Sörensen values which will be the more distinct, the less the impurities function as a buffer with the pure substance. Not all single indicators providing the necessary Sörensen value can be used for this purpose; some will probably react chemically with the substance tested and some may not give a color that is satisfactory. Mixed indicators would here be an advantage.

In the above examples of mixed indicators, the properties given are true when their preparation is carried out as described; different results may be obtained by having a greater proportion of one or the other component. In the case of mixed indicator I it was found, however, that the deviation from the range P_H 5.9–6.8 is less marked when bromothymol blue is made the larger constituent, that is, in proportion greater than 50%. Thus the optimum suitability of a double or mixed indicator will depend not only on the individual indicators mixed but also on their relative proportions chosen for simultaneous use.

A spectroscopic study of the examples of mixed indicators given should provide a fuller insight into the exact nature of the equilibria involved in attempting to correlate ionization, tautomerization and light absorption phenomena.

Summary

1.   Differences of subjective color are enhanced when two indicators are partially transformed at the same hydrogen-ion concentration.

2.   The colorimetric determination of hydrogen-ion concentration can, therefore, be rendered more precise where necessary and in certain titrations sharper end-points obtained. These advantages apply especially to colored liquids.

LONDON, ENGLAND

ELASTICITY OF PURIFIED GELATIN JELLIES AS A FUNCTION OF HYDROGEN-ION CONCENTRATION

BY S. E. SHEPPARD, S. S. SWEET AND ANBER J. BENEDICT

In a previous communication entitled "The Elastic Properties of Gelatin Jellies"[1] two of the present writers have given the results on the measurements of the rigidity of gelatin jellies from commercial gelatins, at various concentrations and under different conditions of preparation. Certain rather anomalous effects were observed when the rigidity was determined for jellies containing different concentrations of acid and alkali, the Sörensen values of which had been determined electrometrically in solutions.

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[1] Sheppard and Sweet, THIS JOURNAL, **43**, 539 (1921).

From the work of Loeb and others[2] on the effects of hydrogen-ion concentration on the properties of gelatin, the following results seem applicable. The hydration of the gelatin is a minimum at the iso-electric point, about P_H 4.7, and rises on either side to maxima, on the acid side at P_H = 2.5, on the alkaline side at P_H = 12. Now, in the previous communication it was shown that addition of alcohol, and glycerol up to certain amounts, greatly increased the rigidity. These are dehydrating agents, and, from the foregoing, it might be expected that gelatin jellies would show maximum rigidity near the iso-electric point. Our previous results are not sufficient to test this, since they were made with commercial gelatin; although of good grade and with an ash content of about 1%, this latter might have been sufficient to influence the results.

Preparation of Ash-free Gelatin

The de-ashing process which has been developed in this Laboratory is carried out in two stages; the first consists in electrolyzing the jelly, the second in precipitating the gelatin from this with acetone. The electrolysis is carried out in a large wooden cell, of inside dimensions 79 cm. (length) × 51 cm. (width) × 50 cm. (height). In the middle of this is placed a porous inner compartment of Filtros,[3] having the inside dimensions 36.7 × 35.5 × 36.7 cm., but extending to and imperviously cemented to both the bottom and the sides of the wooden tank. This internal porous cell has a capacity of about 48 liters and is nearly filled with a solution of good grade gelatin of 5% concentration. The two end compartments are filled with distilled water, eventually conductivity water, and contain the electrodes. These consist of a gold *anode*, 10.5 × 12.7 cm., and a silver *cathode*, 25.4 × 25.4 cm., both of thickness sufficient for rigidity. Current from the service d. c. line at 110 volts is passed through; the time of electrolysis is approximately 2 weeks, but varies with the original ash content; intermediate ash analyses are made, and while 2 weeks is sufficient to reduce a 1.5% ash to 0.2 or 0.1%, this requires about 3 weeks for a 3% ash. About 2 g. of thymol is added as antiseptic. The *current* at the start is about 1 to 0.8 amperes, but falls off rapidly, eventually to about 0.02 amperes. The *temperature* of the gelatin solution or jelly is not allowed to rise above 40°. After 2 or 3 days' run the jelly shows considerable syneresis, a relatively opaque gel of higher concentration separating as the iso-electric point is approached. The water in the anode and cathode compartments is changed every day for the first 3 days, which helps to keep down the temperature rise by reducing the current.

Precipitation.—When the ash has been reduced to between 0.1 and

[2] J. Loeb, *J. Gen. Physiol.*, **1,** 39 (1918).

[3] Filtros is a porous silica septum, made by the Filtros Company, East Rochester, N. Y.

0.2%, the jelly, of approximately 8 to 10% concentration, is removed, melted, and the gelatin precipitated with an equal volume of pure redistilled acetone. The precipitated gelatin is drained off, and excess of acetone distilled at a temperature not exceeding 70°. Conductivity water is then added to make the solution up to 10%. This is coated and set on a polished nickel or steel chill-table (previously wiped with gasoline to ensure stripping), cut into sheets, and dried under uniform conditions on netting.[4] The precipitation not only further reduces the ash content, but removes the greater part of any hydrolysates (gelatose, gelatin peptones, etc.).

The yield is about 75 to 80% of the original gelatin of good grade. There is readily obtained an iso-electric gelatin (P_H 4.8) of average ash 0.03 to 0.02%, which can be made less than 0.01% by a single repetition of the process. Although somewhat slow, the process requires but little. attention most of the time and gives a satisfactory de-ashed material. The gelatin prepared in this way for the work on rigidity had an ash content of 0.015%. The greater part of this—up to 70%—consisted of silica with a small amount (about 0.001% of the gelatin) of iron oxide (Fe_2O_3), and only traces of alumina and phosphoric acid.

Preparation of Test Pieces

The test cylinders of jelly, at different concentrations and hydrogen-ion adjustments, were prepared as previously described. All the jellies were kept for 16 to 20 hours at 0° to 5°. On the acid side hydrochloric acid was used, on the alkaline sodium hydroxide. The determinations of the hydrogen-ion concentration of the gelatin sols were made electrometrically for the 4, 5 and 7% systems, at 35° to 40°, using an Acree-Elliott hydrogen electrode and a potentiometer, the potentials being corrected for temperature and barometric pressure. The Sörensen values for 10% were determined colorimetrically. Investigation has shown that the protein error with gelatin is small for P_H 3 to 8, but increases on either side of this range. The gelatin as used had a moisture content of 10.1% (referring to gelatin dried at
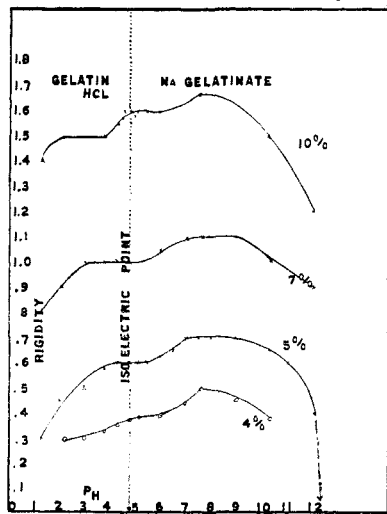

Fig. 1.

[4] Boiled-out fish line.

100–105°); the concentrations of the jellies are referred to the air-dry material.

TABLE I

RIGIDITY, N

P_H	4%	5%	7%	10%
1.3	..	0.3	0.8	1.4
2.1	0.3	0.45	0.9	1.5
3.0	0.3	0.50	1.0	..
3.7	0.35	0.55	..	..
3.8	..	..	1.0	1.5
4.3	0.35	0.60	1.0	1.55
4.5	..	..	..	1.55
4.6	..	..	..	1.55
4.7	0.36	0.60	1.0	1.60
5.3	0.40	0.60	1.0	1.60
5.5	..	0.60	..	1.60
6.0	0.40	0.65	1.05	1.60
7.0	0.45	0.70	1.10	..
7.6	0.50	0.70	1.10	1.67
8.0	..	0.70	1.10	..
9.0	0.45	0.70	1.10	..
10.3	0.40	0.65	1.00	1.50
11.0	..	0.60	..	..
12.0	..	0.40	0.90	1.20
12.3	..	0.00	..	..

These results do not agree entirely with those previously obtained with technical gelatins[1] since they do not show the maxima and minima found there. It appeared possible, from other work on the influence of aluminium and other salts on the properties of gelatin at various hydrogen-ion adjustments, that these variations might be due to the influence of the ash constituents. This was verified to some extent, by measuring the rigidity of a 7% jelly of the same ash-free gelatin, over a range of hydrogen-ion adjustments, but with amounts of potassium alum added, to bring the content of alumina (Al_2O_3) within a range (0.01 to 0.10% of dry gelatin) commonly found in technical gelatins. The results obtained are given in the following table and curve.

TABLE II

INFLUENCE OF ALUMINA ON GELATIN RIGIDITY

% Al_2O_3									
0.001		0.01		0.02		0.04		0.10	
P_H	N	P_H	N	P_H	N	P_H	N	P_H	N
1.29	0.8	1.0	0.6	1.2	0.9	1.18	0.8	1.2	0.7
2.09	0.9	1.5	0.85	...	..	...	..	...	..
3.80	1.0	2.0	1.00	2.08	1.2	...	..	...	..
4.34	1.0	3.0	1.10	2.50	1.3	3.01	1.5	3.10	1.4
4.58	1.0	3.5	..	...	..	...	..	...	..
4.82	1.0	4.0	1.1	4.35	1.4	4.3	1.4	4.06	1.65

4.90	1.0	4.3	1.2	4.50	1.3	4.3	1.4	4.10	1.70
5.10	1.0	4.5	1.2	4.95	1.25	4.3	1.4	4.30	1.70
5.30	1.0	..	..	5.6	1.20	5.1	1.4	4.50	1.70
5.39	1.0	..	..	...	..	7.77	1.5	5.6	1.8
7.60	1.1	11.5	1.30	10.7	1.6	10.48	1.51	9.0	1.7
10.30	1.05	12.0	1.3	11.75	1.2	11.70	1.3	11.5	1.6
12.06	0.9	12.3	0.9	12.35	1.1	...	..	...	..
12.25	..	..	..	12.56	0.8	12.6	0.6	12.6	0.8

The very considerable influence on the rigidity of the jellies produced by small amounts of aluminum is evident from these data. The rigidity curves do not show exact agreement with any of those obtained for commercial gelatins; but the more pronounced variation of the curve with amounts of alumina less than 0.10% of the gelatin does strengthen the conclusion that the presence of ash constituents (aluminum, iron and calcium, phosphoric and sulfuric acids, and silica) could give oscillations of the rigidity with the Sörensen value of the character observed. The
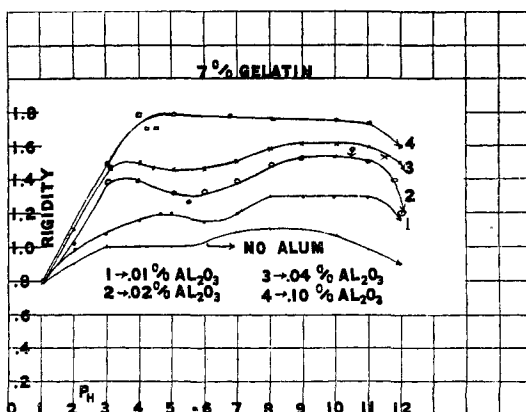

Fig. 2.

effects of aluminum observed do not appear to follow those found by J. Loeb[5] for aluminum salts on other physical properties of aqueous gelatin systems, but rather to be related to the progressive precipitation of hydrous alumina. This commences at P_H 3 and is complete at p_H 7. The data are insufficient at present to allow a decision regarding the extent to which chemical combination (formation of aluminum gelatinate, and possibly also of internal complexes) and mechanical admixture of a finely divided solid are respectively responsible. In connection with this, however, it is interesting to note that the electrometric titration curves of ash-free gelatin to which definite amounts of potassium alum have been added indicate a shift of the iso-electric point. In Fig. 3 are given three

[5] J. Loeb, *J. Gen. Physiol.*, **1**, 503 (1919).

curves, for 1% ash-free gelatin alone, and with alum equivalent to 0.04 and 0.10% of Al_2O_3 on dry gelatin.   The curves for 0.01 and 0.02% have been omitted for the sake of clarity, since they run very close to each other and to the 0.04% curve.   The values of the iso-electric point, deduced from the titration curves,[6,1] are: ash-free gelatin 4.83; plus 0.01, 0.02, and 0.04% of Al_2O_3, 4.5 to 4.3; plus 0.10% of Al_2O_3, 4.2; which indicate a displacement of the iso-electric point of gelatin in the presence of aluminum salts.   Other evidence, from the melting points of gelatin jellies, in agreement with this, will be reported elsewhere.   On the other hand, the results in Table I do not support the existence of a maximum rigidity at the iso-electric point.   The curve shows no pronounced maximum, exhibits only a shoulder in the region of the iso-electric point, rises to a
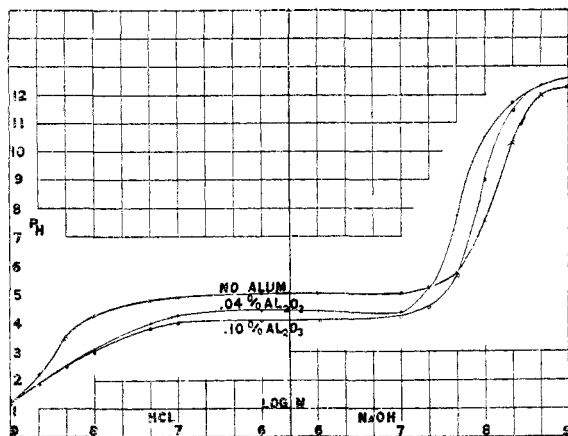

Fig. 3.

flattish maximum between P_H 7 to P_H 9 and then declines gradually.   It is possible, however, that the rigidity and elasticity of gelatin gels are not determined solely by the conditions referred to.   According to Maxwell's theory of elasticity, $E = \dfrac{\eta}{\Theta}$, where E is the elasticity, η the viscosity, and Θ the time of relaxation.   Now the change of viscosity with hydrogen-ion concentration, when dissociated from hydrolytic factors, shows close parallelism with the swelling—P_H curve.[7]   Supposing this parallelism to persist from the sol to the gel condition, we should have a minimum of

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[6] Compare Patten and Kellems, *J. Biol. Chem.*, **39**, 383 (1920).

[7] We have made an extended study of the relations of viscosity of gelatins, both commercial, and purified iso-electric gelatin, to hydrogen-ion concentration, temperature, etc.   Our results on the influence of hydrogen-ion concentration on purified gelatin agree with Loeb's, rather than those of Davis, Oakes and Browne, ["Viscosity of Gelatin Solution," THIS JOURNAL, **43**, 1526 (1921)] in that a second maximum for P_H values higher than the iso-electric point is found and a minimum at P_H 4.8.

elasticity at the iso-electric point, provided Θ remained unchanged.   If then the value of Θ, the time of relaxation, also followed the viscosity in giving a minimum at the iso-electric point, this would tend to give a flattened curve for the elasticity, similar to that observed in this work. Some work has been done on the time of relaxation,[8] mostly by study of the artificial double refraction under strain, and recently E. Hatschek[9] has suggested that the optical and mechanical relaxations differ considerably.   We are, therefore, investigating the effect of hydrogen-ion concentration on the relaxation.

Poisson's Ratio for Gelatin Jellies.—In our previous paper we compared our values for the modulus of rigidity at various gelatin concentrations with A. Leick's[10] values for the modulus of stretch at various concentrations by the following relation.   The modulus of stretch, E, (Young's modulus) is related to the rigidity by the equation

$$N = \frac{E}{2(1 + \mu)}$$

where $\mu = \dfrac{\Delta D}{D} : \dfrac{\Delta l}{l}$, the ratio of lateral to longitudinal strain, known as Poisson's ratio.   We then stated: "According to experiments of Maurer, Bjerkén and others, the volume of a gelatin jelly is practically constant, even for relatively large stretching loads.   Hence μ can be taken as equal to $1/2$, and $N = E''/3$.   Although, as will be noted directly, our results are not affected, nor the comparison with Leick's figures, the above statement is not quite correct.

The actual value of the ratio $\dfrac{\Delta D}{D} : \dfrac{\Delta l}{l}$ for a material which does not change its volume when stretched (or compressed) must *diminish* as the extension becomes greater, from approximately 0.5 for very small extensions.   In this latter case μ is as defined for infinitely small extensions as dealt with by the elastic theory, giving the above mentioned relation between the elastic constants.   In the statements concerning Poisson's ratio for gelatin jellies there is a misleading identification of the true Poisson's ratio μ, for infinitesimal deformations, with the value $\mu' = \dfrac{\Delta D}{D} : \dfrac{\Delta l}{l}$ for finite deformations.   This appears to have originated with some statements of Leick, which, correct for his particular conditions, seem to have misled subsequent writers on the subject, notably H. Freundlich[11] and E. Hatschek.[9]   Thus Leick remarks, referring to the determination of constrained double refraction in gelatin plates,[11] "If it be noted that as soon as the plate is stretched its thickness D is altered, and that for aque-

[8] Reiger, *Physik. Z.*, **2**, 213 (1901).   Maurer, *Wied. Ann.*, **28**, 628 (1886).

[9] Hatschek, *Kolloid-Z.*, **28**, 211 (1921).

[10] Leick, *Ann. Phys. Chem.*, [4] **14**, 139 (1904).

[11] Freundlich, "Kapillarchemie," Akad. Verlagsgesell., Leipzig, **1909**, p. 481.

ous gelatins we may set the ratio of the lateral contraction to the elongation $\mu = 0.5$ (as shown by R. Maurer[8]) then we may write

$$n_e - n_o = \frac{\Delta\lambda}{D(1-0.5l/L)},$$

Actually, however, this is permissible only for infinitesimal values of l/L, the relative elongation, which Leick failed to notice. Thus in regard to the calculation of the elastic modulus of stretch E from the extension of loaded jelly plates he remarks: "If P denote the load in grams, Q the cross section in sq. cm. and l/L the relative elongation, then the elastic modulus is

$$E = \frac{P}{Q} : \frac{l}{L}$$

the cross-section Q being readily obtained from the thickness D and the breadth B as $Q = D.B(1-0.5\frac{l}{L})^2$." Here again the formula is correct only for infinitesimal extensions, for which alone $\mu = 0.5$.

What was observed and clearly stated by earlier investigators is the following: substances which alter their volume very little on stretching have for very small stretches a value of μ closely approaching 0.5, a fact first mentioned by Thomson and Tait. Röntgen[12] confirmed this for rubber and Maurer[8] for gelatin jellies, but as pointed out by Bjerkén,[13] Röntgen noted in this connection, that if a volume alteration does *not* take place, μ in terms of finite differences must *decrease* with increasing extension. Röntgen determined this decrease for rubber, and Bjerkén has done so for gelatin jelly, of approximately 20% concentration. His table is reproduced here.

P G.	L Mm.	B Mm.	μ'	V	P G.	L Mm.	B Mm.	μ'	V
0	51.0	25.5	...	...	0	50.5	47.0	...	...
30	57.0	24.0	0.500	0.990	100	55.0	44.8	0.525	0.989
50	62.0	23.3	0.400	1.013	200	60.5	43.0	0.430	1.003
70	67.0	22.2	0.413	0.997	300	66.2	41.0	0.411	0.997
90	71.0	21.5	0.400	0.989	400	72.0	39.5	0.375	1.006
110	77.0	21.0	0.346	1.025	500	77.0	38.0	0.365	0.998
...	77.5	20.8	0.355	1.012	600	81.8	37.0	0.343	1.003
...	82.0	20.2	0.342	1.009	700	85.5	36.0	0.338	0.993
...	86.0	19.6	0.337	0.997	800	99.0	35.2	0.321	1.000
210	97.5	18.4	0.305	0.997	900	93.5	34.4	0.315	0.993
230	102.0	17.9	0.298	0.985	1000	97.5	33.8	0.302	0.999
250	106.0	17.7	0.284	1.002	1100	101.5	33.1	0.293	0.996
			Mean $V =$	1.001				Mean $V =$	0.998

The first series was made with a strip of 25.5mm. breadth and 1 mm.-thickness, the second with one of 58.5mm. breadth and 2.0mm. thickness

[12] Röntgen, *Pogg. Ann.*, **159**, 601 (1876).
[13] von Bjerkén, *Wied. Ann.*, **43**, 817 (1891).

Bjerkén remarks later: "As Maurer found by direct volume measurements for small extension, so here also, at the greatest extensions which can be effected, the volume remains constant, at least to a high degree of approximation, much higher than with caoutchouc."

Our tentative results so far confirm Bjerkén's results. It appears, therefore, evident that H. Freundlich[11] in his valuable "Kapillarchemie" is in error in his reference to Poisson's ratio for gelatin jellies. Referring to the elastic properties of these, he states: "To these quantitative results is only to be added that

$$\mu = \frac{\Delta 2r}{2r} : \frac{\Delta l}{l},$$

according to investigations of Maurer, Bjerkén and Fraas, is equal to $^1/_2$ for small extensions; *this means, as a comparison of the expressions for cylinders $\pi r^2 l$ and $\pi(r - \Delta r)^2$ $(l + \Delta l)$ shows, that the total volume does not change in extension.*[14] Further, for gelatin gels, as Bjerkén has shown, the volume is nearly strictly constant even for large extension." While individual conclusions here are correct, the part of the statement italicized by us is evidently incorrect and misleading. If the volume $V = \pi(r - \Delta r)^2$ $(l + \Delta l)$ remain constant, then

$$\frac{\Delta 2r}{2r} : \frac{\Delta l}{l} = \mu'$$

cannot remain equal to 0.5 but must decrease as $\frac{\Delta l}{l}$ increases. Without this qualification, the following statement of E. Hatschek[4] also assigns a misleading eminence to the value $\mu = 0.5$ for gelatin gels:[15] "Both Maurer and Leick determined Poisson's ratio for gels of various concentrations, and found it to be 0.5 within the limits of error, a result which is not astonishing in view of the high content of fluid." It seems probable that the last sentence refers to a constant volume condition as being associated with the approximation of μ to 0.5.

Returning to Leick's results for the modulus E and the comparison of our results with his, no considerable error appears to be involved by the use of $\mu' = 0.5$ by Leick, and hence in our comparison, since Leick's values of l/L (extension of unit length) did not exceed 16%; according to Bjerkén's results within this limit μ' would not fall below 0.5, although not constant.

Summary

1. Investigation has been made of the relation of the modulus of rigidity of purified gelatin jellies (demineralized and freed from hydroly-

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[14] Not italicized in original.

[15] A very similar case of confusion of the elastic constant μ for very small deformations with μ', the empirical ratio of transverse contraction to longitudinal extension, has been ably discussed for rubber by Prof. G. Stafford Whitby in his "Plantation Rubber and the Testing of Rubber," Longmans, Green and Co., 1920, Chap. 21.

sates) at different gelatin concentrations, over a wide range of hydrogen-ion adjustments. Except at very high and very low ($>$ 2 and $<$ 11) values of P_H, the rigidity does not vary very rapidly, the maximum being at P_H 7 to P_H9.

2. Amounts of aluminum equivalent to 0.01 to 0.1% of aluminum trioxide based on dry gelatin, produced considerable changes in the rigidity —P_H curve, and markedly increased the rigidity.

3. These results are discussed in connection with the theory of gelatin viscosity and elasticity.

4. A misleading statement on Poisson's ratio (for gelatin jellies) in a previous paper and in the literature of the subject is corrected.

ROCHESTER, NEW YORK

ADSORPTION BY ACTIVATED SUGAR CHARCOAL. I[1]

BY F. E. BARTELL AND E. J. MILLER

The greater part of the vast amount of work that has been done in connection with the study of the mechanics of adsorption of substances from solution by charcoal has been done with animal or blood charcoal. In view of the fact that the highly complex blood charcoal and the almost equally complex, but less active, wood or vegetable charcoal are not readily purified, it is not surprising that the results obtained with them have varied greatly in the hands of different investigators.

The recent development of methods for the activation of charcoal[2,3,4] for the adsorption of gases suggested to us the possibility of preparing from sugar an active charcoal which would be free from the objectionable features of animal charcoal, such as high ash, high nitrogen content, and the necessity of treatment with reagents for its purification, and using this charcoal in a study of the nature of adsorption of electrolytes from solution.

Preparation of Activated Sugar Charcoal

Ten-pound lots of cane sugar were repeatedly recrystallized from conductivity water in order to free the sugar, as far as possible, from inorganic matter, such as calcium, etc. After recrystallization the sugar was carbonized and activated by the following method.

[1] Published as Journal Article No. 24 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

[2] Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, 11, 420 (1919).

[3] Sheldon, *Phys. Rev.*, 16, 165 (1920).

[4] Winter and Baker, *J. Chem. Soc.*, 117, 319 (1920).