346. *The Vapour-pressure Curve of Tetraethyl-lead from* 0° *to* 70°.

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In view of the importance of tetraethyl-lead in the study of the combustion of hydrocarbons, it is desirable to know its vapour pressure over a considerable range. The only published work on the subject is that of Jones, Evans, Gulwell, and Griffiths (J., 1935, 39), but as this is for pressures far greater than are normally required in kinetic experiments, we have studied the vapour-pressure curve by a static method, over the range 0—70°.

Fig. 1.

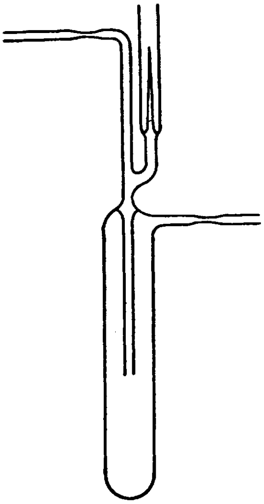
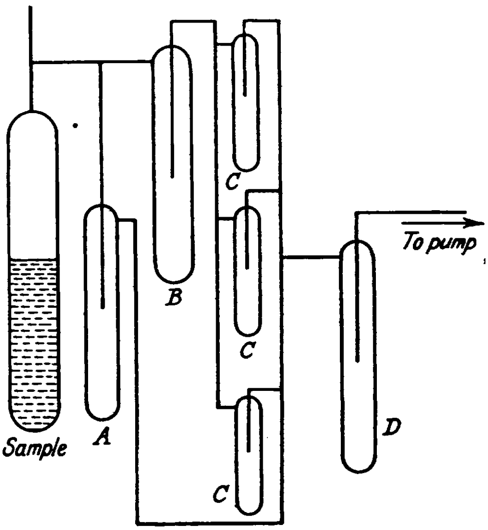


Fig. 2.



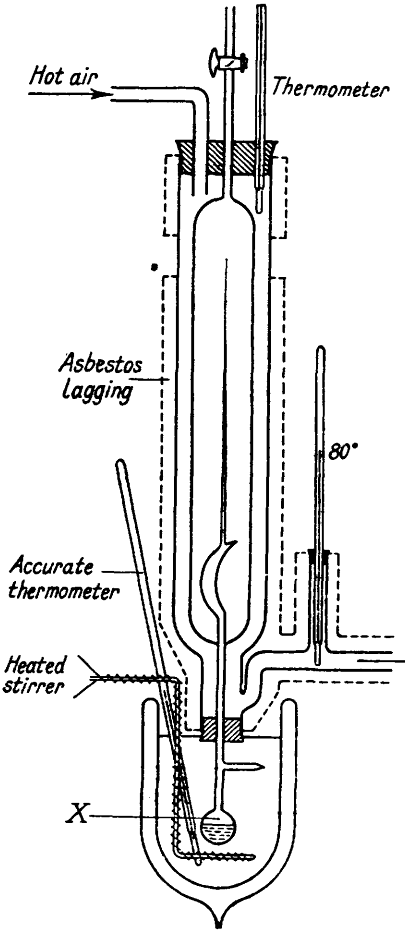
Although the formula we have deduced is not markedly different from that obtained by the previous authors at higher temperatures, the present results indicate that the vapour pressures of pure tetraethyl-lead are 10—15% higher in this range than those extrapolated from their formula.

EXPERIMENTAL.

A sample of commercial tetraethyl-lead, supplied by Imperial Chemical Industries, Ltd., was freed from halides by treatment with silver oxide, and further purified by distillation in a vacuum. As the substance readily decomposes under the influence of light and grease, the apparatus was constructed as free from taps as possible, and the final samples were collected for storage in liquid-air traps fitted with vacuum breakers, and covered with black paint.

A number of these receivers, of design shown in Fig. 1, were connected in parallel, one side being in communication with the crude sample, and the other with a pumping system, which consisted of a two-stage mercury-diffusion pump, backed by a Hyvac rotor pump, both being protected from the vapour of the substance by a trap cooled in liquid air.

FIG. 3.



The apparatus, shown diagrammatically in Fig. 2, was evacuated, and about one-third of the sample distilled into the trap *A*, which was then sealed off and removed. Another one-third was distilled into the trap *B* for further fractionation, and the residue rejected. The contents of *B* were left on the pump until about one-third had distilled into the liquid-air trap *D*, and then solid carbon dioxide–ether mixtures were placed round each of the receivers *C*. In this way the tetraethyl-lead vapour could be condensed, while any volatile decomposition products could be drawn away by the pump. As each receiver filled, it was sealed off in a vacuum, and removed; the residual one-third of the contents of *B* was also rejected. It has not hitherto been recorded that the pure substance is odourless, but the characteristic unpleasant smell developed after it had been in contact with air for a short time.

The vapour pressures were measured by a sensitive Bourdon gauge surrounded by a hot-air jacket, the temperature of which was maintained constant at 80° by passing a stream of hot air from a motor blower through an electrically heated Pyrex tube, consuming about 500 watts. The apparatus was lagged with cotton-wool and asbestos string, and mounted vertically, as shown in Fig. 3.

When the apparatus had reached a steady temperature, both sides of the gauge were evacuated, and a calibration performed against a mercury manometer, by measuring the displacement of the pointer with a travelling microscope, for various pressure differences between the spoon and the external body of the gauge.

Slight fluctuations in the temperature of the jacket were not serious, as it was found that the sensitivity of the instrument only changed by 1 part in 300 between 18° and 80°. The calibration curve was a straight line between $-$ 20 and $+$ 20 mm. of mercury pressure difference in the spoon of the gauge, giving 1 mm. pointer deflection equivalent to 6·18 mm. Hg to within 1 part in 400. As the position of the pointer could be read to within 0·001 mm., the vapour pressures are correct to 0·005 mm. Hg or 0·25%, whichever is the larger.

After the gauge had been calibrated, a sample of purified tetraethyl-lead was introduced by vacuum distillation into a small bulb *X*, connected to the spoon side of the gauge. After the sample had been warmed and refrozen several times, to get rid of dissolved gases, the bulb was sealed off from the pump and supply.

The displacement of the pointer was observed with the bulb immersed in oil at various temperatures, in a Dewar flask. An electrically heated stirrer was used to keep the temperature of the bath steady to within 0·05° while equilibrium was attained. The vapour pressure at each temperature was taken twice, and between each reading the bulb was cooled to − 80°, to ensure that no decomposition of the sample had occurred.

The following vapour pressures (p, in mm. Hg) are direct readings obtained from several experiments, and the graph between $1/T$ (where T is the absolute temperature) and $\log p$ shows a satisfactory linear relation.

Temp.	p.	$10^5/T$.	$\log_{10} p$.	Temp.	p.	$10^5/T$.	$\log_{10} p$.	Temp.	p.	$10^5/T$.	$\log_{10} p$.
0·00°	0·056	366·2	−1·352	27·00°	0·438	333·2	−0·358	48·60°	2·076	310·9	0·317
10·05	0·115	353·3	−0·939	28·80	0·512	331·6	−0·291	51·25	2·483	308·3	0·395
15·00	0·167	347·1	−0·777	30·55	0·556	329·4	−0·255	53·65	2·805	306·0	0·448
15·90	0·183	346·0	−0·738	39·00	1·076	320·4	0·032	58·50	3·756	301·6	0·575
17·00	0·216	344·7	−0·666	45·50	1·608	313·9	0·206	67·00	6·293	294·6	0·799
20·20	0·260	341·0	−0·585								

DISCUSSION.

These results can be expressed by the formula $\log_{10} p = 9{\cdot}428 - 2938/T$ between 0° and 70°. This result differs somewhat from that published for temperatures between 78° and 150° (*ibid.*), *viz.*, $\log_{10} p = 9{\cdot}426 - 2960/T$, which in the present range of 0—70° gives values 10—15% too low. This discrepancy, which is not great, may be ascribed to the magnitude of the extrapolation, and also possibly to errors inherent in the method used by the previous authors, who obtained vapour pressures in a vacuum-distillation apparatus, where it is doubtful whether perfect static equilibrium could be attained between the vapour and the boiling liquid.

It was originally intended to carry the curve to higher temperatures, but slight decomposition occurred when the jacket temperature was 120°. No doubt, decomposition would occur in the distillation apparatus mentioned, but would be less important, since the gaseous products of decomposition would be drawn away continually by the pump.

SUMMARY.

Samples of pure tetraethyl-lead have been prepared, and their vapour pressures determined for temperatures between 0° and 70° by using a hot-air-jacketed Bourdon gauge.

Our thanks are due to the Royal Society and the Chemical Society for grants, to Imperial Chemical Industries, Ltd., for specimens, and to the Department of Scientific and Industrial Research for a maintenance grant to one of us (E. J. B.).

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[*Received, August 8th*, 1936.]