such curves. Nine alternative linear functions have been considered—viscosity, fluidity and logarithmic viscosity, each being taken as an additive property against weight, volume and molecular composition units in turn.

It has been conclusively shown that none of these nine equations are even in approximate agreement with experimental facts. All must, therefore, be entirely devoid of theoretical significance.

A new empirical cube-root formula has been presented, which falls into much closer agreement with observed values. Only for the last system investigated are the divergences appreciable.

Further work is being carried on on similar ideal systems in order to obtain a more definite idea of the merits of this equation.

NEW YORK CITY.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY No. 305.]

THE VISCOSITY OF LIQUIDS. III. IDEAL SOLUTIONS OF SOLIDS IN LIQUIDS.[1]

BY JAMES KENDALL AND KENNETH POTTER MONROE.

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It was hoped that a study of suitable systems of this type might solve the question left undecided at the close of the preceding paper, *i. e.*, whether the relative success of the cube-root viscosity equation there considered was due entirely to chance, or whether it might possess actual theoretical significance.

Previous work on the viscosities of ideal solutions of solids in liquids is extremely scanty.[2] Suggested formulas are, in general, similar in form to those for binary liquid mixtures, and similarly unsatisfactory in practice. Thus the linear equation

$$\eta = (1 + Ax)\eta_0$$

(where η_0 = viscosity of pure solvent; x = weight of solute in unit volume of solution; A = constant) is valid only for very dilute solutions. The logarithmic equation of Arrhenius[3]

$$\eta = A^x.\eta_0\text{; or } \log (\eta/\eta_0) = x \log A$$

also becomes useless at higher concentrations. The fluidity formula of Lees[4]

$$1/\eta = x/\eta_0 + (1 - x)/\eta_1$$

regards the most concentrated solution as a second component with vis-

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[1] Preceding articles; Kendall, *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 25 (1913), and Kendall and Monroe, THIS JOURNAL, **39**, 1787 (1917).

[2] See Dunstan and Thole, *J. Chem. Soc.*, **97**, 1249 (1910).

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

[4] Lees, *Phil. Mag.*, [6] 1, 139 (1901).

cosity η_1 and treats the system as a binary liquid mixture, compositions being expressed in volume fractions. Here again agreement with experimental data is dependent upon the introduction of an additional constant, varying with the particular mixture considered. Various more complex equations, none of which are really satisfactory, have been examined by Green.[1]

Kendall[2] has shown that here, as for binary liquid mixtures, the Arrhenius formula comes into much closer agreement with experimental results when molecular concentration units are employed. In the same article it was also established that the equation, thus modified, was merely a special form of the general liquid mixture formula

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

where η_1 represents the viscosity of the pure solvent and η_2 that of the pure solute *in the liquid state* at the temperature of the experiment.

The second component being a solid, η_2 is here the unknown. The validity of the different possible liquid-mixture equations can consequently be tested by the constancy of the values obtained for η_2 from solutions of varied concentrations.[3] This was carried out with the experimental data available, and the modified Arrhenius equation found to afford the most concordant results. Owing to the few mixtures considered, however, and the uncertainty as to their ideality, the question could not be regarded as finally settled.

In this investigation the following systems have been taken up:

I. Benzene-naphthalene	III. Toluene-naphthalene
II. Benzene-diphenyl	IV. Toluene-diphenyl

Washburn and Read[4] have demonstrated conclusively, by freezing-point determinations, that the first two of these follow the laws of ideal solutions throughout the whole composition range. The full freezing-point curves for the other two mixtures have not been determined, but the fact that several points in each case[5] were found to coincide within experimental error with those for the corresponding benzene solutions of identical molecular composition indicates that these systems are also ideal.[6]

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[1] Green, *J. Chem. Soc.*, **93**, 2023 (1908).

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

[3] If the true formula were known and exact values for η_2 thus obtainable, we should be greatly assisted in the allied problem of the true viscosity-temperature relationship. At present we are held back here by the small temperature intervals available, but by the determination of the viscosities of liquids far below their freezing points by the method indicated above this difficulty would vanish (see p. 1798, note 1).

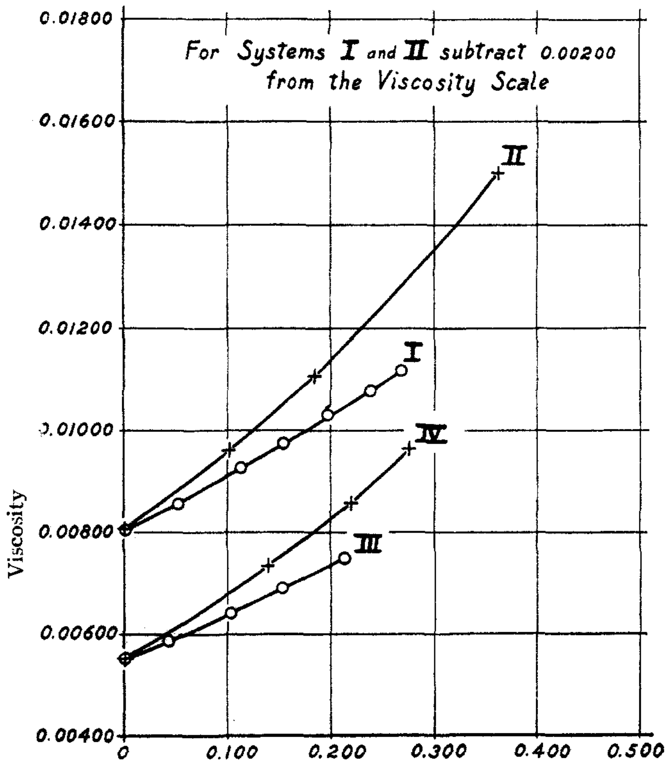
[4] Washburn and Read, *Proc. Nat. Acad. Sci.*, **1**, 191 (1915).

[5] See also Speyers, *Sill. Jour.*, [4] **14**, 295 (1902).

[6] If a given solid forms ideal solutions with various liquids its solubility at any fixed temperature is independent of the particular liquid (Roozeboom, Heterogene Gleichgewichte, Vol. 2, p. 273).

The experimental methods followed were exactly as described in the preceding article. Naphthalene was prepared by sublimation. The product employed melted sharply between 80.4–80.5°. Diphenyl was obtained by the usual method of passing benzene vapor through a hot tube. The crude product was fractionated, crystallized from absolute alcohol several times, and finally sublimed after driving off all traces of alcohol. The samples used gave a sharp melting point between 69.6 and 69.7°.

The viscosity results obtained are shown in the tables on pp. 1805 and 1806[1] and also in the accompanying diagram. As with the mixtures in-



Mol Fraction Solute

I. Benzene—naphthalene. III. Toluene—naphthalene.
II. Benzene—diphenyl. IV. Toluene—diphenyl.

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[1] Volume percentages are derived from density determinations, the assumption being made that no change in volume would occur on mixing the two components in the liquid state. The satisfactory constancy of the extrapolated values thus obtained for the densities of *liquid* naphthalene and *liquid* diphenyl at 25° (1.02 and 1.03 ± 0.005, respectively) indicates that this assumption is valid for all of the four series examined. In view of the long extrapolation necessary, however, volume percentages can be accurate only to the first place of decimals, as given in the tables above.

vestigated in the previous paper, it was found that none of the formulas previously proposed gave good agreement, consequently only the results calculated by the liquid-mixture cube-root equation

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

are presented here.

TABLE I.—BENZENE-NAPHTHALENE AT 25°.

Per cent. naphthalene in mixture.					
Weight.	Volume.	Molecular.	η (Expt.).	η_2 (Calculated).	Percentage deviation from mean value.
0.0	0.0	0.0	0.006048	..	...
8.11	7.3	5.10	0.006565	0.0220	—2.2
17.16	15.2	11.21	0.007261	0.0230	+2.2
22.97	20.6	15.38	0.007707	0.0223	—0.9
28.82	25.8	19.79	0.008263	0.0227	+0.9
34.10	30.8	23.98	0.008764	0.0224	—0.4
37.69	33.9	26.93	0.009178	0.0227	+0.9
				Mean, 0.0225	

In consequence of the great range of the extrapolation for η_2, its constancy affords a very sensitive criterion as to the agreement of the formula with the experimental data. From the figures above it will be seen that the cube-root formula gives consistent results for η_2 (the viscosity of liquid naphthalene at 25°) right up to the most concentrated solutions investigated.

TABLE II.—BENZENE-DIPHENYL AT 25°.

Per cent. diphenyl in mixture.					
Weight.	Volume.	Molecular.	η (Expt.).	η_2 (Calculated).	Percentage deviation from mean value.
0.0	0.0	0.0	0.006051	..	...
18.08	15.8	10.06	0.007585	0.0341	—0.9
30.57	27.3	18.24	0.009014	0.0340	—1.1
53.03	48.9	36.38	0.01298	0.0351	+2.1
				Mean, 0.0344	

Again the constancy of the values for η_2 obtained by the use of the cube-root equation is satisfactory throughout. All other equations considered gave less consistent results.

TABLE III.—TOLUENE-NAPHTHALENE AT 25°.

Per cent. naphthalene in mixture.					
Weight.	Volume.	Molecular.	η (Expt.).	η_2 (Calculated).	Percentage deviation from mean value.
0.0	0.0	0.0	0.005526	..	...
5.73	4.8	4.19	0.005848	0.0181	—1.1
13.72	11.8	10.26	0.006394	0.0180	—1.6
20.12	17.4	15.33	0.006866	0.0183	0.0
27.31	24.1	21.27	0.007470	0.0186	+1.6
				Mean, 0.0183	

Here the values obtained for η_2 are consistent among themselves, but are *not* in agreement with those derived for "liquid naphthalene" at 25° in Table I. This discrepancy is also evident in Table IV.

TABLE IV.—TOLUENE-DIPHENYL AT 25°.

Per cent. diphenyl in mixture.					
Weight.	Volume.	Molecular.	η (Expt.).	η_2 (Calculated).	Percentage deviation from mean value.
0.0	0.0	0.0	0.005520	..	...
21.38	18.6	13.98	0.007335	0.0275	—2.5
32.02	28.2	21.97	0.008587	0.0281	—0.4
38.97	34.8	27.61	0.009627	0.0289	+2.5
				Mean, 0.0282	

The constancy of η_2 is, in this case, not so good as in the previous systems, but still not unsatisfactory until we compare the value with that obtained in Table II. Just as for naphthalene above, a decided difference is evident in the two "calculated" values. It is of interest to note that the ratio [η_2 on benzene basis]/[η_2 on toluene basis] is practically identical for the two solutes, namely 1.23 for naphthalene and 1.22 for diphenyl.

The results of this paper also are consequently indecisive. All previous formulas are certainly useless. The cube-root equation gives good results for any single system, but the values for different systems containing the same solute are conflicting. No explanation of the results obtained can be ventured here, since it is obvious that more systems must be investigated before deductions of any value can be drawn.

NEW YORK CITY.

A STUDY OF THE ALLOTROPY OF CADMIUM.

BY FREDERICK H. GETMAN.

Received July 11, 1917.

Introduction.

To the interesting investigations of Ernst Cohen[1] and his pupils we are indebted for practically all of our knowledge of the phenomenon of allotropy among the metals. By means of the pycnometer, the dilatometer and the potentiometer, he has shown that tin, bismuth, cadmium, copper, zinc, antimony, lead, sodium and potassium exist in different allotropic modifications, each of which possesses a more or less definite range of stability.

In studying the electromotive behavior of cadmium, Cohen[2] made use of a cell set up according to the following scheme, the direction of the current outside of the cell being shown by the arrow:

$$\overset{-}{\text{Electrolytic Cd on Pt}} \xleftarrow{\hspace{6em}} \tfrac{1}{2}\text{ sat. sol. } CdSO_4 \text{ — } 12.5\%\ \overset{+}{\text{Cd}} \text{ amalgam.}$$

Similar cells have also been investigated by Jaeger,[3] Bijl,[4] and Hulett.[5]

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[1] *Verslag Akad. Wetenschappen*, 16, 485, 565, 628, 632, 807 (1913–14); 17, 54, 59, 60, 122, 200 (1914); *Z. phys. Chem.*, 85, 419 (1913); 87, 409, 419, 426, 431 (1914).

[2] *Trans. Faraday Soc.*, 10, 216 (1915).

[3] *Ann. Physik*, [3] 65, 106 (1898).

[4] *Z. phys. Chem.*, 41, 641 (1902).

[5] *Trans. Am. Electrochem. Soc.*, 7, 353 (1905).