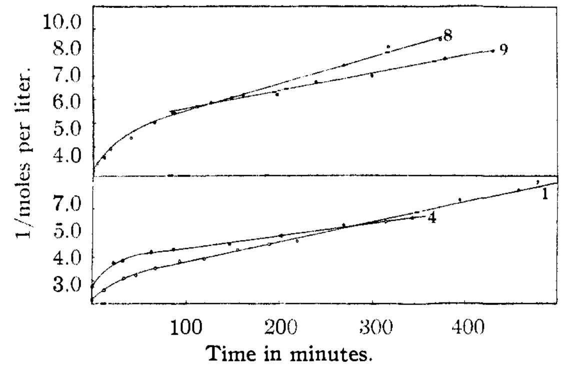


Fig. 3.—Second order rate curves: 1 and 4, thiophenol and 2-ethylethylenimine at 26° and 17°, respectively; 8 and 9, thiophenol and 2,2-dimethylethylenimine at 25° and 15°, respectively.

thiophenol whose concentration increases gradually until a "steady state" is reached. Thereafter, the reaction is a regular bimolecular reaction, thiophenol reacting with the intermediate. The use of the "method of the unstable intermediate"[17] gives the rate equation

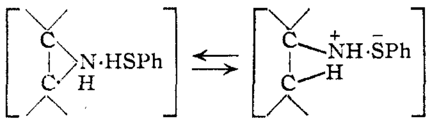
$$-\frac{\mathrm{d}(T)}{\mathrm{d}t} = \frac{k_1k_3(E)(T)^2}{k_2 + k_3(T)}$$

where (T) = concn. of thiophenol, (E) = concn. of imine and k_1, k_2 and k_3 are defined in the diagram above.

In order that the reaction be of second order after the "steady state" is reached, the expression

$$k_{\mathrm{bi}} = \frac{k_1k_3(T)}{k_2 + k_3(T)}$$

must be constant, where k_{bi} = bimolecular rate constant. This means that the rate of the reaction of the intermediate with thiophenol must be much greater than the rate at which it reverts to the starting compounds, and that the rate-determining step is the formation of the intermediate. In view of this argument then, the intermediate is not likely a simple hydrogen-bonded molecular compound, since hydrogen bonding (with its small activation energy[18]) should be a fast reaction. However, it is possible that the intermediate is a mixture of two forms, namely, a hydrogen bonded molecular compound and an ion-pair, which differ only in the position of the proton.[19] In the case of thiophenol and the imines this can be represented as



It is proposed that this ion-pair, in which the C–N bonds are weakened due to a positive charge on the nitrogen,[20] is the reacting species. Such an equilibrium between ion-pair and molecular compound should be measurably slow in the non-polar solvent, carbon tetrachloride, and may be the rate-determining step. In polar solvents such as alcohol and water (in which the reactions yield products of type III) and in the presence of strong acid catalysts, the ion-pair may more easily separate into an anion and a free immonium cation, thus increasing the probability of carbonium ion (IV) formation.

[17] A. Skrabal, *Monatsh.*, **64**, 289 (1934).

[18] Linus Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 284.

[19] R. M. Fuoss, D. Edelson and B. I. Spinrad, THIS JOURNAL, **72**, 327 (1950).

[20] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 303.

PROVIDENCE, RHODE ISLAND RECEIVED NOVEMBER 1, 1950

[CONTRIBUTION FROM THE INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

Sorption of Water Vapor by Proteins and Polymers. IV[1,2]

BY BERNARD KATCHMAN AND A. D. MCLAREN

The water vapor sorption isotherms of a number of polymers and proteins have been acquired in the continuing effort to determine the relative efficiency of site adsorption by polar groups. Unlike many proteins, the first sorbed water apparently does not penetrate the tobacco mosaic virus particles. Crystalline insulin and soya-bean trypsin inhibitor sorb more water than the corresponding amorphous samples. The sorption capacity of polar groups (ether, hydroxyl) can depend on the structure of the polymer. Ester linkages have very little affinity for water vapor. The carboxyl group, like the hydroxyl group, has a strong affinity for water. The over-all results indicate that a one-to-one correlation of polar groups and sorbed water molecules in proteins and polymers is generally not observed as structural relationships tend to limit sorption.

In line with the stoichiometric views of water vapor sorption by polar groups in proteins[3] and nylon,[4] we have examined a few polymeric materials in order to further examine this hypothesis.[5]

Comparative studies have been made with polymethacrylic acid, polyvinyl benzoate, polyisobutyl methacrylate, polyethylene, polyvinylisobutyl ether, methoxypolyglycol, polyacrylonitrile, polyvinyl acetate, ethylene-vinyl alcohol, polyglycine-DL-alanine and polymethyl vinyl ketone. Water vapor uptake by crystalline and amorphous trypsin-inhibitor (STI) protein from the soya bean and insulin have been examined. Tobacco mosaic virus has also been exposed to water vapor with results differing markedly from those found for simple proteins.

Experimental Procedure and Results

The sorption measurements with water vapor were carried

[1] For previous paper see J. A. Cutler and A. D. McLaren, *J. Polymer Sci.*, **3**, 792 (1948).

[2] From Part I of the Ph.D. thesis of B. Katchman, Polytechnic Institute of Brooklyn, 1950. Work done under contract with the Technical Command, Chemical Corps, U. S. Army.

[3] L. Pauling, THIS JOURNAL, **67**, 555 (1945).

[4] M. Dole and A. D. McLaren, *ibid.*, **69**, 651 (1947).

[5] Previous references in this field have been summarized by M. Dole and I. L. Faller, *ibid.*, **72**, 414 (1950).

TABLE I

SORPTION OF WATER BY SYNTHETIC HIGH POLYMERS AT 25 OR 40° (MOLES OF WATER PER 100 G. OF POLYMER)

Symbol	Polymer	Symbol	Polymer
M	Polymethylacrylic acid (du Pont)	A	Polyvinyl acetate (du Pont)
V	Polyvinyl benzoate (du Pont)	E	Ethylene-vinyl alcohol (du Pont)
I	Polyisobutyl methacrylate (du Pont)	P	Polyethylene (du Pont)
X	Methoxypolyglycol 750 (Carbon and Carbide)	B	Polyvinyl isobutyl ether (General Aniline)
N	Polyacrylonitrile (du Pont)	K	Polymethyl vinyl ketone

Polymer → Rel. v. p.	M (40°)	V (40°)	I (40°)	X (25°)	N (25°)	A (25°)	E (25°)	P (40°)	B (25°)	K (25°)
0.05	0.045									
.1	.080			0.004	0.013	0.016	0.011			0.01
.2	.14	0.023		.06	.018	.023	.023			.022
.3	.19	.034	0.02	.12	.026	.031	.034			.037
.4	.26	.045	.025	.22	.035	.042	.046			.053
.5	.34	.055	.03	.38	.043	.055	.063		0.01	.077
.6	.44	.066	.035	.67	.068	.072	.085		.01	.11
.7	.54	.077	.04	1.1	.12	.096	.11	0.03	.02	.16
.8	.70	.088	.06		.22	.14	.14	.04	.03	.22
.9	.91	.099	.08		.42	.17	.21	.05	.065	.29
.95	1.02	.123	.13		.70	.25	.27	.07		

TABLE II

SORPTION OF WATER BY PROTEINS AND A POLYPEPTIDE (MOLES OF WATER PER 100 G. OF SUBSTANCE)

Symbol	Substance	Symbol	Substance
STI-A(25°)	Trypsin inhibitor (amorphous) (M. Kunitz, *J. Gen. Physiol.*, 29, 149 (1946))	I-A(25°)	Insulin amorphous (Eli Lilly and Co.)
STI-C(25°)	Trypsin inhibitor (crystalline)	I-C(40°)	Insulin (crystalline)
		P	Polyglycine DL-alanine (courtesy Dr. F. Eirich)

Rel. v. p. →	0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	0.95
STI-A	0.09	0.15	0.22	0.28	0.35	0.45	0.56	0.67	0.84	1.13	1.4
STI-C	.11	.18	.28	.37	.47	.59	.72	.87	1.10	1.51	1.9
I-A	.12	.17	.24	.31	.38	.46	.54	.65	0.81	1.27	1.96
I-C	.09	.17	.28	.35	.42	.50	.60	.69	.84	1.09	1.27
P(25°)	.10	.14	.19	.23	.29	.36	.46	.62	.90	1.72	3.54
P(40°)	.08	.13	.18	.21	.26	.33	.43	.61	.75	1.60	3.40

out by the method essentially as described by Bull[6] or as modified by Hauser and McLaren.[7]

The sources of the polymers and proteins are indicated in Tables I and II.

In Fig. 1 are shown typical results with the virus. In Tables I and II we have summarized the sorption data by interpolating values from "smoothed" curves in the manner of Bull.[6] The experimental reproducibility is only about 25% at low humidity, about 5% at high humidity and about 10% at *ca.* 0.5 relative vapor pressure for the materials which absorb but small amounts of water vapor. For those materials taking on relatively large amounts of water the reproducibilities are much better, namely, about 8–15%. With the polymers, 0.1–0.3 g. samples were weighed on sensitive quartz spirals.[7] With the proteins, approximately 0.2-g. samples were employed and weighed either with the spiral or in weighing bottles with an analytical balance. In all cases, however, the degrees of accuracy and precision were more than ample for the conclusion here drawn to be valid.

As has been previously noted, the proteins and polymers showed little or no hysteresis.[6,7] The STI was still active as a trypsin inhibitor after being pumped dry under high vacuum with a mercury vapor pump assembly.

With tobacco mosaic virus (TMV) a surprising difference was found between a desorption isotherm from the wet pellet and an adsorption isotherm from a sample pre-dried at 5° over phosphorus pentoxide. (After so drying the sample was still viable.) The wet pellet (prepared by Dr. G. Oster) was obtained by sedimentation in an ultracentrifuge. It contained 24 moles of water per 100 g. dry virus. In desorption the first few points required from 150 to 30 days for equilibrium to be obtained. For the adsorption isotherms less time, of the order of 20 days, was required to reach equilibrium weights in air.

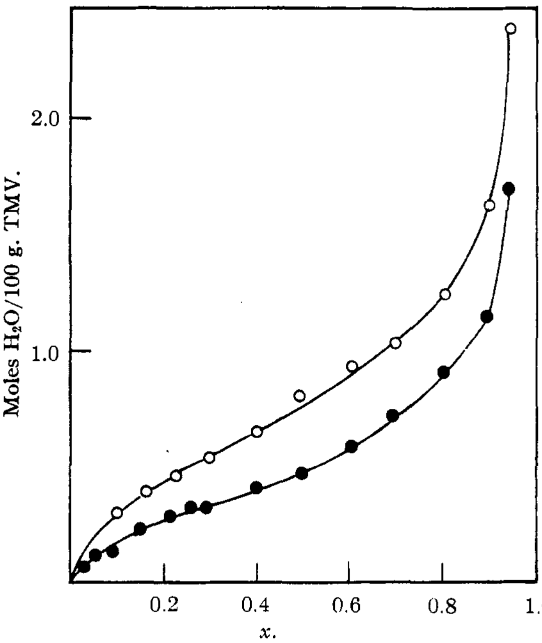


Fig. 1.—Sorption isotherms of TMV at 25°: ○, desorption; ●, sorption.

Discussion of Results

The Polymers.—As has been pointed out previously,[7] typical vinyl polymers give adsorption isotherms having an initial, more or less linear portion

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[6] H. B. Bull, *ibid.*, **66**, 1499 (1944).

[7] P. M. Hauser and A. D. McLaren, *Ind. Eng. Chem.*, **40**, 112 (1948).

extending to a relative vapor pressure in the neighborhood of 0.5. This is followed by a more rapid uptake of moisture giving rise to an isotherm with curvature convex to the x axis (x = relative vapor pressure). This is the case with polyacrylonitrile, polymethyl vinyl ketone, polyvinyl isobutyl ether, polyvinyl benzoate, polyisobutyl methacrylate, polyvinyl isobutyl ether, ethylene-vinyl alcohol and polythene, as shown here, as well as with polyvinyl alcohol, polyvinyl butyral, and vinylidene chloride-acrylonitrile.[7] For these substances (*cf.* Table III) there is not enough water sorbed, even at x = 0.90, to provide one water molecule per polar group except in the case of polyvinyl alcohol (which is soluble in water).[4] Such isotherms do not fall into any of the types described by Brunauer,[8] and no theoretical treatment is available for the entire isothermal curve.

TABLE III

MOLES OF POLAR GROUPS PER 100 G. OF POLYMER COMPARED WITH MOLES OF WATER VAPOR SORBED AT 0.9 RELATIVE VAPOR PRESSURE

Polymer	Moles of polar groups	Moles of water sorbed
Polymethacrylic acid	1.16	0.91
Polyvinyl benzoate	0.676	.1
Polyisobutyl methacrylate	0.705	.08
Methoxypolyglycol	2.27	Dissolves
Polyacrylonitrile	1.89	0.42
Polyvinyl acetate	1.16	.17
Ethylene-vinyl alcohol	1.86	.21
Polyethylene	$\sim$0	.05
Polyvinyl isobutyl ether	1.00	.07
Polymethyl vinyl ketone	1.43	.29
Polyglycine-DL-alanine	1.56	1.72

Qualitatively it may be seen (Table III) that a side chain ether linkage (polyvinyl isobutyl ether) does not give rise to water sorption differing very much from that in polyethylene. An ether linkage in the chain (methoxy-polyglycol), however, has a great affinity for water and ultimately leads to dissolution. Vinyl alcohol esters (polyvinyl acetate and polyvinyl benzoate) have very little attraction for water. The low sorption by polyesters has also been noted by Dole and Faller.[5,9] By contrast the carboxyl group in polymethacrylic acid has an attraction for water comparable in magnitude to that of the hydroxyl group in cellulose[10] and polyvinyl alcohol.[7] As saturation vapor pressure is approached the ratio of moles water absorbed to moles carboxyl per 100 g. of polymer becomes nearly unity. The low attraction of polymethyl vinyl ketone even at high relative vapor pressures may possibly be attributed to hydrogen bonding within the polymer.[3] The relative sorption powers of the polyketone and the polyesters for water is consistent with the greater hydrogen bonding capacity of the former as tested by solubility measurements.[11] The sorption of water by hydroxyl groups is less evident on monomeric units copolymerized with ethylene[11a] than in cellulose or polyvinyl alcohol. That the internal spacial arrangement of hydroxyl groups is probably also involved in the differences in partial molar heats of hydration of polymers has been noted previously.[4,12] Summarizing we can say that the ability of a polymer to sorb water depends on the nature as well as the position of the polar groups present in the molecule.[12a]

The hydration of (1:1) polyglycine-DL-alanine is similar to that with polyglycine ester[12] up to about 70% relative vapor pressure. At high humidity the isotherm for polyglycinealanine is more like that of a water soluble protein, which is to be expected since this polymer is water soluble. That is to say, the uptake of water vapor expressed as moles at 0.95 relative vapor pressure is considerably greater than the number of moles of peptide bonds per hundred grams polymer, indicating an incipient solubility.

The Proteins.—A comparison of hydration of trypsin-inhibitor (STI) samples shows that the crystalline material can hold more water at a given relative vapor pressure than can the amorphous. It is reasonable to postulate that in addition to the water held by polar groups,[3] water may also be held between layers of peptide chains in the crystal, in line with the interpretation of hydration of proteins by Bull.[6] Qualitatively similar results are evident in comparing Robinson's data[13] on crystalline insulin at 25° with our data on amorphous insulin.[14]

As has been shown elsewhere, the first monolayer sorbed by tobacco mosaic virus corresponds to the surface area of the virus.[15] The same result is found at both 25 and 15°, by adsorption. The absorption of water vapor by proteins is believed to occur in the interior portions of the structure,[16] but with TMV the particle seems to be inpenetrable to water, liquid water being taken up between the particles.[17] The tremendous hysteresis effect observed is different from the behavior shown by proteins[4] and polymers. It may be associated with the way the rigid rods pack under the quick non-equilibrium conditions used in drying down the original sample for adsorption study.[18] Further work is needed to clarify this point.

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(8) S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943.

(9) Our results with polyethylene terephthalate are identical with those of Dole and Faller and have therefore been omitted from Table I.

(10) V. L. Simril and S. Smith, *Ind. Eng. Chem.*, **40**, 112 (1948).

(11) C. S. Marvel, J. Harkema and M. J. Copley, THIS JOURNAL, **63**, 1609 (1941).

(11a) Both polyethylene and ethylene vinyl alcohol copolymer are crystalline; C. W. Bunn and H. S. Pesier, *Nature*, **159**, 161 (1947).

(12) E. F. Mellon, A. H. Korn and S. R. Hoover, THIS JOURNAL, **70**, 3040 (1948).

(12a) The influence of polymer molecular weight on sorption has not been explored. It may be considerable for low polymers (cf. "Carbowax Compounds and Polyethylene Glycols," Carbide and Carbon Chemicals Corp., New York, N. Y., 1946.

(13) R. A. Robinson, *J. Chem. Soc.*, 1083 (1948).

(14) Ovalbumin is transformed to plakalbumin by the loss of only 1-2 polar amino acid residues and with an accómpanying change in crystalline habit. The sorption isotherms are identical, however (A. D. McLaren and M. Ottesen, *Compt. rend. Lab. Carlsberg, sér. chim.*, **27**, 325 (1950).

(15) B. Katchman, J. A. Cutler and A. D. McLaren, *Nature*, **166**, 266 (1950).

(16) H. J. Frey and W. J. Moore, THIS JOURNAL, **70**, 3644 (1948).

(17) J. D. Bernal and I. Fankuchen, *J. Gen. Physiol.*, **25**, 111 (1941).

(18) It should be noted that an undried sample was used for the desorption isotherm and a pre-dried sample, dried at 5°, was used for adsorption measurements (see under experimental). This is thus not a true hysteresis cycle in the usual sense. We wish to thank Dr. G. Oster for the sample of pure salt free virus.

Acknowledgment.—The authors wish to extend thanks to Dr. J. Cutler for her help in collecting some of the data reported herein.

BROOKLYN 2, N. Y. RECEIVED SEPTEMBER 8, 1950

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

The Thermal Decomposition of Dioxolane[1]

BY WILLIAM B. GUENTHER[2] AND W. D. WALTERS

The homogeneous thermal decomposition of dioxolane has been investigated over the temperature range 455–525° and at initial pressures from 50 to 400 mm. On the basis of (a) aldehyde analyses, (b) mass spectrometric analyses of the gaseous products during and at the end of the decomposition, and (c) measurement of the ratio of the final to the initial pressure, the following decompositions seem to occur: (1) $C_3H_6O_2 \rightarrow CH_2O + CH_3CHO$ and (2) $C_3H_6O_2 \rightarrow CO_2 + C_2H_4 + H_2$ with (1) and (2) occurring at approximately equal rates; the subsequent reactions of the substances formed in (1) and (2) yield the final products, 2CO, H_2, CH_4, CO_2 and C_2H_6. Experiments at different initial pressures indicate an apparent order of reaction of 1.3. The rate of pressure increase is markedly inhibited by the addition of either nitric oxide or propylene, and accelerated by the addition of ethylene oxide.

Introduction

Of the decompositions of cyclic compounds investigated thus far the decomposition of the cyclic ether dioxane appears to be one of the few reactions inhibited by nitric oxide.[3] The very marked inhibition indicates that dioxane decomposes chiefly by a chain reaction. On the other hand in two previous investigations[4,5] of five-membered ring compounds no appreciable inhibition by nitric oxide was observed. It was of interest, therefore, to examine the five-membered cyclic formal dioxolane to ascertain whether its homogeneous decomposition would be a chain reaction similar to that for dioxane. For dioxolane no detailed investigation has been reported. Bilger and Hibbert[6] have pyrolyzed dioxolane in a flow system at 474° in the presence of carbon dioxide. They observed that two of the important products are ethylene and an acid, the yield of the acid being about 35% of that of ethylene. Catalytic pyrolysis of substituted dioxolanes in a flow system has been carried out by Neish, Haskell and MacDonald.[7] They reported that these compounds decompose, presumably by the way of free radicals, to form chiefly carbonyl compounds and, to a lesser extent, unsaturated hydrocarbons.

Experimental

Materials.—The samples of 1,3-dioxolane were kindly donated by the Carbon and Carbide Chemicals Corporation and the du Pont Company. The dioxolane was usually treated with potassium hydroxide pellets and Drierite before vacuum fractionation. For the experiments to determine the order of the reaction, the dioxolane was dried as above and then treated with sodium before it was fractionated under vacuum three times. For the samples used in the present study, the boiling points, read after short boiling times, were within the range 74.6° at 747 mm. to 74.8° at 753 mm. The value of Legault and Lewis[8] is 75.0–75.2° at 760 mm. The index of refraction of the purified dioxolane was found to be $n^{21}{}_D$ 1.3997. Clarke[9] reports $n^{20}{}_\alpha$ 1.39736 and $n^{20}{}_\gamma$ 1.40734. By means of the color tests mentioned in a later section it was found that the dioxolane after purification did not contain formaldehyde or acetaldehyde. Likewise peroxides were absent from the purified dioxolane which had been vacuum-fractionated and stored under vacuum.

Nitric oxide prepared earlier by the method described by Klute and Walters[10] was employed after removal of any impurities non-volatile at −78°. C.P. propylene, 99.5%, from the Ohio Chemical and Manufacturing Company was employed after degassing at −196°. A sample of purified propylene prepared from *n*-propyl alcohol was also used. The ethylene oxide was a specially purified sample from the Dow Chemical Company and was supplied to us by Dr. D. R. Stull. Biacetyl was obtained from the Eastman Kodak Company.

Apparatus and Method.—The furnace and method of temperature regulation for the static experiments were similar to those already described.[5] The temperature was measured with a standardized[11] platinum, platinum–13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer. In most of the experiments a heated stopcock lubricated with Myvacene-S was used next to the reaction vessel. Tests showed that this lubricant did not absorb a manometrically measurable amount of dioxolane under the conditions of the experiments. Moreover, for comparison, a mercury cut-off was employed in place of the above stopcock for a number of runs, but no appreciable difference in the pressure–time curves was observed. The remainder of the vacuum system for the static experiments was of the usual type. With added nitric oxide or propylene, the gas to be added was introduced into the reaction vessel before the dioxolane. With ethylene oxide or biacetyl a known amount of the added material was condensed in a cold finger (−78°) prior to the condensation of the dioxolane. Then the entire mixture was vaporized into the reaction vessel. The effect of surface was tested by installing a reaction bulb packed with lengths of smooth glass tubing which increased the surface to volume ratio by a factor of approximately 35. The apparatus for the flow experiments was similar to that used by Rice and Haynes.[12]

Analyses.—Formaldehyde and acetaldehyde were identified as intermediate products in the decomposition of dioxolane in three ways: (a) by solid derivatives, (b) by color reactions, and (c) by their polarographic half-wave potentials. The flow system was used to obtain sufficient quantities of products for the identification of the aldehydes by means of derivatives. The dioxolane was allowed to flow rapidly at about 15 mm. pressure through a furnace held at approximately 800°. The products which condensed at −196° were dissolved in water and a water solution saturated at 100° with methone (dimedon) was added in ex-

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[1] This work was supported by the Office of Naval Research under Contract N6onr-241, Task Order I, with the University of Rochester.

[2] Abstracted from the M.S. thesis of William B. Guenther.

[3] L. Küchler and J. D. Lambert, *Z. physik. Chem.*, **B37**, 285 (1937).

[4] C. H. Klute and W. D. Walters, THIS JOURNAL, **68**, 506 (1946).

[5] D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

[6] R. M. Bilger and H. Hibbert, *ibid.*, **58**, 823 (1936).

[7] A. C. Neish, V. C. Haskell and F. J. MacDonald, *Can. J. Research*, **25B**, 266 (1947).

[8] R. R. Legault and D. C. Lewis, THIS JOURNAL, **64**, 1354 (1942).

[9] H. T. Clarke, *J. Chem. Soc.*, **101**, 1788 (1912).

[10] C. H. Klute and W. D. Walters, THIS JOURNAL, **67**, 550 (1945).

[11] W. F. Roeser and H. T. Wensel, *J. Research Natl. Bur. Standards*, **14**, 247 (1935).

[12] F. O. Rice and W. S. Haynes, THIS JOURNAL, **70**, 964 (1948).