

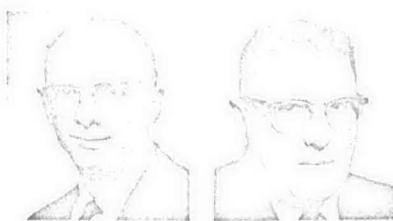
eliminate first- and even some second-order effects directly. Addingley and Whytlaw-Gray (35) were apparently the first to compare directly the gas under investigation with an approximately equimolar quantity of a well-investigated reference gas. They measured the small differences in volume when the gases were at identical pressures. Haman and Pearce (36) and later McGlashen and Potter (37), Figure 14, measured the small difference in pressure when the two gases were confined as nearly as possible at the same temperature and equal volumes. The apparatus is as nearly symmetrical as possible. The test gas is charged to the left buret and the reference gas to the right through the manometer tubes M, with the mercury withdrawn. The mercury levels were then raised to the first buret mark to confine the gases in the same volume and the amount of one adjusted to give the same pressure. Then, the two were successively compressed to fill only two and only one bulb each and the pressure difference measured. The pressures are related directly to the second virial coefficient. To yield an accuracy of 2:1,000 in the second virial, the initial total pressure need only be known to 1:1,000. The need for maximum possible accuracy is concentrated on measurements of the pressure differences.

Interaction second virial coefficients have been measured directly by Knobler, *et al.* (38), and by Magasanik and Ellington (5, 6), Figure 15 and 16. In this case, three vessels of equal volume are held at the same temperature. Two vessels, V_1 and V_2 , are filled with one gas, Figure 16, the third, V_3 , with the second gas, all at precisely the same pressure. Then the contents of vessel V_2 of the first component are mixed with those of the second component in V_3 by repeated flushing into and out of the expansion vessel TP. The mixture is then compressed back to the initial volumes in V_2 and V_3 and the difference in pressure between the mixture and that of the reference volume, V_1 , measured directly with the differential manometer D. This difference can be related directly to the interaction second virial coefficient. Thus, first-order total pressure and second-order pure component second virial effects are screened out to give more accurate interaction coefficients directly.

Recommendations

If recommendations were to be made on the basis of this review, they would be:

1. That more of the experimental efforts for obtaining new P - V - T



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data be directed at obtaining values accurate to 1:5,000 or better.

2. That more efforts be directed toward obtaining data near phase boundaries, and for the dense fluid.
3. That effort be made to extend each new work to existing data and reconcile discrepancies so that larger internally consistent sets will result.
4. That new efforts include relatively extensive ranges of more than one independent variable to obtain full advantage of the smoothing effects obtainable with analytical fits.
5. That effort be made to develop more special methods that will yield data directly on second order effects.

It is recognized that these recommendations are in the direction of increased cost for new efforts, but the added value of them to other investigators and engineers should more than make it worthwhile. #

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