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SECOND CROSS VIRIAL COEFFICIENTS OF BENZENE–GAS MIXTURES FROM HIGH PRESSURE SOLUBILITY MEASUREMENTS

A COMPARISON WITH GAS CHROMATOGRAPHIC VALUES*

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SUMMARY

Values of second cross virial coefficients have been determined from solubility measurements at high pressures for binary mixtures of benzene with He, H_2, N_2, Ar, CH_4, and C_2H_4. The results of these measurements are compared with values obtained using newly developed high pressure gas–liquid chromatographic methods. The agreement between second cross virial coefficients obtained by these two different methods is found to be good.

INTRODUCTION

In recent years there has been considerable interest in the use of gas–liquid chromatography (GLC) as a means of determining thermodynamic properties of two component systems[1-10]. In these studies, the variation of net retention volume of a pure sample with carrier gas pressure is used to determine both the activity coefficient at infinite dilution of the sample component in the stationary liquid phase and the second cross virial coefficient representing deviations from ideality in the gas phase caused by intermolecular pair interactions between molecules of the sample component and those of the carrier gas. Comparisons of activity coefficients obtained using GLC methods and those obtained from static vapor pressure measurements show good agreement[3,5]. Second cross virial coefficient data, determined using other methods, also show good agreement in the few cases where data are available for comparison[8,9,11]. In general, however, there is a paucity of second cross virial coefficient data available for comparison to GLC values, particularly for systems involving gases of moderate complexity such as methane and ethylene whose solubility in the stationary liquid phase cannot be neglected, thus necessitating the introduction of approximate correction factors in GLC second cross virial coefficient determinations[9,10].

Values of second cross virial coefficients involving one solute, benzene, in a series of gases ranging in complexity from helium to ethylene, have been determined

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from solubility measurements at high pressures and are reported here. Temperatures of these measurements (32°, 35°, 50°) have been chosen to maximize comparison with existing GLC values.

EXPERIMENTAL

The experimental technique used here for determining second cross virial co-efficients is a modification of a method used by PRAUSNITZ AND BENSON[12]. The method entails measuring the concentration of benzene vapor in equilibrium with its liquid phase in the presence of a compressed inert gas. The flow system used in these experiments is shown schematically in Fig. 1.

The gas to be studied is allowed to flow under high pressure from its storage cylinder (A) through a Matheson Model 3 pressure regulator (B) into a cylindrical steel equilibrium cell (C) containing liquid benzene. A detailed drawing of the equilibrium cell is shown in Fig. 2. In use, the cell is filled with benzene to a level approximately 2 in. from the top. The high pressure gas entering the bottom of this cell is dispersed into small bubbles by a fritted glass sparger (pore size 14 μ) to insure rapid equilibration between the gas and benzene as the bubbles pass upwards through the liquid phase. There were no problems with benzene entrainment or splashing at the surface provided adequate dead space was provided over the liquid surface. The temperature of this cell was controlled to within $\pm 0.05°$ by a constant temperature oil bath (D).

The vapor–gas mixture leaving the cell passes through a heated section of tubing (E) and is expanded through a heated Matheson stainless steel needle valve (F) into a series of three cold traps (G) which are suspended in a dry ice–acetone bath while
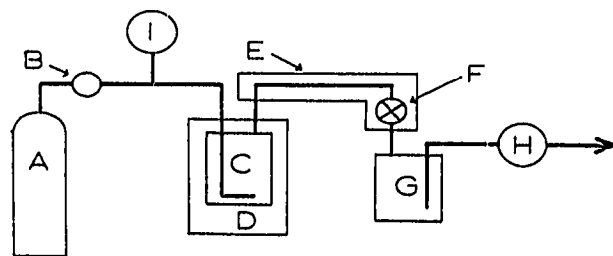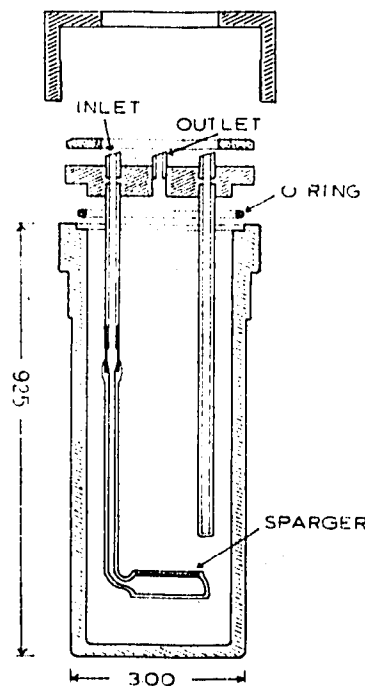

Fig. 1. Schematic diagram of equipment.

Fig. 2. Equilibrium cell. (Dimensions in inches.)

the run is in progress. The temperature of the tubing (E) and valve (F) is maintained at a temperature exceeding that of the equilibrium cell to prevent condensation from occurring until the gas–vapor mixture is expanded into the cold traps. After passing through the traps, the gas stream passes through an American Meter Co. Model AL 17-1 wet-test meter (H) which measures the volume of essentially pure diluent gas at ambient temperature and pressure which has flowed through the system during a given experimental determination. The pressure of the gas–vapor system in the high pressure section between the regulator (B) and the expansion valve (F) is measured with a 1000 lb./sq. in. range bourdon gauge (I) which was calibrated against an Aminco Model 47-2221 dead-weight tester.

The experimental procedure followed in using this apparatus is very simple. The system containing benzene is loaded with the gas to be studied at the pressure of interest and is allowed to come to equilibrium over a period of at least 12 h at the desired temperature. The valve (F) is then adjusted to give the desired flow rate (0.5 l/min–1.0 l/min) with the system being allowed to vent directly to the atmosphere for a period of approximately 30 min to insure attainment of steady state conditions. The traps are then lowered into the cold bath and the flow of the gas–vapor mixture is immediately diverted to the trapping system and wet-test meter. After a period of flow, the flow is again vented to the atmosphere, the traps are sealed, and removed from the cold bath. The quantity of benzene in the cold traps is then determined gravimetrically while the volume of gas is measured at ambient pressure and temperature. Flow rates and durations of flow were adjusted for each run so that generous and approximately constant amounts of benzene (1–3 g) were trapped during each run in order to minimize weighing errors. In all cases, nearly all the benzene collected was found in the first trap, with the second trap never containing more than 1 % of the amount of benzene found in the first trap. No measurable amounts of benzene were ever detected in the third trap. Since the vapor pressure of benzene at dry ice–acetone temperature is insignificant ($\sim 10^{-2}$ mm Hg), it can be confidently assumed that the traps were essentially 100 % efficient in removing benzene vapor from the gas stream. Thus, the mole fraction of benzene in the gas phase in the equilibrium cell at the pressure of the run is readily determined from the measured mass of benzene collected and the volume of accompanying gas.

RESULTS AND DISCUSSION

A single determination of the mole fraction of benzene in a given diluent gas at a known pressure is sufficient information to allow the second cross virial coefficient for benzene and that gas to be determined provided that: (a) the solubility of that gas in benzene is known at that pressure; (b) the second virial coefficients of pure benzene vapor and pure gas are known at the temperature of the experiment; and (c) the pressure is not so great as to require the introduction of third or higher virial coefficients for the description of the gas phase properties of the system in the equilibrium cell.

The fugacity of benzene (component 2) in the liquid phase, $\bar{f}_2{}^L$, is related to the mole fraction of dissolved gas (component 1), X_1, and the total hydrostatic pressure of the system, P, by the relation:

$$\bar{f}_2{}^{L} = \gamma_2{}^{L}(1 - x_1)P_2{}^{\circ}\Phi_2{}^{\circ}\exp\left[\frac{V_2{}^{\circ(L)}(P - P_2{}^{\circ})}{RT}\right] \tag{1}$$

Here $P_2{}^{\circ}$ and $\Phi_2{}^{\circ}$ are the vapor pressure and fugacity coefficient of pure benzene at temperature T, while $\gamma_2{}^{L}$ and $V_2{}^{\circ(L)}$ are the activity coefficient and molar volume of benzene in the liquid phase. For small mole fractions of dissolved gas such as encountered in these experiments, $\gamma_2{}^{L}$ can be taken to be unity without introducing appreciable error. The fugacity of benzene in the gas phase, $\bar{f}_2{}^{G}$, can be expressed in terms of the mole fraction of benzene in the gas phase, y_2, its fugacity coefficient, Φ_2 and pressure P, as:

$$\bar{f}_2{}^{G} = \Phi_2 y_2 P \tag{2}$$

The condition for equilibrium is that $\bar{f}_2{}^{G} = \bar{f}_2{}^{L}$, so that the vapor phase solubility of benzene in a compressed gas is related to the hydrostatic pressure of the system by:

$$y_2 = \frac{(1 - x_1)P_2{}^{\circ}}{P}\left(\frac{\Phi_2{}^{\circ}}{\Phi_2}\right)\exp\left[\frac{V_2{}^{\circ(L)}(P - P_2{}^{\circ})}{RT}\right] \tag{3}$$

If contributions arising from third and higher virial coefficients are neglected the fugacity coefficient of benzene vapor in the gas mixture can be expressed as:

$$\ln \Phi_2 = \frac{2}{V}[y_2 B_{22}(T) + y_1 B_{12}(T)] - \ln Z \tag{4}$$

where y_1 represents the mole fraction of diluent gas in the gas phase, V is the molar volume of the gas phase mixture, and the symbols $B(T)$ denote second virial coefficients representing deviations from ideality caused by pair interactions between molecules of the species designated by subscripts. Z represents the compressibility factor of the gaseous mixture.

Thus, a given experimental measurement of the mole fraction of benzene in the vapor phase with a particular diluent gas at a known temperature and pressure can be used to evaluate the ratio of fugacity coefficients, $\Phi_2{}^{\circ}/\Phi_2$ in eqn. (3). The second cross virial coefficient $B_{12}(T)$ for that particular benzene–gas mixture can then be evaluated from this ratio of fugacity coefficients in an iterative fashion using eqn. (4) with a trial value for $B_{12}(T)$ to make initial estimates of the molar volue, V, and compressibility factor, Z. In the computations that follow, fugacities have been used with Henry's law constants obtained from refs. 13–20 to calculate x_1 of eqn. (3) as a function of pressure for the various benzene–gas systems, Values of pure component second virial coefficients used in these calculations are found in refs. 21–34. P° was obtained at the desired temperatures from data found in ref. 35 while values of the molar volume of liquid benzene at these temperatures were taken from ref. 36.

Table I lists experimentally determined mole fractions of benzene vapor in the various gas mixtures. Fig. 3 is a graphical representation of the data in Table I. In Fig. 3 it is seen that not only does the mole fraction of benzene increase at a given pressure going from the relatively nonpolarizable gas He to ethylene, whose molecules are very polarizable, but further, that in the case of ethylene, the mole fraction passes

TABLE I

VAPOR COMPOSITION IN BINARY SYSTEMS CONTAINING BENZENE

Gas	Temperature (°C)	Total pressure (atm)	Mole fraction of benzene (y_2)
He	50	15.2	0.0225
		36.3	0.00930
		36.3	0.00934
		49.5	0.00687
		50.2	0.00680
		64.3	0.00534
		64.3	0.00519
		64.3	0.00526
H_2	50	22.4	0.0169
		39.0	0.0105
		39.0	0.0104
		39.0	0.0105
		39.4	0.0102
		50.7	0.00856
		50.7	0.00862
		50.7	0.00854
		56.6	0.00770
		57.2	0.00770
		63.8	0.00714
Ar	32	23.7	0.00950
		23.7	0.00968
		36.9	0.00696
		36.9	0.00723
		51.3	0.00608
		51.3	0.00606
		64.0	0.00569
		64.0	0.00577
	50	24.9	0.0173
		36.5	0.0139
		36.5	0.0142
		50.3	0.0118
		50.3	0.0116
		64.6	0.0100
		64.6	0.0105
N_2	35	22.9	0.0106
		22.9	0.0108
		22.9	0.0107
		37.0	0.00773
		37.0	0.00779
		37.0	0.00772
		37.0	0.00777
		37.0	0.00773
		37.0	0.00753
		50.3	0.00680
		50.3	0.00673
		50.3	0.00676
		64.6	0.00601
		64.6	0.00597
		64.6	0.00606
	50	23.4	0.0173
		36.4	0.0142
		36.4	0.0141

TABLE I (*continued*)

Gas	Temperature (°C)	Total pressure (atm)	Mole fraction of benzene (y_2)
		49.9	0.0118
		49.9	0.0115
		62.8	0.0102
		62.8	0.0103
		63.4	0.0101
CH_4	50	21.5	0.0224
		36.7	0.0164
		36.7	0.0167
		52.1	0.0147
		52.1	0.0146
		54.5	0.0143
		64.5	0.0146
		64.5	0.0144
C_2H_4	50	23.4	0.0209
		23.8	0.0205
		30.2	0.0180
		30.2	0.0186
		37.0	0.0177
		37.0	0.0174
		46.2	0.0177
		46.2	0.0174

through a minimum at approximately 40 atm and increases with total pressure beyond this point.

Fugacity coefficients for benzene in the various gases have been calculated from the data of Table I using eqn. 3. Fig. 4 shows the values obtained at 50° plotted as a function of pressure.
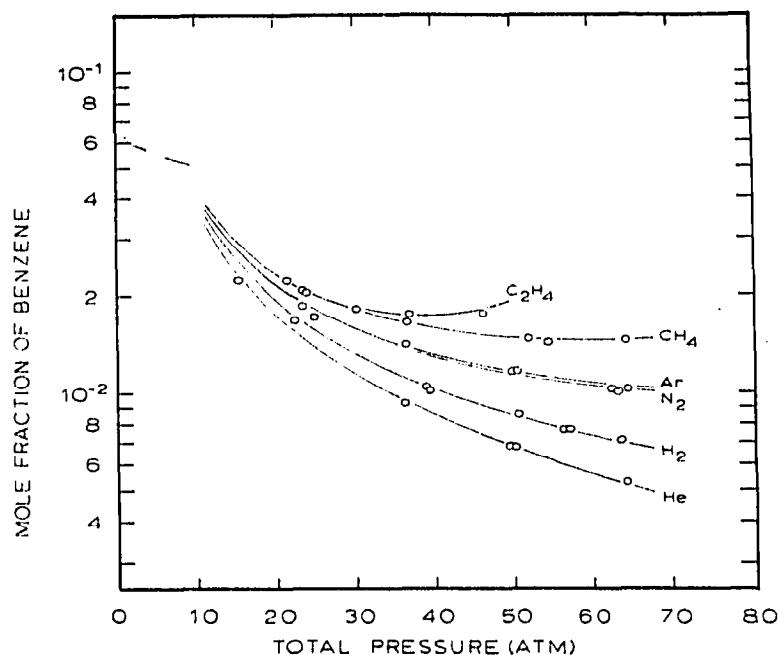

Fig. 3. Vapor phase solubility of benzene in the gases He, H_2, N_2, Ar, CH_4, and C_2H_4 at 50°. (The solid line represents computed values of mole fraction based on experimentally determined second cross virial coefficients listed in Table II.)

Second cross virial coefficients for the various benzene–gas mixtures corresponding to these fugacity coefficients have been calculated using eqn. 4. For each system, excellent agreement was found to exist among values of $B_{12}(T)$ obtained at different pressures. Averages of the values obtained for each benzene–gas system are listed in Table II. Second virial coefficients obtained from GLC methods are also listed in this table for comparison. It is seen that with one exception, a value measured for helium, the second cross virial coefficients obtained here agree within experimental error with values derived from GLC work.
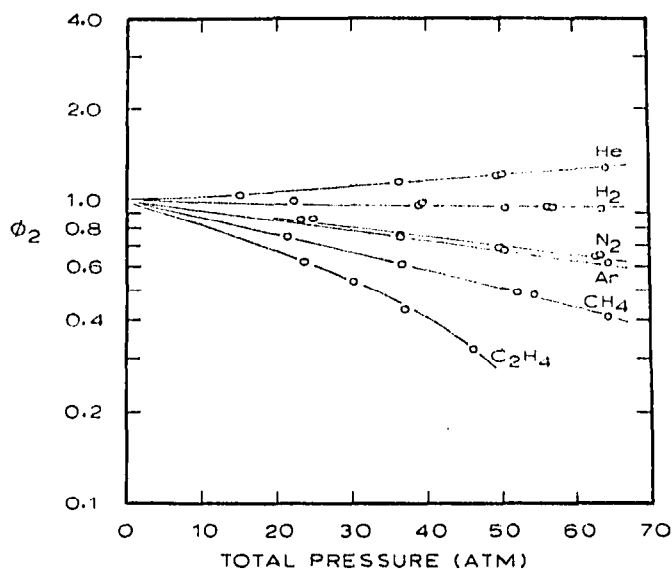

Fig. 4. Fugacity coefficients of benzene in He, H_2, N_2, Ar, CH_4, and C_2H_4 at 50°. (The solid line represents computed values of fugacity coefficients based on the experimentally determined second cross virial coefficients listed in Table II.)

Since the experimental methods used here are completely different from those used in the GLC method, the values for second cross virial coefficients listed here represent an independent check of the results obtained from GLC measurements. The

TABLE II

SECOND CROSS VIRIAL COEFFICIENTS FOR BENZENE WITH VARIOUS GASES

Gas	Temperature (°C)	$B_{12}(T)$ ($cm^3/mole$)	$B_{12}(T)$ GLC ($cm^3/mole$)
He	50	+ 67 ± 4[a]	+ 57 ± 8[b], +49 ± 8[b]
H_2	50	+ 4 ± 3	− 5 ± 8[b]
N_2	35	− 97 ± 3	− 104 ± 10[c]
N_2	50	− 85 ± 3	− 87 ± 8[b], −94 ± 10[c]
Ar	32	−122 ± 3	− 135 ± 10[c]
Ar	50	− 95 ± 3	− 85 ± 8[b], −90 ± 10[c], −88[d]
CH_4	50	−171 ± 3	−155 ± 15[b]
C_2H_4	50	−282 ± 5	—

[a] Experimental error is expressed as average deviation.
[b] Ref. 8.
[c] Ref. 7.
[d] Ref. 5.

good agreement between values obtained by these two methods strongly attest the fact that gas chromatographic methods represent a powerful tool for studying gas phase interactions between dissimilar molecules.

REFERENCES

1 D. H. DESTY, A. GOLDUP, G. R. LUCKHURST AND W. T. SWANTON, in M. VAN SWAAY (Editor), *Gas Chromatography*, Butterworths, London, 1962, p. 67.
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. (London)*, 295A (1966) 259.
5 A. J. B. CRUICKSHANK, M. L. WINDSOR AND C. L. YOUNG, *Proc. Roy. Soc. (London)*, 295A (1966) 271.
6 S. T. SIE, W. VAN BEERSUM AND G. W. A. RIJNDERS, *Separation Sci.*, 1 (1966) 459.
7 B. W. GAINEY AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 349.
8 D. H. EVERETT, B. W. GAINEY AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 2667.
9 R. L. PECSOK AND M. L. WINDSOR, *Anal. Chem.*, 40 (1968) 1238.
10 A. J. B. CRUICKSHANK, B. W. GAINEY AND C. L. YOUNG, *Trans. Faraday Soc.*, 64 (1968) 337.
11 E. M. DANTZLER, C. M. KNOBLER AND M. L. WINDSOR, *J. Chromatog.*, 32 (1968) 433.
12 J. M. PRAUSNITZ AND P. R. BENSON, *Am. Inst. Chem. Engrs. J.*, 5 (1959) 161.
13 J. HORIUTI, *Sci. Papers Inst. Phys. Chem. Res. (Tokyo)*, 17 (341) (1931) 125.
14 M. ELBISHLAWI AND J. R. SPENCER, *Ind. Eng. Chem.*, 43 (1951) 1811.
15 A. LANNUNG, *J. Am. Chem. Soc.*, 52 (1930) 68.
16 H. L. CLEVER, R. BATTINO, J. H. SAYLOR AND P. M. GROSS, *J. Phys. Chem.*, 61 (1957) 1078.
17 E. B. MAXTED AND C. H. MOON, *Trans. Faraday Soc.*, 32 (1936) 769.
18 J. C. GJALDBAEK AND J. H. HILDEBRAND, *J. Am. Chem. Soc.*, 71 (1949) 3147.
19 J. E. JOLLEY AND J. H. HILDEBRAND, *J. Am. Chem. Soc.*, 80 (1958) 1050.
20 P. MILLER AND B. F. DODGE, *Ind. Eng. Chem.*, 32 (1940) 434.
21 R. WIEBE, V. L. GADDY AND C. HEINS, Jr., *J. Am. Chem. Soc.*, 53 (1931) 1721.
22 W. G. SCHNEIDER AND J. A. H. DUFFIE, *J. Chem. Phys.*, 17 (1949) 751.
23 L. STROUD, J. E. MILLER AND L. W. BRANDT, *J. Chem. Eng. Data*, 5 (1960) 51.
24 N. K. KALFOGLOU AND J. G. MILLER, *J. Phys. Chem.*, 71 (1967) 1256.
25 A. MICHELS AND M. GOUDEKET, *Physica*, 8 (1941) 347.
26 A. MICHELS, H. WIJKER AND H. K. WIJKER, *Physica*, 15 (1949) 627.
27 E. WHALLEY, Y. LUPIEN AND W. G. SCHNEIDER, *Can. J. Chem.*, 31 (1953) 722.
28 A. MICHELS, H. WOUTERS AND J. DE BOER, *Physica*, 1 (1934) 587.
29 P. S. KU AND B. F. DODGE, *J. Chem. Eng. Data*, 12 (1967) 158.
30 D. R. DOUSLIN, R. H. HARRISON, R. T. MOORE AND J. P. McCULLOUGH, *J. Chem. Eng. Data*, 9 (1964) 358.
31 A. MICHELS AND M. GELDERMANS, *Physica*, 9 (1942) 967.
32 R. J. L. ANDON, J. D. COX, E. F. G. HERINGTON AND J. F. MARTIN, *Trans. Faraday Soc.*, 53 (1957) 1074.
33 G. A. BOTTOMLEY, C. G. REEVES AND F. R. S. WHYTLAW-GRAY, *Proc. Roy. Soc. (London)*, A246 (1958) 504.
34 G. A. BOTTOMLEY AND T. H. SPURLING, *Australian J. Chem.*, 19 (1966) 1331.
35 A. F. FORZIATI, W. R. NORRIS AND F. D. ROSSINI, *J. Res. Natl. Bur. Std.*, 43 (1949) 555.
36 R. R. DREISBACH (Editor), *Physical Properties of Chemical Compounds*, Vol. II, American Chemical Society, Washington, D.C., 1959.