723. *Some Physical Properties of Pure Benzene.*

By (Mrs.) S. M. Rybicka and W. F. K. Wynne-Jones.

Carefully purified benzene has been found to have f. p. 5·525°, d^{20} 0·87896, and n_D^{20} 1·50141, in good agreement with the best values recently published. The value obtained for the freezing point of benzene is very different from that (5·493°) recorded by T. W. Richards, which clearly should not be used, as has sometimes been recommended, as a secondary fixed point in thermometry.

For many years purified benzene has been regarded as a convenient substance to use as a standard for the measurement of temperature and other physical properties; in particular, since the work of Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, **36**, 1825) the freezing point

of benzene has been accepted as a convenient sub-standard in thermometry and, despite a warning by Masson (*Nature*, 1931, **128**, 726) that it was probably low, the value 5·493°, put forward by Richards as the freezing point of pure benzene, is still widely accepted. We were concerned with the purification of benzene for some kinetic measurements and in the course of this work we determined the freezing point, density, and refractive index, and, while our original intention was to accept Richard's value for checking our thermometers, we were finally convinced that it is undoubtedly low and consequently endeavoured to fix it with greater accuracy.

To obtain pure benzene we adopted a method which, while certainly used previously, has not been explicitly described and we report it in detail since the reliability of our results depends on the validity of our method. Essentially, we fractionally crystallised the benzene and determined the physical properties of the crystallised portion and the mother-liquor, and continued the process until the physical properties of the two portions were identical. This work was carried on during the late war when it was not easy to obtain pure benzene commercially and the AnalaR benzene which we used as the starting material for most of the work evidently contained about 2% of hexane or heptane; we were however fortunate in being able to obtain some of Kahlbaum's purest benzene which, with slight purification, gave a product identical in properties with our other material.

Since the completion of our work there have become available the American Petroleum Institute's tables of the physical properties of hydrocarbons (American Petroleum Institute Research Project 44) and also Egloff's review of these ("Physical Constants of Hydrocarbons," Vol. III, Reinhold, 1946). The table gives Egloff's selected values, our own review of the literature, the recent determinations made by the American Petroleum Institute, and finally our own determinations. It is evident that whereas there is satisfactory agreement between the last three sets of values, those given by Egloff differ appreciably.

	Egloff.	Mean from literature.	A.P.I.	This work.	Refs.
Freezing point	5·49°	5·53°	5·533°	5·525°	1—11
Density, d^{20}	0·87866	0·87900	0·87903	0·87896	2, 6, 12—14
Refractive index, n_D^{20}	1·50096	1·50135	1·50110	1·50141	4, 5, 6, 8, 15, 16

[1] Masson, *Nature*, 1931, **128**, 726. [2] Young, *Proc. Roy. Dublin Soc.*, 1910, **12**, 374. [3] Richards, Carver, and Schumb, *J. Amer. Chem. Soc.*, 1919, **41**, 2019. [4] Gifford and Lowry, *Proc. Roy. Soc.*, 1923, *A*, **104**, 430. [5] Kalff, Thesis, Amsterdam, 1924. [6] Timmermans and Martin, *J. Chim. physique*, 1926, **23**, 747. [7] Huffman, Parks, and Daniels, *J. Amer. Chem. Soc.*, 1930, **52**, 1547. [8] Menzies and Lacoss, *J. Physical Chem.*, 1932, **36**, 1967. [9] Sugden, *J.*, 1933, 768. [10] Kraus and Vingee, *J. Amer. Chem. Soc.*, 1934, **56**, 511. [11] Ziegler and Andrews, *ibid.*, 1942, **64**, 2482. [12] Richards and Shipley, *J. Amer. Chem. Soc.*, 1916, **38**, 989. [13] Zmaczynski, *J. Chim. physique*, 1930, **27**, 503. [14] Fiock, Grinnings, and Holton, *Bur. Stand. J. Res.*, 1931, **6**, 887. [15] Brühl, *Annalen*, 1880, **203**, 363. [16] Williams and Daniels, *J. Amer. Chem. Soc.*, 1924, **46**, 903; 1925, **47**, 1490.

Experimental.

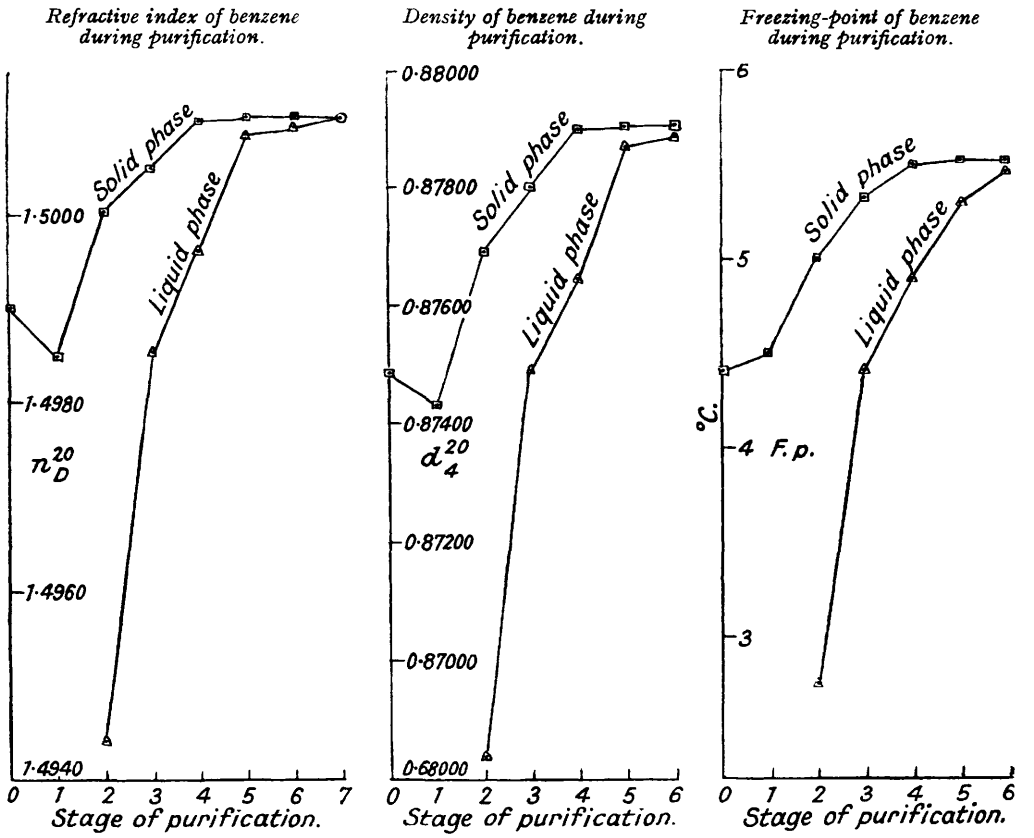
Purification of Benzene.—The benzene used in this work gave a negative reaction for thiophen by the isatin test. It was however noticed that after repeated fractional crystallisation the purified benzene would sometimes give a positive result (brown coloration with concentrated sulphuric acid). This indicates the presence of a substance, such as thiophen, which not only forms mixed crystals with benzene, but also is more concentrated in the mixed crystals than in the solution. The benzene was shaken with five successive lots of concentrated sulphuric acid and then with distilled water until the water gave no acid reaction. It was then refluxed with phosphoric oxide (which remained colourless) and fractionally distilled, the portion boiling within 0·1° being collected. After this preliminary treatment the benzene was fractionally crystallised in the following manner: Benzene (4 l.) was cooled in Winchester bottles placed in a refrigerated tank. The amount of solid formed at each crystallisation was about one-quarter of the total volume; the crystals were always advanced a stage in the scheme of purification and the mother-liquor was pushed back a stage according to the usual procedure; the final volume of purified benzene was rather more than 1 l.

In the figure are shown the values for the various physical properties of the crystals and the mother-liquor during the purification. All these results refer to the moist benzene and the values have no absolute significance since no corrections have been applied for instrumental errors.

It is remarkable that the properties of the original AnalaR benzene were so different from those of pure benzene. It seems that the impurity must be a saturated hydrocarbon since this alone can account for the decrease in all the physical properties. If we assume that heptane is the impurity we calculate its percentage to be 2·11 from the freezing-point lowering, 2·37 from the refractive index decrease, and 2·34 from the density decrease. The agreement is close enough to justify the assumption that heptane or some very similar hydrocarbon with a boiling point close to that of benzene is present.

Determination of Physical Properties.—(a) *Refractive index.* Refractive indices were determined on a Zeiss Pulfrich refractometer, by use of the values given by the manufacturers for the conversion of angles into refractive indices. The instrument was checked with pure water, for which n_D^{20} 1·33300 was consistently obtained. A sodium lamp was used as a source of illumination.

(b) *Density.* The measurements of density were made with pycnometers according to Hartley and Barrett's method (*J.*, 1911, 1072), account being taken of the correction given by Bury and Grindley (*J.*, 1928, 3297). Owing to the considerable coefficient of expansion of benzene the control of temperature is important and this was done by placing the pycnometer in a Dewar vessel immersed in a thermostat. The temperature fluctuations of the Dewar vessel were less than 0·005°.



(c) *Thermometry.* Temperatures were read on a solid-stem thermometer reading from −5° to 30° and graduated to 0·05°; by use of a cathetometer readings could be made to 0·005°. This thermometer had been calibrated at the National Physical Laboratory at every 5° and the maximum graduation error recorded was 0·02°. The zero of the thermometer was checked several times during the progress of the work and the appropriate correction applied. The thermometer was immersed to the reading and in all measurements care was taken to ensure that equilibrium was properly attained. Since the freezing point of benzene is only ½° removed from an actual calibration point, we think it probable that the temperature is known to 0·01°. The same thermometer was used for determining the temperature at which the refractive index and density were measured.

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KING'S COLLEGE, NEWCASTLE-ON-TYNE. [*Received, June 10th*, 1950.]