the weakly yellow vat remains unchanged when shaken with air but acquires a pink color on acidification with acetic acid. The pigment dissolves in alcoholic alkali with a bluish-green color which fades rapidly to a dull red-brown.

The samples analyzed were prepared by mixing filtered solutions of the components and washing the collected product thoroughly with alcohol, water, alcohol, benzene, and glacial acetic acid. The pigments were unmelted at 280°. Analyses of samples dried at 80–105° indicated the presence of approximately one molecule of bound water. The results reported were obtained after drying to constant weight at 150° and 1–2 mm. pressure (several hours).

The pigment from **2-methyl-1,4-naphthohydroquinone** formed dark red microscopic needles having a metallic, golden shimmer.

Anal. Calcd. for $C_{22}H_{15}O_3Cl$: C, 72.82; H, 4.16; Cl, 9.78. Found: C, 72.97; H, 4.28; Cl, 9.48.

The product from **2,6-dimethyl-1,4-naphthohydroquinone** was of similar appearance.

Anal. Calcd. for $C_{24}H_{19}O_3Cl$: C, 73.75; H, 4.90. Found: C, 73.77; H, 4.91.

Summary

The pigments obtainable as described in the literature by condensing α-naphthohydroquinone with various aldehydes in acetic–hydrochloric acid solution are assigned the revised formula $Ar(R)C_{21}H_{12}O_3Cl$, largely on the basis of the isolation of anhydrous picric acid salts. The composition and properties, together with the preparation of pseudo base diacetates and leuco base diacetates, suggest that the pigments are oxonium salts of the anthocyanidin type. A formulation is suggested.

Pigments exhibiting analogous properties are produced by the action of hydrochloric and acetic acids on 2-methyl and 2,6-dimethyl-1,4-naphthohydroquinone. These also appear to be oxonium salts of the anthocyanidin type.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 10, 1941

[CONTRIBUTION FROM WALKER LABORATORY, RENSSELAER POLYTECHNIC INSTITUTE]

The Effect of Ultraviolet Light on Methyl Cellulose in Solution

BY L. SPITZE, A. MOORADIAN, R. H. HARTIGAN AND L. A. HANSEN

Although numerous papers have appeared on the action of ultraviolet light on cellulose and its nitric and acetic esters, such work on the ethers of cellulose is less abundant. In a spectrographic investigation of cellulose and cellulose acetate, Rassow and Aehnelt[1] concluded that cellulose absorbs light strongly; varying the viscosity of the solution of an ester does not affect light absorption, but a change in the number of ester groups does affect it considerably. Rassow and Weber[2] report that depolymerization, low viscosity and low light absorption go together. Clement, Riviere and Beck[3] investigated the effect of ultraviolet light on a number of cellulose derivatives and observed that, with cellulose and hydrocellulose, the action is one of polymerizing. The potassium hydroxide index decreases under the influence of light and the hydrocelluloses become difficultly esterifiable. Berthelot and Gaudechon[4] have shown that nitrocellulose films when subjected to ultraviolet light decompose with the production of carbon dioxide, carbon monoxide, nitrogen, nitrous oxide and nitric oxide. It was also found[3] that acetone solutions of nitrocellulose became yellow and the viscosity was lowered on irradiation. The opinion was expressed that the decrease in viscosity was probably indicative of a depolymerization of the cellulose molecule. Solid ethyl cellulose was stable to light, but a solution showed a marked drop in viscosity. With solid benzyl cellulose, when exposed to ultraviolet light, a large amount of insoluble matter is produced. Mason and Rosevear[5] have studied the degradation of oriented cellulose structures by polarized ultraviolet light using the copper number as a means of measuring the degradation.

The authors thought it would be of interest to study the effect of ultraviolet light on solutions of methyl cellulose, using measurements of viscosity, osmotic pressure and copper number as means of determining whether or not degradation had taken place.

The methyl cellulose (Methocel M-340) was obtained from the Dow Chemical Company. This material is of 50 cp. viscosity type and has a methoxy content of 31.5%. The aqueous solutions of methyl cellulose were prepared

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(1) B. Rassow and W. Aehnelt, *Cellulosechem.*, **10**, 169 (1929).

(2) B. Rassow and F. Weber, Dissertation, Leipzig, 1929.

(3) L. Clement, C. Riviere and A. Beck, *Chimie et industrie*, Special No., 702-706 (March, 1932).

(4) D. Berthelot and H. Gaudechon, *Compt. rend.*, **154**, 201 (1912).

(5) C. W. Mason and F. B. Rosevear, THIS JOURNAL, **61**, 2995 (1939).

by first wetting a weighed amount of the material in hot distilled water (about 80°). The mixture was then diluted to the required concentration with distilled water, cooled in an ice-bath and stirred until complete solution was effected. The solution was then filtered through a fritted glass filter and evacuated to remove dissolved air.

The source of light was a 1000-watt, type H-6, water-cooled, General Electric quartz capillary mercury arc lamp supplied with a quartz jacket. In this preliminary work the complete spectrum was used, no attempt being made to filter out the visible portion of the spectrum, and, further, the intensity of the light was not measured. However, the capillary lamp was frequently cleaned and replaced when signs of devitrification appeared. The solution to be irradiated was contained in a stoppered 800-ml. transparent quartz flask, which was water-cooled and maintained at a distance of 20 cm. from the source of light. Solutions irradiated in a Pyrex flask showed a very much smaller effect than those irradiated in quartz.

Physical Methods of Following Degradation.—Viscosity measurements on samples exposed for various periods of irradiation were made at 20° using a Model C Hoeppler laboratory viscosimeter which has an accuracy of ±1%. In addition, viscosities were determined on solutions of several concentrations of the unirradiated and the highly irradiated sample, made by various dilutions of the respective stock samples. From these measurements the molecular weights of the two samples were computed using the expression of Staudinger[6]

$$\eta_{sp}/C_{gm} = K_m M$$

where $\eta_{sp} = \eta_r - 1$, η_{sp} being the specific, η_r, the relative viscosities in centipoises; C_{gm}, the concentration in basic moles per liter, = 10 (vol.%)/189, where 189 is the weight of the recurring unit in the samples of methyl cellulose used; K_m, an experimentally determined constant, $= 11 \times 10^{-4}$ for methyl cellulose in water[7]; M = molecular weight.

Osmotic pressure determinations on the various samples were run at 20°, using the dynamic method employed by Loughborough and Stamm.[8] The osmometer, constructed of brass, was given a coating of Bakelite resinoid which was baked. Membranes of cellophane were used. The applied air pressure was controlled with a reducing valve, with an air-escape bubbler in parallel with the line to the osmometer. The air-escape bubbler consisted of a sintered glass gas-dispersing tube immersed in water. The manner in which molecular weights were obtained from the data is discussed below.

Evaluation of Degradation by End-group Determination.—While an estimation of the number of reducing terminal groups is commonly used in evaluating the degradation of cellulose, this is not frequently done with the cellulose ethers. A copper reduction method has been used occasionally,[9] but, apparently, has not been systematically investigated. Wolfrom and Lewis[10] report that results obtained with methylated sugars are inaccurate. Some workers have chosen to determine reducing power by a hypoiodite method rather than a copper one. The method of Cajori[11] has been applied to methylated sugars by Wolfrom and Lewis,[10] to cellulose and cellulose acetate by Bergmann and Machemer,[12] and to ethyl cellulose by Okamura.[13]

The copper number method was selected in order to follow the degradation since it is simple and readily adaptable to small samples. While Mark,[14] Amick,[15] Heuser,[16] and others have pointed out that the results obtained with glucose, cellulose, etc., are of questionable reliability as absolute values, results on cellulose materials can be duplicated if conditions are maintained comparable. Mason and Rosevear[5] used this means of following the degradation of ramie fibers subjected to polarized ultraviolet light.

The procedure is a modification of the Heyes micro method[17] which is a scaling-down of the original Schwalb–Braidy determination.[18]

Solutions required:

A. Carbonate–bicarbonate: 150 g. of anhydrous sodium carbonate and 50 g. of sodium bicarbonate in one liter of solution.

B. Copper sulfate: 100 g. of crystalline copper sulfate in one liter of solution.

C. Ferric sulfate: 40 g. of ferric sulfate and 100 cc. of concentrated sulfuric acid per liter of solution.

D. Standard potassium permanganate solution: approximately 0.04 *N*.

A quantity of methyl cellulose solution necessary to give 0.25 g. of methyl cellulose was weighed accurately into a clean 1″ × 6″ test-tube. To 9.5 cc. of solution A was added 0.5 cc. of solution B. The mixture was heated quickly to the boiling point and added to the cold methyl cellulose solution, whereby the methyl cellulose was precipitated in a form readily attacked by the reagents. The weighed test-tube was immersed immediately in an oil-bath of temperature 100 ± 0.03°, and mounted in a wooden rack containing holes large enough to support a number of such test-tubes. The mouth of the tube was covered with a glass pear and the contents heated in the bath for exactly three hours, with occasional stirring with a glass rod. Copper number determinations on samples exposed to ultraviolet light for various periods of time were run simultaneously.

At the completion of the three-hour digestion period, each test-tube was removed from the bath and, *without cooling*, the contents were filtered on either a fritted Jena glass crucible or a Gooch crucible, and washed three times with *boiling* distilled water. (The hot filtration and the use of boiling wash water are necessitated by the solubility of methocel in *cold* water, resulting in a colloidal

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(6) H. Staudinger and W. Heuer, *Ber.*, **63**, 222 (1930); *Z. physik. Chem.*, **153**, 391 (1931); *Ber.*, **65**, 267 (1932); "Die Hochmolekularen organischen Verbindungen," Berlin, 1932, p. 56.

(7) H. Staudinger and F. Reinbeck, *Ber.*, **71B**, 2525 (1938).

(8) D. L. Loughborough and A. J. Stamm, *J. Phys. Chem.*, **40**, 1113 (1936).

(9) W. S. Denham, *J. Chem. Soc.*, **119**, 80 (1921).

(10) M. L. Wolfrom and W. L. Lewis, THIS JOURNAL, **50**, 845 (1928).

(11) F. A. Cajori, *J. Biol. Chem.*, **54**, 617 (1922).

(12) M. Bergmann and H. Machemer, *Ber.*, **63**, 316 (1930).

(13) I. Okamura, *Cellulosechem.*, **14**, 135 (1933).

(14) H. Mark, "Physik und Chemie der Cellulose," Part of "Technologie der Textilfasern," edited by R. O. Herzog, Springer, Berlin, 1932, p. 196.

(15) C. A. Amick, *J. Phys. Chem.*, **31**, 1441 (1927).

(16) H. Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, 1938, Chapter by E. Heuser, p. 1584.

(17) T. F. Heyes, *Soc. Chem. Ind.*, **47**, 90T (1928).

(18) C. Doree, "Methods of Cellulose Chemistry," Chapman and Hall, London, 1933, p. 38.

solution impossible to filter. For the same reason, the subsequent reagents used in the determination are added *hot*.) The crucible was then transferred to a clean suction flask of 100–200 cc. capacity.

1.5 cc. of boiling solution (C) was introduced into the reaction tube which was shaken to remove any adhering cuprous oxide. Without applying any suction, the methyl cellulose on the filter was flooded with this solution, and the solution allowed to remain there until the darkening which took place instantaneously owing to the oxidation of the cuprous oxide to cupric oxide, had passed away. Then the suction was applied, and the solution withdrawn into the filter flask. The vacuum was released and the washing of the reaction tube and irrigation of the methyl cellulose were repeated using 1 cc. of hot solution C. The reaction tube was washed into the filter and the methyl cellulose was finally washed three or four times with 2-cc. lots of boiling distilled water. The filtrate and washings were then promptly titrated in the filter flask with 0.04 *N* potassium permanganate, using a 2-cc. micro-buret with a drawn-out tip, which delivered a drop of 0.015 cc. volume. The first flash of pink through the entire solution is the end-point, even though the color fades after a few seconds.

A blank determination was run on a quantity of water equivalent to that amount present in the weighed sample of methyl cellulose solution, going through the actual procedure described above. Two or three drops of potassium permanganate were required to produce the pink end-point. This volume was deducted from all the final buret readings. The copper number, defined as the number of grams of copper in the cuprous oxide, reduced from the cupric hydroxide by 100 g. of the methyl cellulose, was computed by means of the equation

$$\text{Cu. no.} = \frac{\text{Cc. of } KMnO_4 \times \text{Normality} \times 6.357}{\text{Weight of methyl cellulose in sample}}$$

The accuracy obtained is indicated by the data given in Table I.

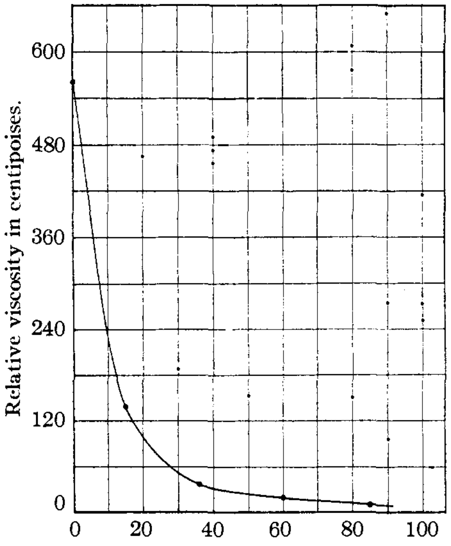

Fig. 1.—Variation of relative viscosity with irradiation: concentration, 4.3% by weight.

Results and Discussion

The values shown in Table I represent a summary of viscosity and copper number measurements on a methyl cellulose solution of concentration =4.3%, after exposure in a quartz flask.

TABLE I

EFFECT OF ULTRAVIOLET LIGHT ON VISCOSITY AND COPPER NUMBER OF AQUEOUS METHYL CELLULOSE SOLUTIONS

Concentration of solution, 4.3% (by weight)

Irradiation, hours	Viscosity, centipoises	Copper number			
0	580	0	0	0.06	0.09
15	138	0.15	0.15	.15	.22
36	35.5	0.85	0.87	.87	.88
60	19.1	1.20	1.30	1.31	1.32
85	8.4	2.64	2.72	2.73	2.88

The variation of viscosity and that of copper number with exposure time are shown graphically in Figs. 1 and 2, respectively. The large drop in viscosity is indicative of degradation of the cellulose chain according to the work of Staudinger, and the corresponding increase in copper number agrees with this.

It should be pointed out that the viscosity of the unirradiated stock samples did not change with time during the course of our experiments.

A complete summary of viscosity, osmotic pressure and copper number measurements on a solution of original concentration =4.85% methyl cellulose is given in Table II.

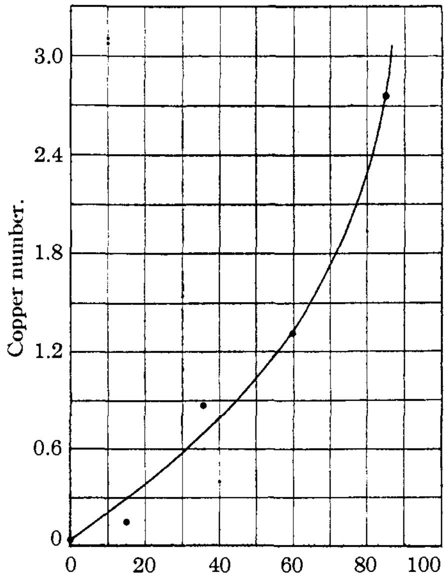

Fig. 2.—Variation of copper number with time of irradiation: concentration, 4.3% by weight.

TABLE II

EFFECT OF ULTRAVIOLET LIGHT ON VISCOSITY, OSMOTIC PRESSURE, COPPER NUMBER OF METHYLCELLULOSE SOLUTIONS, AND VARIATION OF VISCOSITY AND OSMOTIC PRESSURE WITH DILUTION

Concentration of original solution was 4.85% by weight

Irradiation, hr.	Concn., Vol.%	C_{gm}	η_r	η_{sp}	η_{sp}/C_{gm}	C, vol.%	P, cm.H_2O	P/C	Concn., wt.%	Copper no.[a]		
0	0.104	0.0055	1.36	0.36	65.4	0.103	9.2	89.4				
	.207	.0109	1.80	.80	73.1							
	.309	.0163	2.34	1.34	81.9	.299	12.0	40.1				
	.402	.0212	2.93	1.93	90.7	.410	7.6	18.5				
	.507	.0268	3.78	2.78	103.8	.512	6.8	13.3				
	.984	.0521	9.49	8.49	163.1	.961	12.0	12.5				
	2.01	.106	48.7	47.7	448.0	1.77	21.2	12.0	2.00	0.01		
	4.90	.259	815	814	3140				4.85	.01		
8	2.02	.107	37.2	36.2	338.9	1.88	23.8	12.7	2.01	.03	0.03	
	4.90	.259	588	587	2270				4.85	.06	.07	
30	2.00	.106	21.6	20.6	194.8	1.84	24.7	13.4	1.99	.22	.23	
	4.90	.259	226	225	867				4.85	.15	.15	
73	0.100	.00529	1.13	0.13	24.6	0.119	11.0	92.2				
	.203	.0102	1.29	.29	27.0	.215	10.1	46.4				
	.304	.0161	1.43	.43	26.8	.304	7.0	23.0				
	.389	.0206	1.55	.55	26.8	.390	9.0	23.1				
	.500	.0264	1.71	.71	26.8	.454	11.3	24.9				
	.982	.0520	2.77	1.77	34.1	.964	19.0	19.7				
	2.00	.106	6.22	5.22	49.3	1.92	38.2	19.9	1.99	.82	.95	0.95
	4.90	.259	35.4	34.4	132.6				4.85	1.19	1.20	

[a] No comparison of copper numbers of solutions of different concentrations, but of the same irradiation time, can be made inasmuch as values are of significance only when conditions are maintained comparable.

The values of η_{sp}/C_{gm} are plotted against C_{gm} for the unirradiated sample and for that irradiated seventy-three hours, giving the curves shown in Fig. 3. By extrapolating η_{sp}/C_{gm} to $C_{gm} \rightarrow 0$, values are obtained corresponding to a molecular weight, as computed by the equation of Staudinger, of 53,000 for the unirradiated methyl cellulose and 24,000 for the sample irradiated seventy-three hours. These values lie in the range of those obtained by other investigators.[7,19,20,21]

Staudinger and Schulz[21] suggested an equation for computing molecular weights, M, from osmotic pressures, p_c, of concentrated solutions of nitrocellulose, cellulose acetate, and other substances

$$p_c = RTC/M(1 - cS)$$

in which the co-volume, S, is obtained by the relation, $\log p_c = \log k - \lambda \log S$, where $k = 8.25\,(10)^{-6}$, $\lambda = 2.23$ for nitrocellulose. They point out that the behavior of methyl cellulose in water is peculiar, and that the equation does not hold. In spite of this, the authors felt that this expression would be useful in giving approximate molecular weight values, relative only, for solutions of a definite concentration, which concentration approached that of the irradiated solution as nearly as possible and yet could be conveniently used in the osmometer (about 2%). The values thus obtained are shown in Table III.

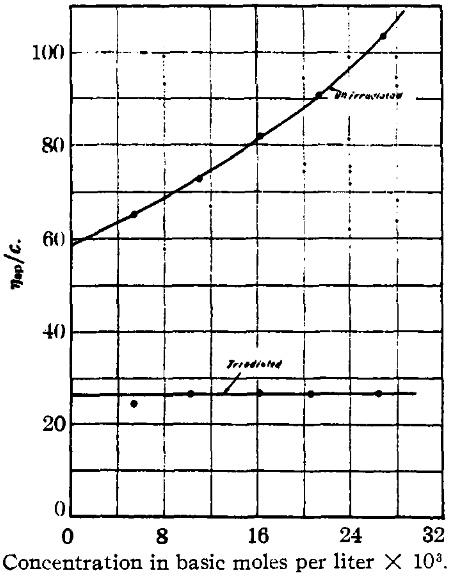

Fig. 3.—Variation of η_{sp}/c with c.

These data furnish convincing proof that the action of ultraviolet light results in shortened chain length with a consequent increase in reduc-

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(19) R. Signer and P. V. Tavel, *Helv. Chim. Acta*, **21**, 535 (1938).

(20) T. Svedberg and K. O. Pedersen, "The Ultracentrifuge," Oxford, 1940, Article by E. O. Kraemer.

(21) H. Staudinger and G. V. Schulz, *Ber.*, **68B**, 2320 (1935).

TABLE III

EFFECT OF ULTRAVIOLET LIGHT ON MOLECULAR WEIGHT OF METHYL CELLULOSE

Irradiation, hours	(M. W.) viscosity, by extrapolation	(M. W.)Osm.p., from approx. 2% soln.	Copper number (2% solution)
0	53,000	44,000	0.01
8		42,000	.03
30		38,000	.22
73	24,000	26,000	.95

ing properties due, probably, to a rupturing of the glycosidic linkages of the substituted "glucose anhydride" units.

Preliminary work on the effect of concentration on the osmotic pressure of methyl cellulose solutions shows that by plotting *p/c versus c* a curve is obtained (see Fig. 4) in which a break occurs at a concentration of about (0.45–0.50%) which is in agreement with that of Schulz[22] although the shapes of the curves are different. However, these curves are similar to those reported by Herz[23] for Cellit in methyl glycolacetate.

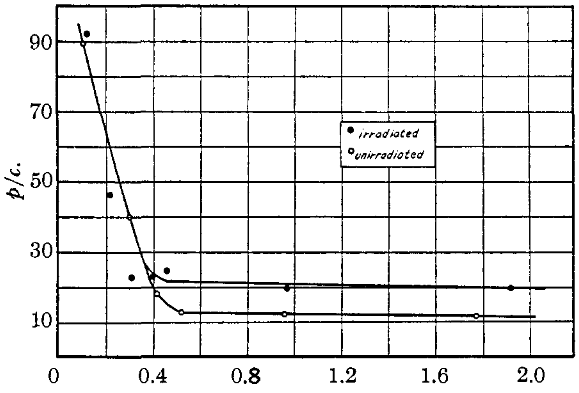

Fig. 4.—Variation of *p/c* with *c*.

Acknowledgments.—The authors are indebted to the Dow Chemical Company for the samples of Methocel furnished for this investigation. They also wish to thank Mr. R. G. MacDonald, Secretary of the Technical Association of the Pulp and Paper Industry, for obtaining certain information concerning end group determinations. Our special thanks go to Mr. M. C. Anderson for making some of the equipment used in this research, and also to Mr. J. R. Murphy for his help in preparing the manuscript.

Summary

Using a quartz capillary mercury arc lamp to furnish ultraviolet light, an out-gassed sample of methylcellulose in water was irradiated in a stoppered quartz flask. Viscosity, osmotic pressure, and copper number data show that the methyl cellulose molecule is degraded. A molecular weight of about 50,000 for methyl cellulose is in harmony with results obtained by other investigators for various cellulose derivatives. A modification of the Heyes micro copper number procedure for cellulose was developed and applied to the degraded methyl cellulose solutions.

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[22] G. V. Schulz, *Z. physik. Chem.*, **A158**, 237 (1932); **A176**, 317 (1936); **A177**, 453 (1936); *Z. Elektrochem.*, **42**, 692 (1936); *Angew. Chem.*, **49**, 863 (1936).

[23] M. Ulmann, "Molekulgrossen-Bestimmungen hochpolymerer Naturstoffe," Leipzig, 1936, p. 78, work of W. Herz in *Cellulosechem.*, **15**, 95 (1934).

TROY, N. Y. RECEIVED MARCH 6, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF BUFFALO AND THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Atomic Weight of Fluorine Calculated from Density and X-Ray Data

BY CLYDE A. HUTCHISON AND HERRICK L. JOHNSTON

A precise value for the density of lithium fluoride, determined by a "temperature of flotation" technique, has been reported recently by Hutchison and Johnston.[1,2] In the present paper this density value is used to compute a value for the atomic weight of fluorine.

The following values are also used in the computation: (a) the ratio between the true grating spaces for calcite and lithium fluoride determined from the X-ray measurements of Bearden and Shaw[3] and of Straumanis, Ievins and Karlsons[4]; (b) the cleavage angles for calcite determined by Bearden[5]; (c) the density of calcite determined by Bearden[5]; (d) the linear coefficient of ex-

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[1] C. A. Hutchison and H. L. Johnston, THIS JOURNAL, **62**, 3165 (1940).

[2] H. L. Johnston and C. A. Hutchison, *J. Chem. Phys.*, **8**, 869 (1940).

[3] Bearden and Shaw, *Phys. Rev.*, **48**, 18 (1935).

[4] Straumanis, Ievins and Karlsons, *Z. physik. Chem.*, **B42**, 143 (1939).

[5] Bearden, *Phys. Rev.*, **38**, 2089 (1931).