The Second Virial Coefficient of Benzene

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EVERETT and Penney[1] have recently reviewed the experimental data on the second virial coefficient (B) of benzene and drawn attention to the disagreement between the results of different experimenters. This is apparent in Fig. 1 where the values of $-B$ found by Eucken and Meyer[2] and by Baxendale and Enüstün[3] are seen to be considerably larger than those of Lambert, Roberts, Rowlinson, and Wilkinson[4] and of Casado, Massie, and Whytlaw-Gray.[5]

In this note we report two independent series of measurements aimed at resolving these discrepancies.

The measurements at Reading were made in a "Boyle's apparatus" similar to that described by Alexander and Lambert.[6] Two different samples of benzene were used. The first of these was prepared at Reading by treatment with sulfuric acid followed by fractional distillation and then by repeated fractional crystallizations. The purity of the sample so prepared was calculated

from the shape of the freezing point curve and was found to be 99.95 ± 0.05 moles percent. The second sample was kindly supplied by Professor J. Timmermans from the Bureau International des Etalons Physico-chimiques in Brussels. Considerable care was taken to de-gas the liquid so as to ensure that a gas-free sample of vapor was introduced into the burette. The results are given below.

Reading sample:

$t°C$	43.1	51.9	60.0	62.9	65.7	75.1	85.9	94.2	99.1,
$-B/\text{cm}^3\,\text{mole}^{-1}$	1300	1198	1064	1112	1099	1090	1004	947	916.

Brussels sample:

$t°C$	58.1	72.1	90.8,
$-B/\text{cm}^3\,\text{mole}^{-1}$	1137	1075	1006.

The measurements at Sydney were made by a comparative method which has been described before.[7]

Mr. I. Brown, C.S.I.R.O., Melbourne, kindly supplied a purified sample of benzene for these determinations. The pressures were between 15 percent and 75 percent of the saturation pressure of benzene, and in this range no virial coefficients higher than the second are needed to describe the behavior of the vapor. The results are given below:

$t°C$	70	80	100	100	125,
$-B/\text{cm}^3\,\text{mole}^{-1}$	1035	971	852	839	733.

Both sets of data have been plotted in the diagram. They lie close to the curve

$$B/\text{cm}^3\,\text{mole}^{-1} = 70 - 13.2 \times 10^7 / T^2,$$

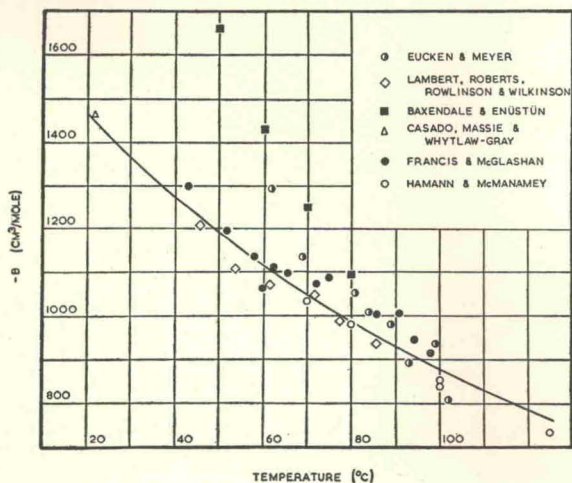which Everett and Penney selected after rejecting Baxendale and Enüstün's results, and they provide further justification for that choice.

FIG. 1. Second virial coefficient of benzene.

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[3] Baxendale and Enüstün, Phil. Trans. Roy. Soc. (London) **A243**, 176 (1951).
[4] Lambert, Roberts, Rowlinson, and Wilkinson, Proc. Roy. Soc. (London) **A196**, 113 (1949).
[5] Casado, Massie, and Whytlaw-Gray, Proc. Roy. Soc. (London) **A207**, 483 (1951).
[6] Alexander and Lambert, Trans. Faraday Soc. 37, 421 (1941).
[7] Hamann and Pearse, Trans. Faraday Soc. 48, 101 (1952).