

SECOND VIRIAL COEFFICIENTS OF SOME ARGON-HYDROCARBON MIXTURES AND THEIR COMPARISON WITH CHROMATOGRAPHIC VALUES*

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INTRODUCTION

Gas chromatography finds increasing use in non-analytical applications. The basic simplicity of the technique and the speed with which measurements can usually be made make it attractive as a means of physico-chemical research. (In fact, the better understanding of gas chromatography obtained by such studies often proves to be directly useful in the main field of analytical gas chromatography.) The non-analytical applications of gas-liquid chromatography (henceforth GLC) fall into two groups. Firstly, observation of the broadening of individual bands of material as they pass through the column make it possible to study gas-liquid diffusion¹, and secondly, accurate measurement of retention volume gives direct access to the partition coefficient of the sample between the stationary liquid and the carrier gas. This coefficient is a thermodynamic quantity and from it we can determine activity coefficients and information concerning the equation of state of the sample-carrier gas mixture. It is this last type of measurement with which we are concerned here.

At low densities the equation of state of a gas mixture may be written as:

$$PV = RT [1 + B(T)/V],$$

where P is the pressure, V is the molar volume, T is the temperature, R is the gas constant, and B is the second virial coefficient. For a binary system, B is given by the equation:

$$B = x_1^2 B_{11} + 2 x_1 x_2 B_{12} + x_2^2 B_{22}$$

in which B_{11} and B_{22} are the second virial coefficients of the pure components, x_1 and x_2 are the mole fractions, and B_{12} is the virial coefficient which arises from interactions between unlike molecules. It is this *interaction* virial coefficient which is obtainable from GLC experiments.

Recently a number of experiments have been reported²⁻⁵ in which high-pressure gas chromatography has been used to determine interaction second virial coefficients. The GLC method involves studying the effect of carrier gas pressure on

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the partition coefficient and in practice this is accomplished by studying the variation of the retention volume of a pure sample as the carrier gas pressure is increased. To a good approximation, the net retention volume (V_N) of a pure sample is related to B_{12} by³:

$$\ln V_N = \ln V_N^\circ + \beta p_o J_s^4 \quad (1)$$

where:

$$\beta = (2 B_{12} - v_1^\infty)/RT.$$

v_1^∞ = partial molal volume of the sample at infinite dilution in the stationary liquid

J_s^4 = is a function only of the inlet and outlet column pressures, p_i and p_o :

$$\ln V_N^\circ = \ln \frac{n^l RT}{\gamma_1^\infty p_1^\circ} - \frac{(B_{11} - v_1^\circ) p_1^\circ}{RT} \quad (2)$$

where:

γ_1^∞ = the activity coefficient of the sample at infinite dilution in the stationary liquid

v_1° = molar volume of the pure sample

n^l = number of moles of stationary liquid on the column

p_1° = vapour pressure of the pure sample at column temperature

B_{11} = second virial coefficient of the pure sample.

Thus, from the slope of a plot of $\ln V_N$ versus $p_o J_s^4$ a value for B_{12} can be obtained, and from its intercept a value of γ_1^∞ . The B_{12} is for the mixture of sample vapour + carrier gas and should be independent of the nature of the stationary liquid. The γ_1^∞ is for the sample in the stationary liquid and should be independent of the nature of the carrier gas.

That the activity coefficients are correct has been verified in the case of several systems for which accurate static data are available³. Generally the agreement between the static and the GLC determinations is excellent, and thus there is reasonable confidence that the GLC method for obtaining γ_1^∞ is reliable.

However, when one comes to make a comparison between the second virial coefficients obtained chromatographically and those obtained statically one finds that none of the gas mixtures for which there is a published GLC result have ever been studied by other means. In general B_{12} data are scarce, but data for permanent gas-hydrocarbon mixtures are almost non-existent.

It is important that this comparison be made because it is difficult to assess accurately the validity of some of the assumptions that were made in deriving the GLC theory (e.g. neglect of third virial coefficients, neglect of the solubility of the carrier gas in the stationary liquid). In previous work⁴ values of virial coefficients were obtained by the application of the principle of corresponding states and compared with the chromatographic results.

The prediction of the second virial coefficient of a pure substance by this procedure requires a knowledge of its critical temperature and its critical volume. The

prediction of an *interaction* second virial coefficient involves not only a knowledge of the critical temperatures and volumes of the pure components but also the use of some empirical combining rules to obtain from the parameters for the pure components a set of *pseudo*-critical parameters characteristic of the mixture. It has been found that the GLC data are usually in rough agreement with corresponding states values⁴, but this agreement depends on which combining rules are used. Thus, this comparison is not quite satisfactory as a test of the chromatographic results. For this reason we have used a static method to determine experimental B_{12} values for five mixtures previously studied by gas chromatography.

EXPERIMENTAL METHOD

The technique employed for determining interaction virial coefficients has been described in detail elsewhere⁶. Briefly, the measurement consists of determining the pressure change when two gases are mixed at constant volume and temperature. Three 2 l bulbs are immersed in a thermostatic bath. Two of the bulbs (A, B) are filled with one component to a pressure P and the other bulb (C) is filled with the other component to the same pressure as can be observed with a sensitive differential pressure transducer. The contents of bulbs B and C are then mixed and any pressure change, ΔP , which results is observed by comparing the pressure in B and C with the original pressure in the reference bulb A.

The excess second virial coefficient \mathcal{E} , defined as:

$$\mathcal{E} = B_{12} - \frac{1}{2} (B_{11} + B_{22}), \quad (3)$$

is related in first order to the pressure change on mixing by the relation:

$$\mathcal{E} = 2 RT \Delta P / P^2. \quad (4)$$

(The higher order terms are small and easily evaluated for the conditions of our experiments⁶.) With this technique it is possible under optimum conditions to determine excess virial coefficients with a precision of $\pm 2 \text{ cm}^3/\text{mole}$. However, it is clear from eqn. 4 that the pressure difference observed depends quadratically on the filling pressure and in these studies the maximum pressure in the apparatus is limited by the low saturation pressure of the hydrocarbon component. For this reason the precision of the measurements has been considerably reduced.

The pentane, hexane, 2,2-dimethylbutane and 2-methylpentane used in the experiments were research grade (minimum 99.9% purity), obtained from the Phillips Petroleum Company. The 2-methylbutane was Matheson, Coleman and Bell spectroquality. The argon contained 0.005% maximum impurity. All of the hydrocarbon samples were degassed by repeated freezing and pumping before use. The measurements were made at 25.0° with the exception of one hexane mixture, which was studied at 50.0°.

RESULTS AND DISCUSSION

The values of \mathcal{E} obtained from our measurements and listed in Table I are

TABLE I

EXPERIMENTAL RESULTS AND B_{12} VALUES FOR HYDROCARBON MIXTURES WITH ARGON

Hydrocarbon component	$\mathcal{E}(\text{cm}^3/\text{mole})$	$-B_{12}(\text{cm}^3/\text{mole})$	$-B_{12}GLC(\text{cm}^3/\text{mole})$
<i>Temperature: 25°</i>			
Pentane	469 ± 4	136 ± 18 ^{7*} 125 ± 23 ⁸	98 ± 20
Hexane	807 ± 48	149 ± 65 ⁷ 80 ± 73 ⁹ 180 ± 50 ¹⁰	124 ± 20
2,2-Dimethylbutane	577 ± 16	156 ± 26	115 ± 20
2-Methylpentane	701 ± 39	147 ± 49	125 ± 20
2-Methylbutane	408 ± 4	178 ± 14 ⁷	94 ± 20
<i>Temperature: 50°</i>			
Hexane	614 ± 7	148 ± 27 ⁷ 108 ± 32 ⁹ 120 ± 9 ¹⁰	107 ± 20

* References refer to value of virial coefficients of pure hydrocarbon used in calculation of B_{12}

averages of at least three measurements which agree within the stated uncertainty. The precision of the measurements is essentially determined by the sensitivity of the pressure transducer and, as noted above, for the hydrocarbons with higher vapor pressures this results in a smaller uncertainty for the measurement.

In order to obtain values of B_{12} from these data it is necessary to have values of the second virial coefficients of the pure components, and these are listed in Table II. There are a large number of determinations of B for Ar at the temperatures of interest and they vary by no more than $\pm 1 \text{ cm}^3/\text{mole}$ from the particular values chosen; the choices of virial coefficient values for the hydrocarbons are less clear-cut.

TABLE II

VIRIAL COEFFICIENTS FOR PURE SUBSTANCES

	$-B(\text{cm}^3/\text{mole})$	References
<i>Temperature: 25°</i>		
Argon	16.4 ± 1	15
Pentane	1197 ± 20 1172 ± 30	7 8
Hexane	1896 ± 20 1758 ± 50 1958 ± 3	7 9 10
2,2-Dimethylbutane	1450 (± 20)	11 (calculated, $n = 5.2$)
2-Methylpentane	1680 (± 20)	11 (calculated, $n = 5.2$)
2-Methylbutane	1160 (± 20) 1155	11 (calculated, $n = 5.4$) 13
<i>Temperature: 50°</i>		
Argon	11.5 ± 1	15
Hexane	1513 ± 20 1423 ± 50 1456 ± 3	7 9 10

Direct determinations of second virial coefficients have been made only for pentane and hexane, most recently by McGLASHAN AND POTTER⁷, who showed that their data were represented essentially within experimental error by a semi-empirical corresponding states equation. It is their smoothed values which are given in the table. For pentane these results are in good agreement with the other value cited which was obtained by graphically extrapolating from 35° the measurements of GARNER AND MCCOUBREY⁸. Two other sets of data for hexane are to be found in the literature^{9,10} and these, too, are listed in the table. It is clear that if one accepts the claimed precision of these results there are large systematic differences between the different B values for this substance.

No direct measurements of the second virial coefficients of the branched hydrocarbons have been performed, but it has been shown for similar substances¹¹ that by using the McGLASHAN AND POTTER corresponding states equation, which was designed for normal hydrocarbons, reliable virial coefficients can be predicted by employing a fictitious carbon chain length. The chain length is determined from an analysis of either vapor pressure data or critical constants in a procedure essentially identical to that utilized by PITZER¹² for determining values of his acentric factor. The values for the branched hydrocarbons cited in the table have been obtained by this technique and the error estimates are representative of the accuracies obtained for a number of trial systems¹¹. The validity of these predictions for the systems studied here is lent credence when the computed second virial coefficient for 2-methylbutane is compared with a value, also listed, obtained from an analysis of heats of vaporization¹³.

Using the tabulated virial coefficients for the pure components we have calculated the interaction virial coefficients given in Table I by means of eqn. 3. The stated uncertainties represent the sum of the errors in our measurements of ϕ and the errors estimated for the pure hydrocarbons. Although it is not possible at present to specify which of the hexane values is most probable it should be noted that the McGLASHAN AND POTTER data are most likely to be consistent with the results for the other systems since they all conform to the same corresponding states equation.

For comparison the interaction virial coefficients obtained from GLC⁴ are also listed in the table. With the exception of the 2-methylbutane mixture the static results agree within experimental error with the GLC work, although the chromatographic data seem to lie in magnitude systematically lower than the present data. One does expect small systematic errors in the GLC values due to the approximations made in the theory. In order to obtain B_{12} from β in eqn. 1 it is necessary to know v_1^∞ , the limiting partial molal volume of the hydrocarbon in the stationary liquid, and in the actual calculations this has been replaced by v_1° , the molar volume. Some rough measurements indicate that this value may differ from the limiting partial molal volume by as much as 10 cm³/mole. In addition, recent approximate calculations¹⁴ indicate that the effect of solubility of Ar carrier gas in the stationary liquid may cause an error of $-5 (\pm 5)$ cm³/mole in B_{12} at 50°. At 25° this effect would be roughly 3 cm³/mole larger in magnitude due to increased solubility. Therefore, even though the precision of the GLC data is about ± 6 cm³/mole, taking these systematic errors into account it is probable that the actual uncertainty in the GLC results is of the order of ± 20 cm³/mole. Also, the sign of at least one of the errors is such as to bring the chromatographic data in closer agreement with the static results.

This work has involved a completely independent check of the B_{12} results obtained from GLC; these two experiments are so very different in nature that the general agreement between them gives added confidence in the new GLC theory. Previous comparisons with static measurements have attested to the correctness of the interpretation of the intercept of the $\ln V_N$ versus $p_0 J_3^4$ curve, and this test now suggests that the interpretation of the slope is reliable. (This simple treatment will not be expected to hold in cases where the carrier gas is appreciably soluble in the stationary liquid or where third virial coefficients cannot be neglected.) Any more sensitive test of the theory and its limits by comparisons between interaction virial coefficients will require either more reliable second virial coefficients for pure hydrocarbons or, better, a study by GLC of a wider range of systems for which static results are available.

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SUMMARY

New measurements of the interaction second virial coefficient (B_{12}) of some mixtures of argon with various low molecular weight hydrocarbons are presented. Recently, several workers have proposed and examined methods of measuring B_{12} by means of high-pressure gas chromatography, and these argon mixtures have been measured, primarily, in order to provide a comparison with those results obtained chromatographically. Although experimental error is still quite high (due mainly to lack of accurate values for second virial coefficients of the pure hydrocarbons), the agreement is good and the GLC results appear to be reliable.

REFERENCES

- 1 J. H. PURNELL, *Endeavour*, 23 (1964) 142.
- 2 D. H. DESTY, A. GOLDUP, G. R. LUCKHURST AND W. T. SWANTON, in M. VAN SWAAY (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 67.
- 3 A. J. B. CRUICKSHANK, M. L. WINDSOR AND C. L. YOUNG, *Proc. Roy. Soc. (London)*, Ser. A, 295 (1966) 259.
- 4 A. J. B. CRUICKSHANK, M. L. WINDSOR AND C. L. YOUNG, *Proc. Roy. Soc. (London)*, Ser. A, 295 (1966) 271.
- 5 S. T. SIE, W. VAN BEERSUM AND G. W. A. RIJNDERS, *Separation Sci.*, 1 (1966) 459.
- 6 C. M. KNOBLER, *Rev. Sci. Inst.*, 38 (1967) 184.
- 7 M. L. MCGLASHAN AND D. J. B. POTTER, *Proc. Roy. Soc., (London)*, Ser. A., 267 (1962) 478.
- 8 M. D. G. GARNER AND J. C. MCCOUBREY, *Trans. Faraday Soc.*, 55 (1959) 1524.
- 9 J. D. LAMBERT, G. A. H. ROBERTS, J. S. ROWLINSON AND V. J. WILKINSON, *Proc. Roy. Soc. (London)*, Ser. A, 196 (1949) 113.
- 10 G. A. BOTTOMLEY AND C. G. REEVES, *J. Chem. Soc.*, (1953) 3794.
- 11 E. A. GUGGENHEIM AND C. WORMALD, *J. Chem. Phys.*, 42 (1965) 3775.
- 12 G. N. LEWIS AND M. RANDALL, (Revised by K. S. PITZER AND L. BREWER), *Thermodynamics*, McGraw Hill, New York, 1961, p. 605.
- 13 D. W. SCOTT, J. P. MCCULLOUGH, K. D. WILLIAMSON AND G. WADDINGTON, *J. Am. Chem. Soc.*, 73 (1951) 1707.
- 14 D. H. EVERETT, B. W. GAINEY AND C. L. YOUNG, private communication.
- 15 J. H. DYMOND, *A Compilation of Second and Third Virial Coefficients*, Oxford University, England, 1964.