[CONTRIBUTION FROM SCHOOL OF MINERAL INDUSTRIES, THE PENNSYLVANIA STATE COLLEGE]

Polymorphism of Ga_2O_3 and the System Ga_2O_3–H_2O

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An investigation of freshly precipitated gallia gel by X-ray and electron diffraction techniques has led to the conclusion that the gel is at first a gallia–water complex, not α-Ga_2O_3 as supposed by Weiser and Milligan. On aging, the gel transforms to the GaO_2H structure, but the gel may dehydrate, before the GaO_2H lattice can develop, to form α-Ga_2O_3 or γ-Ga_2O_3. Besides α-, β- and γ-Ga_2O_3, two new polymorphs called herein δ-Ga_2O_3 and ϵ-Ga_2O_3 have been found. X-Ray data and the conditions under which these structures appear are given. The stable form of gallia from room temperature to its melting point is β-Ga_2O_3. Data for the system Ga_2O_3–H_2O were obtained over the pressure range 50 to 25,000 p.s.i., at temperatures up to 800°. The temperature of transformation of GaO_2H to β-Ga_2O_3 plus water as determined by Laubengayer and Engle (300°) was confirmed and it was found that this temperature is not affected appreciably by pressure in the range used.

Introduction

It is to be expected, and has been known, that the gallium ion closely resembles the aluminum ion and substitutes for it in several structures. In an investigation of phase equilibria in the system Al_2O_3–Ga_2O_3–H_2O,[1] the authors have shown that extensive solid solution exists between the alumina and gallia end members in five stable structures designated as α-Al_2O_3, β-Ga_2O_3, $GaAlO_3$, diaspore (AlO_2H) and boehmite ($Al_2O_3 \cdot H_2O$). Two polymorphs of alumina, the stable α-Al_2O_3 (corundum) and the spinel-like metastable γ-Al_2O_3, have been well-known for a long time and, in addition, several other forms are reported in the literature. It was thus of considerable interest to investigate the existence of polymorphs of Ga_2O_3 and their stability relations.

Interest in the structure of the gels of the hydrated sesquioxides has centered on the question of whether or not these gels are crystalline and, if so, what the nature of the crystalline phase is. In this study recent improvements in X-ray and electon diffraction equipment have made possible a re-evaluation of earlier work.

Method of Investigation

Equipment.—In the hydrothermal experiments, starting materials were enclosed in platinum envelopes and inserted in pressure vessels. The latter were of three types: bombs after the design by Morey and Ingerson,[2] pressure vessels described by Tuttle,[3] and the "test-tube" type pressure vessels.[4] The first was used for runs up to 500°, while the other two vessels operated satisfactorily at all desired temperatures, the maximum used being 850°. All vessels were connected by pressure tubing to a pump which delivered water at pressures up to 30,000 p.s.i. Pressure was measured with a Bourdon tube gage, accuracy of control being of the order of ±3%. Temperature was controlled to ±3° and was measured by means of chromel–alumel thermocouples. Further details of experimental procedure have been reported.[4]

For determination of phase changes taking place in air at one atmosphere, mixtures were heated in platinum crucibles at controlled temperatures in platinum wound muffle furnaces. In addition, for runs above 1700°, a platinum–40% rhodium strip furnace[5] was used. Temperatures in the latter were measured with an optical pyrometer, calibrated at the liquidus temperature, 1698°,[6] of the mixture 15% CaO, 85% SiO_2.

Starting Materials.—Two sources of gallium were used: Ga_2O_3 obtained from the Eagle–Picher Company, and gallium metal from the Aluminum Company of America. The former, which was used for most of the work, was from lot No. 1277-902 for which the following batch analytical data were given: 0.001% Mg, 0.0001% Fe, 0.01% Cu, 0.001% Ca, 0.001% Pb, 0.005% Sn, sub-spectroscopic In. Identical experimental results were obtained from the different materials.

For most runs gallia gel was used as the starting substance, prepared from an aqueous solution of the nitrate by adding ammonia while the system was maintained at the desired temperature in the range 0–50°. The precipitate was filtered on a buchner funnel, transferred to an electrodialysis cell, and electrodialyzed until free of nitrate ions. When necessary, as in the study of the gel structure, the process of gel preparation was accelerated to give an elapsed time of not over 10 minutes including preparation of the electron microscope sample.

Identification of Phases.—Identification of phases with light microscopes was not possible in most cases because of the small particle size. Virtually every sample, therefore, was examined by X-ray diffraction techniques. A Norelco Geiger-counter spectrometer, using copper radiation, filtered through nickel foil was used for most of the work. A high temperature furnace was used in conjunction with the spectrometer for the study of phase changes at high temperatures. Electron diffraction patterns were obtained on RCA models: EMB, EMU and EMD. The EMD unit was especially useful for obtaining patterns with only a few seconds exposure. Studies of shape and particle size were made with electron microscopes.

Experimental Results

The Structure of Gallia Gel.—When most R_2O_3 gels age by standing, they form crystalline hydrates as revealed by their X-ray diffraction patterns. Gallia gel is no exception, and converts to GaO_2H, the monohydrate of gallia with the diaspore structure. Weiser and Milligan,[7] however, report that although the aged gallia gel may have the GaO_2H structure, the first formed precipitate is α-Ga_2O_3, a conclusion based on electron diffraction studies. It is difficult to understand this proposed sequence whereby the first precipitate is anhydrous gallia which then transforms to a hydrous phase by standing at room temperature.

X-Ray diffraction patterns of freshly precipitated gels were obtained where the entire process of precipitation and recording of the pattern required 30 minutes or less. On these patterns two broad bands appeared, located close to the maximum intensity reflections for α-gallia, but at distinctly different positions. The largest spacing gel band of maximum intensity corresponded to $2\theta = 28°$ ($d = 3.18$) as compared with the α-gallia maxima of $2\theta = 33.8°$ and $36.1°$ ($d = 2.65$ and 2.49). During the first hour of aging, the broad maxima in the gel pattern became less and less pronounced. This was

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[1] V. G. Hill, R. Roy and E. F. Osborn, *J. Am. Ceram. Soc.*, **35**, in press (1952).

[2] G. W. Morey and E. Ingerson, *Am. Mineral.*, **22**, 1121 (1937).

[3] O. F. Tuttle, *Am. J. Sci.*, **246**, 628 (1948).

[4] R. Roy, D. M. Roy and E. F. Osborn, *J. Am. Ceram. Soc.*, **33**, 152 (1950).

[5] We are indebted to our colleague Prof. M. L. Keith of the Division of Geochemistry for the use of this equipment constructed by him.

[6] J. W. Greig, *Am. J. Sci.*, **13**, 1–44 and 133–154 (1927).

[7] H. B. Weiser and W. O. Milligan, *J. Phys. Chem.*, **44**, 1081 (1940).

TABLE I

INTERPLANAR SPACINGS FOR POLYMORPHIC FORMS OF Ga_2O_3 (Å.)

br = Very broad peak, maximum value given. d = Average value for double peak which was not satisfactorily resolved.

GaO_2H			α-Ga_2O_3			β-Ga_2O_3		γ-Ga_2O_3		δ-Ga_2O_3			ϵ-Ga_2O_3	
d	*I/I₀*	*hkl*	*d*	*I/I₀*	*hkl*	*d*	*I/I₀*	*d*	*I/I₀*	*d*	*I/I₀*	*hkl*	*d*	*I/I₀*
4.906	0.05	020	3.636	0.21	110	4.72	0.05	2.56 br.	1.00	2.863	0.61	222	6.42	0.04
4.580	.02		2.933	.03		3.68	.03	1.47 br.	0.25	2.499	1.00	400	4.67	.04
4.134	1.00	110	2.651	1.00	200	2.965	.82			2.36	0.32	411	3.24	v.w.
3.34	0.10	120	2.490	0.68	101	2.955	.61			2.26	v.w.	420	3.17	0.26
2.659	.35	130	2.237	.03	111	2.833	.94			2.13	0.09	332	2.926	.50
2.543	.12		2.176	.13		2.678	.22			1.95	.08	431	2.693	1.00
2.49	.01		2.057	.02		2.555	1.00			1.91	.06	511	2.528	0.40
2.45	.03		1.804	.32	220	2.41	0.37					333		
2.414	.40	111	1.665	.46		2.347	.64			1.71	.10	433	2.434	.60
2.286	.04		1.583	.02		2.108	.18			1.504	.45	622	2.328	.64
2.214	.08	121	1.564	.11		2.03	.05			1.45	.11	631	2.25	.03
2.161	.11	140	1.465	.25		1.982	.32			1.33	.08	642	2.22	.10
1.981	.04		1.436	.27		1.875	.23						2.17	v.w.
1.894	.02		1.33	.04	400	1.839	.07						1.96	0.12
1.781	.08		1.281	.15		1.794	.04						1.91	.04
1.697	.29		1.243	.07	202	1.75	.03						1.83	.04
1.671	.09	240	1.208	.05		1.684	.12						1.706	.24
1.64	v.w.		1.17	.04		1.628	v.w.						1.55	.64
1.583	0.04		1.138	.06		1.601	0.34						1.52	v.w.
1.541	.12	002	1.125	.08		1.56	v.w.						1.494	0.48
1.486	.08					1.543	0.33						1.452	0.40
1.453	.05					1.523	.36						1.42	v.w.
1.432	.04					1.503	.17						1.40	0.08
1.40	.02					1.45	v.w.						1.37	.04
1.38	.04					1.441(d)	0.90						1.32	.03
1.36	.02					1.355	.24						1.30	v.w.
1.34	.04					1.337	.22							
1.30	.02					1.304	.11							
1.27	v.w.					1.299	.14							
1.25	v.w.					1.23	.04							
1.19	0.02					1.21	.04							
1.13	.04					1.17	.01							
1.11	.03					1.15	.12							

observed by obtaining diffraction patterns every five minutes or so. Beyond this stage, the bands began to sharpen but the maxima were then at different positions. Within three hours the new bands had resolved themselves into a recognizable pattern of GaO_2H. The X-ray data therefore suggest that the first precipitated gel is perhaps a gallia–water complex, not α-Ga_2O_3, which on aging crystallizes to the monohydrate.

Preliminary electron diffraction studies of fresh precipitates gave inconsistent results. On various samples, patterns for α-Ga_2O_3, GaO_2H, γ-Ga_2O_3, and an "amorphous" substance were obtained. Where the gels had first been aged for a few hours, however, the electron diffraction pattern obtained was invariably that of GaO_2H. In a later series of experiments, a thicker layer than usual of fresh gel was placed in the beam of the EMU microscope and the intensity of the beam increased to the maximum. The pattern obtained first showed no trace of crystallinity. After about 30 seconds, broad regions of dark and light bands began to appear. In two minutes a diffuse pattern was observable, and in five minutes a pattern which was stable and could be photographed was obtained. It was not possible to photograph the patterns at the various stages, because exposures necessary were of the order of $^1/_2$ to 1 minute. It was, however, demonstrated that the fresh gel does not give the electron diffraction pattern of α-Ga_2O_3 or indeed any recognizable pattern; and moreover, it was directly observed that during exposure to the beam a pattern develops. It is concluded that the heat of the electron beam can dehydrate the gel to give α-Ga_2O_3 or γ-Ga_2O_3 before there is time for the gel to transform to the GaO_2H structure. Both X-ray and electron diffraction studies therefore support the thesis that the freshly precipitated gel is not an anhydrous gallia phase but is a gallia–water complex; that this gel on aging is transformed to the GaO_2H structure, and that the gel may be dehydrated easily, for example in an electron beam (before the GaO_2H lattice can develop), to form a α-Ga_2O_3 or γ-Ga_2O_3. However, once the GaO_2H has been formed by aging, dehydration does not occur readily, a phenomenon also enencountered with AlO_2H. Furthermore aged, crystalline gels give thinner dispersions for use as electron diffraction samples than the fresh gel and, therefore, absorb less heat from the electron beam.

Polymorphs of Ga_2O_3.—Three forms of Ga_2O_3 have been previously reported, designated as α-, β- and γ-Ga_2O_3. The first is hexagonal, analogous to α-Al_2O_3, with a = 5.31 Å., α = 55°50'.[8] This

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(8) W. H. Zachariasen, "Crystal Structure of the Sesquioxides and Compounds of the Type ABO_3," Norske Vid. Akad. Oslo, Mat. Kl. IV, pp. 1-165, 1928.

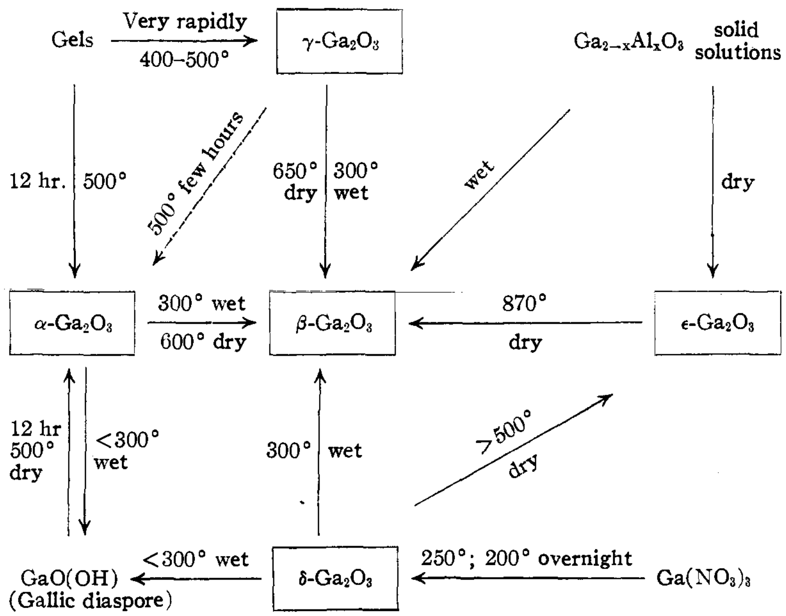

Fig. 1.—Chart illustrating transformation relationships among the forms of gallia and its hydrates. Conversion (wet) of the structure designated as $Ga_{2-x}Al_xO_3$ to β-Ga_2O_3, occurs only where $x < 1.3$; where $x > 1.3$, an α-Al_2O_3 structure forms.[1]

form is obtained on heating GaO_2H in air between 450° and 550°. The second form, β-Ga_2O_3, has a diffraction pattern somewhat similar to that of β-alumina ($Na_2O \cdot 11Al_2O_3$), and is the only stable form of Ga_2O_3 known. Melting points of 1900°[9] and 1740 ± 20°[10] have been reported for β-Ga_2O_3. Using a strip furnace, we have determined the melting point of β-Ga_2O_3 as 1715 ± 15° on the basis of the temperature scale used by Greig,[6] or about 1725 ± 15° (Int.). This stable form of Ga_2O_3 is obtained when any other form of Ga_2O_3, or its hydrate, is heated in air above 1000° or hydrothermally above 300° at any water pressure we have used (15 to 30,000 p.s.i.). We have obtained single crystals of β-Ga_2O_3 both hydrothermally and from the melt ranging up to 1 mm. in size. Böhm[11] reported the third form, γ-Ga_2O_3, supposedly analogous to γ-Al_2O_3, having a unit cell edge of 8.35 Å. In our attempts to prepare this form, following the described procedure,[12] material was obtained having an X-ray diffraction pattern which showed a few broad bands with intensity maxima at *d*-values of 2.56 and 1.47 Å. The pattern is distinct from those of other forms of Ga_2O_3 but shows no obvious relationship to γ-Al_2O_3.

Two additional forms of Ga_2O_3 have been encountered in the present study and designated as δ-Ga_2O_3 and ϵ-Ga_2O_3. X-Ray data obtained for all forms are summarized in Table I. Conversion relationships among the forms are indicated in Fig. 1.

δ-Ga_2O_3.—The Ga_2O_3 as received from the Eagle–Picher Company was found to have an X-ray diffraction pattern unlike those of known forms of Ga_2O_3. It was understood[13] that this substance was prepared by dissolving the metal in nitric acid, heating the residue after evaporation to 250° to decompose the nitrate, followed by heating at 200° for about 12 hours. By following essentially this procedure, we obtained a substance having the same X-ray diffraction pattern as that of the commercial Ga_2O_3 but much more diffuse. The particle size was extremely small with no indication of anisotropy in the crystals, whereas the commercial preparation was composed of birefringent particles apparently of much larger size, with an apparent index of refraction of approximately 1.80. The relatively large size of the crystals in the latter material is apparently due to the formation of aggregates, as in clay minerals, for after shaking in water and examining under the electron microscope the particle size of most of the sample was found to be of the order of 0.02–0.05μ while some particles which may still be aggregates varied up to 1μ in diameter. The fine size is also suggested by the line broadening in the X-ray pattern.

This new, metastable form, called δ-Ga_2O_3, corresponds to the C-type structure of the rare earths,[9] and is analogous structurally to Mn_2O_3, In_2O_3, Tl_2O_3, etc. This structure is body centered, cubic, space group T-5, with a unit cell edge of 10.00 Å. Goldschmidt,[9] in a study of In_2O_3–Ga_2O_3 solid solutions could not obtain high Ga_2O_3-content crystals with the C-type structure, but predicted that if Ga_2O_3 could be obtained with this structure, the unit cell edge would be 9.52 Å. The observed value of 10.00 Å. suggests considerable strain in the structure as would be expected with the relatively small gallium ion. It is not clear whether the anomalous birefringence is due to absorption of water, or whether it may be accounted for by deviations from the Tl_2O_3 structure, which quite possibly have not been detected due to the diffuse nature of the pattern. The density of δ-Ga_2O_3 as calculated from X-ray data is 4.98, and as determined by pycnometric methods is 5.18.

ϵ-Ga_2O_3.—When δ-Ga_2O_3 is heated by differential thermal techniques, a small broad endothermic peak appears at about 550° and a sharper exothermic peak at 925°. These heat effects are related, respectively, to the inversion of δ-Ga_2O_3 to ϵ-Ga_2O_3, and inversion of the latter to β-Ga_2O_3. The X-ray pattern of this fifth form of Ga_2O_3 is similar to, but quite distinct from that of β-Ga_2O_3. The structure of ϵ-Ga_2O_3 could not be determined. The powder pattern (Table I) was, however, normally sharp, and showed no evidence of line broadening characteristic of γ-Al_2O_3 and δ-Ga_2O_3 patterns. The structure is not analogous to that of valentinite,

(9) V. M. Goldschmidt, T. F. W. Barth and G. Lunde, "Geochemische Verteilungsgesetze der Elemente," Skr. Norske, Ved. Akad Oslo Mat. Kl, I-VIII, 1925.

(10) H. van Wartenburg and Reusch, *Z. anorg. Chem.*, **207**, (1932).

(11) J. Böhm, *Angew. Chem.*, **53**, 131 (1940).

(12) Fresh gel, quickly dried between filter paper sheets after filtration on a buchner funnel, was heated to 450–500° for periods of 10 to 60 minutes.

(13) H. S. Harner, Eagle-Picher Co., personal communication (1950).

claudetite, or other common ABX_3 structures which were examined for analogies. The symmetry of ϵ-Ga_2O_3 is apparently lower than hexagonal or tetragonal. That ϵ-Ga_2O_3 is not merely a chance intermediate structure obtained under very specific conditions, but is a definite structure is borne out by the fact that when $GaAlO_3$, or its solid solutions with Ga_2O_3 and Al_2O_3, is heated in air 100° above the equilibrium transformation temperature, a series of ϵ-phase solid solutions form,[1] showing a regular displacement of lines in the X-ray pattern with increasing aluminum content.

Using a furnace adapted for use with the X-ray spectrometer, the pattern of δ-Ga_2O_3 was found to disappear and that of ϵ-Ga_2O_3 appear at 525° within 30 minutes. This inversion was effected at 500° but not at 475° when held at temperature for one week. The inversion of ϵ-Ga_2O_3 to β-Ga_2O_3 occurs readily at 870 ± 15° with a marked heat effect.

Equilibrium Relations in the System Ga_2O_3–H_2O.—Laubengayer and Engle[14] investigated phase relations in the system Ga_2O_3–H_2O using closed bombs and under limited pressure conditions. They reported the occurrence of a metastable trihydrate obtained at 170°, and a monohydrate stable from room temperature to 300°, above which β-Ga_2O_3 is the stable phase. We were unable to prepare or prove the existence of $Ga_2O_3 \cdot 3H_2O$, but in other respects our data agree with those of Laubengayer and Engle. Only one monohydrate, GaO_2H completely analogous to AlO_2H, diaspore, was obtained; under no conditions could we obtain a boehmite structure. Data obtained from some 200 runs have extended the work to pressures from 50 to 25,000 p.s.i. up to 800°. Starting from α-Ga_2O_3, δ-Ga_2O_3, GaO_2H and gels, with time of reaction varying from half an hour to over two weeks, GaO_2H was obtained below and β-Ga_2O_3 above 300 ± 5°. Pressure had very little effect on the decomposition temperature of GaO_2H. The possible existence of a low-pressure stability field for α-Ga_2O_3 was investigated. At pressures as low as 50 p.s.i. the conversion of α-Ga_2O_3 and GaO_2H to β-Ga_2O_3 was realized. Failure to obtain the conversion at 15 p.s.i. pressure is ascribed to sluggishness of the reaction. The equilibrium diagram has only two fields, those for β-Ga_2O_3 and GaO_2H, separated by a univariant line at 300 ± 5°.

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(14) A. W. Laubengayer and H. R. Engle, THIS JOURNAL, **61**, 1210 (1939).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

Polarographic Maxima Suppression in Alcohol–Water Mixtures

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The various factors involved and their influences on polarographic maxima are studied here. The concentrations of colloidal agents necessary to suppress maxima, the M.S.P. values, are seen to increase with increasing alcohol content of the solvent. A linear relationship is noted. An empirical maxima suppression equation is deduced and discussed. The results are interpreted in terms of previously reported micelle phenomena.

The relationship between maxima suppression and micelle formation (for colloidal type suppressors) was examined and reported[1] earlier. The suppressor concentration, precisely sufficient to eliminate the maximum under consideration, has been termed the maximum suppression point (M.S.P.). It has been shown that in order to avoid possible misinterpretation of polarographic results, particular attention should be given to the quantity of suppressor used. For each given suppressor, the role played by: (a) the reducible species, (b) the supporting electrolyte, and (c) the solvent, in relation to the maximum suppression point (M.S.P.), bears investigation. The present report deals with this problem in alcohol–water mixtures.

As in previous work, highly surface-active (nonreducible) colloidal agents are used so that both "positive" and "negative" maxima will be reduced by all the suppressors; and, therefore, Heyrovsky's sign rule[2] need not be considered. Neutral supporting electrolytes are employed throughout to eliminate the effect of acidity. The three colloidal agents investigated here are: gelatin, lauryltrimethylammonium bromide and methyl cellulose (not previously studied). These represent[3] typical cationic and non-ionic colloidal agents. Where possible, a study of the systems dealt with earlier has been extended into the alcohol region. Additional systems have also received attention so that the effect of valence, both in the ions of the reducible species and in the supporting electrolyte, might be observed.

Experimental

A Sargent–Heyrovský Polarograph, Model XII, equipped with a Sargent Circulator and Thermostat, S-181835 and S-84805, was used at 25.00 ± 0.05°. The capillary passed 2.867 mg./sec. (open circuit), for an average drop time of 2.50 sec. in 0.50 *M* aqueous sodium nitrate, when under a pressure of 78.5 cm. of mercury. A drop time of 3.0 sec. was employed in all the maxima suppression experiments. The nitrogen gas was freed of oxygen by means of several vanadium–zinc amalgam wash bottles placed in series.[4] The oxygen free nitrogen was then passed through a sodium hydroxide solution and finally water and/or the concentration of alcohol under investigation before introducing the

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(1) E. L. Colichman, THIS JOURNAL, **72**, 4036 (1950).

(2) (a) J. Heyrovsky, "Actualites scientifiques et industrielles," No. 90, Paris 1934; (b) J. Heyrovsky and M. Dillinger, *Collection Czechoslov. Chem. Communs.*, **2**, 626 (1930).

(3) The gelatin used here will act as cationic material, see exptl. section of ref. 1 for justification.

(4) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).