

[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY]

Adsorption of Strontium and Barium Ions and Their Exchange on Hydrous Ferric Oxide

BY J. D. KURBATOV, J. L. KULP AND EDWARD MACK, JR.

Introduction

In the past it has been shown that the adsorption of divalent positive ions such as strontium, barium, and radium by ferric hydrous oxide depends on the pH of the solution, if the quantities of adsorbate and adsorbent and all other experimental conditions are identical.^{1,2}

The aim of the present work is to compare the adsorption at different concentrations of strontium and barium on hydrous ferric oxide at a pH of 8, and at a temperature of 25°. Two procedures are employed for this study. The one which is called *coprecipitation* consists in the coagulation of the hydrous ferric oxide in the presence of strontium or barium in solution. The other procedure, which can be called simply *adsorption*, consists in the formation of the precipitate of hydrous ferric oxide in the absence of divalent ions in solution, the latter being introduced subsequently.

Radioactive tracer technique has some advantages in the study of the adsorption of strontium or barium on hydrous ferric oxide since this technique allows rapid determination of adsorbed quantities. A radioactive isotope of strontium (Sr^{89}) possesses a half-life of 85 days and is easily produced in the cyclotron by activation of strontium oxide with deuterons.³ A radioactive isotope of barium (Ba^{133}) possesses a half-life of 39 hours, and is produced by activation of cesium.^{4,5} Because of the considerable difference in their half-lives, each one of these isotopes can be determined even in the case of their simultaneous presence.

Experimental

Preparation of Radioactive Tracers

Spectroscopically pure strontium carbonate was decomposed to strontium oxide and about 0.2 g. of the oxide bombarded for six hours with 10 Mev. deuterons in the Ohio State University cyclotron. A platinum target was used instead of the usual copper target to avoid the impurities arising from activation of copper.

Since the oxide of strontium was bombarded, the radioactive isotopes of oxygen and the radioactive isotopes of fluorine, F^{17} and F^{18} , were produced. However, since they are all of short half-life and the strontium, Sr^{89} , has a half-life of fifty-five days, they were allowed to disintegrate for about two days so that they would not contribute any activity to the strontium. The purification of Sr^{89} , therefore, is concerned mainly with the removal of Y^{86} ($T = 87$ days) and of Rb^{86} ($T = 19.5$ days).^{6,7}

After the bombardment was completed, the sample was dissolved in concentrated hydrochloric acid, and purified three times by making basic with ammonium hydroxide, to a pH of 8-9, filtering, reacidifying, and then concentrating the solution. In this way yttrium is removed on the filter paper. It is especially desirable to eliminate any yttrium present since Y^{86} , ($T = 87$ days) would cause erroneous results if mixed with the strontium tracer. To check the extent of yttrium removal the third filter paper was washed with hydrochloric acid and the solution evaporated. The residue was measured on an electrometer giving the following results:

$$\begin{array}{r} \beta + \gamma \text{ activity} \dots\dots 0.12 \text{ unit} \\ \gamma \text{ activity} \dots\dots 0.002 \text{ unit}^{7a} \end{array}$$

Since the gamma radiation comes mainly from Y^{86} , the very small intensity of gamma radiation proves that the yttrium was almost completely removed on the first two filter papers.⁸ The final filtrate was also checked for the presence of Rb^{86} by addition of potassium, as carrier for Rb^{86} , to the solution of strontium and precipitation of strontium. About 0.01 unit of activity was found in solution of rubidium, and no gamma radiation observed in strontium precipitate.

The solution after the last separation was diluted to 100 ml. (I). Then 10 ml. of this was taken for a gravimetric determination of the strontium content and another 10 ml. diluted to 1000 ml. (II). Part of the second dilution was measured on the electrometer over a period of time to check the removal of all radioactive isotopes other than the 55-day strontium. The purity of Sr^{89} was confirmed by obtaining a disintegration curve corresponding to $T = 55$ days.

A gravimetric analysis was carried out by precipitating the strontium as the sulfate and from this analysis the second dilution of the active strontium was calculated to contain 0.00585 mg./ml. In the adsorption experiments the concentration of this active strontium solution was increased by adding common strontium in varying amounts.

To prepare the barium tracer, cesium chloride was bombarded with deuterons giving radioactive isotope Ba^{133} .

A different procedure was used in this case to obtain the pure barium tracer in minute quantities. The bombarded cesium chloride was dissolved in dilute hydrochloric acid, ferric chloride added and radioactive barium removed from solution at pH 9 by adsorption on iron. The precipitate of ferric hydrous oxide with adsorbed radioactive barium was filtered off, then placed in hydrochloric acid of pH 5.5, and the desorbed barium filtered off from the iron. By this procedure the radioactive isotope Ba^{133} was obtained without addition of common barium. It was purified a few times by repeating the previously described procedure.

In the experiments that follow, common barium was added to obtain the required barium concentrations since the active barium solution contained only minute quantities of barium, that is, of the order of less than 1×10^{-9} g. per experiment.

Tracer Procedure

The procedure in determining the fraction of divalent ions adsorbed and the fraction left in solution consisted in removal of part of the liquid

(7a) The total number of units of β radiation, due to Sr^{89} was estimated to be 1830.

(8) Kurbatov and Kurbatov, *J. Phys. Chem.*, **46**, 441 (1942).

- (1) Kurbatov, *J. Phys. Chem.*, **36**, 1241 (1932).
- (2) Kurbatov, Pool and Law, *Phys. Rev.*, **59**, 919 (1941).
- (3) Stewart, *ibid.*, **56**, 629 (1939).
- (4) Cork and Smith, *ibid.*, **60**, 480 (1941).
- (5) Weimer, Pool and Kurbatov, *ibid.*, **63**, 67 (1943).
- (6) Helmholtz, Pecher and Stout, *ibid.*, **59**, 902 (1941).
- (7) Pecher, *ibid.*, **58**, 734 (1940).

phase and measuring its activity on the Geiger-Müller counter. Knowing the total volume of the liquid, the adsorbed quantities were calculated. For control measurements, in some experiments, two portions of the liquid phase were removed from the same sample and the solid phase along with a small known volume of liquid was acidified and all three parts were measured.

In the experiments where two radioactive tracers, strontium and barium, were used simultaneously the procedure was the same except that the samples of the liquid phase were measured for a period of time in order to determine the activity due to each of the tracers.

Since the two tracers have a considerable difference in their half-lives, it is sufficient to follow the drop in counts through about ten days. Then, knowing the half-lives of strontium and barium, the initial activities for Sr⁸⁹ and Ba¹³³ were evaluated.

The activities were measured directly in solution using a Geiger-Müller immersion tube, avoiding the preparation of thin solid samples of uniform geometry.

Since the number of ionizing electrons that get through to the inside of the immersion tube is not proportional to the amount of solution surrounding the tube, shortened graduated cylinders of identical diameter, exceeding by only 2 mm., the diameter of tube were used in all experiments. The containers were tested before experiments.

Furthermore, it was found that if the counts measured remain in an optimum range of 100-400 counts/minute the dilution of measured samples to a constant volume does not affect the measurement appreciably.

In Table I are given results on the calibration of the counter in the range of activity of Sr⁸⁹ from 88 to 603 counts/minute.

TABLE I

VARIATIONS IN GEIGER-MÜLLER COUNTER MEASUREMENTS ON DIFFERENTLY DILUTED SAMPLES OF BOMBARDED STRONTIUM

Description of sample	Counts/min. measured	Counts/min. calcd. for 10 cc. of Sr ⁸⁹
1 cc. Sr ⁸⁹ + 6 cc. H ₂ O	88	880
3 cc. Sr ⁸⁹ + 4 cc. H ₂ O	265	884
5 cc. Sr ⁸⁹ + 2 cc. H ₂ O	426	852
7 cc. Sr ⁸⁹ —no H ₂ O added	603	861

Experimental Results

A. Adsorption isotherms of strontium and barium have been obtained in the range for strontium from 0.33×10^{-6} to 402×10^{-6} g. atoms per experiment and for barium from 1×10^{-11} to 404×10^{-6} g. atoms per experiment. The following experimental conditions were maintained constant: 2.85×10^{-3} g. atom of ferric chloride was introduced into a 50-cc. weighing bottle, radioactive and common strontium or barium chlorides were added, then the solution was brought to a pH of 8.00 ± 0.05 by ammonia,

a Leeds and Northrup pH-meter being used for determination of pH. A concentration of ammonium chloride was maintained constant during all experiments. The temperature was $25 \pm 0.5^\circ$ for the strontium isotherm and for barium was 26° . Final volume was 30 ml.

After the samples were brought to a pH of 8.0 the vessels were stoppered and set aside for thirty minutes. In some experiments described later, different times for settling were used. However, thirty minutes were found to be sufficient to establish a quasi-static state and to obtain reproducible results.

In Table II are presented the data for adsorption of strontium in the middle region of concentrations studied.

TABLE II

ADSORPTION OF STRONTIUM IONS FROM SOLUTION AT pH 8 BY HYDROUS FERRIC OXIDE

10.76×10^{-6} to 60.9×10^{-6} g. atoms of Sr/experiment in 30 cc. vol. with 2.85×10^{-3} g. atoms of Fe.

Total g. atoms of Sr. per exp., $\times 10^4$	Activ. in counts/min. before adsorp.	Counts/min. in soln. after adsorp.	G. atoms Sr/cc. after adsorp. $\times 10^7$	Total g. atoms Sr adsorbed $\times 10^4$	G. atoms Sr adsorbed per g. atom Fe $\times 10^3$	Sr, % adsorbed
10.71	1120	736	2.34	3.68	1.29	34.4
13.72	1120	730	2.98	4.77	1.67	34.8
16.75	1120	760	3.79	5.38	1.89	32.2
16.75	907	609	3.76	5.47	1.92	32.8
17.77	2370	1510	3.77	6.45	2.26	36.4
20.75	1120	755	4.67	6.75	2.36	32.6
30.75	1125	768	6.99	9.77	3.11	31.7
40.8	1125	798	7.67	11.80	4.15	29.1
50.9	1120	815	12.3	13.93	4.89	27.4
60.9	1125	828	15.0	16.0	5.62	26.3

When the log of adsorbed strontium or barium is plotted against the log of concentration the curve approaches a straight line in the region of 1×10^{-6} to 2×10^{-6} g. atoms/cc. as can be seen in Fig. 1. For concentrations greater than 2×10^{-6} g. atom/cc. the barium adsorption became considerably higher than strontium.

In the lowest concentration regions of strontium and barium the two adsorption isotherms are superimposable, as shown by the plot in Fig. 2. This plot was made on direct scale for better comparison of data.

In order to evaluate the saturation region, that is, the region in which adsorbed quantities closely approach the same value for different initial concentrations in solutions, experiments were made on adsorption of strontium with a reduced quantity of iron. In Table III the results are given for initial concentrations of strontium from 41.7 to 121.7×10^{-6} g. atom with 0.713×10^{-3} g. atom of iron as adsorbent. The highest adsorption was found to be nine atoms of strontium per thousand atoms of iron under the conditions specified.

It was found by measuring the adsorption of strontium at two time intervals, ten and thirty

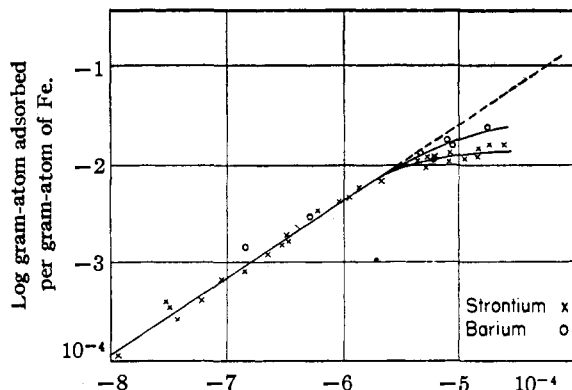


Fig. 1.—Log of gram-atom per cc. of solution.

TABLE III

ADSORPTION OF STRONTIUM IONS FROM SOLUTION AT pH 8 BY HYDROUS FERRIC OXIDE

41.7 × 10⁻⁶ to 121.7 × 10⁻⁶ g. atom Sr/experiment in 30 cc. vol. with 0.713 × 10⁻³ g. atom Fe.

Total g. atoms of Sr. per exp. × 10 ⁶	Activ. in counts/min. before adsorp.	Counts/min. in soln. after adsorp.	G. atoms Sr/cc. after adsorp. × 10 ⁴	Total g. atoms Sr adsorbed. × 10 ⁴	G. atoms Sr adsorbed per g. atom Fe × 10 ⁴	Sr, % adsorbed
41.7	930	875	13.1	2.5	3.51	6.0
61.7	930	875	19.3	3.8	5.33	6.0
91.7	930	875	28.7	5.5	7.72	6.0
121.7	930	879	38.4	6.6	9.25	5.4

minutes, that the half-hour period between titration and taking sample is sufficient to establish a quasi-static state. These data were obtained by removing two 7-cc. samples, one after ten minutes and another after an additional twenty minutes.

TABLE IV

ADSORPTION OF STRONTIUM MEASURED AT TWO TIME INTERVALS AFTER COPRECIPITATION WITH IRON

Vol., 30 cc. per experiment; Fe, 2.85 × 10⁻³ g. atom.

Total g. atoms of Sr. per exp. × 10 ⁶	Time interval, min.	Counts/min. before adsorp.	Counts/min. in soln. after adsorp.	Total g. atoms Sr adsorbed. × 10 ⁴	G. atoms Sr adsorbed per g. atom Fe × 10 ⁴	Sr, % adsorbed
0.84	10	2371	480	0.67	0.24	80.3
0.84	30	2371	472	0.67	0.24	80.1
1.68	10	2371	1080	0.91	0.32	54.5
1.68	30	2371	1062	0.92	0.32	55.2
17.77	10	2371	1510	6.45	2.26	36.4
17.77	30	2371	1460	6.85	2.41	38.5
202	10	2440	2070	30.9	10.8	15.3
202	30	2440	2035	34.0	11.9	16.8

B. Coprecipitation and adsorption procedures for strontium and barium were compared using a time interval of thirty minutes. All other conditions for coprecipitation were the same as previously described. For the adsorption procedure, the ferric chloride and strontium chloride solutions were separately brought to pH 8 and later mixed.

The experiments were arranged in pairs, that is, identical concentrations of strontium or barium

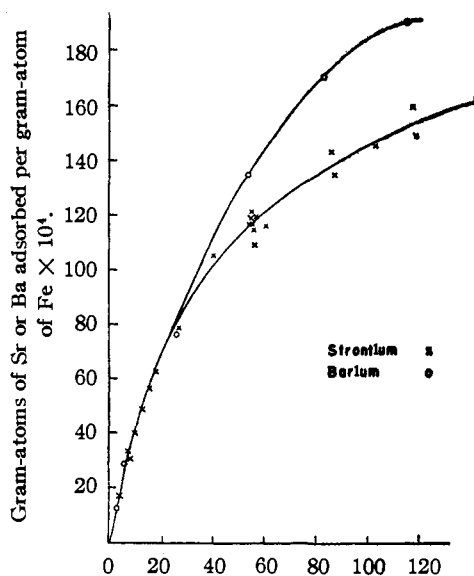


Fig. 2.—Gram-atoms of Sr or Ba per cc. of solution after adsorption × 10⁴.

were used for coprecipitation and adsorption. As can be seen in Tables V and VI, the results obtained showed for all quantities from 1 × 10⁻¹² for barium, to 3.0 × 10⁻⁴ g. atom/exp. for strontium or barium that the coprecipitation

TABLE V

COMPARISON OF COPRECIPITATION AND ADSORPTION PROCEDURES USING STRONTIUM

1.67 to 303 × 10⁻⁶ g. atom Sr/experiment in 30 cc. vol. with 2.85 × 10⁻³ g. atom Fe. Duration of experiment, 30 min. Coprecipitation designated C and adsorption procedure A.

Procedure	Total g. atoms of Sr. per exp. × 10 ⁶	Activ. in counts/min. before adsorp.	Counts/min. in soln. after adsorp.	Total g. atoms Sr adsorbed. × 10 ⁴	G. atoms Sr adsorbed per g. atom Fe × 10 ⁴	Sr, % adsorbed
C-1	1.67	907	468	0.81	0.28	48.5
A-1	1.67	907	549	0.66	0.24	39.5
C-2	16.7	907	609	5.47	1.92	32.8
A-2	16.7	907	695	3.95	1.41	23.5
C-3	202	907	750	30.0	10.5	14.9
A-3	202	907	804	22.6	7.78	11.3
C-4	303	915	809	35.3	12.4	11.7
A-4	303	915	830	27.5	9.65	9.1

TABLE VI

COMPARISON OF COPRECIPITATION AND ADSORPTION PROCEDURES USING BARIUM

30 cc. vol. with 2.85 × 10⁻³ g. atom Fe. Duration of experiment, 30 min. Coprecipitation designated C and adsorption procedure A.

Procedure	Total g. atoms of Ba per exp. × 10 ⁶	Activ. in counts/min. before adsorp.	Counts/min. in soln. after adsorp.	Total g. atoms Ba adsorbed. × 10 ⁴	G. atoms Ba adsorbed per g. atom Fe × 10 ⁴	Ba, % adsorbed
C-1	<10 ⁻⁶	1212	210	82.7
A-1	<10 ⁻⁶	1162	308	73.5
C-2	300	1181	990	48.8	17.1	16.2
A-2	300	823	724	37.0	13.0	12.3

procedure always results in a higher percentage adsorbed than the adsorption procedure. The ratio of adsorbed quantities for the two procedures remains approximately the same for different concentrations of strontium or barium.

However, in case the pairs of experiments are allowed to stand for several days after final titration to pH 8, the quantities adsorbed were found to be identical for both procedures. In Table VII the results are shown only for strontium, since Sr⁸⁹ is of sufficiently long half-life.

TABLE VII

COMPARISON OF COPRECIPITATION AND ADSORPTION PROCEDURES USING STRONTIUM

1.67 to 202 × 10⁻⁸ g. atom Sr/experiment in 30 cc. vol. with 2.85 × 10⁻³ g. atom Fe. Duration of experiment, 1 week. Coprecipitation designated C and adsorption procedure A.

Procedure	Total g. atoms of Sr. per exp., × 10 ⁶	Activ. in counts/ min. before adsorp.	Counts/ min. in soln. after adsorp.	Total g. atoms Sr adsorbed, × 10 ⁶	G. atoms Sr adsorbed per g. atom Fe. × 10 ⁴	Sr, % adsorbed
C-1	1.67	940	348	1.05	0.37	63.0
A-1	1.67	940	348	1.05	0.37	63.0
C-2	16.7	940	514	7.67	2.55	45.3
A-2	16.7	940	523	7.41	2.60	44.4
C-3	202	940	795	31.1	10.9	15.4
A-3	202	940	795	31.1	10.9	15.4

However, the quantity of strontium adsorbed after seven days is higher for the same concentrations than the quantity adsorbed after thirty minutes even in the coprecipitation procedure. Thus, while the adsorption of strontium or barium on ferric hydrous oxide approaches the same values in some time intervals, it remains strictly not independent of the duration of the experiments. Consequently, the results should be considered reproducible only if experiments are performed with the same time interval.

C. Exchange of Adsorbed Strontium or Barium with Ions of Strontium or Barium in Solution.—A pertinent question in adsorption, the clarification of which has been attempted in the present work, can be stated as follows: To what extent does the exchange of already adsorbed strontium or barium ions, with their ions present in solution, take place in the time interval of the adsorption experiments? It can be expected from theoretical considerations and from the experiments described above that the exchange of identical ions may require a very considerable time as compared with the thirty minutes of the coprecipitation procedure. To study this problem, the experiments were divided into groups: (1) exchange of adsorbed atoms with identical ions in solution, (2) exchange of the lighter atoms of strontium for the heavier barium and (3) exchange of the heavier atoms of barium for the lighter strontium. The experimental conditions such as quantity of adsorbent, pH, temperature, salt concentration and volume were maintained as previously.

The procedure for exchange study was as follows: after strontium or barium was coadsorbed on hydrous ferric oxide at a pH of 8, part of the solution above the precipitate was removed and replaced by an equal volume of another solution of the same pH and temperature containing only ammonium chloride of the same concentration as the concentration in the liquid removed. Thus, the concentration of strontium in solution was decreased as shown in the odd numbered experiments of Table VIII.

The last two columns show the results calculated, assuming: (1) there is no exchange or redistribution of the strontium ions that were initially adsorbed on the surface, (2) complete redistribution of the total strontium present accord-

TABLE VIII

EXCHANGE OF ADSORBED STRONTIUM WITH STRONTIUM OR BARIUM IONS IN SOLUTION

30 cc. vol. with 2.85 × 10⁻³ g. atom Fe. Strontium was coprecipitated with iron. Part of the solution was then removed and replaced (a) by NH₄Cl solution (odd numbered experiments) or (b) by barium and ammonium chloride (even numbered experiments). Duration of experiments, 30 min.

Exp.	Total g. atoms of Sr per exp., × 10 ⁶	G. atoms Sr removed from soln., × 10 ⁶	G. atoms Ba added to soln., × 10 ⁶	Activ. in counts/ min. before adsorp.	Counts/ min. in soln. after adsorp.	Total g. atoms Sr adsorbed, × 10 ⁶	Calcd. total g. atoms Sr adsorbed, no redistn., × 10 ⁶	Calcd. total g. atoms Sr adsorbed, complete redistn., × 10 ⁶
1	0.84	0.17	0.00	2135	322	0.64	0.67	0.45
2	0.84	.17	.17	2135	322	.64	.67	.45
3	1.68	.38	.00	1840	660	.84	.91	.71
4	1.68	.38	.38	1840	710	.80	.91	.71
5	17.8	5.43	.00	1641	819	6.18	6.45	4.45
6	17.8	5.43	5.43	1641	860	5.85	6.45	4.45
7	202	101	0	1405	1000	34.0	34.0	25.0
8	202	101	101	1388	1080	25.0	33.0	24.5
9	202	142	0	1015	647	31.0	34.0	19.7
10	202	142	142	1015	755	21.7	34.0	19.7
11	302	131	0	1303	1008	38.8	40.0	31.0
12	302	131	131	1303	1099	27.6	40.0	31.0
13	402	179	0	1277	1039	41.6	44.5	35.0
14	402	179	179	1277	1080	34.6	44.5	35.0

TABLE IX

EXCHANGE OF ADSORBED STRONTIUM WITH BARIUM IONS IN SOLUTION

30 cc. vol. with 2.85×10^{-3} g. atom Fe. Strontium was coprecipitated with iron. Part of the solution was then removed and replaced by barium solution. Two radioactive tracers were used: Sr⁸⁷ and Ba¹³³. Duration of experiments, 30 min.

Total g. atoms of Sr per exp., $\times 10^6$	G. atoms Sr removed from soln., $\times 10^6$	G. atoms Ba added to soln., $\times 10^6$	Activ. in counts/min., before adsorp.	Counts/min. in soln., after adsorp.	Total g. atoms Sr or Ba adsorbed, $\times 10^6$	Calculated total g. atoms Sr or Ba adsorbed, no redistn., $\times 10^6$	Calculated total g. atoms Sr or Ba adsorbed, complete redistn., $\times 10^6$
302	0	0	Sr, 2400	Sr, 2080	Sr, 40.2		
302	104	0	Sr, 1509	Sr, 1187	Sr, 40.3	Sr, 40.2	Sr, 31.0
302	104	104	Ba, 794	Ba, 525	Ba, 55.2	Ba, 0.00	Ba, 28.0
			Sr, 1509	Sr, 1246	Sr, 33.0	Sr, 40.2	Sr, 31.0

TABLE X

EXCHANGE OF ADSORBED BARIUM WITH STRONTIUM IONS IN SOLUTION

30 cc. vol. with 2.85×10^{-3} g. atom Fe. Barium was coprecipitated with iron. Part of the solution was then removed and replaced by strontium solution. Two radioactive tracers were used: Sr⁸⁷ and Ba¹³³. Duration of experiments, 30 min.

Total g. atoms of Ba per exp., $\times 10^6$	G. atoms Ba removed from soln., $\times 10^6$	G. atoms Sr added to soln., $\times 10^6$	Activ. in counts/min., before adsorp.	Counts/min. in soln., after adsorp.	Total g. atoms Ba or Sr adsorbed, $\times 10^6$	Calculated total g. atoms Ba or Sr adsorbed, no redistn., $\times 10^6$	Calculated total g. atoms Ba or Sr adsorbed, complete redistn., $\times 10^6$
303	0	0	Ba, 1215	Ba, 1034	Ba, 45.0		
303	127	0	Ba, 705	Ba, 547	Ba, 39.4	Ba, 45.0	Ba, 33.0
303	127	127	Ba, 695	Ba, 519	Ba, 44.0	Ba, 45.0	Ba, 33.0
			Sr, 913	Sr, 753	Sr, 25.0	Sr, 0.00	Sr, 28.2

ing to the isotherm in the absence of barium. It is obvious by comparing the results of the last three columns of Table VIII that the redistribution of adsorbed strontium after its concentration in the solution is reduced (in fact, halved in these experiments) takes place in a very negligible amount within thirty minutes. However, preliminary experiments made in a period of over twenty-four hours show that about 10% of the adsorbed strontium went back into solution.

The even-numbered experiments in Table VIII show the effect of replacing strontium by an equal quantity of barium in solution. A comparison of odd and even-numbered experiments shows the definite decrease in strontium adsorbed, especially at higher concentrations. This may be due to barium ion exchange with adsorbed strontium.

In Table IX are shown the results of the same type of experiments as above, except that both strontium and barium were traced. By analyzing a sample with the Geiger-Müller counter over a period of time as described above, fractions of strontium and of barium were determined in each phase. These results confirm previous experiments in that some of the barium ions must be exchanging with adsorbed strontium. However, it is interesting to note that a larger quantity of barium ions are adsorbed than merely those necessary to account for the exchange.

In Table X the experiments are shown in which barium is adsorbed, part of the solution removed and then replaced by a solution containing strontium ions. In this case as previously two radioactive tracers were used. Contrary to the results given in Table IX, it may be concluded that adsorbed barium does not exchange with strontium ions in solution, in the limited time of thirty minutes.

The observed adsorption of strontium may be considered as due to the strontium ions added in solution. Additional confirmation of the fact that some of the strontium is adsorbed even on a surface which is nearly saturated with barium is given by experiments on a shift in adsorption.

D. **Shift studies** were conducted in order to determine the difference in quantity of one divalent ion adsorbed for a given concentration in

TABLE XI

SHIFT OF STRONTIUM ADSORPTION IN THE PRESENCE OF BARIUM

30 cc. vol. with 2.85×10^{-3} g. atom Fe. Strontium and barium were coprecipitated with iron and the strontium traced by Sr⁸⁷. Duration of experiments, 30 min.

Total g. atoms of Sr per exp., $\times 10^6$	Total g. atoms of Ba per exp., $\times 10^6$	Activ. of Sr ⁸⁷ in counts/min. before adsorp.	Counts/min. of Sr ⁸⁷ in soln., after adsorp.	Total g. atoms Sr adsorbed, $\times 10^6$	G. atoms Sr adsorbed calcd. from isotherm, $\times 10^6$
22.9	0.0	1042	700	7.5	7.4
11.4	4.8	1070	694	4.0	3.9
5.70	4.5	1070	665	2.2	2.2
0.94	5.8	1070	596	0.5	0.6
22.9	6.3	1042	712	7.2	7.4

TABLE XII

Expt.	Total g. atoms of Sr per exp., $\times 10^6$	Total g. atoms of Ba per exp., $\times 10^6$	Counts/min. of Sr ⁸⁷ in 7 cc. soln. after adsorption
1-C ^a	302	0	188
2-C	302	150	188
3-C	302	300	191
1-A ^b	302	0	194
2-A	302	150	191
3-A	302	300	192

^a C designates coprecipitation procedure. ^b A designates the procedure in which Sr and Ba were added to the precipitated Fe.

the presence of a second divalent ion. The experimental procedure involves the same conditions which were encountered in the adsorption isotherm. Several approaches to the problem were made. First the shift was studied for the strontium isotherm at low and saturation concentrations by introducing simultaneously the second divalent ion, *i. e.*, barium. For one point in the upper concentration region of the strontium the shift was studied using both the coprecipitation and the adsorption procedures to observe whether the two methods resulted differently with regard to this phenomenon.

Then similar experiments were conducted for barium, first in the higher concentration region of the barium isotherm with strontium present in solution. The results are given in Table XIII.

TABLE XIII

SHIFT OF BARIUM ABSORPTION IN THE PRESENCE OF STRONTIUM

30 cc. vol. with 2.85×10^{-3} g. atom Fe. Barium and strontium were coprecipitated with iron and the barium traced by Ba^{133} . Duration of experiments, 30 min.

Total g. atoms of Ba $\times 10^6$	Total g. atoms of Sr per exp. $\times 10^6$	Activ. of Ba^{133} in counts/min. adsorp.	Counts/min. of Ba^{133} in soln. adsorp.	Total g. atoms Ba adsorbed $\times 10^6$	G. atoms Ba adsorbed calcd. isotherm $\times 10^6$
303	0	856	745	40	44
303	150	853	728	44	44
303	302	850	720	46	44

Comparison of adsorption values in the last three tables (XI, XII, XIII) suggest the conclusion that in conventional concentrations under the experimental conditions described a specific effect of heavier ions on adsorption of lighter ones or the reverse is not observable.

However, that the adsorption of divalent ions of one species is not independent of other species has been clearly shown by experiments on adsorption of a minute concentration of barium in the presence of strontium. In Table XIV the results are given for adsorption of the same quantity of barium ($<1 \times 10^{-9}$ g.) in the presence of different conventional quantities of strontium.

TABLE XIV

SHIFT IN ABSORPTION OF MINUTE QUANTITIES OF BARIUM IN PRESENCE OF STRONTIUM

30 cc. vol. with 2.85×10^{-3} g. atom Fe. Minute quantities of Ba^{133} ($<1 \times 10^{-9}$ g.) and inactive strontium were coprecipitated with iron. Duration of experiments, 30 min.

Total g. atoms of Sr added per exp. $\times 10^6$	Activ. of Ba^{133} in counts/min. before adsorp.	Counts/min. of Ba^{133} in soln. after adsorp.	Ba, % adsorbed
0.00	1212	210	82.7
0.56	1204	323	72.8
4.57	1190	442	62.9
67.3	1170	665	43.2

As can be seen from the last column of the table, the per cent. of barium adsorbed decreased

with the addition of strontium. However, adsorbed barium remains higher than the values from the barium isotherm for corresponding concentrations of added strontium.

Acknowledgment.—It is a pleasure to express our gratitude to the Graduate School for support of this research. The grant given by The Ohio State University Development Fund is greatly appreciated by the authors. For activation of tracers in The Ohio State University cyclotron, we are indebted to Dr. M. L. Pool.

Summary

It has been found that the adsorption of strontium and barium ions by a constant quantity of ferric hydrous oxide depends on the concentrations of these ions in solution. The quantity of adsorbent, temperature, pH, salt concentration, time and procedure were maintained constant. The ratio of adsorbed g. atoms of strontium or barium to their g. ions in solution increases with dilution. It reaches a maximum under the conditions defined, for barium at 1×10^{-8} g. ion per experiment, of which 83% is adsorbed by 2.85×10^{-3} g. atom of iron, at 25° and pH 8. Further dilution does not increase the per cent. of barium adsorbed under these conditions. The time interval between titration of the sample and removal of solution for measurement was thirty minutes.

Two procedures were employed in the study of adsorption: (1) the so-called adsorption procedure in which strontium or barium ions in solution were added to already precipitated iron, and (2) the coprecipitation procedure which showed greater adsorption in a thirty-minute interval for all concentrations of strontium or barium studied.

However, it was found that with two similar initial concentrations in a time interval of seven days, identical quantities of barium or strontium are adsorbed with either procedure employed.

The strontium adsorption was found to be irreversible in thirty minutes if the concentration of strontium in solution was reduced. No exchange between adsorbed strontium and strontium ions in solution was detected in this time. However, exchange of adsorbed strontium occurs if barium ions are introduced into the solution. Likewise, adsorbed barium does not exchange in thirty minutes with barium ions in solution. Neither does it exchange with strontium ion if the latter is added to the solution.

In conventional concentrations of strontium or barium the shift in adsorption due to the presence of the second species of divalent ion in solution was not clearly observable. If barium ions are present in quantity less than 1×10^{-9} g., the amount adsorbed depends on the strontium concentration in solution. In this case adsorption of barium decreases with the increase of strontium in solution.

Radioactive isotopes, Sr,⁸⁹ with a half-life of fifty-five days, and Ba¹³³, half-life of thirty-nine hours, were used as tracers.

COLUMBUS 10, OHIO

RECEIVED JUNE 12, 1945

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymer Properties as Functions of Conversion¹

BY FREDERICK T. WALL

When a polymerization reaction is carried out by a batch process, the product obtained will generally exhibit considerable heterogeneity. This heterogeneity is a direct consequence of the fact that the conditions under which the polymerization takes place are constantly changing as the reaction proceeds. Only for a process in which the reaction environment is kept constant can one expect a product possessing a high degree of homogeneity.

In this connection it should be noted that mechanical continuity of polymerization does not necessarily give rise to constancy of reaction conditions.² For example, if a batch or a series of batches are moved through a number of reactors (or through a reaction pipe) while polymerization takes place, mechanical continuity can be realized without attaining uniform reaction environment. To attain uniform conditions it would be necessary to have a steady introduction of raw materials into the reactor accompanied by a steady withdrawal of final product. Such a state of affairs would be difficult, if not impossible, to attain for many polymerization systems, especially those occurring in emulsion.

Recognizing that most polymerizations involve marked variations in the conditions of reaction, it naturally becomes of interest to learn something about the nature of the polymer which forms at each instant during the conversion. For this reason experiments are frequently carried out involving the measurement of various properties at different stages of conversion. Properties most frequently investigated with this idea in mind are the intrinsic viscosity, molecular weight and, in the case of copolymers, composition of the product. Although such measurements constitute a necessary step in the right direction, they do not go far enough, since they do not describe the character of the polymer formed at any given instant. This is true because the measurements are almost invariably carried out on all of the polymer formed up to the conversion of interest; hence the measurements represent over-all average values and not increment values. There will now be derived some equations by means of which such "average" data can be analyzed to obtain the properties of polymer increments.

(1) The work reported in this paper was done in connection with the government research program on synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation (first reported in September, 1944).

(2) K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944).

Weight Average Properties as Functions of Weight Conversion.—Let us first consider a property which for a heterogeneous system averages by weight. Examples of such properties are weight average molecular weight, intrinsic viscosity (but not viscosity average molecular weight, except approximately),³ weight per cent. of a given monomer in a copolymer, etc. If g represents such a property for any given increment and if W is the weight conversion, then by definition the average value of the property corresponding to a particular conversion will be given by

$$\bar{g} = \frac{\int_0^W g dW}{\int_0^W dW} = \frac{\int_0^W g dW}{W} \quad (1)$$

Rearranging (1) there is obtained

$$\int_0^W g dW = \bar{g}W \quad (2)$$

Differentiating (2) with respect to W , one obtains

$$g = \frac{d}{dW} (\bar{g}W) \quad (3a)$$

$$= \bar{g} + W \frac{d\bar{g}}{dW} \quad (3b)$$

It follows from equations (3) that if one knows \bar{g} as a function of W , it becomes possible to obtain increment values. Equation (3a) suggests plotting $\bar{g}W$ vs. W and taking slopes; equation (3b) requires plotting \bar{g} vs. W , taking slopes and then carrying out the indicated calculations. These methods are somewhat suggestive of those involved in determining partial molar quantities. Siggia, Hohenstein and Mark⁴ have made use of this concept in connection with intrinsic viscosity.

Number Average Properties as Functions of Weight Conversion.—Let us now consider properties which form averages by numbers of molecules or moles. The most important example of such a property is the ordinary (or number average) molecular weight. Letting M equal the molecular weight and N the number of moles of polymer corresponding to a weight conversion W , we have by definition

(3) P. J. Flory, *THIS JOURNAL*, **65**, 372 (1943).

(4) S. Siggia, W. P. Hohenstein and H. Mark, *India Rubber World*, **111**, 436 (1945).