# LETTERS TO THE EDITORS

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## A Significant Error in the Determination at Low Pressures of the Virial Coefficients of Vapours

THE differential method[1] which we have developed and which has been applied successfully to the accurate measurement at low pressures of the deviations from ideality of a number of gases has, with vapours, been found to give unreliable results. Usually, with these the $PV/P$ isothermals show a curvature concave towards the pressure axis. This effect was noticed by Casado[2] with benzene vapour, and the literature contains references to curved low-pressure isothermals with several easily liquefiable gases. Hamann and Pearse[3] noticed this behaviour with methyl chloride and methyl bromide. Since, on theoretical grounds, it is very unlikely that a third virial coefficient could produce an effect of the magnitude observed even in benzene, it is clear that an experimental error of some significance is involved. This error is due to adsorption, which hitherto has been neglected by other workers in this field.

Now that a careful investigation of adsorption on 'Pyrex' glass of a series of vapours at various temperatures has been made by one of us[4], it is possible to define the conditions in which this error is at a minimum and to make reliable corrections in volumetric work. It was found that only when the glass surfaces in the volumeters were scrupulously clean and the mercury in contact with them entirely free from even traces of grease that minimum and constant values for adsorption could be obtained.

It was hence imperative to redesign the differential compressibility apparatus so as to avoid entirely the passage of mercury through greased stopcocks. This has now been done by using magnetically controlled mercury valves which permit the necessary fine adjustment[5], and results obtained for benzene vapour at 22° and 35° C. between the pressure limits of 60 and 20 mm. The $PV/P$ graphs, after correcting for adsorption, are very closely linear and the deviations of the experimental points from a mean square line do not exceed 2 parts in $10^5$. The virial coefficient at 22°, deduced from the slope of the line, is $-B = 1,525$ c.c./mol. In the particular apparatus used the increase in surface on expansion is nearly balanced by the decreasing adsorption, so that the total adsorption correction is small and even at the lower temperature does not exceed 30 c.c./mol., or about 2 per cent ; at 35° it is still smaller.

As a check to these results, we have compared the balancing pressures of benzene vapour and nitrogen by means of the microbalance. Originally, Casado, Massie and Whytlaw-Gray[6] compared benzene vapour with oxygen and obtained a value for the molecular weight from the limiting value of the pressure ratio very close to the accepted figure, but for the virial a high degree of accuracy was not claimed and we had reason to suspect that the balance used might not have been sufficiently compensated for adsorption. Imperfect compensation would affect significantly the value of the virial coefficient but would have little influence on the molecular weight. Using a more certain method of compensation for

adsorption, we now find, as the mean of two sets of experiments, $-B = 1,537$ cal./mol. in good agreement with that found with the modified compressibility apparatus. At 35° C. also a satisfactory agreement between the two methods has been attained. Although with the microbalance the accuracy of the results is not as great as with the compressibility method, the agreement supports the view that systematic errors have been avoided.

From the form of the adsorption curves on 'Pyrex' there is a great increase as the saturation point is approached, and on silica at 22° C., although the adsorption is not so great as on 'Pyrex' glass, it increases nearly threefold between 68 and 90 per cent, so that measurements made near the latter point are likely to be adversely affected unless adequately corrected.

It is likely that some of the published data on compressibilities at low temperatures may be in error unless adsorption is taken into account.

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[1] Bottomley, G. A., Massie, Doreen S., and Whytlaw-Gray, R., *Proc. Roy. Soc.*, A, **203**, 201 (1950). Reeves, C. G., and Whytlaw-Gray, R., *ibid.*, A, **232**, 173 (1955).<br>
[2] Casado, F. L., Ph.D. thesis, Leeds (1950).<br>
[3] Hamann, S. D., and Pearse, J. F., *Trans. Farad. Soc.*, **48**, 101 (1952).<br>
[4] Bottomley, G. A., and Reeves, C. G., *Trans. Farad. Soc.*, **53**, 1455 (1957).<br>
[5] Bottomley, G. A., *J. Sci. Instr.*, **34**, 369 (1957).<br>
[6] Casado, F. L., Massie, Doreen S., and Whytlaw-Gray, R., *Proc. Roy. Soc.*, A, **214**, 466 (1952).

## Travelling Disturbances in the Ionosphere : Changes in Diurnal Variation

IN an earlier communication[1] it was reported that the direction of horizontal movement of travelling ionospheric disturbances observed at Sydney, Australia, had a consistent diurnal variation during winter months in the years 1950–52 ; but no significant diurnal variation was then apparent in the summer. These conditions continued until 1955 ; but in the summer of 1955–56 a definite change appeared which was even more marked in 1956–57, the main feature being a marked change of direction from the south-east to the south-west quadrant about midday. The contrast is clearly evident in Fig. 1, which shows the mean diurnal variation in January for the years 1951–54 as compared with the variation for January 1957. The consistency of the results of 1951–54 is shown by the dotted lines, which indicate maximum deviation from the mean. It will be noted that the change from south-east to south-west quadrant in 1957 is quite sudden. This sequence is also found on a number of individual days, though not on all days. There was no significant change in mean speed over this time interval.

Examination of past records starting from the summer of 1949–50 shows that there was a tendency for a similar sequence to occur on occasional days in that year but not sufficiently often to affect the mean curve for the month. This tendency, however, decreased in succeeding years to a minimum in 1953–55. It then increased noticeably in 1955–56 and markedly in 1956–57.

It seems likely that these changes are associated with the sunspot cycle, which showed minimum