\underset{\text{solid}}{BaSO_4} + \underset{\text{solution}}{CrO_4^=} \longrightarrow \underset{\text{solid}}{BaCrO_4} + \underset{\text{solution}}{SO_4^=} \qquad (1)$$

The chromate ions replace part of the sulfate ions in the barium sulfate, and the barium chromate formed is incorporated in the solid phase in the form of mixed crystals. The mixed crystals thus formed are heterogeneous, and become homogeneous, and in thermodynamic equilibrium with the liquid phase, only upon repeated recrystallizations of the solid phase. In previous studies[3] it has been shown that fresh lead sulfate precipitated from 0.1 *M* lead nitrate and potassium sulfate is highly imperfect and perfects itself by repeated recrystallizations when left in contact with the mother liquor. It was expected that, qualitatively, barium sulfate would behave in an identical way and, therefore, that shaking of freshly precipitated barium sulfate with solutions containing sulfate and chromate ions for sufficient periods of time would yield homogeneous mixed crystals of barium sulfate and barium chromate in equilibrium with the liquid phase.

Scholtz and Abegg[4] in their study of the system barium sulfate–barium chromate did not realize the importance of obtaining equilibrium conditions. This explains why no constant value of the distribution coefficient is obtained from their results.

When the mixed crystals are in equilibrium with the liquid phase, the following relation holds

$$\frac{(a\mathrm{CrO_4^=})_S\,(a\mathrm{SO_4^=})_L}{(a\mathrm{SO_4^=})_S\,(a\mathrm{CrO_4^=})_L} = K' \qquad (1)$$

in which "*a*" denotes activity, the subscript S the component in the solid phase, and L the component in the liquid phase. The ratio of the activity coefficients of the sulfate and chromate ions in the solution will remain constant over a wide range of ionic strengths. If this ratio in the solid phase is also constant over a wide range of varying compositions of the mixed crystals, expression (1) can be written in the following way

$$\frac{(\mathrm{CrO_4^=})_S}{(\mathrm{CrO_4^=})_L} = K\,\frac{(\mathrm{SO_4^=})_S}{(\mathrm{SO_4^=})_L} \qquad (2)$$

in which the symbols between parentheses represent mole fractions or the number of moles. If the entire system were ideal the distribution coefficient *K* should be equal to the ratio of the solubility products of barium sulfate and barium chromate.[5]

Experimental

Experiments at Room Temperature (26 ± 1°).—To 50 ml. of 0.10 *M* sodium sulfate in a volumetric flask of 250 ml. was added 25 ml. of 0.10 *M* barium nitrate and 25 ml. of 0.1000 *M* sodium chromate. The suspension was made up with water to 250 ml., thoroughly shaken and transferred to 110-ml. soft glass bottles equipped with paraffined corks. The bottles were then placed on a mechanical shaker and allowed to shake for various lengths of time at 26 ± 1°.

After the shaking period homogeneous samples were taken, centrifuged and an aliquot part of the clear supernatant liquid analyzed for chromate by the standard iodimetric method. The same volume of an appropriate blank was treated the same way. From the original composition of the supernatant liquid and the amount of chromate removed, the necessary data were obtained for calculating *K* in expression (2). The results are given in Table I. The *lines* "Chromate in $BaSO_4$, %" indicate the percentage of the chromate removed from the solution after shaking for the indicated period of time.

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(1) Part of a thesis submitted by G. E. Noponen to the Graduate School of the University of Minnesota in partial fulfilment of the requirements of the degree of Doctor of Philosophy, June, 1936. XV, THIS JOURNAL, **59**, 2029 (1937).

(2) O. Ruff and E. Ascher, *Z. anorg. allgem. Chem.*, **185**, 369 (1929).

(3) I. M. Kolthoff and Ch. Rosenblum, THIS JOURNAL, **56**, 1264, 1658 (1934); **57**, 597, 607, 2573, 2577 (1935); **58**, 116, 121 (1936).

(4) M. Scholtz and R. Abegg, *Z. Elektrochem.*, **12**, 425 (1906).

(5) See H. Flood, *Z. anorg. allgem. Chem.*, **229**, 76 (1936).

TABLE I

DISTRIBUTION OF CHROMATE BETWEEN BARIUM SULFATE AND SOLUTION AT 26 ± 1°

Time of shaking	1/2 hr.	1 hr.	2 hrs.	4 hrs.
Chromate in $BaSO_4$, %	14.8	19.6	24.5	27.8

Time of shaking	19 hrs.	3 days	5 days
Chromate in $BaSO_4$, %	32.4	33.2	33.3

Apparently equilibrium is reached after about a day of shaking. After three to five days the mole percentage of chromate in the precipitate is 33.3 and K is equal to 1.00.

The experiments were repeated, but instead of 25 ml. of 0.100 M chromate, 10 ml. was added. The results are given in Table II.

TABLE II

DISTRIBUTION OF CHROMATE BETWEEN BARIUM SULFATE AND SOLUTION

Time of shaking	1 hr.	4 hrs.	20 hrs.	1 week	2 weeks
Chromate in $BaSO_4$, %	30.8	43.0	45.4	45.1	45.2

Mole percentage of chromate in precipitate is 18; $K = 1.18$.

Again equilibrium was reached after about one day of shaking.

The following experiments were carried out with 50 ml. of 0.01 M chromate instead of 25 ml. of 0.1 M. A duplicate set shows the good reproducibility, especially of the final value of the chromate distribution.

TABLE III

DISTRIBUTION OF CHROMATE BETWEEN BARIUM SULFATE AND SOLUTION

Time of shaking, hr.		1	2	3	6	19
Chromate in $BaSO_4$, %	Set I	38.8	44.5	..	49.0	..
	Set II	40.1	..	48.1	..	52.4

Time of shaking		23 hrs.	7 days	9 days	16 days
Chromate in $BaSO_4$, %	Set I	50.0	50.7	..	
	Set II	..	..	50.7	50.7

Mole percentage of chromate in precipitate is 5.07; $K = 1.14$.

From the results given in Tables I to III it is inferred that the value of K is constant at mole percentages of chromate in the barium sulfate between 5 and 33 and is equal to 1.1.

Effect of Order of Addition of Reagents.—In the following experiments the same amounts of reagent were used as in those of Table I, but the barium nitrate was added to the mixture of sodium sulfate and chromate (Table IV).

TABLE IV

CHROMATE COPRECIPITATED WITH BARIUM SULFATE

Time of shaking	1/2 hr.	1 hr.	2 hrs.	24 hrs.
Chromate in $BaSO_4$, %	42.5	43.0	43.2	42.7

Time of shaking	7 days	1 month	2 months
Chromate in $BaSO_4$, %	43.2	45.4	50.4

Evidently no equilibrium is obtained even after two months of shaking. Indications were obtained that upon addition of the barium nitrate to the sulfate–chromate mixture part of the chromate precipitates as barium chromate and not in the form of mixed crystals. Apparently, the barium chromate has a much smaller speed of recrystallization than the fresh barium sulfate or the imperfect mixed crystals. The results of Table IV indicate that no true equilibrium will be reached when barium chromate is shaken with a sulfate solution. This conclusion will be subjected to further experimental test.

Experiments at 95°

The barium sulfate suspensions were prepared in a manner similar to that at room temperature (see text before Table I). After they had been transferred to the 110-ml. bottles they were preheated for five minutes in a boiling water-bath, stoppered and the bottles fastened on a rotator in an oven kept at 95 ± 1°. The bottles were rotated once every five seconds. After various periods of heating, samples were removed, cooled quickly and centrifuged. The chromate was determined iodimetrically in an aliquot part of the supernatant liquid.

In the following experiments to 50 ml. of 0.1 M sodium sulfate in a volumetric flask of 250 ml. was added 25 ml. of 0.1 M barium nitrate and 25 ml. of 0.1 M sodium chromate; the suspension was treated further as described above.

The percentage of chromate removed from the solution after shaking for various periods of time is given in Table V.

TABLE V

DISTRIBUTION OF CHROMATE BETWEEN BARIUM SULFATE AND SOLUTION AT 95°

Time of shaking at 95°	1 hr.	4 hrs.	24 hrs.	2 days
Chromate in $BaSO_4$, %	13.8	15.4	17.3	20.4

Time of shaking at 95°	6 days	2 weeks	1 mo.
Chromate in $BaSO_4$, %	20.1	20.3	20.2

Equilibrium value 20.2%, corresponding to a value of K of 0.38 at a mole percentage of chromate in the solid phase of 20.2.

The above experiments were repeated using 10 ml. of 0.1 M sodium chromate instead of 25 ml. The results are given in Table VI.

TABLE VI

AS TABLE V WITH LESS CHROMATE

Time of shaking at 95°	1 hr.	2 days	1 week
Chromate in $BaSO_4$, %	21.4	24.1	24.3

Time of shaking at 95°	2 weeks	1 month
Chromate in $BaSO_4$, %	24.7	24.7

Equilibrium value 24.7%, corresponding to a value of K of 0.40 at a mole percentage of chromate in the solid phase of 9.9.

In the experiments given in Table VII 25 ml. of 0.01 M sodium chromate was added instead of 25 ml. of 0.1 M (Table V).

TABLE VII

AS TABLE VI WITH LESS CHROMATE

Time of shaking at 95°	1 hr.	46 hrs.	1 week	1 month
Chromate in $BaSO_4$, %	25.5	27.2	31.9	25.7

Equilibrium value 25.7%, corresponding to a K value of

0.36 at a mole percentage of chromate in the solid phase of 2.6.

From Tables V, VI and VII it is inferred that within a range of mole percentages of chromate in the solid phase between 2.6 and 20.2 K, is constant at 95° and equal to 0.38.

Discussion

1. The value of the distribution constant of 1.10 at 26° is of the same order as the ratio of the solubility products of barium chromate and barium sulfate. From the fact that the distribution constant at 95° is about one-third of the value found at room temperature, one may infer that the solubility of barium chromate increases more with increasing temperature than that of barium sulfate. From data in the literature it follows that the solubility of barium sulfate increases 1.5 times and that of barium chromate 2.2 times between 0 and 30°, a result in qualitative agreement with the above inference.

Our results are not in agreement with those of Scholtz and Abegg[4] who report the same distribution of chromate between mixed crystals and solution at room temperature as 100°.

2. A comparison of the speed of distribution at room temperature (Tables I, II and III) with that at 95° (Tables V, VI and VII) reveals the unexpected result that the speed of reaching equilibrium is greater at the lower temperature. It should be realized that in the experiments at higher temperature the suspensions were formed at room temperature and then heated to 95°. Under these conditions during the pre-heating period mixed crystals are formed which contain much more chromate than corresponds to the equilibrium value at 95°. At 26° $K = 1.1$; at 95° $K = 0.38$. Moreover, recrystallization (and perfection) is proceeding rapidly during this period. Consequently, when the system has reached a temperature of 95°, the solid phase, containing too much chromate, is much more perfect than at room temperature, and more time is required to reach final equilibrium. In a subsequent study on the mixed crystal formation between barium and lead sulfate it will be shown that with this system the distribution constant does not change with temperature and that final equilibrium is reached much faster at 95° than at 26°.

3. It would be more convenient to carry out the experiments with an air-dried sample of fresh barium sulfate. In experiments with lead sulfate in which the speed of distribution of thorium B was determined it has been shown[3] that such a procedure yielded satisfactory results. In the present work a larger sample of fresh air-dried barium sulfate was prepared in the following way. To 200 ml. of 0.20 M sodium sulfate, stirred by a mechanical shaker, was added quickly from a pipet 200 ml. of 0.2 M barium nitrate. The suspension was centrifuged immediately, washed once with water, centrifuged again, then washed twice with absolute ethanol. The sample was then placed in a current of dry air for a period of forty-eight hours. One-half gram samples of the air-dried product were transferred to 200 ml. of a mixture 0.1 M in sodium sulfate and 0.1 M in sodium chromate and the suspensions shaken for various periods of time at 26°. After twenty days of shaking 24.2% of the chromate was found to be removed from the solution, after fifty days, 25%. The latter value corresponds to a mole percentage of 23.3 chromate in the solid corresponding to a value of K of 0.51. Apparently no equilibrium was reached after fifty days of shaking as the equilibrium value of K at room temperature is 1.1. The barium sulfate behaves as if it had aged considerably as a result of the above treatment. A similar conclusion was arrived at when the experiments were carried out at 95°. Samples of the air-dried product weighing 0.100, 0.250 and 0.500 g., respectively, were transferred to 50 ml. of a mixture 0.01 M in sodium sulfate and 0.01 M in sodium chromate. The suspensions were heated to 95° and shaken at this temperature for thirty-seven hours. The percentages of chromate which had disappeared from the solution were 12.8 (0.1 g. $BaSO_4$); 27.8 (0.25 g. $BaSO_4$) and 43.0 (0.5 g. $BaSO_4$) corresponding to values of K of 0.21, 0.34 and 0.28, respectively, whereas the true distribution constant at 95° was found to be equal to 0.38.

Summary

The distribution coefficient K of chromate between barium sulfate and solution was found to be equal to 1.1 at 26° in the range of mole percentages of chromate in the solid phase between 5 and 33. At 95° K has a value of 0.38 in the range of mole percentages of chromate in the solid phase between 2 and 20. No equilibrium value is obtained after long periods of shaking when a mixture of sulfate and chromate is precipitated with barium nitrate. This is also true when fresh air-dried samples of barium sulfate are used instead of the original suspensions.

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