

CHREV. 81

## DETERMINATION OF SECOND-INTERACTION VIRIAL COEFFICIENTS BY GAS-LIQUID CHROMATOGRAPHY

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### 1. INTRODUCTION

#### A. What are virial coefficients?

The ideal gas law, given by the familiar equation  $PV = nRT$ , is based on an ideal model; however, real gases generally fail to obey it. Rather than formulate a new law, however, the ideal gas law is modified so as to conform more closely to the actual behavior of gases. Several such "modified" laws have been used, including the Van der Waals, Dieterici, Berthelot, and Beattie-Bridgeman equations<sup>1</sup>. An alternate form is the virial expansion of the ideal gas law, which for one mole of gas becomes:

$$PV = RT \left( 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \dots \right) \quad (1)$$

where  $B, C, D, \dots$  are called the second, third, fourth, . . . virial coefficients. Obviously, given enough coefficients, the experimental data for any gas can be fitted to the ideal, albeit modified, gas law.

Eqn. 1 gives the gas law as an expansion of volume terms, so that  $B, C, D, \dots$  are a function of temperature only. The expansion could just as easily be written in terms of pressure, however:

$$PV = RT + BP + CP^2 + DP^3 + \dots \quad (2)$$

Eqs. 1 and 2 are used interchangeably in the literature; they are easily related by setting  $P = (RT/V)(1 + B/V)$  in eqn. 1 (ignoring higher coefficients) and substituting for  $P$  in the right-hand side of eqn. 2.

Virial coefficients are of more than superficial importance for chemists. For example, the true fugacity of a real gas is given by the expression<sup>2</sup>:

$$\ln f = \ln P + \frac{BP}{RT} + \frac{1}{2}(C - B^2) \left(\frac{P}{RT}\right)^2 + \dots \quad (3)$$

Furthermore, the second, third, fourth, . . . virial coefficients can be related to binary, ternary, quaternary, . . . molecular interactions via statistical mechanics<sup>3</sup>. Expressions for the thermodynamic properties of real gases should also contain virial terms, for example:

$$\Delta G = RT \ln P_2/P_1 \quad (\text{ideal}) \quad (4)$$

$$\Delta G = RT \ln P_2/P_1 + B(P_2 - P_1) + \dots \quad (\text{real}) \quad (5)$$

Finally, since gas chromatography (GC) involves the elution of a solute with a gas, chromatographers should be aware of the effects of non-ideal carrier gas behavior on retention parameters, which in some cases can be appreciable.

### B. Gaseous mixtures

The Helmholtz free energy for one mole of an ideal gas is given by<sup>2</sup>:

$$A = \mu^0 - RT + RT \ln \left(\frac{RT}{p^0V}\right) \quad (6)$$

where  $\mu^0$  is the chemical potential of the gas at a standard pressure,  $P^0$ . For  $n$  moles of a gas, eqn. 6 becomes:

$$A = n \left[ \mu^0 - RT + RT \ln \left(\frac{nRT}{p^0V}\right) \right] \quad (7)$$

When the second virial coefficient (representing gas imperfections) is included, we have:

$$A = n \left[ \mu^0 - RT + RT \ln \left(\frac{nRT}{p^0V}\right) \right] + nRT \left(\frac{nB}{V}\right) \quad (8)$$

For two perfect gases in an ideal mixture, Dalton's law of partial pressures may be written as:

$$A = \sum_i n_i \left[ \mu_i^0 - RT + RT \ln \left(\frac{n_i RT}{p^0 V}\right) \right] \quad (9)$$

That is, the system is described by a simple summation of the properties of each component. For a mixture of two non-ideal gases, eqn. 8 therefore becomes:

$$\begin{aligned} A = & n_1 \left[ \mu_1^0 - RT + RT \ln \left(\frac{n_1 RT}{p^0 V}\right) \right] + \\ & n_2 \left[ \mu_2^0 - RT + RT \ln \left(\frac{n_2 RT}{p^0 V}\right) \right] + \\ & (n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}) \frac{RT}{V} \end{aligned} \quad (10)$$

where  $B_{11}$  and  $B_{22}$  are the second virial coefficients for species 1 and 2 as if each were present exclusively, and  $B_{12}$  is the cross-coefficient (or, the mixed second virial coefficient) for the two gases. That is,  $B_{12}$  represents the non-ideal interactions between species 1 molecules and species 2 molecules. The  $B_{12}$  values are often called second-interaction virial coefficients, because they represent the non-ideal gas-phase interactions between two dissimilar species.

Eqn. 10 is now differentiated with respect to volume at constant temperature to obtain<sup>2</sup>:

$$PV = (n_1 + n_2) RT + (n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}) \frac{RT}{V} \quad (11)$$

Eqn. 11 describes the behavior of a non-ideal gaseous mixture in terms of the ideal gas law and virial coefficients, and is applicable to GC, where a gaseous solute is eluted by a carrier, also a gas. As is most often the case, solute molecules are very different from carrier species, so that the virial corrections to the ideal gas law (given by eqn. 11) may be appreciable. This is in fact the case when carrier gases other than helium or hydrogen are used at pressures greater than 2 atm, and is a contributing factor to the non-reproducibility of GC data. Much of the work by chromatographers has been oriented toward the determination of  $B_{12}$  values, however, rather than the use of virial coefficient data (which is admittedly scarce) to correct for gas-phase non-ideal behavior. As will be shown, these effects are in some cases very large, and must be dealt with when physico-chemical measurements are made by GC.

## 2. THEORY OF THE DETERMINATION OF VIRIAL COEFFICIENTS BY GAS-LIQUID CHROMATOGRAPHY

In 1961, Everett and Stoddart<sup>4</sup> reported the determination of activity coefficients for several hydrocarbon solutes in di-*n*-nonyl phthalate at 30° by gas-liquid chromatography (GLC). They also noted that the true activity coefficient for a single component when converted to fugacity, is only approximately given by:

$$\ln \gamma_f^z = \ln \gamma_p^z - \frac{B p_1^0}{RT} \quad (12)$$

and, for an infinitely dilute solute vapor in a carrier gas, is actually:

$$\ln \gamma_f^z = \ln \gamma_p^z - \frac{p_1^0}{RT} (B_{11} - v_1^0) + \frac{\bar{p}}{RT} (2 B_{12} - B_{22} - v_1^z) \quad (13)$$

where  $p_1^0$  is the pure solute vapor pressure,  $v_1^0$  the pure solute molar volume,  $\bar{p}$  is the average column pressure, and  $v_1^z$  is the solute molar volume at infinite dilution. In 1962, Goldup and co-workers<sup>5</sup> noted that the separation of several hydrocarbons could be dramatically altered merely by changing the carrier gas. The suggestion was made that second-interaction virial coefficients ( $B_{12}$  values) were responsible, and an empirical formula was proposed to account for the behavior:

$$\ln k' = A + \frac{2 \bar{p} B_{12}}{RT} \quad (14)$$

where  $k' = K_L V_L / V_G$ , the capacity factor, and  $A$  is an empirical constant. At constant  $T$  and  $\bar{p}$ ,  $\ln k'$  was indeed shown to be a linear function of  $B_{12}$  for methylcyclopentane, 2,2-dimethylpentane, 2,4-dimethylpentane, and benzene, with helium, hydrogen, nitrogen, argon, and carbon dioxide carrier gases.

Desty and co-workers<sup>6</sup> evaluated the use of capillary columns in 1962, and concluded that  $B_{12}$  values could be determined via the following equation:

$$\ln V_x = \ln V_x^0 + \beta p_o J_2^3 \quad (15)$$

where  $V_x$  is the solute net retention volume, and:

$$\ln V_x^0 = \ln \frac{n_L RT}{\gamma_1^\infty p_1^0} - \frac{(B_{11} - v_1^0) p_1^0}{RT}$$

$$\beta = \frac{2 B_{12} - v_1^z}{RT}$$

$n_L$  is the number of moles of stationary phase in the column,  $p_o$  is the column outlet pressure, and

$$J_2^3 = \frac{2}{3} \left[ \frac{(p_i/p_o)^3 - 1}{(p_i/p_o)^2 - 1} \right]$$

following the nomenclature of Everett<sup>7</sup>:

$$J_n^m = \frac{n}{m} \left[ \frac{(p_i/p_o)^m - 1}{(p_i/p_o)^n - 1} \right]$$

Everett<sup>7</sup> also derived a virial equation which was different from Desty's. The ideal gas law was written as a summation:

$$PV = n_G RT + \frac{RT}{V^2} \sum_{ij} B_{ij} X_i X_j \quad (16)$$

where  $n_G$  is the total number of moles of gas phase, and  $X_i$  is the mole fraction of the  $i$ th component. Everett then derived the following expression for the activity coefficient:

$$\ln \gamma_1^\infty = \ln \gamma_1^{z,*} - \frac{(B_{11} - v_1^0) p_1^0}{RT} + \frac{(2B_{12} - B_{22} - v_1^z) \bar{p}}{RT} \quad (17)$$

where

$$\gamma_1^{z,*} = \frac{n_L RT}{K_L V_L p_1^0} \left[ 1 + \frac{B_{22} \bar{p}}{RT} \right]$$

Thus,

$$\ln \gamma_1^x = \ln \frac{n_L RT}{K_L V_L p_1^0} - \frac{(B_{11} - v_1^0) p_1^0}{RT} + \frac{(2B_{12} - v_1^z) \bar{p}}{RT} \quad (18)$$

where the approximation:

$$\ln \left( 1 + \frac{B_{22} \bar{p}}{RT} \right) \cong \frac{B_{22} \bar{p}}{RT}$$

has been made.

Eqn. 18 is formally similar to eqn. 15 by Desty. However, Everett subsequently derived the following:

$$\ln K_L = \ln K_L^0 + \beta \bar{p} \quad (19)$$

where

$$\ln K_L^0 = -\ln \gamma_1^z + \ln \frac{n_L RT}{V_L p_1^0} - \frac{(B_{11} - v_1^0) p_1^0}{RT}$$

and

$$\beta = \frac{(2B_{12} - v_1^z)}{RT}$$

as before. The net retention volume was then shown to be:

$$V_N = K_L^0 V_L (1 + \beta p_o J_3^z) \quad (20)$$

Or, since  $K_L^0 = V_N^0/V_L$ ,

$$K_L = K_L^0 (1 + \beta p_o J_3^z) \quad (21)$$

A plot of  $V_N$  (or  $K_L$ ) vs.  $p_o J_3^z$  should have a slope of  $K_L^0 V_L \beta$  (or  $K_L^0 \beta$ ), and an intercept of  $K_L^0 V_L$  (or  $K_L^0$ ). The true activity coefficient should therefore be given by:

$$\ln \gamma_1^z = \ln \frac{n_L RT}{K_L^0 V_L p_1^0} - \frac{(B_{11} - v_1^0) p_1^0}{RT} \quad (22)$$

Martire and Pollara<sup>8</sup> also considered expressions for the activity coefficient, and used the following:

$$\ln \gamma_1^z = \ln \gamma_p^z + \frac{(2B_{12} - v_1^0) \bar{p}}{RT} - \frac{(B_{11} - v_1^0) p_1^0}{RT} \quad (23)$$

where  $v_1^z$  has been replaced by  $v_1^0$  in the second term on the right-hand side of eqn. 23. They noted that this equation should be used for all carrier gases except helium, which is nearly ideal, and for which the following approximation is probably valid to  $\pm 1\%$ :

$$\ln \gamma_1^z = \ln \gamma_p^z - \frac{p_1^0 B_{11}}{RT} \quad (24)$$

Cruickshank *et al.*<sup>9</sup> and Windsor and Young<sup>10</sup> reconsidered the equations of

Desty and Everett. They also expanded the theory to include the effects of carrier gas solubility and third virial coefficients:

$$\ln V_N = \ln V_N^0 + \beta p_o J_3^2 + \xi (p_o J_3^2)^2 \quad (25)$$

where:

$$\xi = \frac{(3C_{122} - 4B_{12}B_{22})}{2(RT)^2} \quad (26)$$

$C_{122}$  is a mixed third virial coefficient<sup>11</sup>, and is probably negligible up to 20 atm. Eqn. 25 is only approximate if  $\beta$  is defined as before. More correctly, however<sup>12,13</sup>,

$$\beta = \frac{(2B_{12} - v_1^{\infty})}{RT} + \lambda \left[ 1 - \left( \frac{\partial \ln \gamma_1^{\infty}}{\partial X_2} \right) \right] \quad (27)$$

where  $\lambda$  is the carrier gas molal solubility in the stationary phase,  $X_2$  is the carrier mole fraction in the stationary phase, and  $(\partial \ln \gamma_1^{\infty} / \partial X_2)$  represents the change of the solute activity coefficient with changing amount of dissolved carrier. When the corrections given by eqns. 26 and 27 are ignored, eqn. 25 reduces to:

$$\ln V_N = \ln V_N^0 + \beta p_o J_3^2 \quad (28)$$

Three equations had thus been derived by different workers, eqns. 15, 20, and 28, which are given below in terms of the net retention volume:

$$\ln V_N = \ln V_N^0 + \beta p_o J_2^3 \quad (\text{Desty } et al.^6) \quad (15)$$

$$\ln V_N = \ln V_N^0 + \ln (1 + \beta p_o J_3^2) \quad (\text{Everett}^7) \quad (20)$$

$$\ln V_N = \ln V_N^0 + \beta p_o J_3^2 \quad (\text{Cruickshank } et al.^9) \quad (28)$$

Each of these involves a different plotting procedure to obtain  $\beta$  (and hence  $B_{12}$ ). Cruickshank *et al.*<sup>9</sup> and Windsor and Young<sup>10</sup> compared the three equations by assuming a value for  $\beta$ , then calculating  $V_N$  for a range of  $p_i$  and  $p_o$  values. Each of the three plotting procedures given by eqns. 15, 20, and 28 above were then used to retrieve  $\beta$ ; eqn. 28 consistently gave  $\beta$  values within 0.3% of the initially assumed value (even for conditions similar to capillary columns), and was usually much better than 0.3%. The only difference between eqns. 15 and 28 is in the  $J$  term, and results from either equation were not appreciably different as long as  $B_{12}$  was less than about 150 ml/mole.

Sewell and Stock<sup>14</sup> investigated the solubility of nitrogen in squalane and found it to be negligible. Cruickshank and co-workers<sup>12,13</sup> also considered the magnitude of the  $\xi$  and modified  $\beta$  terms given above. Neglecting  $\xi$  will give an error in the virial coefficient of about  $\pm 2$  ml/mole, but ignoring the term

$$\lambda \left[ 1 - \left( \frac{\partial \ln \gamma_1^{\infty}}{\partial X_2} \right) \right] \quad (29)$$

may lead to appreciable errors: for hydrocarbon solutes and stationary phases at

column pressures less than 5 atm, the  $B_{12}$  values will be erroneous by  $3 \pm 3$  ml/mole ( $H_2$  carrier),  $6 \pm 6$  ml/mole ( $N_2$  carrier), and  $10 \pm 10$  ml/mole (Ar carrier). The carrier effects will be even larger at pressures greater than 5 atm due to the increased solubility of the carrier in the stationary phase.

Pecsok and Windsor<sup>15</sup> extended the study of carrier gas effects to include methane and ethane, with the use of a very sensitive katharometer<sup>16</sup>. Their equation was of the form:

$$\ln V_s \left[ \frac{(1 + b\bar{p})}{(1 + bp_s)} \right] = \ln V_s^0 + \beta p_s J_3^2 \quad (30)$$

where  $b = B_{22}/RT$ ,  $\bar{p} = p_s J_3^2$ , and  $\beta$  is given by eqn. 27 above. The pressure drop in their work was very small ( $\bar{p} - p_s < 0.1$  atm), so that  $(1 + b\bar{p})/(1 + bp_s)$  was close to unity; the discrepancy in the data with ethane as a carrier was only 2 ml/mole when the factor was ignored. The carrier solubility was expected to be appreciable, since the stationary phase was squalane. Virtually no data exist for the value of  $\{1 - [(\partial \ln \gamma_1^x)/(\partial X_2)]\}$ , however, and so the approximation was made that it lies between 0 and 1, that is:

$$\left[ 1 - \left( \frac{\partial \ln \gamma_1^x}{\partial X_2} \right) \right] = 0.5 \pm 0.5$$

A further approximation was the assumption that the solubility behavior of the carrier gases was ideal<sup>17</sup>. The corrections to  $B_{12}$  values, when the term given by eqn. 29 is included in eqn. 27, were  $-22 \pm 22$  ml/mole for methane carrier, and  $-153 \pm 153$  ml/mole for ethane carrier at 25°. These were very approximate, however, and indicated that much more accurate determinations of  $\bar{z}$  and  $[(\partial \ln \gamma_1^x)/(\partial X_2)]$  are required when hydrocarbons are used as carrier gases.

Dantzler *et al.*<sup>18</sup> critically compared static<sup>19</sup> and GLC-determined  $B_{12}$  values, and found that the agreement was within the experimental error of the two techniques. They also noted that replacing  $v_1^x$  by  $v_1^0$  in eqn. 27 may give an error of 10 ml/mole in the  $B_{12}$  values determined by GLC. Ignoring carrier gas solubility (when fixed gases are used) may additionally cause an error of  $\pm 5 - 10$  ml/mole, so that while the precision of GLC experiments can be as good as  $\pm 6$  ml/mole, the overall error of the method may be as high as  $\pm 20 - 30$  ml/mole. Cruickshank *et al.*<sup>20</sup> attempted to avoid the carrier solubility problem by using a polar stationary phase (glycerol), where the solubility of  $N_2$  and  $CO_2$  was estimated to be less than 10% of the solubility of these gases in hydrocarbon phases. Gainey and Pecsok<sup>21</sup> used a series of closely related stationary phases for a number of hydrocarbon solutes and nitrogen carrier, and found the agreement between GLC and calculated values was excellent when  $N_2$  solubility in the stationary phases was taken into account.

Vigdergauz and Semkin<sup>22</sup> have reported the determination of  $B_{12}$  values from the change of retention index with pressure:

$$\frac{\Delta I}{\Delta P} = \frac{(I_1 - 100 Z)(\beta_{z+1} - \beta_z) - 100(\beta_x - \beta_z)}{-b_2} \quad (31)$$

where  $\Delta I = I_2 - I_1$  (the retention indices of the solute of interest measured at  $P_2$

and  $P_1$ ),  $Z$  and  $Z + 1$  are the carbon numbers of the standards,  $\Delta P = P_2 - P_1$ ,  $X$  is the solute of interest, and:

$$\beta_i = \frac{2B_{12,i} - v_i^2}{2.303 RT}$$

$$b_2 = \log \frac{V_{g,Z+1}}{V_{g,Z}}$$

where  $b_2$  is the log of the ratio of specific retention volumes of the standards at  $P_2$ . In addition, they described a capillary column method which used benzene and styrene standards, PEG 400 as the stationary phase, and pressures up to 30 atm for the determination of  $B_{12}$  values for several aromatic hydrocarbons. A method was also proposed which allows calculation of the  $[(\partial \ln \gamma_1^2)/(\partial X_2)]$  term by choosing one of the solutes as a standard. Finally, Spertell and Chang<sup>23</sup> have derived a method of determining solute-solute ( $B_{11}$ ) virial coefficients by GLC, where the solute is an isotope of the carrier gas: the proposed method appears to be valid, but is severely limited by the isotopic requirements of the solute, and has not yet been experimentally verified.

### 3. EXPERIMENTAL ASPECTS

#### A. Apparatus

The apparatus requirements for the determination of virial coefficients by GLC are essentially the same as for any physico-chemical measurement<sup>24</sup>, with the added consideration that the pressure must be variable over a range of several atmospheres. Many authors have reported GC apparatus capable of medium-to-high pressure operation, including Young<sup>25</sup>, Pecsok and Windsor<sup>15-16</sup>, Tsuda *et al.*<sup>26</sup>, and Cruickshank *et al.*<sup>27-28</sup>. Goedert and Guiochon<sup>29,30</sup> have also described a high-precision apparatus capable of reproducing retention times to hundredths of a second. The device described by Tsuda *et al.*<sup>26</sup> is of particular interest, since organic solvents such as carbon tetrachloride, benzene, and ethanol were used as carrier gases. These of course exhibit large gas-phase non-ideal effects, but may prove useful in the separation of some components, especially in light of the findings of Goldup and co-workers<sup>5</sup>, where the elution behavior of petroleum hydrocarbons was markedly altered merely by changing the carrier gas.

Two excellent papers have also appeared which describe useful apparatus for the static measurement of  $B_{12}$  values. Coan and King's method<sup>31</sup> used an entrainment procedure to determine the mole fraction of benzene in various gases over a range of 40 atm. The mixed virial coefficients were then found from the ratio of fugacity coefficients of benzene and the benzene-gas mixtures. Knobler<sup>19</sup> has also described a device which was employed by Dantzler *et al.*<sup>18</sup> in order to compare GLC and static  $B_{12}$  values.

#### B. Calculated $B_{12}$ values

Good agreement has been obtained between virial coefficients calculated from molecular properties, and those determined by GLC. Cruickshank and co-workers<sup>12,32</sup>



first reported the use of the "method of corresponding states", due to Hudson and McCoubrey<sup>33</sup>. The principle of corresponding states requires that if two different gases have the same value for two reduced variables (*e.g.*, pressure and temperature), they will also have approximately the same value for the third reduced variable (*e.g.*, volume), and are said to be in corresponding states<sup>34</sup>. This principle has been used by several workers to calculate  $B_{12}$  values, notably McGlashan *et al.*<sup>35,36</sup>, and Guggenheim *et al.*<sup>37,38</sup>. Gainey and Hicks<sup>39,40</sup> have recently reviewed four methods of predicting  $B_{12}$  values, and it now appears that solute mixed virial coefficients can be readily calculated, even with a paucity of experimental information regarding the molecular properties of the compounds of interest.

### C. GLC procedure

Mixed virial coefficients are determined most accurately by GLC with eqn. 28:  $\ln V_N$  is plotted vs.  $p_o J_3^2$ , which should give a straight line of slope  $\beta$ .  $B_{12}$  values are then found from this slope and eqn. 27: several examples are given by Littlewood<sup>41</sup>, where plots of  $\log V_N$  vs.  $p_o J_3^2$  are presented for benzene in squalane with various carrier gases (taken from ref. 28). Helium gives almost a horizontal line, indicating that virial effects are negligible up to several atmospheres. The heavier carrier gases, however, show appreciable (greater than 1%) virial deviation from ideal behavior beyond 2 atm. Values for the second-interaction virial coefficients determined in this way will not be more accurate than  $\pm 20$  ml/mole, however, unless the effects of carrier solubility in the stationary phase are known, or can be negated<sup>22</sup>. In addition, the average column pressure should be kept below approximately 10 atm so that third virial coefficients ( $C_{ijk}$ ) are negligible (eqn. 26). Interestingly enough, Czubryt *et al.*<sup>42</sup> have shown that gas-solid chromatography is not a suitable technique for the determination of  $B_{12}$  values unless the carrier gas adsorption isotherm at the column temperature is known exactly, and the relative amounts of adsorbed carrier and solute on the packing surface can be determined.

$B_{12}$  values are most often employed to calculate corrected (fugacity) activity coefficients: the use of eqns. 13, 23, or the following by Conder and Purnell<sup>43</sup>:

$$\ln \gamma_1^f = \ln \frac{n_L RT}{K_L V_L p_1^0} + \frac{(B_{11} - r_1^0) p_1^0}{RT} + \frac{(2B_{12} - r_1^f) p_o J_3^2}{RT} \quad (32)$$

requires knowledge of the solute virial coefficient,  $B_{11}$ , in addition to  $B_{12}$  values.  $B_{11}$  values have been calculated by various methods, including that by Rowlinson<sup>44</sup>, Guggenheim and McGlashan<sup>37</sup>, Kobe and Lynn<sup>45</sup>, Hirschfelder *et al.*<sup>46</sup>, and McGlashan and Potter<sup>35</sup>. A simplified apparatus has recently been described with which  $B_{11}$  values can be determined directly<sup>47</sup>; a few examples are presented in Table I.

Vapor pressure data ( $p_1^0$  values) are also needed, and can usually be found in physical properties compendia, or calculated from various forms of the Antoine equation<sup>48</sup>. Solute molar volumes can easily be measured, but infinite-dilution molar volumes ( $r_1^f$ ) generally must be approximated (often, merely by substituting  $r_1^0$ ); in selected cases,  $r_1^f$  values can be calculated with some degree of accuracy<sup>12,49</sup>.

TABLE 1  
SOLUTE-SOLUTE VIRIAL COEFFICIENTS<sup>9-11</sup> ( $B_{11}$ ) AT 25°

Solute	$B_{11}$ (ml/mole)
<i>n</i> -Pentane	-1033
<i>n</i> -Hexane	-1468
<i>n</i> -Heptane	-1968
Benzene	-1326
Cyclohexane	-1510

#### 4. RESULTS

At least 17 papers have now appeared which list  $B_{12}$  values for well over 200 organic compounds with various carrier gases and stationary phases. A few representative examples are given in Tables 2 and 3: Table 2 compares values of pentane for various carriers and stationary phases, and Table 3 presents the virial coefficients for a variety of hydrocarbons. Most of the  $B_{12}$  determinations have been for normal and branched alkanes and alkenes, but a few aromatic hydrocarbons have also been studied<sup>22</sup>.

TABLE 2  
COMPARISON OF  $B_{12}$  VALUES FOR PENTANE

Solvent	Carrier	$T$ (°C)	$B_{12}$ (ml/mole)	Reference
Squalane	N <sub>2</sub>	25	-100	27
Squalane	H <sub>2</sub>	25	+ 1	27
Squalane	N <sub>2</sub>	25	- 76	7
Squalane	H <sub>2</sub>	25	+ 3	7
Squalane	He	25	+ 28	6
Squalane	CH <sub>4</sub>	25	+204	15
Squalane	C <sub>2</sub> H <sub>6</sub>	25	-414	15
<i>n</i> -Hydrocarbons	Ar	25	- 98	18
1-Phenylalkanes	N <sub>2</sub>	40	- 86	21
<i>n</i> -Octadecane	N <sub>2</sub>	35	- 85	12
Di- <i>n</i> -nonyl phthalate	Ar	50	- 82	22
Di- <i>n</i> -nonyl phthalate	Ar	80	- 68	22
Di- <i>n</i> -nonyl phthalate	N <sub>2</sub>	80	- 60	22
Di- <i>n</i> -nonyl phthalate	CO <sub>2</sub>	80	- 76	22

##### A. Comparison of the GLC technique with other methods

Chromatographic data are usually evaluated by comparing GLC  $B_{12}$  values to static measurements, or calculated virial coefficients. The  $B_{12}$  values for benzene determined by the static method of Coan and King<sup>31</sup> are compared to GLC measurements in Table 4; agreement between the two techniques is within the experimental errors of the methods (Table 2, ref. 31). Dantzler *et al.*<sup>18</sup> also found that agreement between their static and GLC  $B_{12}$  values was within experimental error, which was said to be as high as  $\pm 20$ -30 ml/mole. This is not overly distressing, since at  $\bar{p} = 1$  atm, a  $B_{12}$  value of  $\pm 50$  ml/mole will yield an activity coefficient accurate to  $\pm 0.4\%$ , as shown by Conder and Purnell<sup>43</sup>.

TABLE 3  
SELECTED VIRIAL COEFFICIENTS FOR HYDROCARBONS DETERMINED BY GLC

<i>Solute</i>	<i>Solvent</i>	<i>Carrier</i>	<i>T</i> (°C)	<i>B</i> <sub>12</sub> (ml/mole)	<i>Reference</i>
<i>n</i> -Hexane	1-Phenylalkanes	N <sub>2</sub>	40	-110	21
<i>n</i> -Heptane	1-Phenylalkanes	N <sub>2</sub>	40	-110	21
<i>n</i> -Octane	1-Phenylalkanes	N <sub>2</sub>	40	-134	21
<i>n</i> -Hexane	Squalane	CH <sub>4</sub>	25	-292	15
2-Methylpentane	Squalane	CH <sub>4</sub>	25	-317	15
2,2-Dimethylbutane	Squalane	CH <sub>4</sub>	25	-216	15
Cyclohexane	<i>n</i> -Octadecane	N <sub>2</sub>	35	-122	12
Benzene	<i>n</i> -Octadecane	N <sub>2</sub>	35	-104	12
Hexafluorobenzene	1-Phenylalkanes	N <sub>2</sub>	40	-126	21
Toluene	Polyethylene glycol 400	CO <sub>2</sub>	50	-248	22
Ethylbenzene	Polyethylene glycol 400	CO <sub>2</sub>	50	-271	22
<i>o</i> -Xylene	Polyethylene glycol 400	CO <sub>2</sub>	50	-289	22
<i>m</i> -Xylene	Polyethylene glycol 400	CO <sub>2</sub>	50	-282	22
<i>p</i> -Xylene	Polyethylene glycol 400	CO <sub>2</sub>	50	-284	22

In addition to the static experimental methods already cited, good agreement has also been found between calculated and GLC virial coefficients, as noted earlier. Conder and Langer<sup>50</sup>, Gainey and Young<sup>13</sup>, Gainey and Pecsok<sup>21</sup>, and Gainey and Hicks<sup>39,40</sup> have all shown that the method of McGlashan and Potter<sup>35</sup> in conjunction with the combining rule of Hudson and McCoubrey<sup>33</sup> gives the best theoretical prediction of virial coefficients for conditions appropriate to GLC, and that values calculated in this manner agree with GLC results to 1-10%, as shown in Table 5. Thus, it appears that the GLC method of  $B_{12}$  measurement is accurate to about  $\pm 10$ -20 ml/mole, and can be significantly better, providing the carrier solubility and third virial coefficient effects can be determined, or experimental procedures chosen so that they can be neglected. In any event, agreement between static, calculated, and GLC mixed virial coefficients lies within the experimental error of the respective methods, but the GLC technique is significantly faster and simpler, since it requires only a gas chromatograph and the determination of the solute net retention volume at several column pressures.

TABLE 4  
COMPARISON OF STATIC AND GLC-DETERMINED  $B_{12}$  VALUES FOR BENZENE

<i>Carrier gas</i>	<i>T</i> (°C)	<i>B</i> <sub>12</sub> (ml/mole)	
		<i>Static</i> <sup>31</sup>	<i>GLC</i> <sup>15,17</sup>
He	50	+ 67 ± 4	+ 57 ± 8
H <sub>2</sub>	50	- 4 ± 3	- 5 ± 8
N <sub>2</sub>	35	- 97 ± 3	-104 ± 10
N <sub>2</sub>	50	- 85 ± 3	- 87 ± 8
Ar	32	-122 ± 3	-135 ± 10
Ar	50	- 95 ± 3	- 85 ± 8
CH <sub>4</sub>	50	-171 ± 3	-155 ± 15
C <sub>2</sub> H <sub>6</sub>	50	-282 ± 5	-

TABLE 5  
CALCULATED AND GLC  $B_{12}$  VALUES FOR BENZENE-NITROGEN<sup>13</sup>

Solvent	T (°C)	$B_{12}$ (ml/mole)	
		GLC	Calc.
n-Hexadecane	20	-120 ± 12	-120
	25	-109 ± 10	-116
	30	-107 ± 10	-111
n-Octadecane	35	-104 ± 10	-107
n-Eicosane	50	-94 ± 10	-96
	60	-93 ± 10	-89

## 5. DISCUSSION

There are two areas of significance for chromatographers arising from virial coefficient studies, the first is the effect of gas-phase non-ideal behavior on GC data, and the second, the use of organic solvents as carrier gases. Virial effects are now recognized as a potential source of significant error in GC results, but these gas imperfections may in some cases be used to separate components. Each of these topics is therefore now examined in detail.

### A. Virial effects on $V_a$ and $K_L$ values

Littlewood<sup>11</sup> has considered the problem of non-ideal (virial) effects and relative distribution coefficients. He defined the distribution coefficient,  $K_L$ , in terms of mass:

$$K_L = \frac{\text{weight of solute per gram stationary phase}}{\text{weight of solute per milliliter carrier gas}}, \text{ ml/g}$$

and showed that:

$$K_L = \frac{RT}{\gamma_1^0 MW_L p_1^0}, \text{ ml/g}$$

where  $MW_L$  is the molecular weight of the liquid phase. The true distribution coefficient,  $K_L'$  (corrected for carrier non-ideal behavior), was then given as:

$$K_L' = K_L \exp \left[ \frac{(v_1^0 - B_{11}) p_1^0}{RT} + \frac{(2B_{12} - v_1^z) \bar{p}}{RT} \right] \quad (33)$$

The ratio of  $K_L'$  to  $K_L$  will thus be a measure of virial effects on the distribution coefficients:

$$\ln \frac{K_L'}{K_L} = \frac{(v_1^0 - B_{11}) p_1^0}{RT} + \frac{(2B_{12} - v_1^z) \bar{p}}{RT} \quad (34)$$

Cruickshank and co-workers<sup>9</sup> have correctly pointed out that even if  $B_{12} = 0$ , the term  $(-v_1^z/RT)$  is not zero under any conceivable GLC conditions, so that the ratio will always differ from unity, even at  $p_a J_3^z = 0$ , at which point:

$$\ln \frac{K_L'}{K_L} = \frac{(v_1^0 - B_{11}) p_1^0}{RT} \quad (35)$$

Conder and Langer<sup>50</sup> have also considered the effects of gas-phase non-ideal behavior on retention volumes. They showed that:

$$\ln \frac{V_g(I)}{V_g(II)} = \frac{2 p_0 J_3^2}{RT} [B_{12}(I) - B_{12}(II)] \quad (36)$$

where  $V_g(i)$  and  $B_{12}(i)$  are the specific retention volume and virial coefficient for carrier gas,  $i$ , with the same liquid phase. Eqn. 36 predicts that the ratio of specific retention volumes is independent of  $B_{11}$  or  $B_{22}$  values, and the effect of changing the carrier gas (assuming it is insoluble) is independent of the stationary phase. This was demonstrated to be the case for butyl tetrachlorophthalate and benzoquinoline. Thus, while the absolute specific retention volumes were appreciably different for the two phases, the ratio  $\ln [V_g(I)]/[V_g(II)]$  was the same for both phases. Conder and Langer<sup>50</sup> also found that the difference in  $V_g$  values was 1–2% for a variety of aliphatic and aromatic hydrocarbons when helium and nitrogen were compared as carrier gases, which is certainly negligible for most analytical packed-column work (especially since commercially available chromatographs are rarely capable of reproducing and controlling column temperature and flow-rate to better than  $\pm 5\%$ ). However, they also noted that since capillary columns often require an appreciable pressure drop across long narrow-bore tubing to maintain an adequate flow-rate, virial effects can become appreciable, which will yield non-reproducible relative retention volumes as well as absolute values, unless the pressure conditions are duplicated exactly from laboratory to laboratory. This of course applies equally well to packed-column work whenever the pressure drop across the column exceeds 2 atm. These contributing factors to the non-reproducibility of GC data are not recognized by most chromatographers: and, while it is often true that most analytical laboratories are not concerned with reproducibility of better than 5–10%, such inaccuracy can lead (for example) to the incorrect identification of compounds in complex mixtures, for which capillary columns are now primarily used, and for which virial effects may be pronounced.

### B. Use of organic carrier gases

The use of carrier gases such as benzene<sup>20</sup> may prove very useful in the separation of mixtures, since  $B_{12}$  values should be large. For example, Laub and Pecsok<sup>51,52</sup> and Purnell and co-workers<sup>53,54</sup> have recently examined the charge transfer interactions of benzene, toluene, and the xylenes with various complexing agents in a variety of stationary phases. A very interesting experiment would be the use of benzene as a carrier gas with a column containing di-*n*-butyl phthalate and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ: a strong complexing agent<sup>51</sup>). Presumably, the stationary phase would quickly become saturated with benzene, which would then complex with the dissolved DDQ. Solutes such as toluene and the xylenes would be forced to compete with benzene for sites of complexation, thus offering an additional column variable for purposes of separation, similar to the competition between carrier gases and solutes for surface sites in gas-solid chromatography. Alternatively, one could conceivably begin with a carrier of *p*-xylene (or various dilutions thereof in fixed gases) which forms stronger complexes than the other xylenes, and attempt the elution of the aromatic hydrocarbons. It is anticipated that frontal or displacement forms of GLC would also prove useful in these studies. Luckhurst<sup>55</sup>, and Conder

and Purnell<sup>53</sup> have in fact considered the determination of activity and virial coefficients when the solute concentration is not at infinite dilution, and Conder<sup>23</sup> has pointed out the advantages of several finite-concentration GLC methods.

The technique of Coan and King<sup>51</sup> would appear to be particularly useful as an independent measure of  $B_{12}$  values where an organic carrier gas is used, such as ethane or benzene. Of perhaps potentially greater importance, however, would be a comparison of the static values to the GLC virial coefficients in order to determine the effects of carrier gas solubility in the stationary phase. It may also be feasible to use a combined McBain balance<sup>56</sup>-DeNouy tensiometer<sup>57</sup> system to measure carrier solubility directly, analogous to the determination of GLC surface adsorption effects<sup>58-63</sup>. Regardless of the procedure or measurement, however, the use of carrier gases other than helium, hydrogen, or nitrogen is a much neglected area of research, and it seems feasible that carrier selectivity in GC could become as important as solvent elution in high-performance liquid chromatography.

## 6. CONCLUSIONS

It should now be abundantly clear that virial effects can be very important in physico-chemical studies by GLC, particularly when activity coefficients are to be determined. As discussed earlier, the error in  $\gamma_1'$  values will be as much as 5-10% if virial effects are ignored, and it is not difficult to realize that since chromatographic distribution phenomena depend inversely on  $\gamma_1'$ , data from non-physico-chemical applications (such as separation and identification) will similarly be in error. These effects will be most pronounced when large pressure drops across a column are used, resulting in the possibility of serious discrepancies in retention data. The alteration of retention times or volumes by changing the carrier gas, however, may be a very useful separation tool for analytical work.

An excellent example of other virial effects can be found in the work reported by Yeremian *et al.*<sup>64</sup>, who studied the influence of "inert" diluent gases on the reaction rate and activation energy of the oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  with  $\text{V}_2\text{O}_5$  catalyst at 375-450°. Arrhenius plots showed that there was a 100% difference in the reaction rate when helium was substituted for argon as the diluent gas, and an increase in the molecular weight of the gas increased the rate, precisely the opposite of what was expected. Furthermore, adsorption of the inert gas on the surface of the catalyst was discounted as minimal at the temperature of interest (although this may be open to question), so that physico- or chemisorption could not be used to explain the anomalous rate behavior; these phenomena have yet to be explained, but are of considerable interest in a wide variety of industrial applications, and therefore continue to be studied in detail<sup>65</sup>. Such investigations are of course directly amenable to the GLC or GSC methods developed for rate and catalysis studies<sup>66</sup>; for example, a glance at Tables 2 and 4 shows that He and Ar give virial interactions which are different by as much as 160 ml/mole (benzene at 50°). A useful approach to the question of  $\text{SO}_2$  catalysis would therefore involve the determination of the virial coefficients of He and Ar with  $\text{SO}_2$  (undoubtedly, these effects are pronounced with species such as  $\text{SO}_2$ ). Carrier gas effects could then subsequently be examined by GSC, where  $\text{V}_2\text{O}_5$  would be employed as the column packing.

Finally, it is now apparent to chemists of all disciplines that gas-liquid chro-

matography is of far more importance than a mere tool for separations. Nowhere is this more true than in physical chemistry, where GLC is becoming an increasingly attractive method of examining solution phenomena and related topics<sup>17,51-54,67-71</sup>. Concerning virial phenomena, the trend in GLC has for the most part been in the direction of determining  $B_{12}$  values, rather than the use of virial coefficients to obtain more accurate (hence more reproducible) distribution data. Yet, it does little good to construct a high-precision instrument, and not correct the data so obtained for carrier gas non-ideal effects. It is hoped, therefore, that this review will prompt chromatographers at least to consider virial phenomena, not only in physico-chemical applications, but in straightforward separations as well. There are many areas awaiting development in the study of virial imperfections, not the least of which is the use of common organic solvents as GC carrier gases. Lastly, this review should serve to indicate the fulfillment of an expectation by Purnell<sup>72</sup>, who in 1962 expressed confidence that GC would one day assume an established place among purely physico-chemical disciplines.

## 7. SUMMARY

The determination of second-interaction virial coefficients ( $B_{12}$  values) by gas-liquid chromatography is reviewed. The precision apparatus and experimental procedures required to measure  $B_{12}$  values are considered, and the importance of virial coefficients is also discussed. It is shown that in some cases, carrier gas imperfections lead to very pronounced solute elution effects, especially in kinetic studies. It is concluded that virial coefficients should always be taken into account whenever physico-chemical measurements are made by gas chromatography, and that virial effects should also be recognized to be of potential importance in other analytical (separation and identification) studies.

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