LV.—*The Effect of Intensive Drying on Certain Physical Properties of Benzene.*

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It is now usual to discuss the experimental data of the intensive drying of liquids in terms of hypotheses postulating that a chemically pure liquid is a system of two or more components in equilibrium, the equilibrium in the "wet" liquid being so mobile that the system behaves as if one component only were present. That these components consist of molecules or molecular aggregates differing in size and behaving in certain circumstances as individual molecular species was originally suggested by Baker and Baker (J., 1907, **91**, 1862; 1912, **101**, 2339) and appears to be accepted by others who have propounded explanatory hypotheses (*e.g.*, Smits, *Z. physikal. Chem.*, 1922, **100**, 477; "Theory of Allotropy," 1922, p. 319; J., 1926, 2655; G. N. Lewis, *J. Amer. Chem. Soc.*, 1923, **45**, 2836; Mali, *Phil. Mag.*, 1928, **5**, 609).

The basis for this view lay in the changes, apparently far greater than any conceivable experimental error, observed in the boiling point, vapour pressure, and surface tension of liquids sealed up with phosphoric oxide in glass apparatus.

Subsequently the changes which might be brought about by intensive drying were summarised by Smits (*loc. cit.*) as the fixing of a specific proportion between the components after the normal equilibrium had either not been displaced or had been shifted in one or other of the two possible directions. Later work, mainly by the same author, has been directed towards realising these theoretical conclusions in practice, and the criteria adopted have been measurements of vapour pressure. Some three years ago, when the work here described was under contemplation, the available evidence suggested the probability that a considerable movement in the equilibrium preceded its fixation (Baker, J., 1922, **121**, 563), and the authors then felt and still feel it to be inconceivable that any considerable molecular association or dissociation could occur in a liquid without causing readily measurable changes in density as well as in surface tension. Surface-tension changes had already been observed (Baker, *loc. cit.*) in statically dried bromine, benzene, and hexane, which could be held to imply increases in the mean molecular weight of 49, 165, and 244%, respectively, but in spite of these indications of extensive association no change was found in the density of benzene, carbon tetrachloride, carbon disulphide, ether, bromine, sulphur dioxide, or nitrogen tetroxide after intensive drying, although the dilatometric method used should have sufficed to show changes as small as 1 part in 10,000 parts. This serious discrepancy between density and surface-tension data is still unexplained, although certain doubts have recently been thrown by Smits (J., 1928, 2399) on the validity of Baker's surface-tension measurements. The present investigation was begun with the express purpose of measuring from time to time the density and surface tension of pure benzene during the progress of its drying with phosphoric oxide. Some of the pieces of apparatus used were designed so that these measurements could be made on the liquid as a whole or on a head, middle, or tail fraction of it. The results of the first experiment led to an extension of the inquiry in two directions, *viz.*, (i) the effect of contact between the liquid and the drying agent, and (ii) the effect of the mode of preparation of phosphoric oxide. To facilitate the drying process, the volume of each piece of apparatus was kept as small as possible, the quantity of phosphoric oxide was made relatively large, and in most cases the liquid was continuously circulated by evaporation and condensation. Surface tensions were measured by the method of capillary rise, and densities by means of glass floats as previously described (Robinson and Smith, J., 1926, 1273).

EXPERIMENTAL.

Materials.—After some preliminary experiments with ether, benzene was selected as a suitable liquid, because it has less tendency to react chemically with either phosphoric oxide or metaphosphoric acid than any other material at once so accessible and so easily purified. The stock benzene used for all the experiments described below was prepared from A.R. material supplied by British Drug Houses; this was freed from thiophen by repeated treatment with sulphuric acid, washed several times with caustic soda solution and water, dried for some months over calcium chloride, and finally twice fractionally distilled from fresh calcium chloride through an 18-inch glass-spiral column.

Phosphoric oxide was prepared by redistilling good quality oxide in an apparatus * in which the distillation could take place at temperatures up to 600° in an atmosphere of either air or oxygen, and the product could be collected and sealed up in tubes 1″ × 9″ without coming in contact with undried air.

Preparation of Apparatus.—After being carefully tested for air leaks, each piece of glass-ware was steeped in chromic–nitric acid mixture, thoroughly washed with water, and then successively

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* This apparatus was specially constructed by Mr. T. W. Parker, B.Sc., and one of us (P. L. R.), and will be described in a subsequent communication.

with alcohol and ether, and dried at 150° in an electrically heated oven. Immediately before use, the apparatus was finally dried by 7 days' heating at 400° in a large electrically heated oven of special design, while there passed through it a slow current of clean air dried by passing first through concentrated sulphuric acid in two Drechsel bottles and an inclined tube 3 feet long, and finally through a 5-foot tube packed with phosphoric oxide and glass wool.

The capillaries used for surface-tension measurements were specially drawn for us from Pyrex glass. All the capillaries were specially selected for circularity of cross section and uniformity of bore, the former by examination with a microscope, and the latter by measurement of the length of a thread of pure dry mercury in overlapping positions after the tubes had been cleaned in the manner described above. Lengths of suitable uniformity were cut from the tested sticks, and the radii determined by the two-thread method (Harkins, *J. Amer. Chem. Soc.*, 1919, **41**, 499). All lengths were measured with a travelling microscope (made by the Cambridge Scientific Instrument Co.) reading directly to 0·01 mm. and by estimation to 0·002 mm., and the weighings were made with calibrated weights and have an error not exceeding 0·02 mg. The capillary rises were measured with a special cathetometer reading to 0·02 mm. and made by the same firm. As single tubes were used in all cases, no great absolute accuracy is claimed for the surface-tension measurements, because the level of the liquid outside the capillary cannot be measured with the same accuracy as that of the liquid within it (see Mills and Robinson, J., 1927, 1823), but by taking as the outer level that part of the larger meniscus which could be very sharply focussed, comparative results consistent to within ± 0·05 dyne/cm. could be readily obtained. All measurements were taken on a falling thread and were continued until the required degree of constancy with time was attained.

The floats were made from Durosil tubing of suitable bore and wall thickness, and were kept as short as possible so that they could be used in small volumes of liquid. They were calibrated either in " stock " benzene before introduction to the apparatus or in the liquid to be dried immediately after sealing up. It was found that floats of this character change in density if maintained at 400° for long periods (probably owing to slight yielding of the glass under pressure), hence only those not treated in this manner could be calibrated before sealing up in the apparatus. The flotation temperatures recorded are in each case the mean of not less than eight individual readings, and are corrected for stem exposure.

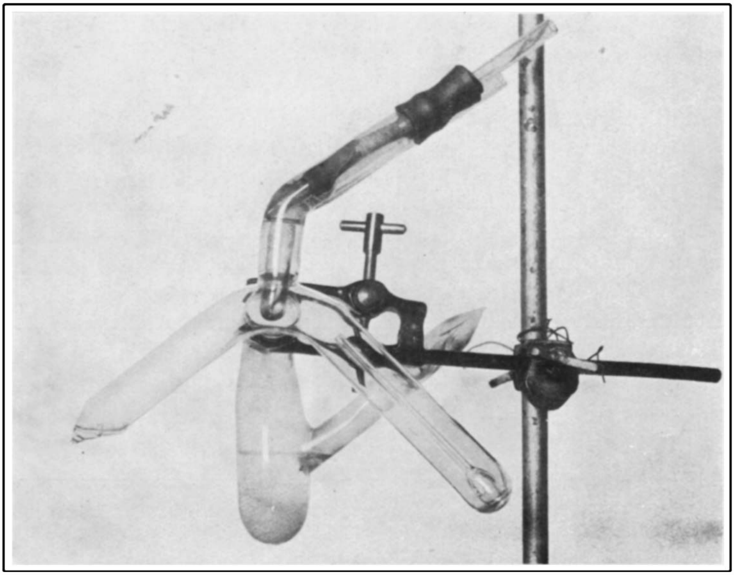

PLATE I.

[*To face p.* 370.]

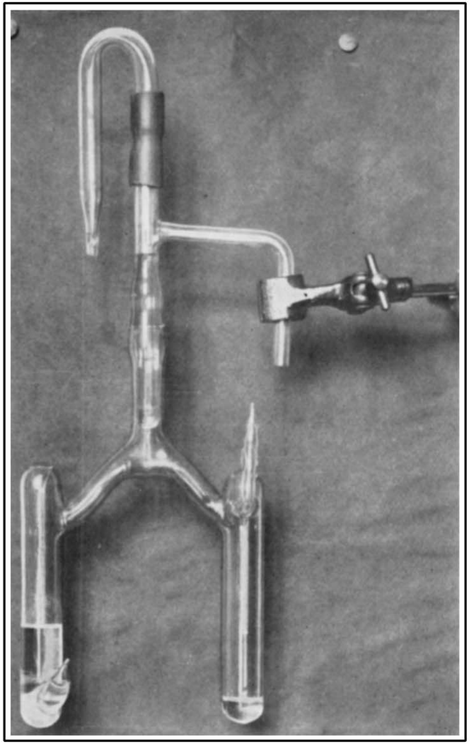

PLATE II.

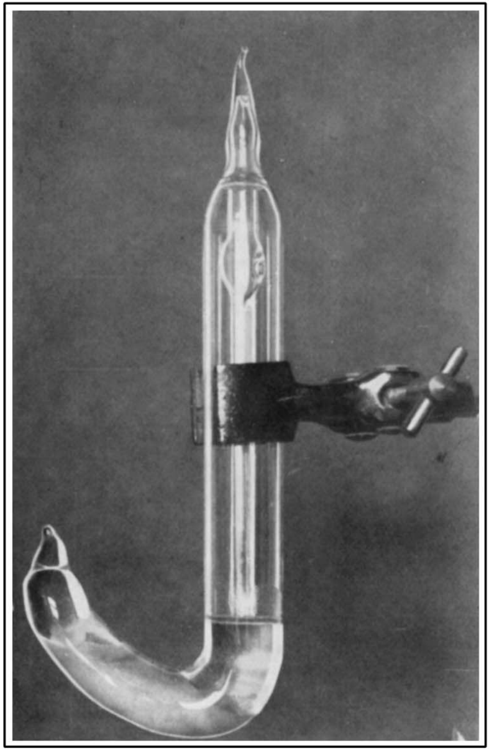

PLATE III.

Experiment I.—This apparatus (Fig. 1; Plate I) was of Pyrex glass freed from capillaries by the method of Smits (J., 1926, 2658), special care being taken that the portion *A* was as cylindrical and as free from optical distortion as possible. It consisted essentially of three limbs, *A*, *B*, and *C*, meeting at the internal condenser *D* which, by a suitable inclination of the apparatus, could deliver condensate into any desired limb. To the bottom of *A* was fused the perforated conical base piece carrying the capillary, as illustrated in Fig. 1 (i), and the two floats were placed in *B*, after which *E* was drawn down to a fine capillary. The end of *G* was closed and the apparatus placed in the heater (represented by the broken lines), leaving the ends of *H* and *E* protruding as inlet and outlet respectively for the current of dry air.

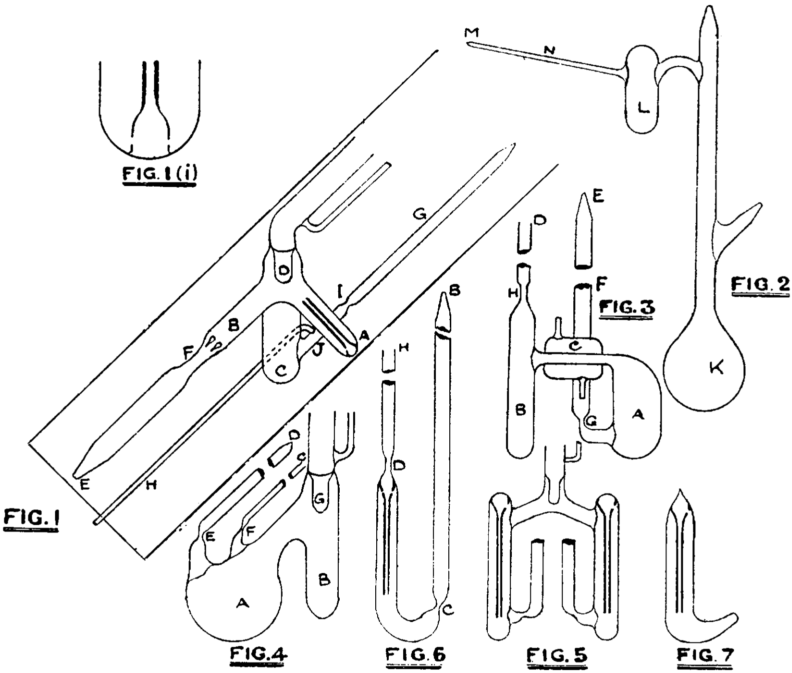

FIG. 1 (i)

FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 6

FIG. 5

FIG. 7

After the final heating already described, the apparatus was allowed to cool with a slightly increased air stream, and then the floats were slid into position and *E* was sealed off at *F*. Finally *G* was opened, by cracking off the taper portion, and fitted with a 3-inch extension of stiff rubber tubing of the same diameter into which was quickly thrust a tube containing distilled phosphoric oxide, the tapered end of which had been smashed the instant previously by means of a pair of pliers. The oxide, which had been distilled in oxygen at a red heat, was shaken as a non-adherent powder down *G* into *C*, and *G* was sealed off at *I*. During this operation a positive pressure of dry air was maintained in the apparatus. Stock benzene, dried for a month over redistilled phosphoric oxide in the evacuated apparatus shown in Fig. 2, was distilled from *K* to *L*, the tip *M* was broken, and the required quantity of liquid was poured down *H* (Fig. 1) immediately after the removal of the tube delivering air. Then the benzene in *C* was gradually cooled while the apparatus was thoroughly evacuated through *H* and sealed off at *J*.

The data for the capillary tube, which was normally used between the 4- and 5-cm. positions, and the float calibrations are given in Table I, the densities of benzene found by Tyrer (J., 1914, **105**, 2540) being employed.

TABLE I.

Uniformity of Capillary.

Approx. position.	Length of thread, mm.	Approx. position.	Length of thread, mm.	Approx. position.	Length of thread, mm.
7·5	17·935	5·0	17·940	2·0	17·935
7·0	17·930	4·0	17·960	1·0	17·910
6·0	17·910	3·0	17·950	0·0 (bottom)	17·915

Mean radius of capillary : 0·215 mm.

Calibration of Floats.

	Flotation temp.	Density at flotation temp.
I	20·283°	0·878635
II	11·695	0·887927

Within a short time of filling, the whole of the benzene was distilled into *B* and the flotation temperature of each float was carefully determined. In calculating the density from the flotation temperature it was assumed that the benzene was still of normal density. Subsequently the liquid was transferred to *A* and the capillary rise of the liquid as a whole was determined. Periodically densities and surface tensions of various fractions were measured, with the results recorded in Tables II and III respectively. During most of the intervals between readings the apparatus was tilted so that the liquid refluxed from the phosphoric oxide. Generally the difference between the temperature of the laboratory and that of the water supply sufficed to maintain a steady movement of material, and when, as occasionally happened in summer, the water was too warm, evaporation was assisted by the heat from a carbon filament lamp.

TABLE II.

(t = Flotation temperature; d = density.)

	Tail fraction.		Head fraction.		Whole.	
Date.	*t.*	*d.*	*t.*	*d.*	*t.*	*d.*
July 4/27					11·695° 20·283	0·87894
6					11·684 20·278	0·87894
8			(11·684°) 20·267	0·87892	(11·684) 20·274	0·87894
11					(11·684) 20·267	0·87892
27			(11·677) 20·264	0·87892		
28	(11·627°) 20·281	0·87894				
Aug. 15			(11·677) 20·266	0·87892		
17	(11·677) 20·288	0·87895				
Oct. 30			(11·669) 20·248	0·87890		
31	(11·669) 20·265	0·87892				
Jan. 23/28					11·669 (20·260)	0·87892
May 2			(11·669) 20·248	0·87890		
3					(11·667) 20·253	0·87891
4					(20·253) 11·666	0·87891
11	(11·669) 20·256	0·87891				
14	11·664 (20·256)	0·87891				
Oct. 29					(11·664) 20·258	0·87891

N.B.—The flotation temperatures in parentheses were determined by estimation, not experimentally.

TABLE III.

(h = Capillary rise; γ = surface tension.)

	Tail fraction.		Head fraction.		Whole.	
Date.	*h.*	γ.	*h.*	γ.	*h.*	γ.
July 6/27					30·96	28·7
11					30·64	28·4
27			30·49	28·3		
28	30·51	28·3				
Aug. 15			30·64	28·4		
17	30·60	28·4				
Oct. 30			30·58	28·4		
31	30·40	28·2				
Jan. 23/28					30·59	28·4
April 27			30·48	28·3		
May 3					30·58	28·4
14	30·52	28·3				
Oct. 27					30·60	28·4

Experiment II.—Two cylindrical vessels, *A* and *B* (Fig. 3), were joined by a horizontal tube with a water-jacket *C*, all made of capillary-free Pyrex glass, and a float of suitable density was introduced into *B*. After the heating at 400° for 7 days, with a slow current of dry air passing in at *D* and out through the fine jet *E*, the apparatus was allowed to cool, phosphoric oxide which had been distilled in oxygen at red heat was introduced through the wide tube *F* in the same expeditious manner as described in Exp. I, and *F* was removed by sealing off at *G*. About 10 c.c. of stock benzene, not previously dried with phosphoric oxide, were poured into the apparatus through *D*. For this purpose the tube carrying air was removed and, after the liquid had been poured in, was replaced by the tube from the pump, the interval during which the tube *D* was open to air being made as small as possible. The liquid was cooled and the apparatus evacuated with the Hyvac pump and finally sealed off at *H*. The flotation temperature (*t*) of the float was accurately determined as soon as possible, and further readings were made from time to time. During some of the intervals the liquid was refluxed from the phosphoric oxide, whilst in others it stood in either *B* or *A*. As only one float was used, the results (Table IV) are not converted to densities.

TABLE IV.

Date ...	July 19, 1927.	July 27.	Aug. 17.	Jan. 23, 1928.	May 2.	Oct. 30.
t	16·556° (calibration)	16·481°	16·607°	16·606°	16·520°	16·575°

Experiment III.—In this apparatus (Fig. 4), also of capillary-free Pyrex glass, a large chamber *A* led into a narrow float vessel *B*, so that density measurements could be made on a small volume of liquid and a larger proportion of phosphoric oxide could be used. The usual heating at 400° was conducted with the air current entering at *C* and emerging at *D*. In this case, before the addition of phosphoric oxide, which had been distilled at 450—500° in oxygen, the two floats which had been previously calibrated in " stock " benzene were introduced into *D* and slid over into *B*. Afterwards, *D* was sealed off at *E*, 8 c.c. of stock benzene were introduced through *C*, the liquid was cooled, and the apparatus evacuated and sealed off at *F*. The quantity of oxide was such that when the whole of the benzene was in *A* no liquid was visible. From time to time density measurements were made on the whole of the liquid (Table V), and in the intervals the liquid was sometimes refluxed from the phosphoric oxide by means of the internal condenser *G* or allowed to stand in either *A* or *B*. The pre-sealing calibration of the floats gave 19·957° and 14·544°, corresponding respectively to densities 0·878988 and 0·884853 at these temperatures.

TABLE V.

Date.	Flotation temps.		d.	Date.	Flotation temps.		d.
—	14·544°	19·957°	0·87894 (calibration)	Oct. 25	14·687°	20·090°	0·87909
1927.				1928.			
Oct. 17	14·605	20·057	0·87905	Jan. 26		20·102	0·87910
18	14·650	20·075	0·87907	May 2		20·106	0·87911
21	14·655	20·069	0·87906	Oct. 29		20·105	0·87911

Experiment IV.—This apparatus (Fig. 5) consisted essentially of two cylindrical vessels, with sealed-in capillary tubes cut from the same stick and of very nearly uniform diameter (0·460 mm.). The connecting tube carried an internal condenser (see Plate II) which could be used for delivering condensate into either capillary vessel. After the usual drying, the apparatus was charged with phosphoric oxide (distilled at red heat in a current of oxygen) and with 20 c.c. of benzene as already described. This benzene had been sealed up with phosphoric oxide in the vessel (Fig. 2) since part of it had been used in Experiment I. Surface-tension measurements were made with the liquid both in contact with and out of contact with phosphoric oxide (Table VI).

TABLE VI.

	Liquid in contact with P_4O_{10}.		Liquid not in contact with P_4O_{10}.	
Date.	h.	γ.	h.	γ.
(Calibration)			28·90	28·7
Feb. 3/28	29·20	29·0	29·32	29·1
24	29·20	29·0		
April 26	29·34	29·1		
May 14	29·20	29·0		
July 6	29·23	29·0		
Oct. 4	28·96	28·7		
27	29·14	28·9		

Experiment V.—This apparatus was of soft glass and had the form illustrated in Fig. 6. The air used during drying passed in at *H* and out at *B*. It was charged through *B* with phosphoric oxide (distilled at 500° in oxygen), sealed off at *C* and the stock benzene added through *H*, which after cooling and evacuation was sealed off at *D*. The quantities were arranged to give a layer of liquid into which the end of the capillary ($r = 0·213$ mm.) dipped just overlying the phosphoric oxide as illustrated in Fig. 7 (Plate III). Before surface tension readings were taken, the liquid was invariably allowed to pass twice or thrice up and down the capillary tube by tilting the apparatus so as to ensure wetting of the capillary walls. The results are given in Table VII.

TABLE VII.

Date.	*h*.	γ.	Date.	*h*.	γ.
Feb. 11/28	31·90	28·3	May 14	31·90	28·3
13	31·78	28·2	July 6	32·02	28·5
April 25	32·12	28·5	Oct. 4	31·94	28·3
May 1	32·02	28·5	27	32·10	28·5
2	32·01	28·5			

Experiment VI.—The apparatus, of soft glass, was identical with that used in Expt. V, but in this case it was not dried at 400° and the phosphoric oxide used was commercial oxide, free from lower oxides but not distilled, the method of charging being by dropping plugs of the oxide, compressed in a glass tube, into the apparatus without the use of a counter-current of dry air. Stock benzene was used, and the radius of the capillary was 0·206 mm. Results are given in Table VIII.

TABLE VIII.

Date.	*h*.	γ.	Date.	*h*.	γ.
Feb. 14/28	31·34	28·7	July 6	31·41	28·7
April 25	31·24	28·6	Oct. 4	31·38	28·7
May 2	31·42	28·7	27	31·53	28·7
14	31·44	28·7			

Discussion of Results.

The mean densities of the head and tail fractions of the benzene in Expt. I, comprising in each case about one-third of the volume of the liquid, are 0·87892 and 0·87893 respectively, whilst that of the whole material is 0·87893. During the 16 months of contact with phosphoric oxide, these portions show a fall in density of 0·00002, 0·00003, and 0·00003, respectively. The capillary rises for head and tail portions show only very slight changes in surface tension over the period, but for the liquid as a whole a fall of 0·30 unit is observed, occurring almost entirely in the first few days. The flotation temperatures obtained in Expt. II may indicate density changes of the order of 0·00007, but nevertheless show that these changes are but temporary, the liquid regaining its original density. Expt. III indicates that an increase in density of the order of 0·0001 may take place in ordinarily dry benzene immediately after it has been brought into contact with phosphoric oxide. Subsequently a steady increase amounting to 0·00005 over the total period of drying is recorded, which is comparatively small and is, strangely enough, opposite in sense to the corresponding change in Expt. I. Expt. IV was set up to test whether the surface tension of benzene was affected by contact with a surface of phosphoric oxide in the manner described by Baker (J., 1927, 949) for other catalysts, whilst Expt. VI carried on the same inquiry in a rather similar manner in an apparatus of soft glass with benzene which had not been subjected to a treatment with phosphoric oxide. Neither these nor Expt. V, which differed somewhat from them, gave indication of significant change in surface tension at the date of the last observation (Oct. 1928).

The changes in density now recorded do not exceed about 5—7 parts in 100,000 parts, and thus support Baker's previous conclusion (*loc. cit.*) that intensively dried benzene does not change in density by 1 part in 10,000 parts. This conclusion has now been extended, however, to include not only the liquid as a whole, but also the various fractions obtainable from it by distillation. When first brought into contact with phosphoric oxide, benzene increases in density by about 1 part in 8,000 parts: the view that this is due to dissolution of the oxide is supported by the observation that the evaporation of benzene in contact with phosphoric oxide invariably left white striæ of residue which could be removed by repeated washing with distilled benzene.

The unexpected discordance between the present surface-tension measurements and those previously recorded by Baker is disconcerting and difficult to explain. In 16 months, under conditions designed in every way to facilitate drying, the maximum observed change in capillary rise is 0·4 mm., and that in the direction of a *decrease* in surface tension, whereas the *increase* in surface tension recorded by Baker after a year's drying would have given, even in these wider capillaries, an increased capillary rise of about 6 mm. Though material changes may yet occur, the conclusion at this stage is, evidently, that intensive drying has not produced any change in the density or surface tension of benzene such as would justify an assumption of appreciable change in degree of association or of fractional separation of pseudo-components. It may be said that the duration of these experiments is insufficient, but there are numerous cases cited in the literature where effects attributed to intensive drying have been observed in shorter periods, and, though our experiments cannot yet suffice to prove a negative, it seems useful to record at this stage the evidence they have so far afforded. The experiments will be continued and may yield results of interest some years hence.

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