the sodium ion fraction would be relatively increased, and a "back transference" of potassium would occur, both of which conditions would give an additive tendency to explain the results obtained in both investigations, and which satisfy both the first and fourth possible causes mentioned.

Summary.

It has been shown that over a range of total concentration from 0.2 N to 1.6 N with equivalent mixtures of sodium and potassium chlorides a relatively higher amount of sodium is transferred than is called for by calculation, on the basis of the isohydric principle, from the conductance of the simple salt solutions.

The increase of sodium transferred, over this range of concentration, is roughly a linear function of the total salt concentration.

The results are in harmony with those of Smith and Ball,[1] according to which they find that the sodium ion-fraction increases with increase of total salt concentration over this same range of concentration.

The results may be explained on the basis of complex formation, the simplest form of which, in accordance with these results, may be expressed thus,

$$NaCl + KCl \rightleftharpoons Na(KCl_2) \rightleftharpoons Na^+ + KCl_2^-.$$

URBANA, ILLINOIS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF COLUMBIA UNIVERSITY, No. 337.]

THE VISCOSITY OF LIQUIDS. IV. IDEAL MIXTURES OF THE TYPES ETHER-ETHER AND ESTER-ESTER.

JAMES KENDALL AND ALEXANDER HOLLAND WRIGHT.

Received April 27, 1920.

Previous attempts to derive a general equation for representing the viscosities of ideal liquid mixtures have been critically examined, and new lines of attack discussed, in earlier papers of this series. In the first article,[2] all existent formulas were tested by means of the available experimental data and a modification of an equation proposed by Arrhenius[3] was shown to give most satisfactory agreement. This equation may be written

$$\log \eta = x \log \eta_1 + (1 - x) \log \eta_2 \qquad (1)$$

(where η_1 and η_2 are the viscosities of the pure components, and the composition, x, is expressed in molecular fractions). Later investigation by Egner[4] has confirmed the approximate accordance of this formula with the results of experiment.

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[1] *Loc. cit.*

[2] Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 25 (1913).

[3] Arrhenius, *Z. physik. Chem.*, **1**, 285 (1887).

[4] Egner, *Medd. K. Vetenskapsakad. Nobelinst.*, **3**, No. 22 (1917).

On more detailed examination[1] of these experimental data, however, it was recognized that, in all systems studied, the differences between the physical constants of the pure components were entirely insufficient to afford a decisive test of the relative merits of the several formulas. Not only were viscosities, in general, only slightly different in value, but also variations in molecular weight and density were too narrow to permit definite conclusions on the proper method for representation of composition. Volume, weight and molecular units have all been suggested by different investigators, and the calculated curves for any one system were in most cases so closely clustered around the experimental curve that no real discrimination was possible.

Several selected systems, as nearly ideal as possible, were, therefore, made the subject of exact experimental study, all of the above mentioned factors being varied as widely as possible. It was found, in consequence, that *none* of the previously proposed formulas agreed even approximately with the experimental data (in one typical series the maximum divergences ran from 27 to 204%) although the logarithmic formula (1) was superior to any other. A new equation, of the form,

$$\eta^{1/3} = x\,\eta_1^{1/3} . + (1-x) . \eta_2^{1/3} \qquad (2)$$

(η_1, η_2 and x having the same significance as in Equation 1) was suggested, which reproduced the observed values very accurately for the majority of the systems examined. In one case, however, the divergences were sufficiently pronounced to force the conclusion that this equation also possessed no general theoretical foundation.[2]

The present article continues the quest for the fundamental viscosity formula for ideal liquid mixtures by an examination of 2 additional series of systems. It was hoped that further accurate data for carefully chosen mixtures (as nearly as possible ideal and with components of widely divergent viscosities, densities and molecular weights) might enable us at least to narrow down still more the possible limits between which the true equation lies by the final rejection of formulas obviously beyond these limits, even if no ultimate success were obtained in establishing the ideal relation. In particular, it was desired to compare the relative merits of Formulas 1 and 2 more stringently than had been done in previous work.

Experimental.

The liquids selected were representative *ethers* and *esters*, 3 systems of each type (ether-ether and ester-ester) being examined.

As the starting point for each substance, standard preparations of reliable firms were taken, and subjected to careful purification. *Ethyl*

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[1] Kendall and Monroe, THIS JOURNAL, **39**, 1787 (1917).

[2] The results obtained by the application of this equation to ideal solutions of solids in liquids were also not entirely satisfactory (see Kendall and Monroe, *ibid.*, **39**, 1802 (1917).

ether was washed with small amounts of water, then with sodium carbonate solution, dried for several months over sodium and fractionated. *Phenetol* was fractionated under constant low pressure (about 20 mm.) by means of a specially devised form of apparatus[1] which allowed change of receivers without break of the vacuum. The fractionation was repeated until no further change in the physical constants of the product could be noted. *Diphenyl ether* was fractionated under low pressure and then fractionally crystallized several times. *Ethyl acetate* was washed with small amounts of water, then with sodium carbonate solution, dried over phosphorus pentoxide and specially fractionated. *Ethyl benzoate* was washed, dried over calcium chloride and fractionated repeatedly. *Benzyl benzoate* was very carefully purified[2] by successive fractionations under constant low pressure.

The portions employed possessed the following constants:

Liquid.	Freezing pt. ° C.	Boiling pt. (760 mm.) ° C.	Density 25°/4°.	Viscosity.	Spec. conductivity.
Ethyl ether.............	...	34.6	0.7139	0.002233	.....
Phenetol...............	...	170.1	0.9618	0.01158	.....
Diphenyl ether..........	27.05	..	1.0706	0.03864	.....
Ethyl acetate...........	...	77.15	0.8948	0.004239	$<1 \times 10^{-9}$
Ethyl benzoate..........	...	209.1	1.0431	0.02014	$<1 \times 10^{-9}$
Benzyl benzoate.........	19.4	323.0±0.2	1.1121	0.08504	$<1 \times 10^{-9}$

A comparison of these constants with those obtained by previous workers indicates that the more laborious methods of purification here adopted have been justified by the removal of final traces of impurities. Thus the benzyl benzoate employed by Kendall and Monroe[3] gave m. p., 18.8°: $\eta_{25°} = 0.08454$. The same workers obtained for ethyl benzoate $\eta_{25°} = 0.01990$. Since all likely impurities would tend to lower the observed viscosity, the present values are preferred. Previous accurate determinations for the remaining liquids are rare, the value $\eta_{25°} = 0.004193$ obtained by Dunstan[4] for ethyl acetate may, however, be cited.

With regard to the ideality of the mixtures examined, it must be admitted that the first liquids in each series (ethyl ether and ethyl acetate), in particular, are not perfectly normal liquids, but the similarity in the nature of the components of each system will be sufficient to render any deviations from ideality only slight.[5] No appreciable heat or volume

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[1] To be described in a later article (P. M. Gross and A. H. Wright).

[2] The difficulty of purifying benzyl benzoate has recently been discussed by the Earl of Berkeley, *J. Chem. Soc.*, **109**, 520 (1916).

[3] Kendall and Monroe, *loc. cit.*, p. 1796.

[4] Dunstan, *Z. physik. Chem.*, **49**, 590 (1904). The values obtained for phenetol and diphenyl ether by Sachanov and Rjachowsky, *ibid.*, **86**, 529 (1914) are by no means in such satisfactory agreement.

[5] The factors affecting ideality have been examined in detail by Hildebrand, THIS JOURNAL, **38**, 1452 (1916).

changes were noted on admixture of equivalent volumes of the 2 components in any one case.

Viscosity measurements were carried out with the use of the Bingham[1] type of viscometer, the experimental procedure and calculation of results being exactly as recorded in earlier articles of this series. Densities (which are required, for this method, only for use in a correction factor) are appended in the tables below to facilitate conversion of the results from molecular to volume units, but accuracy beyond the third place is not claimed.[2]

Results.

In the following tables, the first column gives the composition of the mixture in molecular units, the second its density, the third its absolute

Series A. Mixtures of Diethyl Ether and Phenetol.

Mol. % ethyl ether.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	0.7139	0.002233	....	...	....	...
90.04	0.7458	0.002674	0.002646	—1.1	0.002757	+3.0
83.03	0.7656	0.003057	0.002952	—3.4	0.003171	+3.7
74.85	0.7891	0.003494	0.003377	—3.3	0.003704	+6.0
68.82	0.8059	0.003866	0.003730	—3.5	0.004133	+6.9
60.48	0.8283	0.004406	0.004278	—2.9	0.004780	+8.5
55.79	0.8387	0.004809	0.004629	—3.8	0.005176	+7.6
51.06	0.8488	0.005154	0.004996	—3.0	0.005587	+8.3
45.01	0.8628	0.005713	0.005519	—3.3	0.006151	+7.7
35.16	0.8853	0.006667	0.006489	—2.7	0.007148	+7.2
30.26	0.8970	0.007152	0.007035	—1.6	0.007682	+7.4
25.23	0.9083	0.007856	0.007642	—2.7	0.008256	+5.1
18.55	0.9230	0.008671	0.008530	—1.6	0.009274	+7.0
9.75	0.9427	0.009993	0.009860	—1.3	0.01025	+2.5
7.45	0.9471	0.01027	0.01024	—0.3	0.01052	+2.4
0.00	0.9618	0.01158	....	...	....	...

Series B. Mixtures of Diethyl Ether and Diphenyl Ether.

Mol. % ethyl ether.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.) Cube rt. eqn.	Percentage divergence.
100.00	0.7139	0.002233	....	..	....	..
90.92	0.7601	0.003106	0.002893	— 6.8	0.003344	+ 7.3
78.26	0.8213	0.004552	0.004150	— 8.8	0.005433	+19.3
70.88	0.8554	0.005733	0.005122	—10.6	0.006978	+21.3
60.76	0.8974	0.007614	0.006835	—10.2	0.009539	+25.3
51.02	0.9311	0.009926	0.009022	— 9.0	0.01253	+26.0
42.45	0.9583	0.01258	0.01152	— 8.4	0.01563	+24.0
32.97	0.9862	0.01631	0.01509	— 7.5	0.01962	+20.2
21.93	1.0181	0.02153	0.02068	— 3.9	0.02505	+16.3
13.18	1.0387	0.02737	0.02654	— 3.0	0.03000	+ 9.6
7.04	1.0542	0.03158	0.03161	+ 0.1	0.03382	+ 7.0
0.00	1.0706	0.03864	....	..	....	..

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[1] Bingham, *J. Ind. Eng. Chem.*, **6**, 233 (1914); Bingham, Schlesinger and Coleman, This Journal, 38, 27 (1916).

[2] In a few cases the values given are interpolated.

viscosity. The viscosity calculated according to Equation 1 and its percentage divergence from the observed value are presented in the next 2 columns. Similarly the last 2 columns show the viscosity calculated from Equation 2 and its percentage divergence from the experimental results.

SERIES C. MIXTURES OF PHENETOL AND DIPHENYL ETHER.

Mol. % phenetol.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	0.9618	0.01158	...	...	...	...
90.06	0.9755	0.01309	0.01305	—0.3	0.01337	+2.1
81.27	0.9870	0.01451	0.01451	0.0	0.01510	+4.1
70.37	0.9993	0.01632	0.01654	+1.4	0.01745	+6.8
60.02	1.0111	0.01862	0.01879	+0.9	0.01990	+6.9
51.05	1.0206	0.02096	0.02088	—0.4	0.02218	+5.8
37.31	1.0346	0.02455	0.02460	+0.2	0.02602	+6.0
32.53	1.0396	0.02630	0.02611	—0.7	0.02748	+4.5
20.72	1.0510	0.03003	0.03012	+0.3	0.03127	+4.1
13.67	1.0573	0.03264	0.03277	+0.4	0.03363	+3.1
0.00	1.0706	0.03864	...	...	...	...

SERIES D. MIXTURES OF ETHYL ACETATE AND ETHYL BENZOATE.

Mol. % ethyl acetate.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage. divergence.
100.00	0.8948	0.004239	....	...	....	...
89.92	0.9204	0.005188	0.004960	—4.4	0.005173	—0.3
79.77	0.9440	0.006178	0.005810	—6.0	0.006234	+0.9
69.89	0.9598	0.007247	0.006778	—6.4	0.007419	+2.4
59.98	0.9740	0.008478	0.007909	—6.8	0.008736	+3.1
50.44	0.9866	0.009851	0.009177	—6.8	0.01014	+3.0
39.73	0.9992	0.01157	0.01074	—7.1	0.01190	+2.9
31.31	1.0101	0.01292	0.01236	—4.3	0.01341	+3.7
20.88	1.0223	0.01514	0.01455	—3.9	0.01545	+2.0
12.16	1.0320	0.01704	0.01667	—2.2	0.01731	+1.5
00.00	1.0431	0.02014	....	...	....	...

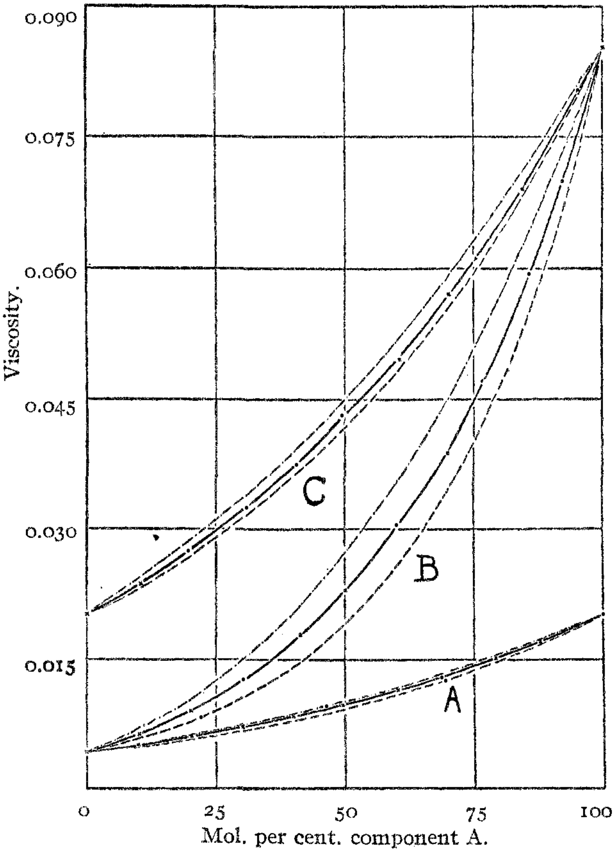
SERIES E. MIXTURES OF ETHYL ACETATE AND BENZYL BENZOATE.

Mol. % ethyl acetate.	Density 25°/4°.	η (expt.).	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	0.8948	0.004239	....	..	....	..
89.80	0.9394	0.006406	0.005756	—10.1	0.006876	+ 7.4
79.90	0.9720	0.009116	0.007746	—15.0	0.01032	+13.2
69.73	0.9988	0.01275	0.01051	—17.5	0.01489	+16.5
58.63	1.0247	0.01789	0.01467	—18.0	0.02122	+18.7
50.00	1.0454	0.02299	0.01900	—17.3	0.02724	+19.0
40.01	1.0625	0.03047	0.02570	—15.6	0.03536	+16.0
30.02	1.0778	0.03881	0.03460	—10.9	0.04528	+16.8
23.47	1.0867	0.04711	0.04210	—10.7	0.05258	+11.6
14.26	1.0975	0.05938	0.05520	— 7.0	0.06412	+ 8.0
7.84	1.1048	0.07003	0.06728	— 4.0	0.07307	+ 4.3
0.00	1.1121	0.08514	....	..	....	..

SERIES F. MIXTURES OF ETHYL BENZOATE AND BENZYL BENZOATE.

Mol. % ethyl benzoate.	Density 25°/4°.	η (expt.)	η (calc.). Log eqn.	Percentage divergence.	η (calc.). Cube rt. eqn.	Percentage divergence.
100.00	1.0431	0.02014	...	...	...	...
89.63	1.0524	0.02371	0.02339	—1.4	0.02426	+2.5
80.23	1.0603	0.02749	0.02678	—2.5	0.02845	+3.5
69.06	1.0683	0.03249	0.03146	—3.2	0.03402	+4.7
59.41	1.0760	0.03740	0.03616	—3.3	0.03938	+5.2
50.54	1.0825	0.04309	0.04109	—4.6	0.04478	+3.9
39.45	1.0910	0.04948	0.04821	—2.6	0.05219	+5.4
29.73	1.0967	0.05695	0.05546	—2.6	0.05933	+4.2
24.75	1.1005	0.06108	0.05960	—2.4	0.06323	+3.5
15.49	1.1053	0.06898	0.06825	—1.1	0.07091	+2.8
4.65	1.1104	0.08039	0.07961	—1.0	0.08069	+0.4
0.00	1.1121	0.08514	...	...	...	...

The results for the esters are also reproduced graphically in the diagram. It will be found, by reference to this diagram and to the tables above, that neither the logarithmic nor the cube root formula expresses the experimental results in a satisfactory manner. The experimental curve lies in all cases[1] between the 2 calculated curves, the logarithmic equation



A = ethyl acetate—ethyl benzoate.
B = ethyl acetate—benzyl benzoate.
C = ethyl benzoate—benzyl benzoate.
— x — Experimental.
— — — — Log. eqn.
— · — · — · — Cube root eqn.

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[1] In one case (for the system: phenetol—diphenyl ether) the logarithmic formula is practically identical with the observed values, the average divergence being only 0.2%. The ratio between the viscosities of the 2 components, however, is smaller here than for any other system studied; the average divergence for the cube root equation is only 4.8%.

giving values consistently too low, the cube root equation giving values consistently too high. The maximum divergence for the 62 mixtures examined is —18.0% for the logarithmic equation, the average divergence —4.8%. For the cube root equation the maximum divergence is +26.0%, the average divergence +7.9%.

The divergences in each case become greater as the ratio between the viscosities of the 2 components of the mixture is widened. In the system ethyl acetate-benzyl benzoate this ratio is more than 20 to 1, the variation being greater than in any system hitherto studied. The divergences here are much larger than for the 2 remaining ester systems, as will be evident from the diagram.

Neither equation can, therefore, be claimed as the ideal formula. The 2 formulas, however, clearly do furnish us with limits within which this unknown relation may be confidently predicted to lie. All other previously proposed equations (such as fluidity formulas, or equations with weight or volume composition units) give hopelessly discordant values, as in the systems investigated by Kendall and Monroe.

The following brief mathematical analysis of the situation which thus presents itself is instructive. The original linear viscosity equation

$$\eta = x\eta_1 + (1 - x)\eta_2 \qquad (3)$$

is equivalent to the statement $d\eta/dx = k$. As indicated in previous articles[1] and also in the diagram here given, however, the experimental viscosity curve is not linear but considerably "sagged;" in other words $d\eta/dx$ increases as η increases. The fluidity formula of Bingham[2]

$$1/\eta = x/\eta_1 + (1 - x)/\eta_2 \qquad (4)$$

which is equivalent to the statement $d\eta/dx = k\eta^2$, errs in the opposite direction, indicating that $d\eta/dx$ does not increase so rapidly as η^2.

We should, therefore, expect some power of η less than the second to give approximate constancy for $d\eta/dx$. The logarithmic Equation 1 reduces, in point of fact, to the statement $d\eta/dx = k\eta$, while the cube root Equation 2 reduces to $d\eta/dx = k\eta^{4/3}$. The former gives results consistently low, the latter gives results consistently high. It would obviously be a simple matter, therefore, to devise an empirical formula, with an index for η lying between 1 and $^4/_3$, which would represent exceedingly well the experimental data for all of the systems investigated.

Such a procedure, however, would hardly ameliorate the present unsatisfactory status of the problem, for it is difficult to conceive how such a formula could possibly be invested with any theoretical significance. Since all efforts to substantiate a simple ideal equation from the experimental side have failed (all possible simple relations being put, indeed,

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[1] Kendall and Monroe, *loc. cit.*, p. 1788.

[2] Bingham, *Am. Chem. J.*, 34, 481 (1905); *Phys. Rev.*, 35, 407 (1912).

outside the pale of error limits) it would seem inadvisable to continue the attack until considerable progress has been made in neighboring sectors which will open up some weak point at present unsuspected. The conclusions drawn from an earlier article[1] may here be emphasized: "It may be, of course, that the true equation is so exceedingly complex (other factors, such as internal pressure, average molecular volume,[2] etc., entering into consideration) that it can never be arrived at except theoretically. Even in that case, however, the data presented in these articles will prove of immediate service in verifying or disproving any such theoretical equation as soon as propounded."

The difficulties confronting any attack from the theoretical side should not be minimized. First of all, an exact and comprehensive kinetic-molecular theory of liquids must be established.[3] Secondly, the nature of the forces conditioning the flow of molecules past one another in the interior of a liquid must be more intimately understood. An exhaustive physico-mathematical treatment of the forces involved must undoubtedly precede any real advances in this field, the fundamental importance of which is, at present, insufficiently realized both by physicists and by chemists. The valuable results attending recent work on the viscosities of gases[4] ought certainly to encourage similar efforts to advance our knowledge of viscosity in the liquid state[5] beyond its present chaotic condition.

Summary.

The viscosity curves for the following liquid systems have been determined with the use of the Bingham viscometer: (1) ethyl ether-phenetol; (2) ethyl ether-diphenyl ether; (3) phenetol-diphenyl ether; (4) ethyl acetate-ethyl benzoate; (5) ethyl acetate-benzyl benzoate; (6) ethyl benzoate-benzyl benzoate.

Although these mixtures are certainly very nearly ideal, yet the experimental data are not reproducible satisfactorily by means of any known simple formula. The logarithmic viscosity equation of Arrhenius and Kendall gives values uniformly a little low, the cube root viscosity equation of Kendall and Monroe gives values uniformly a little high. All other proposed formulas are altogether out of agreement with the figures of experiment.

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[1] Kendall and Monroe, *loc. cit.*, p. 1801.

[2] Tinker, *Phil. Mag.*, [6] 33, 430 (1917).

[3] A recent monograph by Kleeman ("A Kinetic Theory of Gases and Liquids," John Wiley and Sons, 1920) contains many new and exceedingly interesting suggestions on the physico-mathematical development of viscosity relationships from this standpoint.

[4] See, for example, Rankine, *Phil. Mag.*, 29, 552 (1915); *Proc. Roy. Soc. A.*, 91, 201 (1915), and earlier articles.

[5] A differentiation between viscous flow in liquids and in gases has been attempted by Bingham, THIS JOURNAL, 36, 1383 (1914).

From a brief mathematical consideration of the results obtained, the conclusion has been drawn that further progress in this field must be preceded by fundamental advances on the theoretical side of the subject. The experimental work has, at present, reached as far as it can go alone in showing that all simple solutions of the problem hitherto proposed are certainly insufficient.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DENVER FOOD AND DRUG INSPECTION STATION, BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A COLOR TEST FOR OXALIC ACID.[1]

BY LEWIS H. CHERNOFF.

Received May 22, 1920.

Recently Sacher[2] suggested a color test involving the use of a dilute solution of a manganous salt. This is treated with sodium or potassium hydroxide solution and allowed to stand till the manganous hydroxide is partially oxidized by the air. On adding an aqueous solution of oxalic acid, drop by drop, the precipitate dissolves and a red coloration is produced. Reducing substances, also excess of oxalic or any other acid, prevent the color formation.

Dorronsoro and Fernandez[3] have observed a color reaction while working with pinene derived from Spanish oil of turpentine. When pinene was oxidized, a substance, supposed to be nopic acid, was produced which gave a *green* coloration with resorcinol and sulfuric acid. This substance was later identified as oxalic acid.[4]

The writer has confirmed this reaction with oxalic acid and has further developed it for use as a general test for oxalic acid. Under certain conditions described below, a *blue* color is obtained instead of green.

While resorcinol forms colorations with a great number of organic compounds, the colors are mostly red, pink or violet. When nitrates or nitrites are dissolved in conc. sulfuric acid and a crystal of resorcinol is added, a deep blue color is produced. If a little water is added, however, the color becomes brown to red. The writer is unaware of any other compound which gives a *blue* color *under the conditions described below*, although it is quite probable that such compounds exist. Some substances, such as carotin, xanthophyll, some terpenes, etc., give a *blue* color with sulfuric acid alone. It is best, therefore, in many cases to re-

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[1] Published by permission of Secretary of Agriculture, U. S. Department of Agriculture.

[2] Sacher, *C. A.*, 9, 2043 (1915).

[3] Dorronsoro and Fernandez, *Ibid.*, 9, 2522 (1915).

[4] Details of this reaction are not given in the abstract. The original article (*Anales. soc. españ. fis. quim, II*, 441–3 (1913)) was not available.