III.—*The Study of Binary Mixtures. Part I.
The Densities and Viscosities of Mixtures contain-
ing Phenol.*

By ARTHUR BRAMLEY.

THE study of the physical properties of binary mixtures has engaged the attention for a great many years of a large number of chemists and physicists. It rarely happens that any physical property of a mixture of two substances is exactly the same as that calculated according to a simple mixture rule, but often the difference between the actual and calculated values is small compared with the magni-

ture of the property itself. These differences are generally ascribed to constitutional changes brought about by the interaction of the component substances. When the substances brought together react chemically, the physical properties of the product frequently differ enormously from those of the original substances; on the other hand, when mixing is not accompanied by chemical action, the physical properties of the mixture generally approach closely the values calculated. In a large number of cases where two liquids mix it is very difficult to ascertain whether the mixing is accompanied by chemical action, and still more difficult, if not impossible, to determine the extent of such action. The study of this last class of mixtures really consists in a critical examination of their physical properties, and comparing the values obtained by direct measurement with those calculated according to some formula. It has long been known that the viscosities of mixtures differ from those calculated to a much greater extent than most other physical properties; in contradistinction from other physical properties, the constitutional effect is large compared with the additive value. For this reason, the study of the viscosity of pure and mixed liquids has attracted a considerable amount of attention, but so far no satisfactory explanation of the effect of the interaction of two liquids on the viscosity is forthcoming.

The viscosity-concentration curves of liquid mixtures have been classified by Dunstan and Thole into three divisions according as they deviate but slightly from a straight line, exhibit a maximum, or a minimum. The first class includes mixtures of liquids that are chemically indifferent towards each other, the molecules of which are not associated. In the second class the constituents of each mixture are supposed to react chemically, forming a compound which is the cause of the high viscosity. The third class consists of mixtures of liquids which do not form a compound with one another, and at least one of which contains associated molecules, the low viscosity of the mixture being attributed to the dissociation of complex into simpler molecules as a result of the interaction of the two substances.

This method of classification frequently leaves one in doubt about the category to which some mixtures belong. No mixture has an exactly linear viscosity-composition curve, and it is obviously only necessary to choose two substances which are chemically indifferent towards each other and of about the same viscosity to obtain a mixture having a minimum on its viscosity-composition curve, yet the deviation from linearity may be very small. Further, there are a considerable number of mixtures which show no minimum on their viscosity-composition curves, but the latter lie far below the straight

lines representing the simple mixture rule. Examples of such are mixtures of phenol with benzene, chlorobenzene, nitrobenzene, and acetone, which are described later. The cause of the very great deviations in these cases is undoubtedly the dissociating effect of the second substance on the molecular complexes of phenol. Again, there are many mixtures which have viscosities considerably higher than those calculated according to the simple mixture formula, but their viscosity-composition curves show no maximum. These cases are not provided for in the above system of classification.

Much importance is attached to the existence of a maximum on the viscosity-composition curve by Dunstan and his collaborators (T., 1904, **85**, 817; 1905, **87**, 11; 1907, **91**, 83; 1908, **93**, 1919; 1909, **95**, 1556); Tsakalotos (*Bull. Soc. chim.*, 1908, [iv], **3**, 234), and Faust (*Zeitsch. physikal. Chem.*, 1912, **79**, 97). As regards the cause of a maximum, the general consensus of opinion seems to be that it is the result of the formation of a compound, the latter having a higher viscosity than either of the pure substances. Nearly all attempts to determine the composition of the complex, however, from the position of the maximum have proved futile. This is only to be expected, since in almost every case the position of the maximum point depends on the temperature. Faust (*loc. cit.*) found that with rise in temperature the maximum point on the viscosity-composition curve for mixtures of acetone and chloroform disappears, as also does the minimum point on the acetone-carbon disulphide curve. The mixtures of alkylthiocarbimides and secondary bases examined by Kurnakov and Shemtschushni (*Zeitsch. physikal. Chem.*, 1913, **83**, 481) are exceptional. The viscosity isotherms for these mixtures rise to a definite cusp at a concentration corresponding with equimolecular proportions; moreover, the composition of the mixture which has the maximum viscosity does not vary with temperature. Other investigators, notably Findlay (*Zeitsch. physikal. Chem.*, 1909, **69**, 203) and Denison (*Trans. Faraday Soc.*, 1912, **8**, 20), attribute more importance to the position of maximum deviation of the viscosity curve from a straight line. Denison examined the viscosity curves of a number of mixtures, and found that for each mixture the position of maximum deviation was constant at different temperatures, and occurred at a point corresponding with some simple molecular proportion; this he took to indicate the composition of the compound formed. In a large number of cases Denison's test of maximum deviation fails, because not only does it draw no distinction between deviations which are positive and negative, that is, above and below the straight line, but, as will be shown subsequently, the position of maximum deviation frequently varies considerably with the tem-

perature. Findlay (*loc. cit.*), presumably with the object of obtaining conditions approximating to those of corresponding states, measured the viscosities of a number of mixtures at temperatures just below their boiling points. His results failed to reveal any simple relationship between either the maximum viscosity or the maximum deviation and the nature of the compound formed.

Denison's method of analysing the viscosity-composition curves, although yielding definite results in but few cases, suggests another system of classification, which appears simpler and preferable to that of Dunstan and Thole. Two classes only are required:

Class A.—The viscosity-composition curves lie below the straight line joining the viscosities of the pure components.

Class B.—The viscosity-composition curves lie above the straight line joining the viscosities of the pure components.

In general, class A consists of mixtures of substances which do not react chemically with one another to form a compound, the only effect of the interaction of the two pure substances being one of dissociation of complex into simpler molecules. Since there are no linear viscosity isotherms for mixtures, this would imply that all liquids contain some more or less associated molecules, a conclusion for which there is at present no entirely satisfactory criterion. Class B consists of mixtures of substances which react chemically, forming compounds with each other. Some exceptions arise, as, for example, mixtures of phenol and acetone; this pair of substances yields viscosity isotherms of the type A, although the formation of a compound undoubtedly takes place. There are also a number of mixtures giving inflected viscosity isotherms. A discussion of these exceptions will be given subsequently.

The work described below was undertaken with the object of determining what factors influence the viscosity of liquid mixtures, and whether it is possible to ascertain from viscosity measurements the composition of a compound that might exist in a liquid mixture of two substances. For this purpose it was decided to determine the densities and viscosities of mixtures of phenol and several bases of different strengths over as wide a range of temperature as possible. In order to be able to compare the viscosity-composition curves of these mixtures with the general type of curve given by mixtures of phenol and indifferent substances, mixtures of phenol with benzene, chlorobenzene, and nitrobenzene were examined.

EXPERIMENTAL.

In the determination of the densities of the liquids examined, pycnometers of the Sprengel type were employed. For temperatures up to 20° a pycnometer of about 8 c.c. capacity with a bulb

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on one limb was used. Two plain Sprengel tubes of about 10 c.c. capacity were employed for the higher temperatures. Duplicate experiments with different pyknometers showed that the figure in the fourth decimal place was trustworthy, but a general consideration of the different factors influencing the determinations of density indicate that this was about the limit of accuracy attained. All the densities are referred to that of water at 4°.

The viscosities were measured by means of viscometers of the Ostwald type. On account of the great differences in the viscosities of the liquids examined, three pairs of viscometers were used. One pair was suitable for liquids of low viscosity, another pair for liquids of intermediate viscosity, and a third pair for liquids of high viscosity. In this way the periods of flow for the different liquids were of about the same order. The hygroscopic nature of the substances used rendered it necessary to protect them from the moisture in the air; this was done by attaching tubes containing anhydrous calcium chloride to the viscometers. The periods of flow were measured by means of two tested stop-watches, which marked off time in fifths of a second. In the calculation of absolute viscosities, Thorpe and Rodgers's value for water at 25°, namely, 0.00891, was taken as standard.

It is well known that in the determination of viscosities of liquids generally, the maintenance at a steady temperature of the bath in which the viscometer is placed is of great importance. Few experiments, however, had been made in the early part of this investigation before it became apparent that, on account of the enormous temperature-coefficients of the viscosity of some of the liquids at the lower temperatures, the precision with which the temperatures of the baths must be maintained was of a high order. This will be evident from the following example: The viscosity of phenol at 20° is 0.1104; at 10° it is 0.2010; for a temperature interval of 10° the viscosity has almost doubled; hence, if an accuracy of 0.1 per cent. is to be attained, the temperature must not vary more than 0.01°. The thermo-regulation of a bath so that its extreme variations never exceed this amount is a matter of some delicacy, especially so when the temperature required is below that of the room. For a constant temperature bath at 0° a 4-litre beaker was filled with a mixture of clean ice broken into small pieces and distilled water. The following arrangement was found to be suitable for temperatures between about 5° and that of the room. The bath consisted of a rectangular copper vessel with two opposite sides of glass, and had a capacity of about 30 litres. Cooling was accomplished in the following way: A coil of about 10 metres of lead tubing (1.2 cm. in diameter) was embedded in

roughly broken ice in a tank of about 30 litres capacity; one end of this coil was connected to a water-tap, and the other to one end of a second coil of similar tubing having a dozen turns of 7.5 cm. diameter. The other end of this coil, which was immersed in the constant-temperature bath, was connected to a pipe leading to a sink. A steady stream of water was run from the tap through the first coil, where it was cooled to a temperature near zero; it then passed through the second coil, thus cooling the water in the bath; finally, it escaped to the sink. The speed of the water was adjusted so that it would cool the bath to a temperature two or three degrees below that required, the final adjustment of the temperature being made by means of an electrical heater actuated by an electrical thermo-regulator of the form described by Gouy (*J. Physique*, 1897, **6**, 479). A full description, with diagrams, of this excellent regulator is given by Barnes (*Phil. Trans.*, 1902, [A], **199**, 208). For temperatures between that of the room and 50° the same method was used, excepting, of course, the cooling arrangement, which was dispensed with. Auxiliary heating by means of a small gas flame was necessary for temperatures above 30°. The water in the tank was kept thoroughly mixed by means of a turbine stirrer. Trial runs, extending over a full day, showed that, by the above method, the temperature of the bath could be kept constant within two or three thousandths of a degree. For the more viscous liquids, the temperature-coefficient of viscosity diminishes rapidly with rise in temperature; consequently the very high degree of precision in the maintenance of a constant temperature which is required for the lower temperatures is not so necessary for higher temperatures. The baths used for temperatures above 50° were beakers of 4-litres capacity, and ordinary toluene thermo-regulators were employed. Above 100° the water in the baths was replaced by glycerol, and aniline was used instead of toluene in the regulators.

The substances used were purified as follows:

Phenol.—Pure phenol was distilled, and the middle fraction, which had a constant boiling point, was used.

Benzene.—Pure commercial benzene was shaken with successive portions of concentrated sulphuric acid until the latter was no longer coloured; the benzene was then washed several times with water, and dried, first with calcium chloride and afterwards with sodium. Finally, it was distilled through a fractionating column, the portion of constant boiling point being used.

Chlorobenzene.—Kahlbaum's chlorobenzene was kept over anhydrous calcium chloride for a few days, and then distilled. Its boiling point was constant.

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Nitrobenzene.—Some nitrobenzene of unknown origin was washed with sodium carbonate solution, then with water, dried over calcium chloride, and distilled. It had a constant boiling point.

Aniline.—Commercial aniline was fractionated several times; finally a quantity was obtained which had a constant boiling point.

FIG. 1.

- I. Phenol and benzene.
 II. " " chlorobenzene.
 III. " " nitrobenzene.

Dimethylaniline.—Kahlbaum's preparation was redistilled, and the middle fraction of constant boiling point used.

p-Toluidine, *Diphenylamine*, and *Diphenylmethylaniline*.—These substances, obtained from Kahlbaum, were redistilled under diminished pressure, the first and last portions being rejected.

Quinoline.—Kahlbaum's synthetic quinoline was allowed to remain in contact with solid potassium hydroxide for several days, and then distilled; a portion of constant boiling point was obtained.

Pyridine.—Pure commercial pyridine was kept in contact with

solid potassium hydroxide for several days, and then fractionated by distillation. This process was repeated several times, and ultimately a quantity was obtained which had a range of boiling point less than one-tenth of a degree.

Phenetole.—This substance, obtained from Kahlbaum, was redistilled. It had a constant boiling point.

Acetone.—Commercially pure acetone was treated with aqueous potassium permanganate solution, and allowed to remain for three or four days, more permanganate solution being added as the colour disappeared. The acetone was distilled off on the steam-bath, dried over calcium chloride, and finally distilled, using a fractionating column. From 2500 c.c. of commercial acetone, 1500 c.c. were obtained, which had a range of boiling point of less than one-tenth of a degree.

Mixtures of phenol with (*a*) benzene, (*b*) chlorobenzene, and (*c*) nitrobenzene were examined at one temperature only, namely, 20°. The values obtained are given in tables Ia, Ib, and Ic, and Fig. 1 represents graphically the relations between the viscosity and composition of these mixtures. The density-composition curves for these mixtures are almost straight lines; they lie very slightly below the linear.

TABLE Ia.

Mixtures of Phenol and Benzene.

Weight per cent. of phenol.	Density at 20°.	Viscosity at 20°.
0.00	0.8772	0.00629
6.04	0.8880	0.00683
9.84	0.8949	0.00724
20.01	0.9133	0.00865
32.40	0.9370	0.01126
42.09	0.9549	0.01401
53.02	0.9766	0.01911
63.65	0.9976	0.02642
74.11	1.0194	0.03811
83.20	1.0383	0.0535
100.00	1.0752	0.1104

TABLE Ib.

Mixtures of Phenol and Chlorobenzene.

Weight per cent. of phenol.	Density at 20°.	Viscosity at 20°.
0.00	1.1051	0.00768
4.93	1.1034	0.00825
9.78	1.1018	0.00888
21.73	1.0980	0.01122
30.43	1.0954	0.01374
38.90	1.0930	0.01673
49.90	1.0898	0.02218
58.15	1.0874	0.02748
71.41	1.0836	0.04070
81.45	1.0806	0.05555
100.00	1.0752	0.1104

TABLE Ic.

Mixtures of Phenol and Nitrobenzene.

Weight per cent. of phenol.	Density at 20°.	Viscosity at 20°.
0.00	1.2021	0.01931
4.16	1.1957	0.01975
8.84	1.1888	0.02041
18.12	1.1756	0.02208
27.41	1.1635	0.02460
37.96	1.1495	0.02845
49.73	1.1346	0.0353
58.64	1.1233	0.0419
71.03	1.1085	0.0540
84.68	1.0927	0.0759
100.00	1.0752	0.1104

The densities and viscosities of mixtures of phenol and aniline were determined for a number of temperatures ranging from 20° to 125°. Tables II and IIa contain the results obtained, and the viscosity isotherms are shown in Fig. 2. The viscosity-composition curves were drawn on a large scale for each temperature, and the position of maximum deviation from the straight line joining the viscosities of the two components was determined. The composition of the mixtures which show the greatest divergence in viscosity from the values calculated according to the simple mixture rule, together with the corresponding temperatures, are given in table IIb. These quantities are represented graphically in the small curve inset in Fig. 2. The density curves for these mixtures are almost straight lines, the densities found being slightly higher than those calculated. The viscosities of mixtures of phenol and aniline have been measured for one temperature, namely, 35°, by Thole, Dunstan, and Mussell (T., 1913, 103, 1114).

FIG. 2.

Phenol and aniline.

TABLE II.
Mixtures of Phenol and Aniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	30°	40°	60°	80°	30°	40°	60°	80°
0.00	1.0131	1.0045	0.9872	0.9700	0.03145	0.02405	0.0154	0.01100
7.58	1.0185	1.0099	0.9925	0.9752	0.0366	0.0274	0.0169	0.01175
15.96	1.0242	1.0156	0.9982	0.9809	0.0434	0.0315	0.0188	0.01280
23.33	1.0292	1.0206	1.0032	0.9858	0.0507	0.0361	0.02083	0.01375
31.65	1.0347	1.0260	1.0086	0.9911	0.0595	0.0410	0.02285	0.01480
39.14	1.0394	1.0307	1.0133	0.9959	0.0685	0.0461	0.02485	0.01570
47.17	1.0442	1.0355	1.0180	1.0005	0.0770	0.0510	0.0267	0.01662
54.00	1.0448	1.0394	1.0220	1.0047	0.0836	0.0545	0.0279	0.01720
61.84	1.0521	1.0434	1.0259	1.0085	0.0889	0.0573	0.0290	0.01768
69.28	1.0557	1.0470	1.0296	1.0122	0.0907	0.0583	0.0294	0.01793
76.86	1.0590	1.0504	1.0330	1.0156	0.0889	0.0573	0.0292	0.01777
84.80	1.0617	1.0531	1.0358	1.0185	0.0834	0.0546	0.02835	0.01745
92.50	1.0646	1.0561	1.0388	1.0215	0.0768	0.0511	0.0269	0.01670
100.00	1.0668	1.0584	1.0414	1.0242	0.0709	0.0476	0.0252	0.01580

TABLE IIa.

Mixtures of Phenol and Aniline.

Weight per cent. of phenol.	Densities.		Viscosities.	
	20°.	125°	20°.	125°.
0.00	1.0219	0.9288	0.0428	0.00637
7.94	1.0276	0.9342	0.0509	0.00666
15.31	1.0326	0.9390	0.0610	0.00693
23.34	1.0380	0.9436	0.0735	0.00723
31.28	1.0434	0.9482	0.0889	0.00749
39.39	1.0485	0.9527	0.1059	0.00770
47.56	1.0532	0.9571	0.1215	0.00788
53.81	1.0569	0.9606	0.1320	0.00799
62.50	1.0611	0.9648	0.1418	0.00811
69.52	1.0644	0.9690	0.1447	0.00817
77.02	1.0675	0.9727	0.1421	0.00818
85.02	1.0704	0.9762	0.1331	0.00813
92.28	1.0729	0.9795	0.1221	0.00797
100.00	1.0750	0.9828	0.1104	0.00770

TABLE IIb.

Mixtures of Phenol and Aniline.

Weight per cent. of phenol ...	63.0	62.5	62.0	61.25	60.5	59.5
Temperature.....	20°	30°	40°	60°	80°	125°

Mixtures of phenetole and aniline were examined at several temperatures ranging from 0° to 80°. The figures obtained for the densities and viscosities are given in table III. The density-composition curves for mixtures of these substances are straight lines, the values found coinciding with those calculated. Fig. 3 contains the viscosity isotherms, the character of which, it will be seen, is altogether different from that of the corresponding curves for mixtures of phenol and aniline.

FIG. 3.

Aniline and phenetole.

TABLE III
Mixtures of Phenetole and Aniline.

Weight per cent. of phenetole.	Densities.							Viscosities.						
	0°	9.9°	20.2°	29.6°	40.0°	60.0°	80.0°	0°	9.9°	20.2°	29.6°	40.0°	60.0°	80.0°
0.00	1.0390	1.0303	1.0214	1.0134	1.0045	0.9872	0.9700	0.1005	0.0631	0.0426	0.0315	0.02405	0.01545	0.01100
11.74	1.0326	1.0239	1.0149	1.0070	0.9980	0.9809	0.9637	0.0799	0.0523	0.0364	0.0270	0.02080	0.01395	0.01013
21.75	1.0272	1.0184	1.0094	1.0014	0.9922	0.9748	0.9573	0.0655	0.0443	0.0317	0.0238	0.01865	0.01280	0.00944
32.30	1.0216	1.0128	1.0037	0.9956	0.9864	0.9688	0.9511	0.0548	0.0375	0.0275	0.02115	0.01675	0.01171	0.00877
43.68	1.0155	1.0066	0.9974	0.9893	0.9801	0.9623	0.9444	0.0451	0.0321	0.0239	0.01870	0.01500	0.01065	0.00814
54.66	1.0096	1.0007	0.9916	0.9833	0.9740	0.9560	0.9379	0.0379	0.0276	0.0210	0.01670	0.01355	0.00977	0.00758
65.69	1.0036	0.9946	0.9854	0.9771	0.9677	0.9497	0.9315	0.03205	0.02385	0.0184	0.01495	0.01225	0.00896	0.00706
76.54	0.9978	0.9888	0.9795	0.9712	0.9616	0.9434	0.9249	0.02720	0.02075	0.01630	0.01335	0.01106	0.00826	0.00659
88.49	0.9914	0.9823	0.9729	0.9644	0.9547	0.9363	0.9176	0.02265	0.01780	0.01428	0.01169	0.00982	0.00753	0.00603
100.0	0.9852	0.9760	0.9666	0.9580	0.9483	0.9298	0.9110	0.01860	0.01530	0.01240	0.01030	0.00875	0.00687	0.00558

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Tables IV and IVa contain the densities and viscosities of mixtures of phenol and *p*-toluidine for several temperatures between 40° and 175°. The densities are somewhat higher than the calculated values; consequently, the density curve is slightly concave towards the composition axis. The viscosity curves are shown in Fig. 4. Table IVb contains the composition of mixtures the viscosities of which show a maximum deviation from the calculated values, together with the corresponding temperatures. These were obtained as already described for phenol and aniline, and the small curve inset in Fig. 4 depicts the relationship between the two.

This mixture has been examined at 30° by Thole, Dunstan, and Mussell (*loc. cit.*), who found that the maximum point on the viscosity-composition curve was at 63 per cent. of phenol. According to the experiments described in this paper, the position of the maximum point on the viscosity curve corresponds with a composition of 67 per cent. of phenol, and since, in this case, the position of the maximum does not vary appreciably with the temperature, there appears to be a discrepancy of about 4 per cent. in the composition of the mixture of maximum viscosity. Independent experiments carried out in this laboratory, in which Kahlbaum's chemicals, redistilled before use, were employed, gave the following results for a temperature of 31·5°:

Weight per cent. of phenol	50·6	63·3	66·0	68·8	70·7	79·1	86·0
Viscosity	0·0846	0·0921	0·0931	0·0931	0·0926	0·0867	0·0803

These figures indicate a maximum viscosity at a point corresponding with a composition of about 67·5 per cent. of phenol, which agrees well with the value found by the author.

FIG. 4.
Phenol and p-toluidine.

TABLE IV.
Mixtures of Phenol and p-Toluidine.

Weight per cent. of phenol.	Densities.					Viscosities.				
	39.9°	59.9°	79.8°	99.9°	125°	39.9°	59.9°	79.8°	99.9°	125°
0.00	0.9703	0.9534	0.9365	0.9189	0.8962	0.02080	0.01398	0.01006	0.00776	0.00608
9.85	0.9808	0.9640	0.9470	0.9295	0.9068	0.02632	0.01649	0.01149	0.00869	0.00655
20.67	0.9913	0.9744	0.9574	0.9398	0.9172	0.03352	0.01983	0.01323	0.00969	0.00706
29.86	1.0004	0.9835	0.9665	0.9488	0.9261	0.04090	0.02283	0.01469	0.01050	0.00749
38.57	1.0087	0.9919	0.9750	0.9575	0.9348	0.0482	0.02564	0.01600	0.01123	0.00790
46.25	1.0160	0.9991	0.9820	0.9645	0.9418	0.0543	0.02810	0.01705	0.01175	0.00820
55.09	1.0239	1.0069	0.9898	0.9723	0.9495	0.06015	0.03015	0.01805	0.01226	0.00842
62.70	1.0305	1.0135	0.9965	0.9795	0.9567	0.0629	0.03115	0.01858	0.01245	0.00851
71.11	1.0372	1.0201	1.0031	0.9856	0.9628	0.0627	0.03110	0.01857	0.01240	0.00847
80.19	1.0441	1.0270	1.0099	0.9924	0.9696	0.05915	0.02990	0.01804	0.01210	0.00830
89.76	1.0512	1.0340	1.0170	0.9995	0.9766	0.0538	0.02780	0.01711	0.01171	0.00806
100.00	1.0585	1.0414	1.0243	1.0065	0.9833	0.0479	0.02520	0.01581	0.01115	0.00770

TABLE IVa.

Mixtures of Phenol and p-Toluidine.

Weight per cent. of phenol.	Densities.		Viscosities.	
	150°.	175°.	150°.	175°.
0.00	0.8734	0.8502	0.00491	0.00423
16.62	0.8898	0.8668	0.00541	0.00456
23.11	0.8961	0.8732	0.00560	0.00468
34.42	0.9069	0.8842	0.00594	0.00490
38.24	0.9105	0.8878	0.00603	0.00496
45.61	0.9172	0.8943	0.00619	0.00507
56.31	0.9264	0.9034	0.00636	0.00517
65.69	0.9341	0.9110	0.00641	0.00520
76.25	0.9421	0.9188	0.00635	0.00515
79.43	0.9443	0.9210	0.00630	0.00512
86.34	0.9491	0.9256	0.00618	0.00508
100.00	0.9572	0.9337	0.00592	0.00492

TABLE IVb.

Mixtures of Phenol and p-Toluidine.

Weight per cent. of phenol..	61.5	60.0	59.0	58.0	57.0	56.0	55.0
Temperature	39.9°	59.9°	79.8°	99.9°	125°	150°	175°

Mixtures of phenol and dimethylaniline were examined at eight temperatures between 10° and 180°. The figures obtained are given in tables V and Va. The viscosity-composition curves are given in Fig. 5. On account of the sinuous nature of these curves, the deviations from the straight line are both positive and negative, that is, some of the viscosities are greater and some less than the values calculated according to the simple mixture rule. Table Vb contains the composition of mixtures the viscosities of which show a maximum positive deviation and the corresponding temperatures. The connexion between the two is shown graphically by the curve inset in Fig. 5. The densities of these mixtures are but slightly higher than the calculated values.

TABLE Vb.

Mixtures of Phenol and Dimethylaniline.

Weight per cent. of phenol.....	87.5	84.0	82.0	80.0	78.0	76.0	73.0	71.5
Temperature	10°	20°	29.8°	40.2°	59.9°	80.0°	126.0°	177°

FIG. 5.

Phenol and dimethylaniline.

TABLE V.
Mixtures of Phenol and Dimethylaniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	10°	20°	126°	177°	10°	20°	126°	177°
0·00	0·9647	0·9564	0·8679	0·8225	0·01654	0·01387	0·00461	0·00341
9·07	0·9752	0·9670	0·8776	0·8318	0·02076	0·01684	0·00482	0·00352
17·30	0·9851	0·9768	0·8863	0·8403	0·02586	0·02045	0·00508	0·00362
23·94	0·9932	0·9849	0·8939	0·8472	0·03145	0·02415	0·00531	0·00372
33·08	1·0041	0·9959	0·9040	0·8568	0·04185	0·03085	0·00565	0·00386
40·39	1·0136	1·0053	0·9127	0·8647	0·05315	0·0377	0·00594	0·00398
48·27	1·0236	1·0150	0·9216	0·8733	0·0696	0·0470	0·00627	0·00410
55·75	1·0327	1·0243	0·9302	0·8817	0·0869	0·0564	0·00653	0·00422
62·82	1·0413	1·0330	0·9387	0·8895	0·1094	0·0675	0·00680	0·00432
69·97	1·0500	1·0416	0·9471	0·8978	0·1347	0·0801	0·00703	0·00442
78·14	1·0595	1·0512	0·9564	0·9069	0·1639	0·0940	0·00728	0·00453
85·39	1·0678	1·0595	0·9648	0·9152	0·1850	0·100	0·00745	0·00460
92·76	1·0759	1·0676	0·9734	0·9237	0·1964	0·1087	0·00761	0·00467
100·00	1·0835	1·0752	0·9815	0·9315	0·2010	0·1104	0·00770	0·00490

TABLE Va.
Mixtures of Phenol and Dimethylaniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	29.8°	40.2°	59.9°	80.0°	29.8°	40.2°	59.9°	80.0°
0.00	0.9482	0.9400	0.9234	0.9070	0.01173	0.01021	0.00799	0.00658
7.93	0.9574	0.9492	0.9325	0.9159	0.01351	0.01159	0.00878	0.00707
16.61	0.9677	0.9593	0.9425	0.9258	0.01629	0.01354	0.01001	0.00782
24.60	0.9772	0.9688	0.9520	0.9352	0.01936	0.01570	0.01123	0.00852
32.71	0.9872	0.9788	0.9619	0.9449	0.02315	0.01840	0.01267	0.00937
41.46	0.9981	0.9895	0.9724	0.9553	0.0283	0.02185	0.01428	0.01025
49.19	1.0076	0.9990	0.9818	0.9645	0.0333	0.02510	0.01587	0.01119
56.14	1.0158	1.0073	0.9899	0.9726	0.0393	0.02855	0.01760	0.01213
63.95	1.0252	1.0166	0.9991	0.9817	0.04705	0.0334	0.01960	0.01312
70.99	1.0329	1.0243	1.0069	0.9895	0.05325	0.03715	0.02100	0.01379
78.83	1.0431	1.0346	1.0171	0.9997	0.06025	0.0415	0.02270	0.01472
86.08	1.0516	1.0431	1.0256	1.0082	0.0648	0.0440	0.02380	0.01523
93.19	1.0594	1.0509	1.0335	1.0162	0.0686	0.0459	0.02665	0.01567
100.00	1.0668	1.0584	1.0414	1.0242	0.0709	0.0474	0.02530	0.01585

Phenol and diphenylamine mixtures were examined at four temperatures between 30° and 81° , and the results obtained are given in table VI. The figures in brackets for the viscosities of diphenylamine at 30° and 40° were obtained by extrapolation. Fig. 6 shows graphically the relationship between the viscosity and composition of these mixtures. The density curves in this case

FIG. 6.
Phenyl and diphenylamine.

are straight lines. A few mixtures of these two compounds have been examined at 50° by Thole, Dunstan, and Mussell (*loc. cit.*).

Mixtures of phenol and diphenylmethylaniline were examined at six temperatures between 10° and 80° , and the measurements are recorded in tables VII and VIIa. The density curves are almost straight lines, the calculated densities being slightly higher than

TABLE VI.
Mixtures of Phenol and Diphenylamine.

Weight per cent. of phenol.	Densities.				Viscosities.			
	30°	40°	61°	81°	30°	40°	61°	81°
0.0	—	—	1.0543	1.0377	(0.1357)	(0.0852)	0.0417	0.02525
7.87	1.0790	1.0711	1.0533	1.0366	0.1257	0.0795	0.0383	0.0236
15.18	1.0780	1.0700	1.0523	1.0356	0.1165	0.0743	0.0359	0.0224
23.29	1.0769	1.0689	1.0511	1.0344	0.1072	0.0693	0.0339	0.02125
30.87	1.0759	1.0678	1.0501	1.0333	0.1003	0.0652	0.03225	0.02025
38.60	1.0749	1.0668	1.0490	1.0321	0.0947	0.0620	0.03085	0.01955
46.56	1.0738	1.0656	1.0478	1.0309	0.0898	0.0591	0.0296	0.01880
53.43	1.0729	1.0647	1.0470	1.0300	0.0861	0.0568	0.02865	0.01828
59.65	1.0721	1.0639	1.0461	1.0292	0.0828	0.0551	0.0279	0.01782
68.84	1.0709	1.0626	1.0448	1.0278	0.0791	0.0528	0.02685	0.01723
76.60	1.0699	1.0616	1.0438	1.0268	0.0765	0.0513	0.0262	0.01680
84.59	1.0688	1.0605	1.0427	1.0256	0.0742	0.0498	0.02565	0.01640
92.04	1.0678	1.0595	1.0416	1.0245	0.07255	0.04845	0.0253	0.01610
100.00	1.0667	1.0584	1.0405	1.0233	0.0709	0.0474	0.0251	0.01575

the observed values. Fig. 7 shows the connexion between the viscosities and compositions of these mixtures.

FIG. 7.
Phenol and diphenylmethylaniline.

TABLE VII.

Mixtures of Phenol and Diphenylmethylaniline.

Weight per cent. of phenol.	Densities.		Viscosities.	
	9.8°	20.1°	9.8°	20.1°
0.00	1.0595	1.0515	0.1096	0.0722
4.92	1.0605	1.0523	0.1090	0.0708
9.48	1.0615	1.0532	0.1097	0.0715
17.18	1.0632	1.0548	0.1145	0.0730
27.69	1.0657	1.0572	0.1226	0.0764
36.92	1.0679	1.0593	0.1306	0.0798
48.42	1.0708	1.0621	0.1411	0.0845
56.87	1.0728	1.0641	0.1502	0.0885
67.10	1.0753	1.0665	0.1614	0.0935
78.79	1.0782	1.0693	0.1752	0.0995
89.30	1.0809	1.0720	0.1877	0.1048
100.00	1.0836	1.0750	0.2010	0.1104

TABLE VIIa.
Mixtures of Phenol and Diphenylmethylaniline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	30°	40°	60°	80°	30°	40°	60°	80°
0.00	1.0438	1.0359	1.0198	1.0040	0.0513	0.03835	0.02480	0.01735
4.98	1.0449	1.0369	1.0207	1.0048	0.0510	0.03785	0.02435	0.01708
10.21	1.0461	1.0379	1.0217	1.0058	0.0513	0.0376	0.0240	0.01682
20.04	1.0483	1.0401	1.0237	1.0076	0.0519	0.0377	0.0237	0.01650
35.34	1.0519	1.0435	1.0269	1.0104	0.0542	0.0388	0.02375	0.01624
49.87	1.0552	1.0467	1.0301	1.0136	0.0570	0.0402	0.02395	0.01603
62.12	1.0581	1.0495	1.0328	1.0164	0.0597	0.0415	0.02415	0.01594
73.58	1.0607	1.0521	1.0354	1.0188	0.0626	0.0428	0.02445	0.01589
82.22	1.0627	1.0542	1.0373	1.0206	0.0650	0.0440	0.0247	0.01585
90.05	1.0645	1.0560	1.0391	1.0223	0.0673	0.0451	0.02495	0.01586
100.00	1.0668	1.0584	1.0414	1.0242	0.0709	0.0474	0.0253	0.01585

The densities and viscosities of mixtures of phenol and quinoline were determined for eight temperatures ranging from 9.8° to 175° ,

FIG. 8.

Phenol and quinoline.

and the measurements are recorded in tables VIII and VIIIa. Fig. 8 contains the viscosity curves, and the small curve inset shows the connexion between the temperature and composition of the

TABLE VIII.
Mixtures of Phenol and Quinoline.

Weight per cent. of phenol.	Densities.				Viscosities.			
	9.8°	20.1°	125°	175°	9.8°	20.1°	125°	175°
0.00	1.1004	1.0925	1.0085	0.9673	0.04805	0.03635	0.00786	0.00547
7.54	1.1021	1.0944	1.0103	0.9687	0.0619	0.04595	0.00837	0.00564
14.56	1.1037	1.0960	1.0119	0.9698	0.0810	0.05725	0.00901	0.00588
22.73	1.1056	1.0977	1.0133	0.9707	0.1170	0.0785	0.00988	0.00622
29.76	1.1071	1.0992	1.0140	0.9705	0.1677	0.1058	0.01064	0.00642
37.52	1.1078	1.0999	1.0139	0.9696	0.2644	0.1503	0.01121	0.00650
45.08	1.1074	1.0994	1.0127	0.9678	0.3750	0.2031	0.01155	0.00652
53.20	1.1057	1.0977	1.0099	0.9643	0.5065	0.2452	0.01158	0.00649
60.30	1.1030	1.0950	1.0065	0.9602	0.5259	0.2529	0.01119	0.00632
68.21	1.0994	1.0914	1.0021	0.9550	0.4740	0.2327	0.01055	0.00606
76.88	1.0950	1.0869	0.9969	0.9492	0.3836	0.1941	0.00969	0.00570
83.37	1.0916	1.0835	0.9927	0.9445	0.3156	0.1660	0.00918	0.00542
92.06	1.0875	1.0791	0.9876	0.9389	0.2420	0.1337	0.00837	0.00513
100.00	1.0836	1.0750	0.9828	0.9337	0.2010	0.1104	0.00770	0.00492

TABLE VIIIa.
Mixtures of Quinoline and Phenol.

Weight per cent. of phenol.	Densities.				Viscosities.			
	29.9°	40°	60°	80°	29.9°	40°	60°	80°
0.00	1.0851	1.0773	1.0615	1.0458	0.02943	0.02384	0.01671	0.01250
7.77	1.0870	1.0792	1.0635	1.0478	0.03645	0.02885	0.01950	0.01424
14.92	1.0886	1.0808	1.0651	1.0494	0.04495	0.03455	0.02245	0.01603
21.96	1.0904	1.0823	1.0666	1.0509	0.05605	0.04195	0.02615	0.01809
29.82	1.0917	1.0838	1.0679	1.0518	0.07425	0.05335	0.03120	0.02071
37.14	1.0924	1.0843	1.0682	1.0521	0.0965	0.0660	0.03645	0.02308
44.62	1.0917	1.0837	1.0675	1.0514	0.1221	0.0795	0.0410	0.02520
52.31	1.0901	1.0820	1.0658	1.0496	0.1436	0.0887	0.0436	0.02610
59.89	1.0874	1.0793	1.0629	1.0465	0.1480	0.0904	0.0440	0.02582
67.92	1.0837	1.0755	1.0590	1.0425	0.1344	0.0839	0.0410	0.02415
75.75	1.0795	1.0713	1.0548	1.0382	0.1177	0.0748	0.0371	0.02232
83.49	1.0756	1.0672	1.0503	1.0335	0.1010	0.0656	0.03315	0.02028
91.79	1.0711	1.0628	1.0458	1.0288	0.0844	0.05525	0.02875	0.01786
100.00	1.0668	1.0584	1.0414	1.0242	0.0709	0.0476	0.0252	0.01580

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mixture which has a viscosity deviating to the greatest extent from the calculated value. The data from which this curve is drawn were obtained from the viscosity curves as previously indicated, and these are enumerated in the following table:

TABLE VIII*b*.*Mixtures of Phenol and Quinoline.*

Weight per cent. of								
phenol.....	58.0	57.0	56.0	55.5	54.0	53.0	50.5	48.0
Temperature	9.8°	20.1°	29.9°	40.0°	60.0°	80.0°	125°	175°

The broken line curve in Fig. 8 is the density curve for 20.1°. Unlike all the other mixtures described in this paper, the density-composition curve for mixtures of phenol and quinoline has a very pronounced maximum. Moreover, this maximum does not become less marked with rise in temperature; the density curves for the other temperatures run very approximately parallel to the one shown in the figure.

Mixtures of phenol and pyridine were examined at seven temperatures ranging from 10° to 110°, and the results are set out in tables IX and IX*a*. In Fig. 9 are given the viscosity curves. The scale of viscosities for the three highest temperatures, 60°, 80°, and 110°, is considerably extended in order to bring out more clearly the character of the curves. Inset in Fig. 9 is the curve connecting temperature with the composition of the mixture which shows a maximum positive deviation in viscosity. Data for the construction of this curve are given in table IX*b*.

TABLE IX*b*.*Mixtures of Phenol and Pyridine.*

Weight per cent. of phenol ..	93.0	88.0	84.5	82.0	77.0	73.5	70.0
Temperature	10°	20°	30°	40°	60°	80°	110°

The densities of mixtures of these two substances show a considerable deviation from the calculated values; this is especially so with those mixtures containing a greater proportion of phenol. The broken line curve shows the connexion between density and composition for one temperature, namely, 20°. The density curves for all the other temperatures run closely parallel to this.

FIG. 9.

Phenol and pyridine.

TABLE IX.
Mixtures of Phenol and Pyridine.

Weight per cent. of phenol	Densities.						Viscosities.					
	20°	30°	40°	60°	80°	110°	20°	30°	40°	60°	80°	110°
0.00	0.9819	0.9723	0.9627	0.9424	0.9218	0.8900	0.00941	0.00821	0.00714	0.00578	0.00487	0.00385
8.30	0.9916	0.9820	0.9724	0.9524	0.9324	0.9014	0.01109	0.00940	0.00828	0.00656	0.00544	0.00428
16.12	1.0005	0.9909	0.9814	0.9620	0.9428	0.9119	0.01321	0.01106	0.00965	0.00753	0.00614	0.00475
24.36	1.0096	1.0002	0.9909	0.9720	0.9532	0.9234	0.01597	0.01339	0.01152	0.00879	0.00713	0.00535
32.58	1.0187	1.0096	1.0005	0.9821	0.9639	0.9347	0.02010	0.01634	0.01389	0.01032	0.00815	0.00606
38.94	1.0258	1.0167	1.0077	0.9897	0.9718	0.9430	0.02411	0.01963	0.01631	0.01198	0.00934	0.00669
47.13	1.0349	1.0260	1.0173	0.9995	0.9821	0.9535	0.03215	0.02515	0.02042	0.01436	0.01077	0.00751
54.96	1.0429	1.0343	1.0257	1.0083	0.9910	0.9626	0.0437	0.03245	0.02560	0.01727	0.01263	0.00841
63.81	1.0514	1.0426	1.0341	1.0168	0.9995	0.9719	0.05945	0.0429	0.03245	0.02065	0.01446	0.00935
70.49	1.0568	1.0482	1.0397	1.0226	1.0053	0.9779	0.0748	0.0517	0.0380	0.0230	0.01580	0.00988
77.94	1.0620	1.0534	1.0449	1.0279	1.0107	0.9833	0.0907	0.0604	0.04305	0.0250	0.01655	0.01013
85.17	1.0668	1.0583	1.0498	1.0327	1.0155	0.9878	0.1004	0.06625	0.0459	0.0259	0.01670	0.01012
92.45	1.0710	1.0625	1.0540	1.0369	1.0198	0.9923	0.1072	0.06915	0.04705	0.0259	0.01650	0.00985
100.00	1.0752	1.0668	1.0584	1.0414	1.0242	0.9967	0.1104	0.0709	0.0474	0.0252	0.01580	0.00941

TABLE IXa.

Mixtures of Phenol and Pyridine.

Weight per cent. of phenol	Density at 10°	Viscosity at 10°	Weight per cent. of phenol.	Density at 10°	Viscosity at 10°
0.00	0.9916	0.01108	58.46	1.0544	0.0680
17.26	1.0101	0.01594	66.99	1.0618	0.0988
26.01	1.0196	0.02050	76.81	1.0700	0.1416
35.14	1.0294	0.02675	82.86	1.0742	0.1644
45.48	1.0412	0.0376	91.89	1.0787	0.1880
51.89	1.0479	0.0505	100.00	1.0836	0.2010

Tables X and Xa contain a record of densities and viscosities of mixtures of phenol and acetone for five temperatures ranging from 9.95° to 49.8°. The viscosity curves are given in Fig. 10. The densities of these mixtures are almost the same as those calculated; the density curves are almost straight lines.

TABLE X.

Mixtures of Phenol and Acetone.

Weight per cent. of phenol.	Densities.		Viscosities.	
	9.95°	20.05°	9.95°	20.05°
0.00	0.8031	0.7912	0.00360	0.00323
14.19	0.8425	0.8315	0.00486	0.00429
26.72	0.8768	0.8662	0.00635	0.00560
38.06	0.9085	0.8983	0.00868	0.00755
49.43	0.9406	0.9308	0.01256	0.01055
57.79	0.9642	0.9547	0.01688	0.01379
65.22	0.9851	0.9757	0.02358	0.01853
73.74	1.0090	0.9998	0.03670	0.02750
78.94	1.0237	1.0146	0.0495	0.0359
85.39	1.0420	1.0334	0.0748	0.0497
92.85	1.0623	1.0538	0.1193	0.0730
100.00	1.0836	1.0752	0.2010	0.1104

TABLE Xa.

Mixtures of Phenol and Acetone.

Weight per cent. of phenol	Densities.			Viscosities		
	29.8°	40.1°	49.8°	29.8°	40.1°	49.8°
0.00	0.7799	0.7676	0.7559	0.00295	0.00270	0.00248
9.57	0.8056	0.7940	0.7830	0.00360	0.00328	0.00299
19.53	0.8336	0.8223	0.8116	0.00441	0.00399	0.00360
27.70	0.8572	0.8460	0.8335	0.00521	0.00470	0.00422
37.42	0.8855	0.8743	0.8636	0.00670	0.00590	0.00530
44.67	0.9063	0.8952	0.8846	0.00808	0.00711	0.00628
53.79	0.9330	0.9220	0.9115	0.01058	0.00904	0.00794
60.24	0.9520	0.9416	0.9316	0.01319	0.01101	0.00950
67.19	0.9724	0.9625	0.9530	0.01658	0.01363	0.01150
74.25	0.9935	0.9837	0.9733	0.02180	0.01741	0.01425
80.76	1.0115	1.0022	0.9933	0.02910	0.02230	0.01785
87.98	1.0327	1.0237	1.0150	0.03915	0.02875	0.02245
92.81	1.0466	1.0378	1.0293	0.04905	0.03465	0.02615
100.00	1.0668	1.0584	1.0503	0.07100	0.0474	0.0328

FIG. 10.
Phenol and acetone.

Discussion of Results.

A general survey of the work described in the foregoing pages leads to the following general conclusions:

- (1) When a substance, such as phenol, which, in the liquid state,

consists largely of associated molecules, is mixed with another indifferent substance, such as benzene, chlorobenzene, or nitrobenzene, the viscosity of the mixture is considerably lower than that calculated according to the simple mixture rule. The viscosity-composition curve shows a very marked curvature, convex towards the axis of composition.

(2) When the formation of a compound takes place, as, for example, when phenol is mixed with such bases as aniline, *p*-toluidine, and quinoline, the viscosity of the mixture is, in general, higher than that calculated by the simple mixture rule. The viscosity-composition curve is concave towards the composition axis. That the high viscosity of these mixtures is caused by the acidic nature of phenol is shown clearly by displacing the hydroxyl hydrogen by an alkyl group, thus obtaining a neutral substance, phenetole, for example, which, with aniline, yields mixtures the viscosity curves of which are convex towards the axis of composition.

(3) The position of the maximum point on the viscosity curves generally varies with the temperature, and can, therefore, give little indication as to the composition of any compound that might be present. Further, in every case described in this paper, where there is a positive deviation, the composition of the mixture the viscosity of which shows a maximum positive deviation depends on the temperature at which the viscosities are measured; the nature of the relationship between these two quantities is indicated by the small curves inset in the various figures. This is altogether different from what Denison found. On examining these small curves, it will be seen that they are all convex towards the composition axis; they lie entirely on one side of the ordinate representing molecular proportions, and, if produced in the direction of higher temperatures, they would approach this ordinate asymptotically. These peculiarities are, in all probability, the result of an unequal thermal dissociation of the molecular complexes of phenol and of the compound formed, the opposing influence of these two kinds of molecular complexes being altered in favour of the compound. This is well illustrated by the mixtures of pyridine and phenol. At 10°, only a very small portion of the viscosity curve is concave towards the axis of composition. This curve resembles very closely the one for phenol and benzene, and, were it not for the slight inflexion near that end of the curve where the mixtures are rich in phenol, it might be taken as a typical case of a mixture of two indifferent substances, one of which contained associated molecules. Several unsuccessful attempts were made to measure the viscosity of phenol at 0° with the object of ascertaining whether the inflexion

of the viscosity curve would disappear at this temperature. With rise in temperature the part of the curve which is concave towards the composition axis becomes more pronounced, and above 40° a well defined maximum appears. The viscosity curve for this mixture at 10° has only about 15 per cent. of its length above the straight line joining the viscosities of the pure components, whereas at 110° there is only about the same proportion below the corresponding straight line. At the lower temperatures, the effect of the associated phenol molecules on the viscosity is predominant, whilst at the higher temperatures the influence of the pyridine-phenol complexes is more assertive. The development of a maximum on the viscosity curve of a mixture with rise in temperature appears to be rather unusual. Faust found the opposite effect with mixtures of ether and acetone.

The difference between the viscosity curves for mixtures of phenol with aniline and dimethylaniline may be accounted for by the weaker basic nature of the latter.

As regards the viscosity curves for mixtures of phenol with diphenylamine and diphenylmethylaniline, it will be noticed that in neither case do the curves fall as far below the straight line joining the viscosities of the pure components as is the case for mixtures of phenol and benzene. Since there is no reason to suppose that either diphenylamine or diphenylmethylaniline has a weaker dissociating action on the associated phenol molecules than has benzene, the smaller curvature of the viscosity curves for mixtures of phenol and these two very weak bases may be the result of the counteracting influence of compound-formation.

The viscosity curves for mixtures of phenol and acetone, unlike those of phenol and pyridine, show no change in character with rise in temperature. The associated phenol molecules are predominant throughout. It should be borne in mind, however, that the range of temperature over which this mixture has been examined is relatively small, and although, as has been shown by Schmidlin and Lang (*Ber.*, 1910, **43**, 2812), compound-formation certainly takes place, the amount of compound formed is undoubtedly much smaller than in the phenol-pyridine mixtures at the same temperatures.

A number of experiments on the influence of pressure on the viscosity of liquids have been made by Warburg and Sachs (*Ann. Physik.*, 1884, [iii], **22**, 518) and Cohen (*ibid.*, 1892, [iii], **45**, 666), who found that increase in pressure generally causes an increase in viscosity. This increase in viscosity may not be the direct result of the increase in pressure, but of the decrease in volume resulting from the latter. Cohen found that the change in viscosity is not

proportional to the increase in pressure. Bogojawlenski and Tammann (*Zeitsch. physikal. Chem.*, 1898, **27**, 457) investigated the relative effect of pressure on the viscosity and specific volume of water at 0°, and found that they are not proportional. That influences besides mere volume changes play a far more important part in determining the viscosity of a liquid is shown in a most striking manner by the results obtained in this investigation. In every case studied, the density-composition curves for the different temperatures run very nearly parallel; in no case is this so with the viscosity curves. A reference to the mixtures of phenol with quinoline and pyridine will illustrate this. The former of these two mixtures has a marked maximum on the density curves. The maximum increase in density, or the greatest contraction in volume produced by mixing, takes place at all temperatures when the mixture contains about 47 per cent. of phenol, and, further, the amount of this contraction is very approximately the same for every temperature studied. A glance at the viscosity curves in Fig. 8 will show how different these are. In the phenol-pyridine mixtures there is a maximum contraction in volume at 59 to 60 per cent. of phenol. In this case also, both the composition of the mixture which shows maximum contraction and the extent of this contraction are almost independent of temperature. Nothing could be more different than the viscosity curves for this mixture; not only is there a lack of parallelism, but they change in character from one extreme to the other with rise in temperature. If contraction in volume, resulting from whatever cause, were the dominant factor in increasing the viscosity, at least some approach to a proportional relative increase in viscosity and volume-contraction might be expected. Experiment shows that this is not the case.

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THE IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
SOUTH KENSINGTON,
LONDON, S.W.

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