

## SHORT COMMUNICATIONS

### A PROPOSED NEW METHOD FOR THE DETERMINATION OF THE TEMPERATURE VARIATION OF VIRIAL COEFFICIENTS\*

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High precision virial coefficients of vapours, preferably over a wide temperature range and in the absence of mercury vapour, are needed for comparison with values computed from intermolecular potentials. In this note attention is drawn to a novel experimental method which offers distinct advantages over techniques so far exploited.

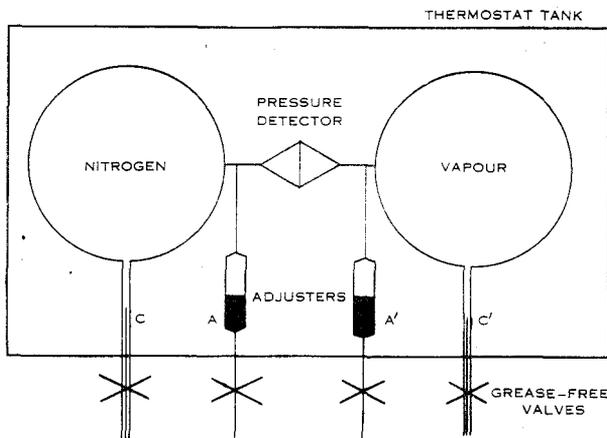


Fig. 1.—General arrangement of apparatus suitable for new method.

The basic scheme is indicated in Figure 1. Samples of nitrogen (provisionally regarded as a perfect gas) and the experimental vapour are confined in the two halves of the symmetrical apparatus and adjusted to the same pressure as indicated by a null-point pressure-sensing device. The temperature is changed substantially and the pressure equality restored by the use of the volume adjuster A' only.

At subatmospheric pressures the equation of state can be taken to be

$$PV = nRT + nBP,$$

which rearranges to

$$B = \frac{V}{n} - \frac{RT}{P}.$$

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If the pressure balance is performed at  $T_1$  and  $T_2$  then, for the vapour,

$$B_1 - B_2 = \frac{V_1}{n} - \frac{V_2}{n} - \frac{RT_1}{P_1} + \frac{RT_2}{P_2}.$$

But the last two terms are equal since the pressure of the vapour on each occasion was equal to that of the ideal gas whose pressure is proportional to the absolute temperature. Hence the remarkable result that

$$B_1 - B_2 = \frac{\Delta V}{n}, \quad \dots \dots \dots (1)$$

so that  $B$  as a function of  $T$  can be obtained from one standard value, the measured volume changes, and the molar quantity of vapour.

When the expansion in terms of  $1/V$  is preferred one can start from

$$\frac{PV}{nRT} = 1 + \frac{nB^*}{V},$$

and similarly deduce

$$\begin{aligned} B_1^* - B_2^* &= \frac{V_1^2 - V_2^2}{n^2 RT/P} - \frac{V_1 - V_2}{n} \\ &= \frac{\Delta V(2V_1 - \Delta V)}{n^2 RT/P} - \frac{\Delta V}{n}. \quad \dots \dots \dots (2) \end{aligned}$$

Note that  $(2V_1 - \Delta V)/(nRT/P)$  is close to 2, so the second term is about half the first.

It is to be especially noted that a small volume change is measured, not—as in most other methods—two closely similar large  $PV$  values which are then differenced with striking loss of precision. There is no need for precision pressure measurements, merely a pressure balancing. Temperature measurement to  $0.1^\circ\text{C}$  suffices, although the thermostat should hold the temperature constant to within  $0.003^\circ\text{C}$ .

It is instructive to substitute numerical values into the basic equations (1) or (2). Consider an apparatus with capacities of 1 l., at pressures of about 500 mm, that is, 0.025 mole. There is no difficulty in admitting this quantity of vapour, known to 1 in 1000 or better, either by gravimetric methods or by volumetric methods plus an assumed preliminary value of  $B$ . With a temperature increase of  $100^\circ\text{C}$  the virial coefficient will commonly change by 200 c.c./mole or more. The volume change will accordingly be 5 c.c. If the pressure-sensing device is sensitive to 0.005 mm the volume adjuster can be positioned to 0.01 c.c., giving an accuracy in  $\Delta B$  of better than 1 c.c./mole.

By loading the apparatus to different initial filling pressures two implicit assumptions in the elementary theory can be tested for if either higher virial coefficients or adsorption effects are significant then  $\Delta V/n$  and  $\Delta B$  will vary with the filling pressure. Corrections for the non-ideality of the nitrogen can be applied using standard isotherm data and a slightly more complex theory.

Rough estimations indicate that the varying adsorption on the walls due to rising pressure and temperature during an experiment might produce errors of the order of 1 c.c./mole with litre vessels. Adsorption is a limiting problem in other types of  $PV$  apparatus. Doubling the size of the vessels, in the present design an easy change, reduces the error to one-half.

In this preliminary paper it is not necessary to recommend detailed procedures\* but some comments on practical points are warranted. The symmetrical design of the apparatus eliminates errors due to thermal expansion of the apparatus and pressure dilation. Suitable corrections will be required for the density change of the volume adjuster working substance. With a liquid manometer as pressure-sensing device it will be necessary to measure the volume over the meniscus surface at every pressure setting. The apparatus makes minimum demands on the amount of confining fluid for the gases as it is never necessary to compress the gases substantially by transfer of liquid as in a Boyle-type apparatus. Liquid metal surfaces are only required at  $A, A', C, C'$ , and possibly in the pressure-sensing device: thus the arrangement is very suitable for use with the expensive gallium as working fluid. With gallium or tin and silica vessels, experiments might conveniently be performed over very long temperature ranges. The basic idea is also applicable to above-atmospheric pressures though at high non-idealities a relatively large volume adjuster is required.

Finally, one important variation may be mentioned. One half of the apparatus can be made *wholly* of glass or silica when a distortion type gauge is used as detector so permitting the examination of the  $PV$  behaviour of mercury vapour or substances corrosive to metals.

\* Much relevant information on the precision manipulation of gases and vapours can be found in the more recent papers of the late Professor R. Whytlaw-Gray and his collaborators.