

CHROM. 5220

## SOME NON-ANALYTICAL APPLICATIONS OF HIGH-PRESSURE GAS CHROMATOGRAPHY

M. VIGDERGAUZ AND V. SEMKIN

*A. E. Arbuzov Institute of Organic and Physical Chemistry, U.S.S.R. Academy of Sciences, Kazan (U.S.S.R.)*

## SUMMARY

Second interaction virial coefficients of more than sixty hydrocarbons and other organic compounds with nitrogen, argon and carbon dioxide have been defined by gas chromatography. The method of calculation of mixed second virial coefficients on the basis of retention indices measured at two pressures has been suggested.

For such cases when the dissolution of the carrier gas in the stationary liquid is noticeable, the interpolation method of mixed second virial coefficients definition has been suggested, including the use of two substances with molecular structure similar with the structure of the substances to be investigated as standards.

One of the most important applications of gas-liquid chromatography is the determination of the physical properties of gases and liquids. GOLDUP *et al.*<sup>1</sup> were the first to show the possibility of applying gas chromatography to the investigation of imperfections in gas mixtures. The change of retention corresponding to a change in the nature of the carrier gas was assigned to the gas imperfection. EVERETT<sup>2,3</sup> and YOUNG *et al.*<sup>4-15</sup> have calculated the second interaction virial coefficients and solute activity coefficients at infinite dilution on the basis of experimental net retention volumes measured at different pressures and with different carrier gases. The correlation between the solute distribution coefficients and the compressibility coefficient has been reported by KOBAYASHI *et al.*<sup>16-23</sup>.

The purpose of this investigation is the chromatographic determination of the second mixed virial coefficients of interaction between the solute and carrier gas on the basis of chromatographic data obtained using packed and open tubular columns.

A more precise relationship for the specific retention volume calculation with the carrier gas compressibility correction may be written as

$$V_g = \frac{t_R - t_0}{g} \cdot v_a \cdot \frac{273.16}{T_p} \cdot (P_0 - P_{H_2O}) \cdot \frac{Z_p}{Z_0} \cdot \frac{J_3^2}{P_0} \quad (1)$$

where  $t_R$  and  $t_0$  are the retention times of the solute investigated and the nonsorbing gas;  $g$  is the weight of the stationary liquid in the column;  $v_a$  is the carrier gas flow rate at the column outlet;  $T_p$  is the flow-meter temperature;  $P_{H_2O}$  is the saturated

vapour pressure at  $T_p$ ;  $Z_p$  is the gas compressibility coefficient at column temperature and at pressure  $P = P_0 \cdot J_2^3$ , which is defined as  $(PV/RT) = (B_{22}/RT)P_0J_4^5$ ;  $Z_0$  is the carrier gas compressibility coefficient at the ambient temperature and the pressure  $P_0$ ;  $V$  is the carrier gas molar volume,  $R$  is the gas constant,  $B_{22}$  is the second virial coefficient of the carrier gas, the pressure drop correction factor, in accordance with EVERETT'S designation,  $J_n^m = n/m \cdot [(P_i/P_0)^m - 1]/[(P_i/P_0)^n - 1]$ ;  $P_i$  is the inlet column pressure.

The specific retention volume is connected with the second mixed virial coefficient according to EVERETT<sup>2,3</sup> and YOUNG *et al.*<sup>4-15</sup> by the equation:

$$\ln V_\theta = \ln V_\theta^0 + \frac{2B_{12} - V_i^\infty}{RT} P_0 \cdot J_3^4 + \lambda \left( 1 - \frac{\partial \ln \gamma^\infty}{\partial x} \right) P_0 \cdot J_3^4 \quad (2)$$

where  $V_\theta$  is the specific retention volume at the average column pressure  $P_0 \cdot J_3^4$ ;  $V_\theta^0$  is the specific retention volume of the same solute at the pressure extrapolated to zero;  $B_{12}$  is the second mixed virial coefficient of interaction of solute and carrier gas;  $V_i^\infty$  is the solute partial molar volume at infinite dilution;  $\lambda$  is the carrier gas molar solubility in the stationary liquid;  $\partial \ln \gamma^\infty / \partial x$  corresponds to the alteration in the solute activity coefficient resulting from a change in the dissolved carrier gas molar fraction.

The log specific retention volume dependence on the average pressure is a straight line the slope of which is connected with the  $B_{12}$  value (if the carrier gas solubility in the stationary liquid is neglected). The distorting influence of the third virial coefficient is noticeable at higher pressures.

As shown in ref. 9, the use of different carrier gases permits one to carry out more precise extrapolation to zero pressure because the  $V_\theta^0$  value is independent of the nature of the mobile phase and corresponds to the point of crossing of the straight lines which corresponds to the same solution but different carrier gas.

The direct second mixed virial coefficients calculation may be found according to the equation

$$-B_{12} = \frac{1.15 RT \Delta \log_{10} V_\theta}{\Delta P} - 0.5 V_i^0 \quad (3)$$

where  $\Delta \log_{10} V_\theta$  is the difference of the logarithms of the solute specific retention volumes, corresponding to a pressure difference  $\Delta P$ ;  $V_i^0$  is the molar volume of the liquid solute. Here  $V_i^\infty = V_i^0$  is allowed. The error connected with this last assumption is about  $\pm 3$  cm<sup>3</sup>/mole according to GAINEY AND YOUNG<sup>10</sup>.

The experiments were carried out with a gas chromatograph equipped with a flame ionisation detector.

A column, 150 cm long with an inner diameter of 3 mm, was packed with Chromosorb W coated with 30% of dinonyl phthalate. The oven temperature was controlled within  $\pm 0.2^\circ$ ; the argon, nitrogen or carbon dioxide carrier gas flow rate was measured with an accuracy up to  $\pm 0.5\%$ .

As shown in Fig. 1, the deviation from the linear relationship of the retention volume logarithm *versus* the average pressure is very small and equal approximately to 0.005 log units for the hydrocarbons and other solutes investigated.

The calculated second mixed virial coefficient values are summarised in Table I which also shows  $B_{12}$  values reported in the literature for comparison.

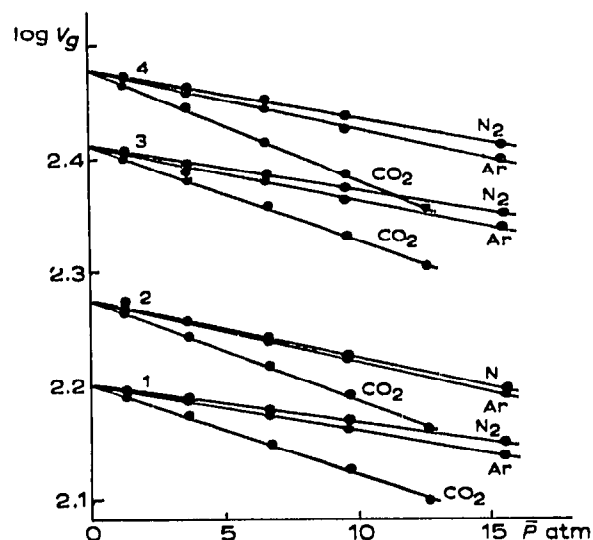


Fig. 1. Logarithm of the specific retention volume (at 80°) plotted *versus* the average column pressure of nitrogen, argon and carbon dioxide. 1 = dioxan, 2 = *n*-octane; 3 = toluene; 4 = butyl acetate.

TABLE I

EXPERIMENTAL SECOND INTERACTION VIRIAL COEFFICIENTS OF SOLUTE-CARRIER GAS MIXTURES ( $-B_{12}$  cm<sup>3</sup>/mole)

No.	Solute	Carrier gas					
		CO <sub>2</sub>		Ar		N <sub>2</sub>	
		80°	50°	50° <sup>98, 13, 25</sup>	80°	80°	80° <sup>98, 10, 11</sup>
1	<i>n</i> -Pentane	76	82	83 ± 20	68	60	49 ± 10
2	<i>n</i> -Hexane	147	106	107 ± 20	81	69	65 ± 10
3	<i>n</i> -Heptane	177	136	---	97	81	80 ± 10
4	<i>n</i> -Octane	227	160	---	122	98	95 ± 10
5	<i>n</i> -Nonane	249	181	---	146	117	---
6	<i>n</i> -Decane	---	---	---	---	130	---
7	Cyclohexane	163	102	---	86	63	50 ± 30
8	2,2,4-Trimethylpentane	147	128	---	87	47	---
9	Benzene	216	117	90 ± 10	105	74	72 ± 10
10	Toluene	235	135	---	120	94	---
11	Styrene	300	169	---	148	117	---
12	Pyridine	207	115	---	95	42	---
13	Nitromethane	188	91	---	62	41	---
14	Nitroethane	247	125	---	97	71	---
15	Chloroform	169	60	---	59	12	---
16	Carbon tetrachloride	154	115	---	67	24	---
17	Ethyl alcohol	95	118	---	46	10	---
18	Isopropyl alcohol	127	80	---	51	---	---
19	Acetone	129	---	---	58	---	---
20	Methyl ethyl ketone	184	86	---	65	36	---
21	Dioxan	136	124	---	86	67	---
22	Butyl acetate	260	138	---	119	79	---

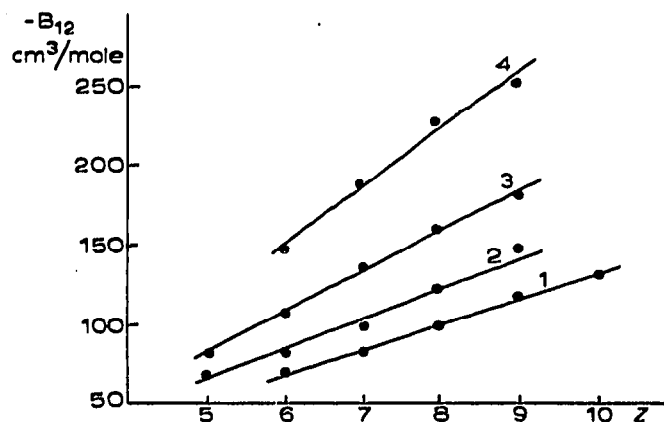


Fig. 2. Mixed second virial coefficient plotted *versus* *n*-paraffin carbon number. Carrier gases: 1 = nitrogen, 80°; 2 = argon, 80°; 3 = argon, 50°; 4 = carbon dioxide, 80°.

The relationship of the  $B_{12}$  values of *n*-paraffins *versus* carbon number is approximately a straight line (see Fig. 2).

It must be pointed out that an error of 1% taking place in the measurement of retention under our experimental conditions leads to a 10% error in the calculated value of the second virial coefficient. The error in  $B_{12}$  determination mainly depends on the experimental errors and the carrier gas solubility in the stationary liquid (the third term in the right part of eqn. 2).

In order to determine the  $B_{12}$  of a complex mixture of components when it is

TABLE II

SECOND INTERACTION VIRIAL COEFFICIENTS OF GASOLINE HYDROCARBONS-ARGON MIXTURES AT 25° CALCULATED ON THE BASIS OF PRESSURE DEPENDENCE OF RETENTION INDEX

No.	Hydrocarbons	$-B_{12}$ ( $\text{cm}^3/\text{mole}$ )	$-B_{12}$ ( $\text{cm}^3/\text{mole}$ ) <sup>25</sup>
1	2,2-Dimethylbutane	108	115 ± 20
2	Cyclopentane	108	
3	2,3-Dimethylbutane	112	125 ± 20
4	2-Methylpentane	115	
5	3-Methylpentane	116	
6	Methylcyclopentane	127	
7	2,2-Dimethylpentane	128	
8	2,4-Dimethylpentane	130	
9	2,2,3-Trimethylbutane	127	
10	Benzene	112	
11	3,3-Dimethylpentane	132	
12	Cyclohexane	130	
13	1,1-Dimethylcyclopentane	134	
14	2-Methylhexane	137	
15	2,3-Dimethylpentane	135	
16	3-Methylhexane	138	
17	<i>cis</i> -1,3-Dimethylcyclopentane	136	
18	<i>trans</i> -1,3-Dimethylcyclopentane	136	
19	<i>trans</i> -1,2-Dimethylcyclopentane	136	

necessary to use open tubular columns, we attempted to measure  $B_{12}$  on the basis of retention indices because their values depend less on changes in the experimental conditions than the specific retention.

It may be shown that the change of the retention index due to a pressure change is

$$\frac{\Delta I}{\Delta P} = \frac{(I_1 - 100z)(\beta_{(z+1)} - \beta_z) - 100(\beta_x - \beta_z)}{-b_2} \quad (4)$$

where  $\Delta P = P_2 - P_1$ ,  $\Delta I = I_2 - I_1$ , and  $I_1$  and  $I_2$  are the solute retention indices measured at the column pressure values of  $P_1$  and  $P_2$ ;

$$\beta_i = \frac{2B_{12i} - V_{1i}^\infty}{2.3 RT}; \quad i = x, z, z + 1; \quad b_2 = \frac{\log_{10} V_{\nu(z+1)}}{\log_{10} V_{\nu z}}$$

is the logarithm of the relative retention of neighbouring  $n$ -paraffins at  $P_2$ ,  $B_{12i}$  is the second mixed virial coefficient of interaction of  $i$ -th solute with the carrier gas. Eqn. 4 permits  $B_{12}$  values of solutes to be determined on the basis of known  $B_{12}$  values for  $n$ -paraffins.

The data obtained on an open tubular column coated with 1-octadecene when a gasoline fraction was separated were used for the calculation<sup>24</sup>. The  $-B_{12}$  values in an argon media for  $n$ -pentane and  $n$ -hexane at 25° used corresponded to 98 and 124 cm<sup>3</sup>/mol<sup>25</sup>. The second mixed virial coefficients calculated according to eqn. 4 are summarised in Table II, where for comparison the two isoparaffin data extracted from the literature are also given.

When the carrier gas solution in the stationary liquid is allowed for, the effective second virial coefficient values may be obtained from eqn. 2:

$$B_{\text{eff.}} = B_{12} + 0.5 \lambda \left( 1 - \frac{\partial \ln \gamma^\infty}{\partial x} \right) RT \quad (5)$$

The absolute value of  $B_{\text{eff.}}$  is much less than the virial coefficient obtained with the same solute and same carrier gas but with a stationary liquid of very small solubilising power for the carrier gas. Therefore it is advisable that the virial coefficient calculation for a series of solutes with similar molecular structure be carried out on the basis of the known  $B_{12}$  values of two solutes of above group, because in this case the possibility of almost neglecting the effect of the third term of eqn. 3 occurs.

It is possible to calculate the second virial coefficients of solute-carbon dioxide mixtures on the basis of retention data of aromatics obtained with an open tubular column coated with polyethylene glycol 400 (pressure—up to 30 atm) using the  $B_{12}$  values of benzene and styrene as standards. The calculation was carried out according to equation

$$\frac{\Delta G}{\Delta P} = \frac{\beta_x - \beta_1 - G(\beta_2 - \beta_1)}{\log_{10}(t'_{R2}/t'_{R1})} \quad (6)$$

where

$$\Delta G = G_2 - G_1, \quad \Delta P = P_2 - P_1, \quad G = \frac{\log_{10} t'_{Rx} - \log_{10} t'_{R1}}{\log_{10} t'_{R2} - \log_{10} t'_{R1}}, \quad \beta \text{ and } t'_R$$

indices correspond to the solute investigated ( $x$ ) and standards (1 and 2), the value  $G_1$  corresponds to the pressure  $P_1$  and  $G_2$  and  $\log_{10}(t'_{R2}/t'_{R1})$  to the pressure  $P_2$ ,

TABLE III

SECOND INTERACTION VIRIAL COEFFICIENTS DETERMINED BY THE INTERPOLATION METHOD (eqn. 6)  
 Standard  $B_{12}$  values: Carbon dioxide carrier gas, benzene = 216 cm<sup>3</sup>/mole, styrene = 300 cm<sup>3</sup>/mole; argon carrier gas, benzene = 105 cm<sup>3</sup>/mole, styrene = 148 cm<sup>3</sup>/mole.

No.	Solute	Ar		CO <sub>2</sub>		No.	Solute	Ar		CO <sub>2</sub>	
		$-B_{12}$ (cm <sup>3</sup> /mole)	$-B_{12}$ (cm <sup>3</sup> /mole)	$-B_{12}$ (cm <sup>3</sup> /mole)	$-B_{12}$ (cm <sup>3</sup> /mole)			$-B_{12}$ (cm <sup>3</sup> /mole)	$-B_{12}$ (cm <sup>3</sup> /mole)		
1	Toluene	123	248	17	1,4-Diethylbenzene	168	342				
2	Ethylbenzene	138	271	18	<i>n</i> -Butylbenzene	168	345				
3	<i>p</i> -Xylene	143	284	19	1,3-Dimethyl-5-ethylbenzene	173	348				
4	<i>m</i> -Xylene	141	282	20	1-Methyl-2-propylbenzene	171	327				
5	Isopropylbenzene	148	286		1,2,3-Trimethylbenzene	165	335				
6	<i>o</i> -Xylene	146	289	21	1,4-Dimethyl-2-ethylbenzene	174	348				
7	<i>n</i> -Propylbenzene	152	292	22	1,3-Dimethyl-4-ethylbenzene	174	350				
8	1-Methyl-3-ethylbenzene	154	309	23	1,2-Dimethyl-4-ethylbenzene	177	354				
9	Iso-butylbenzene	159		24	1,3-Dimethyl-2-ethylbenzene	167	352				
10	1,3,5-Trimethylbenzene	160	325	25	1,2-Dimethyl-3-ethylbenzene	168	349				
11	<i>sec.</i> -Butylbenzene	160	312	26	1,2,4,5-Tetramethylbenzene	183	376				
12	1-Methyl-2-ethylbenzene	158	310	27	1,2,3,5-Tetramethylbenzene	183	380				
13	1,2,4-Trimethylbenzene	156	340	28	1,2,3,4-Tetramethylbenzene	178	386				
14	1-Methyl-3-propylbenzene	167	328	29							
15	1-Methyl-2-iso-propylbenzene	168	329								
16	1-Methyl-4-propylbenzene	169	318								

$t'_R = t_R - t_0$ . The  $B_{12}$  values obtained are summarized in Table III. A similar calculation provided on the basis of retention indices gave results which differ from the literature data when they are compared with those measured above.

The relative  $\partial \ln \gamma^\infty / \partial x$  value may be determined on the basis of the experimental data if one of the solutes investigated is used as a standard. If  $\Delta B = B_{\text{eff.}} - B_{12}$ , it is evident that

$$\Delta B_{\text{rel.}} = \left( 1 - \frac{\partial \ln \gamma^\infty}{\partial x} \right)_{\text{rel.}} \quad (7)$$

The comparative evaluation of the effect of the solubility of the different carrier gases on the solute retention may be found in a similar way.

The values obtained for the second virial coefficients were used in order to make corrections for the gas phase imperfection during the investigation of the thermodynamics of the solution of various organic compounds in polar and nonpolar solvents.

## REFERENCES

- 1 I. A. GOLDUP, G. R. LUCKHURST AND W. T. SWANTON, *Nature*, 193 (1962) 333.
- 2 D. H. EVERETT AND C. T. H. STODDART, *Trans. Faraday Soc.*, 57 (1961) 746.
- 3 D. H. EVERETT, *Trans. Faraday Soc.*, 61 (1965) 1637.
- 4 A. J. B. CRUICKSHANK, M. L. WINDSOR AND C. L. YOUNG, *Proc. Roy. Soc.*, A295 (1966) 259.
- 5 M. L. WINDSOR AND C. L. YOUNG, *J. Chromatogr.*, 27 (1967) 355.
- 6 A. J. B. CRUICKSHANK, M. L. WINDSOR AND C. L. YOUNG, *Proc. Roy. Soc.*, A295 (1966) 271.
- 7 A. J. B. CRUICKSHANK, M. L. WINDSOR AND C. L. YOUNG, *Trans. Faraday Soc.*, 62 (1966) 2341.
- 8 A. J. B. CRUICKSHANK, B. W. CAINEY AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 337.
- 9 A. J. B. CRUICKSHANK, B. W. GAINNEY AND C. L. YOUNG, *VII. Int. Symp. Gas Chromatogr. Copenhagen, 1968*, paper 5.
- 10 B. W. GAINNEY AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 349.
- 11 C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 1537.
- 12 D. H. EVERETT, B. W. GAINNEY AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 2667.
- 13 C. P. HICKS AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 2675.
- 14 C. L. YOUNG, *Chromatogr. Rev.*, 10 (1968) 129.
- 15 A. J. B. CRUICKSHANK, B. W. GAINNEY, C. P. HICKS, T. M. LETCHER, R. W. MOODY AND C. L. YOUNG, *Trans. Faraday Soc.*, 65 (1969) 1014.
- 16 F. I. STALKUP AND R. KOBAYASHI, *J. Chem. Eng. Data*, 8 (1963) 564.
- 17 F. I. STALKUP AND H. A. DEANS, *Amer. Inst. Chem. Eng. J.*, 9 (1963) 106.
- 18 F. I. STALKUP AND R. KOBAYASHI, *Amer. Inst. Chem. Eng. J.*, 9 (1963) 121.
- 19 H. B. GILMER AND R. KOBAYASHI, *Amer. Inst. Chem. Eng. J.*, 10 (1964) 797.
- 20 K. T. KOONCE, H. A. DEANS AND R. KOBAYASHI, *Amer. Inst. Chem. Eng. J.*, 11 (1965) 259.
- 21 H. B. GILMER AND R. KOBAYASHI, *Amer. Inst. Chem. Eng. J.*, 11 (1965) 702.
- 22 R. KOBAYASHI, P. S. CHAPPELEAR AND H. A. DEANS, *Ind. Eng. Chem.*, 10 (1967) 63.
- 23 L. D. HORN AND R. KOBAYASHI, *J. Chem. Eng. Data*, 12 (1967) 294.
- 24 M. S. VIGDERGAUZ AND V. I. SEMKIN, *Neftekhimiya*, 9 (1969) 470.
- 25 E. M. DANTZLER, C. M. KNOBLER AND M. L. WINDSOR, *J. Chromatogr.*, 32 (1968) 433.

*J. Chromatogr.*, 58 (1971) 95-101