TABLE IV

SPECIFIC SURFACE OF VARIOUS PRODUCTS OF BARIUM SULFATE DETERMINED BY THE THREE DIFFERENT METHODS

a = Number of Ba or SO_4 ions × 10^{-18} per gram of barium sulfate. b = Surface in M^2. c = Average particle size in microns.

	Product A			B			C			D			E		
Method	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
Wool violet	37	7.4	0.17	1.0^x	0.19^x	6.9^x	54	10.8	0.12	26	5.2	0.25	3.6	0.7	1.8
Chromate	25	5.0	.26	0.39	.078	17.0	58	11.6	.11	30.5	6.1	.21	2.9	.58	2.2
Thorium B	52	10.4	.13	1.0^x	.19^x	6.9^x									

^{x} Calculations of wool violet and ThB methods based upon the microscopic measurements.

A summary of all the data is given in Table IV. Considering the limitations of the various methods and the assumptions made it is gratifying to see that the order of agreement of the magnitude of the surfaces calculated by the three different methods is satisfactory.

Product C is highly imperfect, causing an uncertainty in the extrapolated value of the amount of chromate exchanged. The ratio of the surfaces of products A (well aged) and C (fresh) by the chromate method was found to be 0.43, and by the wool violet method 0.69. This fair agreement indicates that the internal surface of the imperfect product C in open communication with the liquid phase is very small indeed. The corresponding ratios of products A and D are 0.82 and 1.4 and of products A and E 8.6 and 10.6, respectively. From a practical viewpoint it appears that the wool violet method is the most suitable one for the determination of the specific surface of fresh and aged products of barium sulfate.

Summary

The specific surface of various products of barium sulfate has been determined by three different methods. The simplest method is based on the determination of the amount of wool violet adsorbed in the saturated surface of barium sulfate. The method based upon the exchange between chromate and sulfate ions in the surface of barium sulfate yields valuable results. The thorium B method is limited to well-aged products of barium sulfate.

MINNEAPOLIS, MINN. RECEIVED JUNE 1, 1937
COLUMBUS, OHIO

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

Exchange Adsorption Phenomena with Calcium Oxalate Monohydrate

BY I. M. KOLTHOFF AND E. B. SANDELL

Various examples of exchange between lattice ions in the surface of a slightly soluble precipitate and foreign ions of the same electrical sign in the solution have been found in this Laboratory.[1] In the present paper examples of similar exchanges at the interface of calcium oxalate monohydrate and aqueous solutions of various electrolytes are given. Moreover, it is shown that the saturated solution of calcium oxalate in an electrolyte does not contain equivalent amounts of calcium and oxalate when one of the lattice ions gives an exchange with one of the foreign ions of the solution and the system contains an excess of the solid. The difference between the inequality of calcium and oxalate concentrations increases with increasing amount of surface exposed to the solution, or when dealing with a particular product with increasing amount of solid.

Experimental

Preparation of Calcium Oxalate Monohydrate.—Three products of calcium oxalate monohydrate, prepared as follows, were used in the present work.

Product I.—One liter of hot 0.50 *M* ammonium oxalate solution was added slowly with vigorous stirring to one liter of hot 0.52 *M* calcium chloride solution acidified with one milliliter of concentrated hydrochloric acid. The time of addition of the oxalate solution was ten minutes. The precipitate was washed with redistilled water with the aid of a centrifuge until it was chloride-free. The washed precipitate was suspended in a liter of water, allowed to stand for three days, collected by centrifugation, rewashed and finally mixed with one-half liter of water. The suspension thus obtained was used directly in the adsorption experiments.

Product II.—This product was prepared in the same way as Product I, except that potassium oxalate was used instead of ammonium oxalate in the precipitation.

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[1] For a review see I. M. Kolthoff, *J. Phys. Chem.*, **40**, 1027 (1936); for exchange reactions on the surface of barium sulfate *cf.* I. M. Kolthoff and G. E. Noponen, THIS JOURNAL, **59**, 1237 (1937).

Product III.—The method of preparation was the same as for Product I. This product was made by Sister Gregoire Loyola in this Laboratory.

The precipitates used in the experiments given in Table II were well aged by allowing them to stand in water, changed at intervals, for some weeks or months. The purity of the aged product was tested by shaking 10 to 15 g. with approximately 250 ml. of water for twenty-four hours and comparing the calcium or oxalate concentration of the saturated solution with the corresponding concentration in a solution which had been saturated with 0.1 g. of the precipitate. When no significant difference was found in the two cases, the product was considered sufficiently pure for the purpose.

The size-frequency curve of Product III is given in Fig. 1. The microscopic measurements were made by H. A. Laitinen in this Laboratory.

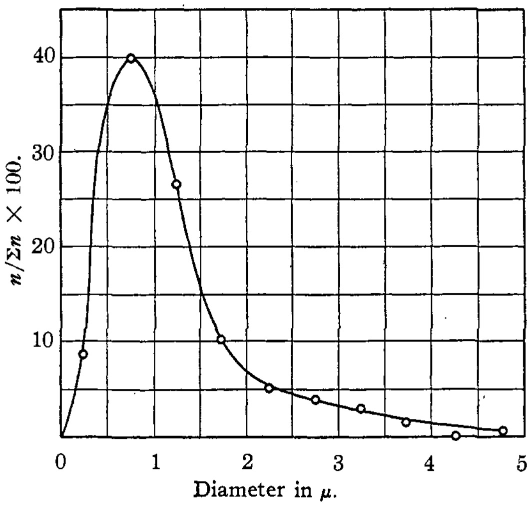

Fig. 1.—Size-frequency curve of calcium oxalate monohydrate (Product III).

Experiments in which Adsorption of Both Cation and Anion Were Determined.—These experiments were confined to a few salts of which cation and anion could both be determined with reasonable precision.

In each experiment, a sufficient volume of calcium oxalate suspension to yield 15 to 20 g. of the monohydrate was transferred to a 250-ml. volumetric flask, mixed with a measured volume of the salt solution being investigated, and made up to the mark with water. The mixture was shaken mechanically in a suitable bottle for twenty hours at room temperature (25 ± 2°). The suspension was centrifuged to remove most of the calcium oxalate, and the supernatant liquid was then filtered with the usual precautions. Both cation and anion were determined in measured volumes of the filtered centrifugate by suitable methods. The concentration of the electrolyte solution added to the calcium oxalate suspension was determined under similar conditions, both the cation and anion being determined. From the amount of calcium oxalate monohydrate taken, determined by evaporating the suspension at the end of the experiment and drying the residue at 110°, and the known density of the monohydrate (2.25), the volume of the liquid phase in the suspension was determined, and therefrom the original concentration of the solute was found.

The various ions involved in these experiments were determined by the following methods. Magnesium was estimated by precipitation as hydroxyquinolate followed by titration of the precipitate by the usual bromate method. When iodate was present it was reduced to iodide with sulfurous acid before the magnesium precipitation. Iodide was determined by oxidation to iodate with chlorine water, and titration of the iodate by the familiar iodometric method. For the determination of ammonium ion the hypochlorite method was used, in which ammonia is oxidized to nitrogen in bicarbonate medium by calcium hypochlorite and excess bromide; the amount of hypochlorite remaining after the reaction was found by iodometric titration in acid solution. Barium and chloride were determined microgravimetrically. These methods were tested with known amounts of the constituents being determined, at comparable concentrations, and were found to give accurate results. The results of these adsorption experiments are given in Table I. It may be mentioned that no significant change in the *p*H of the salt solutions took place on shaking with calcium oxalate.

TABLE I

CATION AND ANION ADSORPTION OF SOME SALTS BY CALCIUM OXALATE MONOHYDRATE

	$CaC_2O_4 \cdot H_2O$	Salt	Concn. *M*	Adsorption in micro-equivalents per gram $CaC_2O_4 \cdot H_2O$ Cation	Anion
1	I	MgI_2	0.002	1.0	0.4
2	I	NH_4IO_3	.002	0.25	1.0
3	II	NH_4IO_3	.002	.1	1.2
4	II	$Mg(IO_3)_2$	.002	3.6	3.0
5	II	$BaCl_2$	.001	6.8	0.6

Determination of Exchange Adsorption of Electrolytes by Calcium Oxalate from the Change in Calcium and Oxalate Concentrations of the Suspension.—In these experiments the exchange adsorption of a number of electrolytes by calcium oxalate was studied by determining the calcium or oxalate concentration of a suspension containing a large amount of precipitate and comparing with the concentration in an electrolyte solution of the same strength containing only a small amount of the precipitate. If equivalent amounts of foreign cation and anion are not adsorbed, there must be produced an increase in the concentration of either calcium or oxalate ion in the suspension of much calcium oxalate as compared with the suspension containing only a little precipitate. Thus if a foreign anion $A^=$ is adsorbed by exchange with oxalate ion, and the foreign cation does not exchange with calcium ion

$$CaC_2O_4 + A^= \rightleftarrows CaA + C_2O_4^=$$

there must be an increase in the oxalate ion concentration, and a corresponding decrease in the calcium-ion concentration, the solubility product remaining constant; conversely, if the foreign cation exchanges, the oxalate concentration decreases. The greater the amount of calcium oxalate suspended in the solution, the more marked will be the decrease in the solubility.

The amount of foreign ion adsorbed by exchange can be calculated easily from the change in either the calcium or oxalate concentration. Let

S = solubility product of $\mathrm{CaC_2O_4 \cdot H_2O}$ in the electrolyte solution
X = moles of the divalent anion $\mathrm{A^{=}}$ removed by exchange from a volume of v ml.
$[\mathrm{C_2O_4^{=}}]$ = oxalate concentration of the electrolyte solution after exchange
$[\mathrm{Ca^{++}}]$ = calcium concentration of the electrolyte solution after exchange
w = weight of calcium oxalate monohydrate in grams

If X moles of $\mathrm{A^{=}}$ are removed by exchange from v ml. of solution, an equal amount of oxalate is sent into the solution, the solubility product of calcium oxalate is exceeded and a certain amount of precipitate is formed. The amount, in moles, of oxalate precipitated from one liter of solution is:

$$\sqrt{S} + (1000X/v) - [\mathrm{C_2O_4^{=}}] \qquad (1)$$

The amount of calcium simultaneously precipitated is

$$\sqrt{S} - [\mathrm{Ca^{++}}] \qquad (2)$$

Since (1) and (2) are equal we have

$$\sqrt{S} + (1000X/v) - [\mathrm{C_2O_4^{=}}] = \sqrt{S} - [\mathrm{Ca^{++}}], \text{ or}$$

$$X = \frac{v}{1000}\{[\mathrm{C_2O_4^{=}}] - [\mathrm{Ca^{++}}]\} = \frac{v}{1000}\left\{[\mathrm{C_2O_4^{=}}] - \frac{S}{[\mathrm{C_2O_4^{=}}]}\right\}$$

The quantity of the foreign anion, in moles, removed by exchange by one gram of the precipitate is therefore

$$\frac{v}{1000w}\left\{[\mathrm{C_2O_4^{=}}] - \frac{S}{[\mathrm{C_2O_4^{=}}]}\right\}$$

The value of S is found by shaking a small amount (50 to 100 mg.) of calcium oxalate with the same electrolyte solution that is used in the adsorption experiment, and determining either the calcium or oxalate concentration of the saturated solution.

For divalent cation exchange the formula becomes

$$X = \frac{v}{1000}\left\{\frac{S}{[\mathrm{C_2O_4^{=}}]} - [\mathrm{C_2O_4^{=}}]\right\}$$

For a univalent cation the expression is

$$X = \frac{2v}{1000}\left\{\frac{S}{[\mathrm{C_2O_4^{=}}]} - [\mathrm{C_2O_4^{=}}]\right\}$$

In carrying out the adsorption experiments, a sufficient amount of suspension to furnish 10 to 15 g. of calcium oxalate monohydrate was transferred to a 250-ml. volumetric flask, a measured volume of the electrolyte solution of known concentration was added, and the mixture made up to the mark with water and weighed. From the known density of the precipitate (2.25) the weight of the calcium oxalate could be calculated; in some experiments the value so obtained was verified by evaporating the suspension to dryness at the end of the experiment. The suspension was then shaken mechanically for twenty hours at room temperature (25 ± 2°). Most of the precipitate was separated from the liquid phase by centrifuging and the last traces by filtration. Calcium or oxalate was then determined in 50 or 100 ml. of the filtrate. The normal solubility of calcium oxalate in the given electrolyte solution was determined by simultaneously shaking 0.1 g. of precipitate with 250 ml. of solution for twenty hours and determining either the oxalate or calcium concentration of the filtered centrifugate.

Calcium was determined by concentrating the solution by evaporation, adding ammonium oxalate, filtering off the precipitate, washing with a saturated calcium oxalate solution and titrating with 0.01 N potassium permanganate. The excess of permanganate was found iodometrically by adding iodide and titrating the liberated iodine with 0.001 N sodium thiosulfate, starch being used as indicator. Oxalate was determined by titrating 50 to 100 ml. of the solution directly with permanganate; the excess of permanganate was found iodometrically as before, the titration with thiosulfate here being made in a 100-ml. graduate in order that the end-point could be perceived sharply in the large volume. It is not possible to concentrate the oxalate solution by evaporation prior to the titration because comparatively much of the oxalate is destroyed in the process. The accuracy of the methods was tested with known amounts of calcium and oxalate, and was found to be satisfactory for the purpose.

Table II contains the results of the experiments in which the exchange adsorption of a number of electrolytes was found from the change in the calcium or oxalate concentration of the calcium oxalate suspension as described above.

Experiment 5 of Table I involving the adsorption of barium chloride was performed immediately after Experiment 17 of Table II on the same prod-

TABLE II

EXCHANGE ADSORPTION BY CALCIUM OXALATE MONOHYDRATE AT 25 ± 2°

(Total volume of suspension 250 ml.)

No.	Electrolyte	Concn., M	$CaC_2O_4 \cdot H_2O$ Product	$CaC_2O_4 \cdot H_2O$ Weight, g.	Normal soly. of $CaC_2O_4 \cdot H_2O$ Ca, $M \times 10^3$	Normal soly. of $CaC_2O_4 \cdot H_2O$ C_2O_4, $M \times 10^3$	S, $M^2 \times 10^8$	Lattice ion concn. after exchange Ca, $M \times 10^4$	Lattice ion concn. after exchange C_2O_4, $M \times 10^4$	Exchange adsorption micromoles per gram $CaC_2O_4 \cdot H_2O$ Cation	Exchange adsorption micromoles per gram $CaC_2O_4 \cdot H_2O$ Anion
1	$(NH_4)_2SO_4$	0.010	II	15.5	0.114	0.116	1.3		0.31		4.1
2	$(NH_4)_2SO_4$	.010	II	15.5			1.5	0.05	.31		4.1
3	$(NH_4)_2SO_4$	.010	II	15.0		.118	1.4		.29		3.8
4	$(NH_4)_2SO_4$	.010	II	14.0			1.3		.25		3.4
5	$(NH_4)_2SO_4$	.001	III	10.6		.077	0.6		.105		1.1
6	$(NH_4)_2SO_4$	.005	III	10.4		.103	1.0		.157		2.2
7	$(NH_4)_2SO_4$	.020	III	10.25		.143	2.0		.23		3.6
8	Na_2SO_4[a]	.010	II	13.6			1.3	.058	.22		2.9
9	Na_2SO_4[a]	.010	II	17.0		.122	1.5		.22		2.3
10	NH_4IO_3	.010	II	13.5	0.089		0.80	.056			3.1
11	$MgSO_4$	.010	II	12.0		.30	9.0		.41		3.9
12	NaOH	.010	II	11.5		.12	1.44		.30		10.8
13	HCl	.001	II	12.0		.21	4.4		.21	0.0	0.0
14	NaCl	.01	II	17.5		.083	0.7		.084	.0	0.0
15	NaCl	.02	II	17.5		.103	1.1		.104	.0	0.0
16	$BaCl_2$	.001	II	16.5		.078	0.6		.029	2.6	
17	$BaCl_2$	.001	II	16.3		.076	0.6		.034	2.1	
18	$MnCl_2$	.01	II	16.0		.48	23		.30	7.1	
19	$MgCl_2$	.01	II, III	13.0		.26	7		.239	1[b]	
20	$AgNO_3$	.0002	III	11.0		.060	0.4		.059	0.0	0.0

[a] Product more aged than in experiments 1–4. [b] Average of 5 experiments.

uct of calcium oxalate. Since the amount of barium adsorbed by exchange should be equivalent to the amount of calcium sent into the solution, the data of one experiment can be used to check the data of the other. In Experiment 5 of Table I, 6.2×10^{-6}, *i. e.* $(6.8 - 0.6) \times 10^{-6}$, equivalent of barium was found to be removed by exchange by one gram of precipitate, or 1.0×10^{-4} equivalent by 16.2 g., the amount of calcium oxalate used in the experiment. The number of moles of calcium sent into one liter of solution by exchange with barium ion should therefore be $(1000/243) \times 5 \times 10^{-5} = 2.06 \times 10^{-4}$; in this expression 243 is the volume of solution in the 250 ml. of suspension used in the adsorption experiment. The final concentration of oxalate in the solution should therefore be given by y in the equation: $(y + 2.06 \times 10^{-4})y = S = 5.9 \times 10^{-9}$.

The value of S was obtained by shaking approximately 0.1 g. of calcium oxalate with 250 ml. of 0.0001 M barium chloride solution and determining the oxalate concentration of the saturated solution. The calculated value of y is found to be 2.6×10^{-5} mole per liter. The experimental value of y was found to be 3.4×10^{-5} in Experiment 17 of Table II. If there had been no replacement of calcium ions by barium the oxalate concentration would have been 7.7×10^{-5} molar. Although the agreement between the calculated and experimental values is not all that might be desired, there is seen to be an approximate correspondence between the decrease in the barium concentration and the increase in the calcium concentration and therewith the decrease in the concentration of oxalate.

A similar calculation can be made for the adsorption of hydroxyl ion from 0.01 N sodium hydroxide solution (Experiment 12 of Table II). In this case the adsorption of hydroxyl was determined directly in the same solution in which the oxalate was titrated. The adsorption of hydroxyl was found to amount to 1.25×10^{-4} mole from 245 ml. of solution for the particular amount of precipitate used. If the assumption be now made that all of the adsorption of hydroxyl takes place by the exchange mechanism and that none of the hydroxyl is adsorbed as sodium hydroxide, the equivalent amount of oxalate displaced is $(1000/245) \times 5 \times 1.25 \times 10^{-5}) = 2.55 \times 10^{-4}$ mole from 1 liter of solution. Therefore the calcium concentration of the solution after exchange should be y, the value of which is found from

$$y(y + 2.55 \times 10^{-4}) = 1.39 \times 10^{-8}$$

The value of the solubility product was found by shaking approximately 0.1 g. of calcium oxalate with 250 ml. of 0.01 N sodium hydroxide and determining the oxalate concentration of the saturated solution. The calculated value of y is 4.7×10^{-5}, whereas the experimental value is 4.6×10^{-5}. This agreement allows the conclusion that all the hydroxyl has been removed by exchange and that, within the experimental error, no true adsorption of sodium hydroxide occurs.

Discussion

1. Conclusive evidence was obtained that sulfate, iodate and hydroxyl ions exchange with oxalate, and that barium, manganese and probably magnesium exchange with calcium ions on the surface of calcium oxalate monohydrate. Thus, if calcium oxalate is shaken with electrolyte solutions containing sulfate, iodate or hydroxyl ions, the saturated solutions contain oxalate in excess of calcium, whereas upon shaking with solutions containing barium, manganese and probably magnesium the saturated solution contains calcium in excess of oxalate. The result of experiment 4 in Table I may indicate a true salt adsorption of magnesium iodate, although it may be interpreted as an exchange between iodate and oxalate on the one hand and of magnesium with calcium on the other.

In the cases investigated a true salt adsorption may have occurred but the amount of such an adsorption is so small as to escape certain detection. If it occurs it is certainly much smaller than the exchange which has been definitely established in the various cases. No indication of exchange has been found between sodium, ammonium and hydronium ions, respectively, and calcium, or between chloride and oxalate. Apparently, only those ions which form slightly soluble salts with the lattice ion of opposite charge can exchange.

2. The results do not allow a conclusion regarding the mechanism of the "exchange." Exchange reactions have been found in various cases in which the exchanging ion does not fit in the lattice of the precipitate. Moreover, it is hard to see how one oxalate ion can be replaced by two iodate or hydroxyl ions, unless one assumes that the interface between the solid and the liquid phases consists of a layer of hydrated lattice ions and that the exchange occurs in this layer. Another interpretation of the experimental results is that no exchange occurs, but that a true adsorption of the "exchanging" ion on the lattice ion of opposite sign takes place. If calcium oxalate is shaken with ammonium iodate, for example, an adsorption of calcium iodate may occur. The mechanism of such an adsorption differs from that of an exchange. In the latter case the oxalate ions which have been liberated by exchange enter the solution and give rise to the precipitation of calcium oxalate until solubility equilibrium is attained. If an adsorption of calcium iodate would occur, calcium ions would be withdrawn from the solution which then becomes undersaturated with respect to calcium oxalate. Instead of obtaining a precipitate of the latter from the solution, some of the solid would have to go into solution to reestablish solubility equilibrium.

Finally a third interpretation has been suggested by Verwey[2] who assumes a true adsorption of the "exchanging ion." This adsorption gives rise to a shift of the location of the isoelectric point (zero point charge) of the precipitate and to the formation of a triple layer. At present no experimental evidence is available to decide which of the proposed mechanisms is correct. It is quite possible that the mechanism may be different in various cases.

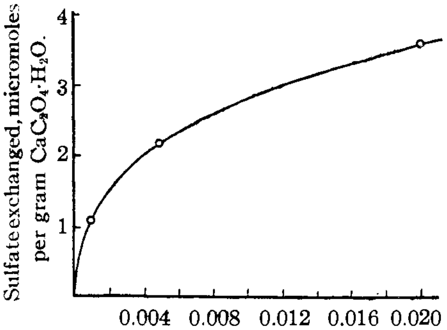

Fig. 2.—Exchange adsorption of ammonium sulfate on calcium oxalate.

3. In Fig. 2 the amount of exchange between sulfate and oxalate has been plotted as a function of the concentration of the sulfate concentration in the solution (product III). Assuming that the mechanism is an exchange the distribution of sulfate and oxalate between the solid and liquid phases may be represented by the equation

$$\frac{[\mathrm{SO_4^=}]_{\mathrm{surface}}}{[\mathrm{SO_4^=}]_{\mathrm{solution}}} = K\,\frac{[\mathrm{C_2O_4^=}]_{\mathrm{surface}}}{[\mathrm{C_2O_4^=}]_{\mathrm{solution}}} \qquad (3)$$

in which K denotes the distribution coefficient. If the number of oxalate ions present on the surface of the original product is x, it is found after exchange equilibrium is attained that

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[2] E. J. W. Verwey, *Kolloid Z.*, **72**, 187 (1935).

$$\frac{[\mathrm{SO_4^{=}}]_{\mathrm{surface}}}{[\mathrm{SO_4^{=}}]_{\mathrm{solution}}} = K\frac{(x - [\mathrm{SO_4^{=}}]_{\mathrm{surface}})}{[\mathrm{C_2O_4^{=}}]_{\mathrm{solution}}} \tag{4}$$

Experiments 5, 6 and 7 given in Table II allow the calculation of the approximate values of K and x. Expressing the number of ions on the surface in micromoles per gram of calcium oxalate monohydrate, and the number of ions in solution in micromoles per liter yields the equations

$$\frac{1.1}{1000} = K\frac{x - 1.1}{105} \tag{5}$$

$$\frac{2.2}{5000} = K\frac{x - 2.2}{157} \tag{6}$$

$$\frac{3.6}{20{,}000} = K\frac{x - 3.6}{234} \tag{7}$$

From (5) and (6): $K = 0.04 \quad x = 3.8$

From (6) and (7): $K = 0.02 \quad x = 5.8$

From (5) and (7): $K = 0.03 \quad x = 5.0$

From the three experiments an average value of K of 0.03 and of x of 5 is found. It is gratifying to find that the number of micromoles of surface oxalate (5) per gram of calcium oxalate monohydrate calculated in this manner is in fair agreement with the value calculated from the microscopic size measurement. From the surface-distribution curve an average particle diameter of 2.4×10^{-4} cm. was calculated. Taking the density of calcium oxalate monohydrate as 2.25 and assuming that the particles are cubical and contain equal amounts of calcium and oxalate ions on the surface, we find the number of micromoles on the surface of 1 g. of the product to be

$$x = \frac{6\left\{\frac{6.06 \times 10^{23}}{146} \times 2.25 \times (2.4 \times 10^{-4})^3\right\}^{2/3}}{2.25 \times (2.4 \times 10^{-4})^3} = 8$$

Although the few experiments reported do not justify a definite conclusion, it seems reasonable to infer that equation (3) expresses the quantitative relation between the exchange of sulfate and oxalate ions on the surface of calcium oxalate monohydrate.

Summary

1. Sulfate, iodate and hydroxyl ions exchange with oxalate, and barium, manganese and probably magnesium exchange with calcium on the surface of calcium oxalate monohydrate. No indication of exchange has been found between sodium, ammonium and hydronium ions, and calcium on the one hand, and of chloride with oxalate on the other on the surface of calcium oxalate monohydrate.

2. The saturated solution of a slightly soluble salt in an electrolyte does not contain equivalent amounts of lattice cation and anion if one of the lattice ions gives an exchange on the surface with one of the ions of the electrolyte. The inequality in the amount of dissolved lattice cation and anion increases with the amount of surface exposed.

3. The mechanism of the exchange has been discussed.

4. A quantitative expression for the distribution of sulfate and oxalate between the surface of calcium oxalate monohydrate and solution has been given and from this the distribution coefficient and the number of moles of surface oxalate per gram of solid have been calculated. The latter value is in reasonable agreement with that calculated from microscopic measurements.

MINNEAPOLIS, MINN. RECEIVED JUNE 1, 1937

[CONTRIBUTION FROM THE JACQUES LOEB LABORATORIES OF STANFORD UNIVERSITY]

Enhanced Polymerization and Depolymerization of Natural Rubber by Quinones and Related Compounds[1]

BY D. SPENCE AND JOHN D. FERRY

Introduction

Oxidizing Agents in Polymerization.—Oxygen and oxidizing agents play a rather puzzling dual role in the chemistry of polyprene substances. Under certain conditions, they cause breakdown and depolymerization of unsaturated hydrocarbon macromolecules. Purified natural rubber, for example, is very susceptible to attack by molecular oxygen, and the absorption of relatively small proportions is sufficient to form a sticky product which lacks tensile strength and dissolves readily in solvents to form solutions of low viscosity.[2] The action of a variety of oxidizing agents, such as potassium permanganate, hydrogen peroxide, and benzoyl peroxide, is similar.[3] On the other hand, the opposite effect, namely, enhanced polymerization by

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[1] The results here recorded form the basis of U. S. Patent applications assigned to The B. F. Goodrich Company.

[2] Kohman, *J. Phys. Chem.*, **33**, 226 (1929); Bloomfield and Farmer, *J. Soc. Chem. Ind.*, **54**, 125T (1935).

[3] Harries, *Ber.*, **37**, 2708 (1904); *cf.* Memmler, "Science of Rubber," Reinhold Publishing Corp., New York, 1934, p. 207 ff.