

of the method is characterized by determinations and $\pm 0.008\%$ respectively. of 0.1 and 0.6% of water, within limits of ± 0.001

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Chemical and X-ray Investigation of Barium Sulfate Contaminated with Permanganic Acid¹

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Introduction

A recent article by Walden and Cohen² reported the results of an investigation of barium sulfate precipitates contaminated with nitrate. The results of this work indicated the necessity of a similar investigation using a contaminating ion of different configuration, such as permanganate ion. Several investigators, notably Grimm and Wagner³ have reported on the precipitation of barium sulfate in the presence of potassium permanganate.

The present investigation deals with (1) the precipitation of barium sulfate in the presence of permanganate ion, hydrogen ion being the only other foreign ion present; (2) the establishment, by chemical analysis, of the complete constitution of these contaminated precipitates, thereby identifying the cation which balances the charge of the coprecipitated permanganate ion; (3) investigation of the character of the precipitates by means of X-ray powder photographs.

It developed that the method of precipitation used by Walden and Cohen,² which for them produced beautifully coarse crystalline precipitates contaminated with nitrate ion, yielded for us precipitates so fine as to appear amorphous even when examined between crossed nicols under an oil-immersion objective, and which gave only a vague trace of an X-ray diffraction pattern. The method of precipitation used by Grimm and Wagner,^{3b} adapted to the new conditions, proved to be apparently the only one which would yield precipitates of the desired coarseness.

Complete analyses of samples prepared by both methods showed that barium and sulfate ions

(1) Dissertation submitted by Philip R. Averell in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University. The material was presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

(2) Walden and Cohen, *THIS JOURNAL*, **87**, 2591 (1935).

(3) (a) Grimm, *Z. Elektrochem.*, **30**, 467 (1924); (b) Grimm and Wagner, *Z. physik. Chem.*, **132**, 131 (1928); (c) Wagner, *ibid.*, **2B**, 27 (1929).

exist in the precipitates always in a mole ratio of 1:1, which shows that the ion accompanying the permanganate ion is not barium, and therefore must be hydrogen or a hydrated hydrogen ion.

X-ray powder photographs showed a definite and fairly regular expansion of the lattice parameters with increased contamination, a conclusive evidence of the existence of solid solution.

Method of Preparation.—The method of precipitation used by Walden and Cohen, adapted to the study of permanganate contamination, consists of the slow addition of a sulfuric–permanganic acid solution to a barium permanganate–permanganic acid solution, the concentrations being so adjusted that the permanganate concentration is the same in both solutions; the sulfuric acid added is sufficient to precipitate less than half of the barium ion. The method of Grimm and Wagner, adapted to the present investigation, is to mix rapidly two solutions containing respectively equimolar quantities of barium permanganate and sulfuric acid. Each solution contains in addition permanganic acid in such amount that the permanganate ion concentrations are equal.

Since the unpreventable spontaneous decomposition of permanganic acid made it impossible to keep the system free of manganese dioxide, it was necessary to use all solutions as quickly after preparation as possible, and to use some means of removing manganese dioxide from the precipitate before final filtration, washing and drying. Accordingly, after the mother liquor was removed, the precipitate was given one washing with either sulfur dioxide solution or dilute hydrogen peroxide acidified slightly with hydrochloric acid, followed by water. All washings were made more effective by centrifugal drainage. As the slow drying of water-wet precipitates also caused decomposition with formation of manganese dioxide, this difficulty was obviated—again using Grimm's procedure—by washing with acetone four or five times, the last washings being colorless, then with anhydrous ether, before drying in air or over concentrated sulfuric acid.

The product thus prepared is a beautiful rose-colored precipitate, showing no traces of manganese dioxide, either to the unaided eye or under a microscope. As in the case of the precipitates described by Grimm, the co-precipitated permanganate ion is chemically very inert. The color is not noticeably bleached by contact with strong reducing solutions even after standing for several days. Heating at 110° for twenty to forty hours produces decomposition only in insufficiently washed precipitates, and in

those of highest contamination; in general, such heating causes not even a detectable loss in weight. One sample, after several hours ignition at 700–800°, showed the presence of undecomposed permanganate when dissolved in concentrated sulfuric acid.

Chemical Analysis

Two methods were used to decompose the barium sulfate precipitates for analysis: (1) fusion with anhydrous sodium carbonate; and (2) solution in concentrated sulfuric acid. In method (1), the melt was decomposed with a small amount of water, and a few drops of hydrogen peroxide added to reduce all the manganese to manganese dioxide. After filtration, the residue of barium carbonate and manganese dioxide was dissolved in dilute hydrochloric acid plus hydrogen peroxide; the barium was precipitated as the sulfate and weighed, while the manganese could be determined in the filtrate. The original filtrate, consisting of sodium sulfate and sodium carbonate, was made acid with hydrochloric acid, diluted to 400 cc., and the sulfate precipitated with barium chloride. In method (2), the coprecipitated permanganate was reduced to manganous ion by passing sulfur dioxide over the surface of the sulfuric acid during solution of the barium sulfate; the latter was then reprecipitated by adding water, washed, filtered, ignited and weighed; the filtrate was analyzed for manganese by the bismuthate method as modified and described by Park;⁴ in place of potassium permanganate as a standard solution, ceric sulfate was used in conjunction with phenanthroline-ferrous ion indicator.⁵ Samples of 0.5–1.5 g. required a titer of 5–10 cc. of 0.1 *N* ferrous sulfate; considering the accuracy of the bismuthate method, as well as the relatively small amount of permanganate ion in such a sample, these small titers yielded adequate precision in the calculations.

X-ray Analysis

Powder photographs were taken with the same apparatus used by Walden and Cohen² with a few mechanical improvements. The lattice parameters were calculated from film measurements by the least squares treatment developed by Cohen.⁶

Data and Interpretation

The equivalence of barium and sulfate ions in the precipitates was established by analyses of several precipitates by the sodium carbonate fusion method; representative precipitates prepared by both methods were analyzed. Table I shows the weights of barium sulfate obtained from the barium ion in the original precipitates (denoted by $BaSO_4$ in the table, and from the sulfate ion (denoted by $BaSO_4$). The upper group consists of precipitates in which the manganese dioxide was dissolved out with sulfur dioxide before the final washings with acetone and ether.

(4) Park, *Ind. Eng. Chem.*, **18**, 597 (1926).

(5) Walden, Hammett and Chapman, *THIS JOURNAL*, **55**, 2649 (1933).

(6) Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935); Cohen, *Z. Krist.*, **94**, 288 (1936).

TABLE I

Ppt. no.	G. sample	G. $BaSO_4$	G. $BaSO_4$	Ratio Ba/SO_4
20	0.7486	0.6944	0.7056	0.984
22	1.0998	1.0429	1.0531	.990
24	0.9221	0.8798	0.8872	.992
42	.5545	.5357	.5418	.988
32	.9208	.8950	.8943	1.001
36	.8339	.7243	.7210	1.005
44	.5141	.4955	.4947	1.002
45	.3838	.3690	.3694	0.999
48	.5192	.4904	.4905	1.000

It will be noted that in these precipitates, the sulfate exceeds the barium by an amount distinctly outside the experimental error. Apparently washing with sulfur dioxide results in added contamination of the precipitate with excess sulfate ion formed on oxidation of the wash solution by manganese dioxide. When hydrogen peroxide solution was substituted for sulfur dioxide, this difference disappeared, as can be seen in the lower group, in which hydrogen peroxide was used to remove manganese dioxide.

As has been indicated above, the charge on the co-precipitated permanganate ion could conceivably be balanced in only three ways: (1) by barium ion, (2) by hydrogen ion or (3) by both barium and hydrogen ion. Since barium and sulfate ions are equivalent in the contaminated precipitates, alternatives (1) and (3) are thus ruled out; the permanganate ions must then be balanced wholly by equivalent hydrogen ions.

The demonstration of the equivalence of barium and sulfate also made it possible to use exclusively the sulfuric acid solution method of analysis, which actually measures only the barium content.

If the precipitates are considered to contain only barium sulfate plus permanganic acid, an appreciable portion of the weight of the original sample is left unaccounted for; that is, the weight of barium sulfate reprecipitated after solution in sulfuric acid, plus the weight of permanganic acid calculated from the manganese found by analysis, does not add up to the weight of sample used. The obvious explanation of this discrepancy is that the precipitates must contain water. Since permanganic acid is a strong acid, it would be present in the precipitating solution as oxonium and permanganate ions rather than anhydrous undissociated hydrogen permanganate molecules, and would be expected to enter the barium sulfate crystals in that form. As a matter of fact, our

analyses, so interpreted, indicate a variable proportion of water, but in only one instance does the determined ratio of moles of water to moles of permanganic acid fall below unity.

The composition of the contaminated precipitates may then be expressed as barium sulfate plus permanganic acid and water in varying proportions. Table II shows the numerical results of analyses of precipitates which were properly prepared, using hydrogen peroxide to clear up manganese dioxide, and which showed no traces of manganese dioxide. Precipitates in which sulfur dioxide was used are omitted.

TABLE II

Ppt. no.	BaSO ₄ , %	HMnO ₄ , %	% H ₂ O by diff.	Mole % hydrated HMnO ₄
32	97.80	1.275	0.92	1.50
33	98.56	0.580	.86	1.13
34	90.25	6.601	3.15	12.5
36	86.53	9.027	4.44	16.9
42	97.08	1.844	1.08	3.57
44	97.57	1.448	0.98	2.81
45	97.48	1.521	1.00	2.95
46	98.54	1.417	0.04	2.72
47	96.20	2.174	1.63	4.21
48	95.43	2.542	2.03	4.93
49	98.18	1.178	0.64	2.28
50	96.26	2.269	1.47	4.89

Since the weight of water was calculated by difference, it was considered advisable to confirm the actual presence of water in the calculated proportion by some other method. Accordingly, weighed samples of different precipitates were given thirty minutes ignition at 700°. The ignited precipitates were weighed, then treated with 18 *M* sulfuric acid, the barium sulfate going into solution, and the residual manganese oxides remaining in suspension. After dilution with water to the proper volume, the barium sulfate being reprecipitated, a measured excess of standard ferrous sulfate solution was added and let stand until the manganese oxides were completely dissolved; the excess of ferrous sulfate was then titrated with standard ceric sulfate. Since the percentage of manganese in each sample was known already, and hence the weight of manganese present, the analysis after ignition yielded the average composition of the manganese oxides in the ignited precipitates. The observed weight loss during the ignition should then consist of the excess water, the water of constitution from permanganic acid, and oxygen from manganese heptoxide to the oxide of the determined average

composition. From these data, the actual loss of water may be determined, and compared with the weight of water calculated by difference from the original analyses (see Table II). Since the oxygen and water of constitution of the permanganic acid amount to only a third of the total observed loss in weight, the remainder cannot be explained by experimental error. The only possible conclusion seems to be that the residual loss must be water, and this residual loss checks very well with the weight of water calculated by difference. The results are shown in Table III.

TABLE III

Ppt. no.	G. sample	H ₂ O by diff., g.	H ₂ O by ignition, g.
32a	1.1584	0.0096	0.0101
32b	1.1778	.0097	.0098
44	0.8989	.0088	.0083
47	.6363	.0077	.0073

This water is held tightly by the crystal lattice as shown by the fact that neither vacuum desiccation over concentrated sulfuric acid for four months, nor heating at 110° for a week caused any appreciable loss in weight. On the basis of this confirmation by a different method of attack, we may say with reasonable assurance that the precipitates definitely contain water.

In order to correlate our observations on permanganate contamination with those of Walden and Cohen on nitrate contamination, it was necessary to have complete analyses of their precipitates, which they had analyzed only for weight per cent. of nitrate ion. Two of the precipitates prepared by Walden and Cohen were selected and fused with anhydrous sodium carbonate to determine the ratio of barium to sulfate ion. As is shown in Table IV (nomenclature the same as

TABLE IV

Ppt. no.	G. sample	G. BaSO ₄	G. BaSO ₄	Ratio Ba/SO ₄
12	0.6269	0.6072	0.5703	1.065
14	.4670	.4516	.4243	1.064

in Table I), the difference between the barium and sulfate precipitates is in both cases about 6% of the sample weight, which is decidedly greater than any possible experimental error. However, the excess of barium does not account for the total nitrate content of the precipitates as given by the analyses of Walden and Cohen. Moreover, the remainder of the nitrate, when calculated to nitric acid, still does not account for the total sample weight, which indicates the

possibility that there may be water taken in as part of the contaminant. Although the data are too meager to warrant any definite statement as to the precise constitution of these precipitates, what does seem to be definite is that the ratio of barium to sulfate is greater than unity, and therefore that at least part of the co-precipitated nitrate has its charge balanced by excess barium ions. In this respect, the nitrate contaminated precipitates differ from those containing permanganate.

X-ray Data and Interpretation

The lattice parameters of the crystalline contaminated precipitates are given in graphical form in Figs. 1 and 2. In Fig. 1 the parameters a_0 , b_0 ,

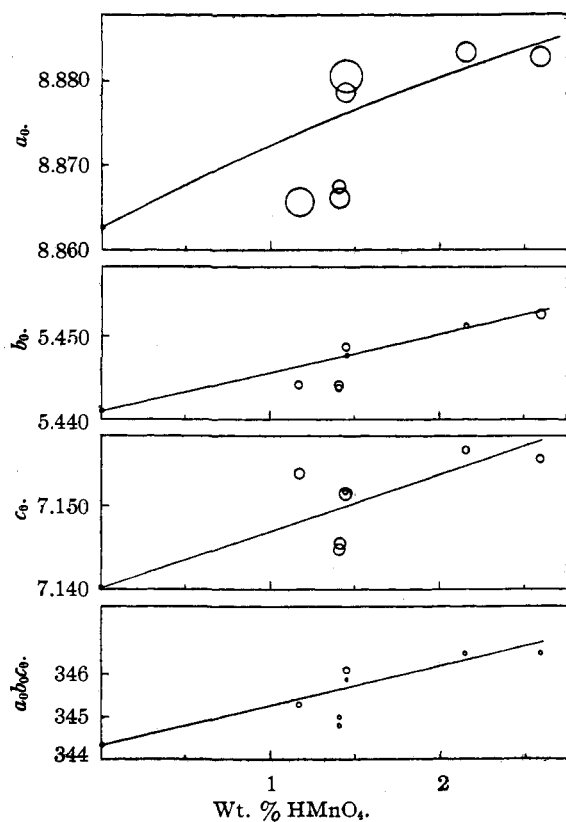


Fig. 1.

and c_0 in Ångström units, and the volume of the unit cell, $a_0b_0c_0$, are plotted against weight per cent. of permanganic acid. In Fig. 2, the abscissa is the weight per cent. of total contaminant, or 100-% BaSO₄. The radii of the circles around the experimental points are the probable errors as determined by the least squares analysis of the films.⁶ It is apparent from the two sets of curves that the lattice parameters vary more regularly

with the percentage of total contaminant than with the percentage of permanganic acid alone. A reasonable interpretation of these results seems to be that the lattice is expanded by the entry of both permanganic acid and water, but not to the same degree. Since, as has been pointed out, the ratio of water to permanganic acid varies in different precipitates, it is not to be expected that the points will lie closely on a smooth curve, as should be the case if the expanding effects were the same, weight for weight. The fact that the lattice parameters vary with increasing percentage of contaminant demonstrates the solid solution character of the precipitates.

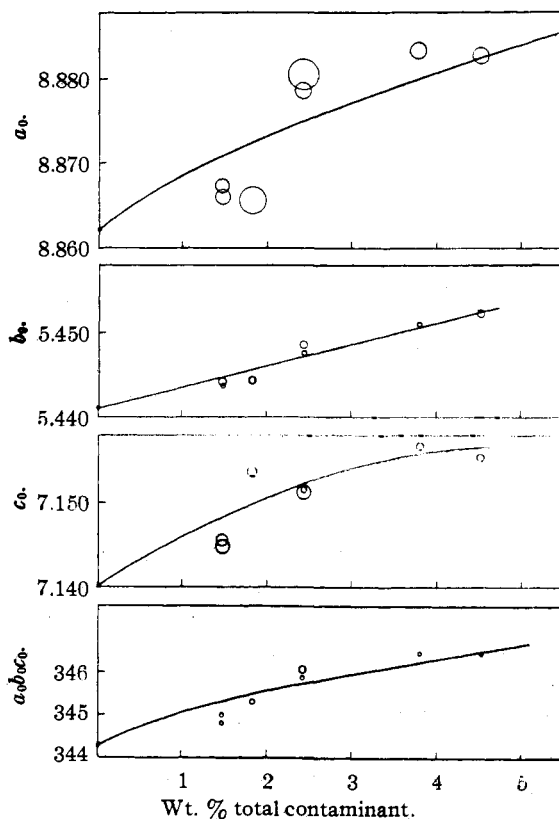


Fig. 2.

Discussion

It might be well at the outset to deal briefly with attacks⁷ which have been made on the assumption of solid solution formation in precipitation systems on the ground that phase-rule studies of such systems show that no solid solution is found to exist in equilibrium with the mother liquor. It should be noted that there is no indication that any precipitate encountered in

(7) Benrath and Schackmann, *Z. anorg. allgem. Chem.*, **218**, 139 (1934).

analytical practice involving coprecipitation of a foreign ion is in actual equilibrium with its mother liquor. Rather it has been observed that such equilibrium is approached exceedingly slowly during prolonged digestion.⁸ Undoubtedly the precipitates investigated by the authors, as well as those of Grimm and Wagner and of Walden and Cohen, are not the results of heterogeneous equilibria, but of kinetic processes localized at the surfaces of the growing crystals.

The data just presented suggest that some of our present ideas with regard to the limitations under which solid solutions may be formed must be revised. The question of crystallographic isomorphism between solvent and solute appears to have as little bearing here as it does in metal systems.⁹ Since large lattice expansions accompanying solid solution are not to be expected, it seems reasonable to suppose that the size, charge and configuration of the entering ions are controlling factors. The possible importance of these factors has already been discussed by numerous investigators.^{3b,10}

This idea appears to be quite consistent with the experimental data just presented. The radius of a complex ion may be defined as the radius of the smallest sphere which can be circumscribed about the whole structure. Both sulfate and permanganate ions consist of four oxygens in regular tetrahedral arrangement about the central atom; the ionic radii, calculated from dimensions given by Wyckoff¹¹ and Pauling,¹² are 3.00 and 3.16 Å., respectively. Obviously the substitution of two permanganate ions for one sulfate ion could take place only with excessive expansion of the lattice. Substitution of a single permanganate ion for a sulfate ion, however, would in itself cause only a small expansion. Such a substitution would necessitate the simultaneous replacement of a barium ion by a univalent cation,¹³ which would likewise cause no large expansion if there were a corresponding similarity of radii.

Although precise values of the radius of an oxonium ion are at present lacking, Volmer's¹⁴

X-ray measurements of ammonium perchlorate and oxonium perchlorate (usually written $\text{HClO}_4 \cdot \text{H}_2\text{O}$) indicate rather definitely that oxonium ion is about the same size as ammonium ion, or slightly larger than barium or potassium ion. The ionic radii given by Wyckoff¹¹ are $\text{NH}_4^+ = 1.50$, $\text{Ba}^{++} = 1.38$ and $\text{K}^+ = 1.33$ Å. Peters¹⁵ was able to prepare barium sulfate precipitates contaminated with as much as 12% of ammonium permanganate, and on the basis of his results predicted that oxonium permanganate should likewise form solid solutions in barium sulfate. Our experimental data fulfil this prediction. Whether the additional water molecules which the precipitates were found to contain are associated with the oxonium ions or are distributed elsewhere through the crystal cannot be decided by the data at our disposal. In either case, they would contribute to the expansion of the lattice, as indeed the experimental evidence indicates.

The nitrate ion has its three oxygens at the apices of an equilateral triangle, close-packed about the central nitrogen atom and planar with it, or nearly so. Since in nitrate-contaminated precipitates a barium ion is balanced by either one sulfate ion or two nitrate ions, it is necessary to have some idea as to what orientation two nitrate ions may assume with respect to each other in replacing a single ion. Such an idea may be obtained by a study of the lattice of barium nitrate.

Barium nitrate has a cubic lattice in which distinct pairs of nitrate ions lie symmetrically about alternate lattice points like the sulfurs in pyrites. The two nitrogens lie on a diagonal of the unit cube with the plane of both ions perpendicular to the diagonal; the oxygens of the two ions are staggered so that their projections on a plane perpendicular to the diagonal are at the apices of a regular hexagon. It seems permissible to assume that a pair of nitrate ions might present a similar configuration when entering the barium sulfate lattice in the place of a single sulfate ion. The radius of the nitrate pair in the barium nitrate lattice is 3.42 Å. These nitrate ions are not close-packed; if they were, the radius would be about 3.1 Å. There is no way to predict how closely the ions would pack if substitution occurred in this manner; however, either value is sufficiently close to the radius of a sulfate ion to suggest that such a substitution would cause no large expansion of the barium sulfate lattice.

(15) Peters, Dissertation, Würzburg, 1930.

(8) Mellor, "Treatise on Quantitative Inorganic Analysis," 1st ed., Griffin, London, 1913, p. 614.

(9) Jette, *Am. Inst. Mining Met. Engrs., Inst. Metals Div., Tech. Pub.* 560 (1934); Hahn, "Applied Radiochemistry," Cornell University Press, Ithaca, New York, 1936, p. 69.

(10) Kolthoff and Moltzau, *Chem. Rev.*, **17**, 293 (1935).

(11) Wyckoff, "The Structure of Crystals," 2d edition, The Chemical Catalog Co., New York, 1931, p. 192.

(12) Pauling, *THIS JOURNAL*, **49**, 765 (1927).

(13) Huggins, *Chem. Rev.*, **10**, 427 (1932).

(14) Volmer, *Ann.*, **440**, 200 (1924).

The correlation of these two cases of contamination involving different analytical results gives strong support to the assumption that size as well as charge and configuration of the ions concerned are very important factors controlling the formation of solid solutions in precipitation systems. The fact that, so far as is known, barium sulfate has only an orthorhombic form, while barium nitrate has only a cubic form, shows that for cases of partial miscibility isomorphism or structural similarity between any two component ion-pairs of the contaminated precipitate is immaterial to the process. Either cation or anion or both can be replaced independently.

Summary

1. Several samples of permanganate-contaminated barium sulfate were prepared in the absence of all foreign ions except permanganate and hydrogen ions, using the procedure employed by Grimm and Wagner.^{3b}

2. Chemical analysis of the rose-colored precipitates shows that the total contaminant consists of hydrogen and permanganate ions in

equivalent quantity, and a variable amount of water.

3. The lattice parameters of these precipitates, obtained by X-ray powder photographs, are all greater than those of pure barium sulfate, and when these are plotted against the weight per cent. of total contaminant present, a reasonably smooth, rising curve is obtained. The precipitates are, therefore, solid solutions.

4. Chemical analysis of nitrate-contaminated barium sulfate prepared by Walden and Cohen² shows that the mole ratio of barium to sulfate is greater than unity, and therefore that the co-precipitated nitrate ions are balanced, at least partially, by barium ions.

5. Comparison of permanganate contamination with nitrate contamination of barium sulfate shows that primary factors controlling the formation of solid solutions in precipitation systems are the size, charge and configuration of the ions entering the lattice. Crystallographic isomorphism and similarity of ionic structure are proved to be unnecessary conditions for cases of limited miscibility.

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The Vapor Pressure of Phosphorus Pentoxide

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Introduction

The vapor pressure of phosphorus pentoxide has been subject to some uncertainty. The disagreement in existing data has already been pointed out by Kelley.¹ The uncertainty, however, is not so much one of magnitude as of reproducibility. Smits and co-workers² obtained measurements which varied from sample to sample. They believed this variation to be due to the presence of two forms of phosphorus pentoxide which could be partially separated by fractional distillation. It necessarily follows that these two postulated forms should be not readily transformable one into the other, and that true equilibrium between them could not have existed

at the time the vapor pressure measurements were made. Entirely reproducible results were obtained by Hoeflake and Scheffer³ but they point out that their distillations were carried out under fairly uniform conditions. Hence, their measurements were not necessarily at variance with those of Smits.

The present investigation was undertaken with the hope of determining definitely whether this phenomenon of Smits exists. The results are interpreted as showing that it does not and that the measurements of Hoeflake and Scheffer are substantially correct.

Description of Apparatus

The Jackson⁴ type gage was used by both Smits and Hoeflake and Scheffer. It consists essentially of a thin-

(1) K. K. Kelley, *Bur. Mines Bull.* 383, 1905, p. 82.
 (2) A. Smits and A. J. Rutgers, *J. Chem. Soc.*, 126, 2573 (1924);
 A. Smits with H. W. Deinum, *Z. physik. Chem.*, A149, 337 (1930).
 The same material is also presented in *Proc. Acad. Sci. Amsterdam*,
 33, 514 (1930).

(3) J. M. A. Hoeflake and F. E. C. Scheffer, *Rec. trav. chim.*, 45, 191 (1926).

(4) Jackson, *J. Chem. Soc.*, 99, 1066 (1911).