XCIH.—*Specific Gravities and Boiling Points of
Mixtures of Benzene and Normal Hexane.*

By D. HAMILTON JACKSON, M.A., B.Sc., Ph.D., and SYDNEY YOUNG,
D.Sc., F.R.S.

IN the fractional distillation of "petroleum ether" from which the aromatic hydrocarbons had not been previously removed by treatment with a mixture of nitric and sulphuric acids, it was observed that the

benzene and toluene, unlike the polymethylene hydrocarbons, did not come over at their true boiling points, but chiefly about 15° lower. Thus the portion richest in benzene* was that boiling at about 65° , the amount of benzene diminishing regularly at higher and lower temperatures. This lowering of the boiling point of benzene, when mixed with hexanes, seemed to indicate that paraffins and aromatic hydrocarbons, although miscible in all proportions, behave as regards distillation in a manner comparable with that of liquids only partially miscible. A few rough experiments on the distillation of mixtures of benzene and normal hexane in different proportions appeared to support this view, and it was thought desirable to make a more complete investigation of the boiling points and specific gravities of mixtures of these hydrocarbons.

Both the normal hexane and the benzene employed were obtained from Kahlbaum. The *hexane* was purified before use, according to the method given in a preceding paper (Trans., 1895, 67, 1071), and then dried with phosphorus pentoxide and with sodium; it boiled at 68.97° (corr.); its sp. gr. $0^{\circ}/4^{\circ}$ was 0.67705. The *benzene* was shaken up with small quantities of strong sulphuric acid, washed with water, and dried with phosphorus pentoxide and with sodium; it boiled at 80.21° (corr.); its sp. gr. $0^{\circ}/4^{\circ}$ was 0.90005.

Determination of the Specific Gravities of Mixtures of Benzene and Normal Hexane.—The method employed was as follows. The benzene was poured from a U-tube drawn out to a capillary at either end, into a small very short-necked mixing flask, the weight of which was known, and the added weight was determined. The hexane was then introduced, and its weight similarly determined. From these data, the composition of the mixture was deduced.

After shaking, the mixed liquids were sucked up into a Sprengel specific gravity tube (Perkin's form) of the capacity 15.325 c.c. at 0° , and the specific gravity was ascertained in the ordinary way. Although the total loss of benzene *plus* hexane in pouring out these liquids from the U-tubes in which they were contained into the mixing flask was not inconsiderable, it was found that the loss during the manipulation of the prepared mixture was such as not sensibly to affect the values of the specific gravity obtained. This was shown by making redeterminations of the specific gravity with the same liquid as follows. Rather more of a mixture was prepared in the mixing flask than was necessary for a single estimation of the specific

* The presence of benzene in such a mixture of hydrocarbons is readily detected, and its amount approximately ascertained, by prolonged treatment—several times repeated if it is desired to remove the benzene completely—with a mixture of concentrated nitric and sulphuric acids. On diluting the acid with water, and allowing it to stand for two or three days, metadinitrobenzene crystallises out.

gravity, and a determination was then made; immediately after, the liquid used was blown back from the Sprengel tube into the mixing-flask and a second determination made; this second value for the specific gravity was not usually greater than the first by 0.01 per cent. The results of the specific gravity determinations are given in the following table.

Mixture.	Percentage of benzene.	Observed sp. gr. 0°/4°.	Observed vol. of a gram $= \frac{1}{\text{sp. gr.}}$	Calculated* vol. of a gram.	Increase of vol. of a gram on mixing.
I.	1.24	0.67896	1.47284	1.47244	0.00040
II.	1.52	0.67952	1.47163	1.47143	0.00020
III.	9.27	0.69212	1.44483	1.44306	0.00177
IV.	12.31	0.69723	1.43425	1.43195	0.00230
V.	15.07	0.70196	1.42458	1.42184	0.00274
VI.	16.95	0.70535	1.41773	1.41497	0.00276
VII.	21.57	0.71342	1.40169	1.39807	0.00362
VIII.	22.41	0.71501	1.39857	1.39499	0.00358
IX.	24.22	0.71821	1.39235	1.38837	0.00398
X.	31.87	0.73258	1.36504	1.36036	0.00468
XI.	33.23	0.73517	1.36023	1.35538	0.00485
XII.	36.51	0.74166	1.34832	1.34338	0.00494
XIII.	38.38	0.74528	1.34178	1.33654	0.00524
XIV.	40.40	0.74936	1.33448	1.32914	0.00534
XV.	41.39	0.75153	1.33061	1.32552	0.00509
XVI.	41.54	0.75184	1.33007	1.32496	0.00511
XVII.	47.03	0.76326	1.31016	1.30489	0.00527
XVIII.	55.30	0.78140	1.27975	1.27463	0.00512
XIX.	63.58	0.80057	1.24910	1.24432	0.00478
XX.	69.18	0.81394	1.22858	1.22385	0.00473
XXI.	70.78	0.81797	1.22253	1.21796	0.00457
XXII.	77.38	0.83492	1.19772	1.19382	0.00390
XXIII.	79.85	0.84142	1.18846	1.18477	0.00369
XXIV.	81.34	0.84548	1.18276	1.17933	0.00343
XXV.	86.27	0.85916	1.16393	1.16129	0.00264
XXVI.	88.61	0.86586	1.15492	1.15273	0.00219
XXVII.	91.58	0.87436	1.14369	1.14184	0.00185
XXVIII.	92.80	0.87802	1.13892	1.13739	0.00153
XXIX.	95.20	0.88514	1.12975	1.12861	0.00114

* That is, on the assumption that there is no change of volume on mixing the benzene and hexane. Let p = percentage of benzene; then, taking 0.90005 as the sp. gr. of benzene, and 0.67705 as that of hexane, we have

$$\frac{p}{100 \times 0.90005} + \frac{100-p}{100 \times 0.67705} = \text{calculated vol. of a gram.}$$

Determination of the Boiling Points of Mixtures of Benzene and Normal Hexane.—For this purpose, Beckmann's boiling point apparatus was used, and the method finally employed was practically the same as that of Nernst in his investigation of the boiling points of benzene and acetic acid (*Zeit. physik. Chem.*, 1891, 8, 110). An upright glass tube, however, was used in place of the usual glass spiral condenser

attached to the inner boiling tube. As the range of temperature between the boiling points of benzene and hexane is considerable, it was decided to substitute for the ordinary Beckmann, an open-scale Geissler thermometer divided into half degrees and easily allowing readings to be made to 0.05° .

The benzene and hexane were placed in U-tubes provided with wide capillaries, and the amount of liquid used in an experiment was ascertained by weighing the tubes before and after pouring. One of the liquids was introduced in the cold; the other was added by pouring it down the straight condenser tube as soon as the first had been brought to steady ebullition. Benzene was the liquid used throughout in the outer jacket of the apparatus.

The height of liquid in the boiling tube in the case of the mixture is, of course, not the same as that of the single liquid (benzene or hexane), so that the observed boiling points are not strictly comparable. It was found, however, experimentally (by observing the boiling point of benzene in the apparatus and then adding further successive quantities of benzene and observing the boiling point) that the error from this cause was negligible, being less than the limit to which the thermometer was read.

To ascertain the error due to change of composition of the mixture during an experiment, the composition of the liquid also *after* the experiment was ascertained by utilising the specific gravity results given above. The latter were plotted out on an open scale against the percentage composition, so that the strength corresponding with a specific gravity could be read off. After a determination of strength and boiling point had been made in the ordinary way, the apparatus was allowed to cool down, the mixture from the inner tube was poured into a small flask, and from the latter it was sucked up into the specific gravity tube. It was found that the strength of the mixture as determined by the two methods was the same to within less than 0.2 per cent., as a rule. Now, if the boiling points given in the table below be examined, it will be seen that an error of 0.2 per cent. in the estimation of the strength is negligible with a thermometer read to twentieths of a degree, except in the case of mixtures containing 90–100 per cent. of benzene where a small change in composition produces a relatively large change in boiling point. In the case of these mixtures, it is probable that the error in the boiling point exceeds one-twentieth of a degree, if the strengths are taken as correct; the indirect method of ascertaining the percentage composition would no doubt be preferable in this case, but its application is difficult owing to the readiness with which mixtures very rich in benzene freeze in the specific gravity tube when cooled to 0° .

The following are the results of the boiling point determinations

the strengths given being those obtained by weighing, and not by the specific gravity method. Probably the true strengths would lie between those obtained by the two methods.

Mixture.	Percentage of benzene.	Boiling point (corr.).*	Mixture.	Percentage of benzene.	Boiling point (corr.).*
I.	5.5	69.00°	XI.	64.9	72.70°
II.	6.5	68.96	XII.	67.3	73.01
III.	11.6	69.00	XIII.	78.0	74.67
IV.	17.2	69.14	XIV.	78.8	74.75
V.	27.3	69.47	XV.	85.2	76.12
VI.	31.6	69.72	XVI.	88.9	76.91
VII.	39.5	70.17	XVII.	90.1	77.20
VIII.	46.6	70.70	XVIII.	92.0	77.75
IX.	47.3	70.70	XIX.	94.0	78.49
X.	53.0	71.42	XX.	95.3	78.80

* dp/dt at 760 mm. = 23.3 mm. for benzene. For hexane, the value is 23.9 mm.; it was given by mistake as 22 mm. in the original paper (Trans., 1895, **67**, 1072). The boiling point of hexane at 760 mm. should be 68.95°, and not 69.0° as previously (*loc. cit.*) stated.

It is well known that the members of many homologous series of organic compounds become less and less soluble in water as the molecular weight increases; this is notably the case with the saturated fatty alcohols, $C_nH_{2n+2}O$, and acids, $C_nH_{2n}O_2$, the lowest members of which, methylic alcohol and formic acid, are miscible with water in all proportions, whilst the very high members are practically insoluble at ordinary temperatures. At the same time, experimental evidence, so far as it goes, points to the conclusion that the contraction and heat evolution diminish with rise of molecular weight. Konowaloff, in his study of the vapour pressures of mixtures of the lower alcohols with water (*Ann. Chem. Phys.*, 1881, [ii], 14, 34), has shown that there is here also a gradual change from the ordinary behaviour of two miscible liquids (methylic alcohol and water), the vapour pressures of which, and also the boiling points, are always intermediate between those of the components, to that of partially miscible liquids, mixtures of which, within certain limits, have vapour pressures higher, and boiling points lower, than that of either component; a somewhat similar result was obtained by the study of the vapour pressure of mixtures of the fatty acids with water.

Konowaloff observed, however, that, starting from the lowest member of a series, the typical form of curve for partially miscible liquids was reached, both with the alcohols and acids, before the liquids ceased to be miscible in all proportions at ordinary temperatures.

Thus methylic, ethylic, and propylic alcohols are each of them

miscible with water in all proportions, but whilst the vapour pressure of methylic alcohol diminishes regularly on dilution, that of ethylic alcohol is hardly affected by the addition of a moderate amount of water; it shows, indeed, a very slight rise at first, but afterwards diminishes at an increasing rate, until, with infinite dilution, the vapour pressure of pure water is reached.

With propylic alcohol and water, there is, at each temperature, a certain mixture which has a very decided maximum vapour pressure considerably higher than that of either component. Conversely, there is at each pressure a particular mixture of propylic alcohol and water which, like a pure liquid, distils at a constant temperature and with constant composition. On distilling stronger or weaker solutions of propylic alcohol and water, the mixture of maximum vapour pressure and minimum boiling point comes over first, followed by mixtures richer in propylic alcohol or water, according to the original composition. It is, therefore, possible to separate either pure propylic alcohol or pure water, but not both, from such a mixture.

With ethylic alcohol and water, since the maximum vapour pressure (and minimum boiling point) differs but very slightly from that of pure alcohol and corresponds with a mixture containing very little water, it follows that a very strong solution of ethylic alcohol must distil over at a nearly constant temperature and almost without change of composition, and that neither pure alcohol nor pure water can be separated from it. On the other hand, it is quite easy to obtain pure water by the distillation of a weak solution of ethylic alcohol.

As the boiling point of methylic alcohol rises steadily on dilution, both components may be separated by distillation of a mixture of the two.

Mixtures of water with acetic acid behave like those of ethylic alcohol and water, except that no maximum vapour pressure has been observed. The vapour pressure of water is but slightly lowered by adding a little acetic acid, whilst that of acetic acid is rapidly raised by the addition of water; and it is quite possible to obtain anhydrous acetic acid by the distillation of a strong aqueous solution, although it is very difficult, if not impossible, to separate either pure water or pure acetic acid by distillation of a weak solution of the acid.

The data given above show that mixtures of normal hexane and benzene behave, on distillation, in a similar manner to mixtures of ethylic alcohol and water or of water and acetic acid. An addition of 10 per cent. of benzene to normal hexane has no appreciable influence on the boiling point, whilst an addition of 10 per cent. of hexane to benzene lowers the boiling point nearly 3° . Again, from a solution containing, say, 10 per cent. of benzene, it is impossible to separate either component by fractional distillation, but it would be

928 FRANCIS AND YOUNG : ACTION OF FUMING NITRIC ACID

easy to separate pure benzene, but not hexane, from a mixture containing, say, 90 per cent. of benzene.

That the liquids do approximate in their behaviour to partially miscible liquids is further shown by the fact that there is always expansion on mixing, the expansion reaching a maximum of about 0.4 per cent.

UNIVERSITY COLLEGE,
BRISTOL.