Interaction Second Virial Coefficients and Binary Interaction Parameters for the CO_2 – C_2H_6 Systems between 250 and 300 K

We have determined the interaction second virial coefficients (B_{12}) for the CO_2 – C_2H_6 system between 250 and 300K using a Burnett-isochoric apparatus. The technique follows a procedure suggested by Hall and Eubank (1973) and extended by Holste et al. (1980). Combined errors for B_{12} are within 1.2 cm^3/mol. In addition, values for the binary interaction parameter k_{12} calculated from our B_{12} values show definite temperature dependence.

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SCOPE

Interaction second virial coefficients, B_{12}, contain information about mixtures which is essential for both theoretical and practical applications. Because of a direct, statistical mechanical basis, B_{12} reflects molecular interactions between unlike molecules and provides insight for theoretical mixture models. On the partial side, B_{12} is necessary for thermodynamic calculations at low pressures when the application dictates use of the (truncated) virial equation. The binary interaction parameter, k_{12}, is an important correlation parameter which we extract from the B_{12}.

The usual method for obtaining B_{12} is by reduction of mixture second virial coefficients. Edwards and Roseveare (1942) apparently pioneered the technique. Knobler et al. (1959) developed a significantly better technique, the differential pressure method. These two methods have produced the bulk of B_{12} data, although reduction of vapor-liquid equilibrium data and of chromatographic data also have provided less precise values. Often the k_{12} have been extracted from vapor-liquid equilibrium data, because extremely precise B_{12} values were not available.

Hall and Eubank (1973) proposed a new, differential method for B_{12} determinations using a Burnett-isochoric apparatus. Holste et al. (1980) applied this technique to the carbon dioxide-helium system with excellent results. We have applied the technique to the carbon dioxide-ethane system and then derived k_{12} from the resultant B_{12}.

CONCLUSIONS AND SIGNIFICANCE

We have determined B_{12} values for the carbon dioxide-ethane system at 10 K intervals from 250 to 300 K using the modified Burnett method proposed by Hall and Eubank (1973) as expanded by Holste et al. (1980). We have utilized established procedures to correct for the effects of higher-order terms in the virial equation, and, after a careful analysis, we have concluded that random errors in these determinations have masked any systematic effects. Therefore, we have determined that the *accuracy* of our measurements is ±1.2 cm^3/mol for B_{12} based upon a 99% confidence limit.

To our knowledge, no measurements, other than the current work, have sufficient precision to demonstrate conclusively that the binary interaction parameter (defined in the conventional manner) depends upon temperature. Our results show the temperature dependence in the low temperature range. Our 3σ effect on k_{12} from the B_{12} errors is ±0.004 which is significantly smaller than even our minimum values of $k_{12} = 0.088$ at 300 K.

Having established the feasibility of our experiment for producing temperature dependent k_{12}, we shall make a systematic study of natural gas and syngas binaries to establish these dependences. A knowledge of the correct temperature dependence for k_{12} can have a profound effect on the results of many useful correlations and thus on the design of units based upon such correlations.

INTRODUCTION

In many theoretical and practical applications of the equation of state, the virial equation is the preferred form for fluids and fluid mixtures. The precise basis of this equation in statistical mechanics is the primary reason for this applicability. The derivation produces two equivalent (mathematically but not practically) forms:

$$Z - 1 = B\rho + C\rho^2 + \ldots = B'P + C'P^2 + \ldots \qquad (1)$$

Statistical mechanics also provides the mixing rules for the virial coefficients

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \qquad (2)$$

$$C_m = \sum_i \sum_j \sum_k y_i y_j y_k C_{ijk} \qquad (3)$$

Higher order coefficients have similar mixing rules. More fundamental mixture information resides in the interaction coefficients (B_{ij}, C_{ijk}, etc.) than in the mixture coefficients (B_m, C_m, etc.), because the latter depend upon the pure fluid virial coefficients

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and the mixture composition. Our purpose in this study is to provide accurate experimental values for the interaction second virial coefficient.

We have chosen the carbon dioxide-ethane system because the expanding economic importance of these fluids has resulted in an increased need for accurate data. Ample information exists for the pure compounds but mixture data are scarce. Our values for $B_{CO_2-C_2H_6}$ cover the range $250 \le T/K \le 300$.

REVIEW OF PREVIOUS WORK

Large amounts of data exist for both carbon dioxide and ethane—as a result we shall only cite reference works or recent efforts. Two principal reviews are available for carbon dioxide: Vukalovitch and Altunin (1968) and Angus et al. (1973). In addition, the review of virial coefficients by Dymond and Smith (1969) contains information on carbon dioxide.

Recently, Michels et al. (1954), Douslin and Harrison (1973) and Mansoorian et al. (1981) have published data for ethane which are in substantial agreement. Dymond and Smith (1969) also report virial coefficients. The major review of available ethane data comes from Goodwin et al. (1976).

Many values for B_{ij} come from a straighforward reduction of the equation for binary mixtures:

$$B_{12} = (B_m - y_1^2B_{11} - y_2^2B_{22})/^2y_1y_2 \qquad (4)$$

For example, Zaalishvili (1956) used this technique to obtain values for CO_2-C_2H_6 in the range $310 \le T/K \le 510$ using data from Reamer et al. (1945). Another technique is the differential pressure method developed by Knobler et al. (1959). Mason and Eakin (1961) used the latter method to determine $B_{CO_2-C_2H_6}$ at 288 K. The technique we used is the one developed by Hall and Eubank (1973) and expanded by Holste et al. (1980).

EXPERIMENTAL

Our basic apparatus for this experiment is a Burnett-isochoric instrument. The Burnett-isochoric method, discussed by Burnett (1963), Pope et al. (1972), Hall and Eubank (1972), and Holste et al. (1980), is a combination of the Burnett method and the isochoric method which possesses advantages over the individual techniques. Figure 1 presents a schematic of the apparatus. Detailed descriptions of the apparatus appear in theses by Watson (1978) and Young (1978).

In our apparatus, the sample fluid remains entirely within the temperature bath (helium gas is the bath fluid). Communication with the external pressure-measurement system is by helium through a Ruska differential pressure cell. Our pressure measurement instruments are Ruska air-lubricated dead weight gauges and an Ideal Arrowsmith manometer. These devices are consistent within 0.01% in their region of overlap and have assigned accuracies of better than 0.02%. Our precision for pressure observation is better than 0.001% using techniques described by Holste et al. (1977). We measure and control temperature in a potentiometric circuit using a standard platinum-resistance element calibrated on IPTS-48. (We report IPTS-68 values, however.) The temperature measurement accuracy is ±0.01 K but control is within 0.002 K.

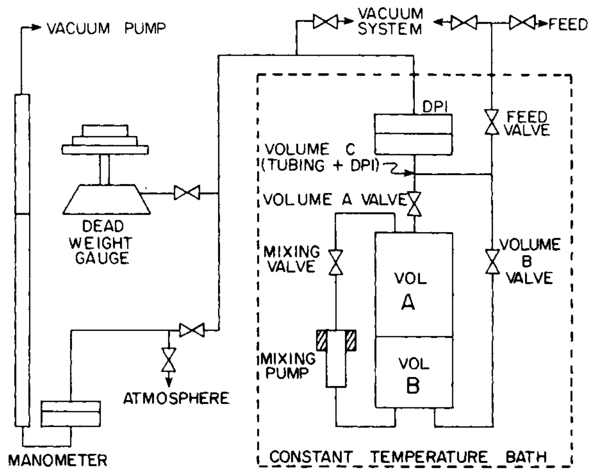

Figure 1. Schematic diagram of the Burnett-isochoric apparatus.

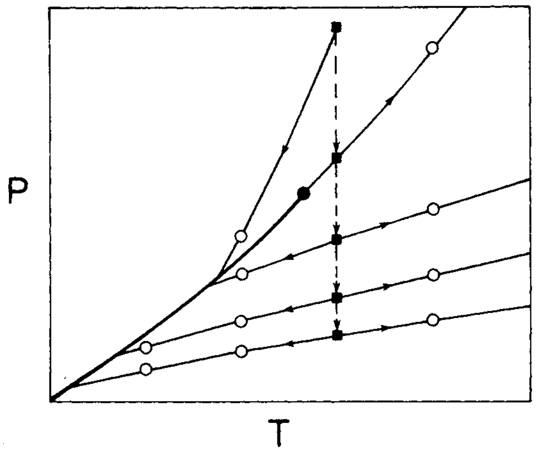

Figure 2. Burnett-isochoric experiment traced upon a *P-T* diagram.

The Burnett-isochoric method consists of filling one cell of the apparatus to a predetermined pressure at a convenient temperature and then running up and/or down in temperature along an isochore. Returning to the initial temperature and pressure provides a leak test for the experiment before expanding the fluid into the other, evacuated Burnett volume. Repeating this procedure until reaching a minimum observable pressure upon expansion constitutes a Burnett-isochoric run. Figure 2 traces the experimental path on a *P-T* diagram. A single filling suffices to generate an entire $P\rho T$ surface which ensures sample integrity. Superimposed upon the Burnett-isochoric experiment is the Burnett-mixing experiment described by Hall and Eubank (1974). In this isothermal experiment, one volume is filled with a pure fluid to a measured pressure, P_1, and a second volume is filled with a second pure fluid to a pressure, P_2. The fluids then are mixed thoroughly, and the equilibrium pressure of the mixture, P_m, is determined. These data and some previously determined pure-fluid properties and apparatus constants provide the information required to calculate properties such as composition, excess volume and interaction virial coefficients. Combining the two experimental techniques produce a single set of mixtures, made at a single temperature, from which we can evaluate B_{12} values over the entire accessible temperature range. Thus, P_1 and P_2 come from isochores run using the mixture.

ANALYSIS

A complete analysis of the experiment for B_{12} appears in Holste et al. (1980) and we report only results here. The basic equation for the isochorically extended experiment is

$$B_{12}^*(T) = \frac{N_1N_2Z_1^bZ_2^bR(T^b)^2}{2P_1^bP_2^bT}\left\{n_m^2P_m - \frac{\eta_1^2P_1}{N_2^2} - \frac{T}{T^b}\left[\frac{P_1^b}{Z_1^bN_1}(\eta_m - \eta_1/N_1) + \frac{P_2^b}{Z_2^bN_2}(\eta_m - \eta_2/N_2)\right]\right\} \qquad (4)$$

where superscript b denotes the base isotherm, N is the Burnett cell constant $[N_i = (V_i + V_j + V_c)/(V_i + V_c)]$, and η_i is a volume-distortion parameter. We have developed an empirical expression for η_i

$$\eta_i = \frac{V_i}{V_i^b} = 1 + [(5 \times 10^{-7}) + (7.04 \times 10^{-6})(P_i^b)^{0.0905}](T - T^b) \qquad (5)$$

The relationship between B_{12}^* (experimentally observable) and B_{12} (desired) is

$$B_{12}^* = B_{12} + \sum_{n=1}^{\infty} A_n(P_2^b/Z_2^b)^n \qquad (6)$$

where A_n are constants. Equation 6 is valid *at any temperature*. A plot of B_{12}^* vs. P_2^b/Z_2^bwill have B_{12} as an intercept. Third-virial contributions introduce slope into the plot while higher-order contributions will introduce curvature. The present method therefore provides an empirical correction for higher-order effects without explicit knowledge of the actual higher-order virial coefficients.

The advantages of the isochorically extended Burnett mixing experiment becomes apparent upon closer inspection of Eqs. 4 and 6. The only experimental data required at temperatures other than the mixing temperature are P_i and T. To account for second-order effects, the cell-distortion parameter must be available from a previous experiment covering the entire temperature range. Explicit information about pure-fluid compressibility factors and apparatus constants is required only at the mixing temperature. As a result, the mixing temperature may be the most convenient temperature in the range, taking into account such factors as temperature control, adsorption effects, and experimental manipulations. The significant reduction in the total number of required mixtures allows increased data production without reduction in quality.

RESULTS

The interaction virial coefficient experiment requires explicit compressibility factor information for the pure fluids only at the mixing temperature. We have used 300 K as the mixing temperature and we report results for carbon dioxide and ethane only at 300 K.

Actually, the carbon dioxide results come from earlier work by Watson (1978) and Bellomy (1976) as reported by Holste et al. (1980). The supplier, Precision Gas Products, certified the carbon dioxide sample as 99.996% pure. When we combine all our error estimates, we conclude that our value for the second virial coefficient of −121.7 cm^3/mol has an uncertainty of ±0.5 cm^3/mol. Precision Gas Products also supplied the ethane sample and certified its purity as 99.99%. Our combined error estimates for the second virial coefficient of ethane, −181.7 cm^3/mol, produce an uncertainty of ±0.5 cm^3/mol.

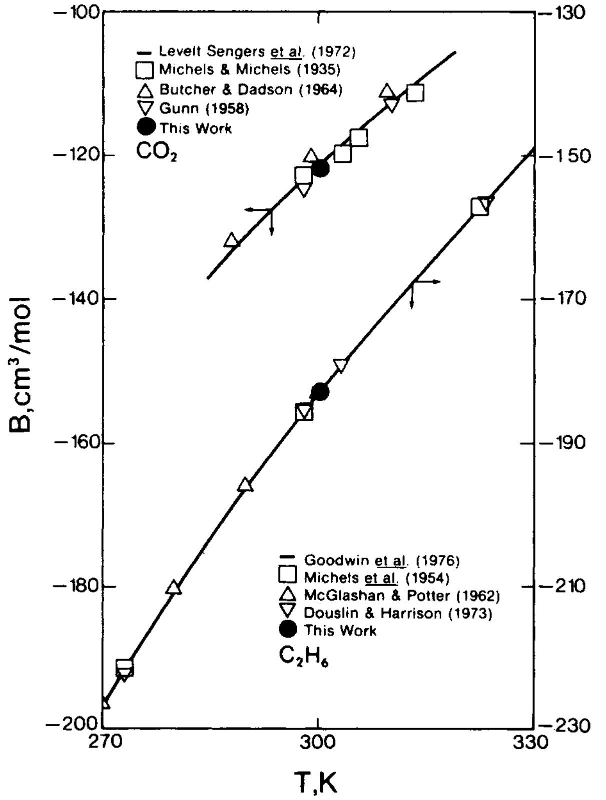

Figure 3. Comparison of second virial coefficients for CO_2 and C_2H_6 from this work at 300 K with other values at similar temperatures.

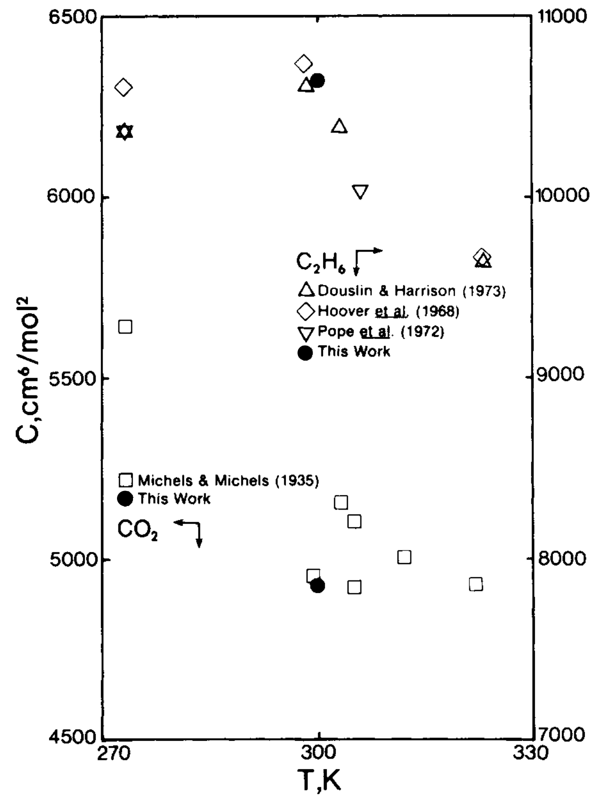

Figure 4. Comparison of third virial coefficients for CO_2 and C_2H_6 from this work at 300 K with other values at similar temperatures.

Figure 3 presents a comparison of our second virial coefficients for carbon dioxide and ethane with those of other investigators. The size of the closed circle representing our value in each case covers our uncertainty estimates. Figure 4 presents similar information on third virial coefficients. In all cases, our pure component results show excellent agreement with those of other investigators. Table 1 presents numerical values for these pure component results.

We utilized the isochorically extended experiment to collect the mixture data. Having selected the desired filling pressures, we ran pure-fluid isochores beginning at the pressure chosen for each pure fluid. Next, we filled the appropriate cell volume to the chosen pressures with each pure fluid and then mixed the fluids. After mixing, we measured an entire mixture isochore. We repeated the experiment for several different starting pressures to provide an unambiguous extrapolation of B_{12}^* to zero pressure.

Figure 5 presents the isochorically extended data with a least squares fit for each temperature. The experimental values of B_{12} are the zero-density intercepts of these least squares fits. Table 2 contains our B_{12} values along with our estimates of their standard deviations. Holste et el. (1980) show that any significant systematic errors would introduce curvature into the isotherms in Figure 5. Because this effect is not apparent, we conclude that random errors mask the systematic ones. Based upon a 99% confidence limit, the average uncertainty for our B_{12} values is ±1.2 cm^3/mol.

Figure 6 compares our results with those reported by Mason and Eakin (1961) and Zaalishvili (1956), and with values calculated by

TABLE 1. VIRIAL COEFFICIENTS FOR PURE COMPONENTS, CARBON DIOXIDE AND ETHANE, AT 300 K

Compound	Purity %	Second Virial Coefficient (cm^3/mol)	Third Virial Coefficient (cm^6/mol^2)
Carbon Dioxide	99.996	$(-121.7_0 \pm 0.5)$	4,926.7
Ethane	99.99+	$(-182.7_1 \pm 0.5)$	10,580

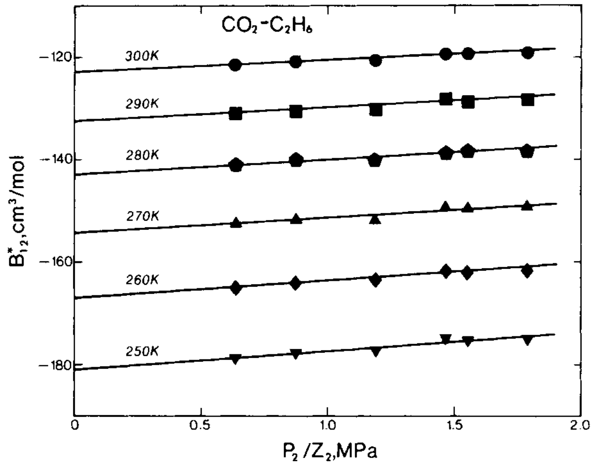

Figure 5. Isochorically extended data with at least squares fit showing extrapolation to zero density.

TABLE 2. INTERACTION SECOND VIRIAL COEFFICIENTS AND BINARY INTERACTION PARAMETERS FOR THE CO_2-C_2H_6 SYSTEM

Temperature (K)	B_{12} (cm^3/mol)	$^\sigma B_{12}$ (cm^3/mol)	k_{ij}[a]
250.00	−181.0	0.58	0.105
260.00	−167.0	0.47	0.100
270.00	−154.4	0.39	0.097
280.00	−142.9	0.35	0.093
290.00	−132.5	0.34	0.090
300.00	−122.9	0.35	0.088

[a] Uncertainty in k_{ij} corresponding to $3\sigma_{B_{ij}}$ is ±0.004.

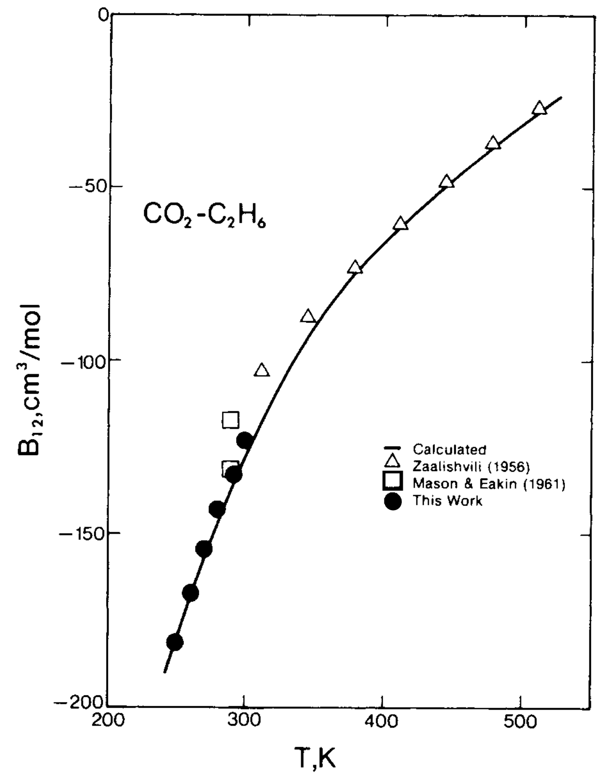

Figure 6. Comparison of B_{12} values from this work with those of other investigators.

assuming a Lennard-Jones potential and the simple mixing rules:

$$\epsilon_{12} = \sqrt{\epsilon_{11}\epsilon_{12}}, \tag{7}$$

and,

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22}). \tag{8}$$

The force constants given by Mason and Spurling (1969) for CO_2 and by Douslin and Harrison (1973) for C_2H_6 produce ϵ_{12}/K = 195.55 K and σ_{12} = 4.443 Å for the CO_2–C_2H_6 interaction potential. Our "calculated" B_{ij} curve uses the generalized Lennard-Jones tables given in Hirschfelder et al. (1954). These calculations assume that only dispersion interactions exist, but we have estimated that the quadrupole—induced dipole contribution should be on-the-order-of 2 cm^3/mol or less and therefore of little significance. The three sets of experimental values are not consistent, but the calculated values are in excellent agreement with all our values, and with those of Zaalishvili above 375 K. We note that Zaalishvili actually reports values calculated from the experimental *PVT* data of Reamer et al. (1945), who did not calculate values for B_{ij}. Holste et al. (1980) also observe excellent agreement between their experimental B_{ij} values for the He-CO_2 system and values calculated using the mixing rules given by Eqs. 7 and 8.

Generalized correlations for B_{ij} based upon the principle of corresponding states usually do not provide accurate quantitative results without the incorporation of a binary interaction parameter, k_{ij}, in addition to the critical properties of the mixture components as pure fluids. This requirement for k_{ij} is not surprising, because the pure fluid properties cannot contain any information about the interactions between unlike molecules, and it is precisely these interactions that give rise to B_{ij}. The conventional definition of k_{ij} is:

$$T_{cij} = \sqrt{T_{ci}T_{cj}}\,(1 - k_{ij}). \tag{9}$$

We have used the Tsonopoulos (1974) modification of the correlation of Pitzer and Curl (1957) to determine our experimental values for k_{ij}. In this situation, the equations are

$$\frac{BP_c}{RT_c} = f^{(0)}(T_r) + \omega f^{(1)}(T_r), \tag{10}$$

where:

$$f^{(0)}(T_r) = 0.1445 - 0.330/T_r - 0.1385/T_r^2 \\ -0.0121/T_r^3 - 0.000607/T_r^8, \tag{11}$$

and:

$$f^{(1)}(T_r) = 0.0637 + 0.331/T_r^2 - 0.423/T_r^3 - 0.008/T_r^8. \tag{12}$$

The equations require mixture critical values for P_c, T_c, and ω to calculate B_{ij} values. Equation 9 gives the mixing rule for T_c, and we have used the forms for P_c and ω given by Tsonopoulos (which do not include k_{ij} explicitly) in our calculations. Our k_{ij} values are calculated by determining the value of T_r which produces our experimental values when used in Eq. 10. This T_r value then is used in Eq. 9 to calculate k_{ij}. The pure fluid critical properties used in the calculation are those given by Reid et al. (1977). We note that a 3σ deviation in B_{ij} produces a corresponding uncertainty of 0.004 in k_{ij}.

Figure 7 shows our experimental values of k_{ij} as a function of temperature. Clearly, k_{ij} exhibits significant temperature dependence, but unfortunately, our temperature range is too restricted to justify any conclusions regarding the precise functional form of this temperature dependence. The temperature dependence of k_{ij} indicates that generalized correlations for B_{ij} derived from the Lennard-Jones interatomic potential are not capable of highly accurate predictions. These shortcomings may be caused by inadequacies of the interatomic potential model, the mixing rules for critical parameters, or both. There is no *a priori* reason that interactions between unlike molecules should give rise to B_{ij} values with different reduced temperature dependences than interactions between like molecules. Our results therefore suggest that further investigations of reduced forms for B_{ij} (perhaps using potentials other than Lennard-Jones) and of appropriate mixing rules will be required to provide theoretical descriptions of accuracy compa-

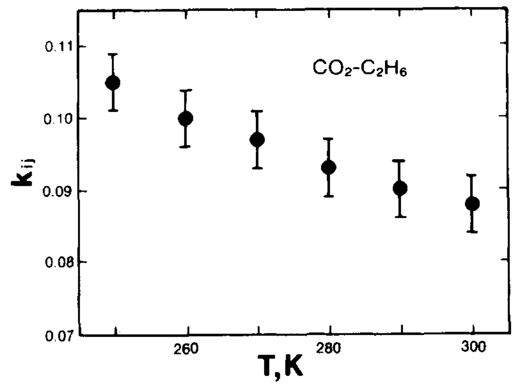

Figure 7. Temperature dependence of the binary interaction parameter, k_{12}. The error bars indicate the 3σ confidence levels of our linear fits.

rable with the experimental results reported here. Unfortunately, few experimental results of comparable accuracy are available for other mixtures, therefore additional experimental measurements will be required to provide an adequate data base for testing future theoretical developments.

ACKNOWLEDGMENTS

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NOTATION

A = constant
B = second virial coefficient (density series)
B' = second virial coefficient (pressure series)
B_{12} = interaction second virial coefficient
B^*_{12} = uncorrected, observed interaction virial coefficient
C = third virial coefficient (density series)
C' = third virial coefficient (pressure series)
k_{12} = binary interaction parameter
N = apparatus cell constant (ratio of volumes)
P = pressure
R = gas constant (8.31441 J/mol·K)
T = temperature
V = volume
Z = compression factor

Greek Letters

ϵ_{ij} = intermolecular potential well depth
η = cell distortion parameter
ρ = density
σ = standard deviation
σ_{ij} = intermolecular collision diameter
ω = acentric factor

Subscripts

c = critical property
i = species i
j = secies j
k = species k
m = mixture
r = reduced property

Superscript

b = base isotherm

LITERATURE CITED

Angus, S., B. Armstrong, and K. M. de Reuck, eds., *International Thermodynamic Tables of the Fluid State: Carbon Dioxide*, Pergamon Press, Oxford (1973).

Bellomy, M. T., "An Experimental Verification of the Hall and Eubank Method of Direct Measurement of the Interaction Second Virial Coefficient," M.S. Thesis, Texas A&M University, College Station, TX (1976).

Burnett, E. S., "Application of the Burnett Method of Compressibility Determination to Multiphase Fluid Mixtures," *U. S. Bur. Mines Rept. Inv.*, **6267** (1963).

Butcher, E. G., and R. S. Dadson, "The Virial Coefficients of the Carbon Dioxide-Ethylene System," *Proc. Roy Soc. London*, **A277**, 448 (1964).

Douslin, D. R., and R. H. Harrison, "Pressure-Volume-Temperature Relations of Ethane," *J. Chem. Thermo.*, **5**, 491 (1973).

Dymond, J. H., and E. B. Smith, *The Virial Coefficients of Gases: A Critical Compilation*, Clarendon Press, Oxford (1969).

Edwards, A. E., and H. E. Roseveare, "The Second Virial Coefficients of Gaseous Mixtures," *J. Chem. Soc.*, **64**, 2816 (1942).

Goodwin, R. D., H. M. Roder, and G. C. Straty, "Thermophysical Properties of Ethane from 90 to 600 K at Pressures to 700 Bar," *Nat. Bur. Stand. Tech. Note*, **684** (1976).

Gunn, R. D., "Volumetric Properties of Non-Polar Gas Mixtures," M.S. Thesis, University of California (Berkeley) (1958).

Hall, K. R., and P. T. Eubank, "Burnett-Isochoric Coupled Data with Application to Adsorbing Gases," *Physica*, **61**, 346 (1972).

Hall, K. R. and P. T. Eubank, "Experimental Techniques for Direct Measurement of Interaction Second Virial Coefficients," *J. Chem Phys.*, **59**, 709 (1973).

Hall, K. R., and P. T. Eubank, "Mixture Compositions and Excess Volumes from the Burnett Apparatus," *AIChE J.*, **20**, 815 (1974).

Hirschfelder, J. O., C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, John Wiley & Sons, New York (1954).

Holste, J. C., P. T. Eubank, and K. R.Hall, "Optimum Use of a Differential Pressure Transducer for High-Precsion Measurements," *Ind. & Eng. Chem., Fund.*, **16**, 378 (1977).

Holste, J. C., M. Q. Watson, M. T. Bellomy, P. T. Eubank, and K. R. Hall, "Interaction Second Virial Coefficients by Direct Determination: Application to the Helium-Carbon Dioxide System," *AIChE J.*, **26**, 954 (1980).

Hoover, A. E., I. Nagata, T. W. Leland, Jr., and R. Kobayashi, "Virial Coefficients of Methane, Ethane, and Their Mixtures at Low Temperatures," *J. Chem. Phys.*, **48**, 2633 (1968).

Knobler, W. H., J. J. M., Beenakker, and H. F. P. Knapp, "The Second Virial Coefficient of Gaseous Mixtures at 90°K," *Physica*, **25**, 909 (1959).

Levelt-Sengers, J. M.H., M. Klein, and J. S. Gallager, "Pressure-Volume-Temperature Relationships of Gases; Virial Coefficients," *AIP Handbook*, 3rd ed., McGraw-Hill, New York (1972).

Mansoorian, H., K. R. Hall, J. C. Holste, and P. T. Eubank, "The Density of Gaseous Ethane and of Fluid Methyl Chloride, and the Vapor Pressure of Methyl Chloride," *J. Chem. Thermo.*, **13**, 1001 (1981).

Mason, D. M., and B. E. Eakin, "Compressibility Factor of Fuel Gases at 60°F and 1 atm," *J. Chem. Eng. Data*, **6**, 499 (1961).

Mason, E. A., and T. H. Spurling, "The Virial Equation of State," 269, Pergammon Press, Oxford (1969).

McGlashan, M. L., and D. J. B. Potter, "An Apparatus for the Measurement of Second Virial Coefficient of Vapours," *Proc. Roy. Soc. London*, **A267**, 478 (1962).

Michels, A., and C. Michels, "Isotherms of CO_2 between 0° and 150°C and Pressures from 16 to 250 atm.," *Proc Roy. Soc. London*, **A153**, 201 (1935).

Michels, A., van Stratten, W., and J. Dawson, "Isotherms and Thermodynamic Functions of C_2H_6 at Temperatures between 0° and 150° and Pressures up to 200 atm.," *Physica*, **20**, 17 (1954).

Pitzer, K. S., and R. F. Curl, Jr., "Empirical Equation for the Second Virial Coefficient," *J. Amer. Chem. Soc.*, **79**, 2369 (1957).

Pope, G. A., P. Chappelear, and R. Kobayashi, "Analysis of Data Obtained by Isochorically Coupled Burnett Experiments," *Physica*, **57**, 127 (1972).

Reamer, H. H., R. H. Olds, B. H. Sage, and W. N. Lacey, "Phase Equilibria in Hydrocarbon Systems: Volumetric Behavior of Ethane-Carbon Dioxide Systems," *Ind. & Eng. Chem.*, **37**, 688 (1945).

Reid, R. C., J. M. Prausnitz, and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd Edition, McGraw-Hill, NJ (1977).

Tsonopoulos, C., "An Empirical Correlation of Second Virial Coefficients," *AIChE J.*, **20**, 263 (1974).

Vukalovitch, M. P. and V. V. Altunin, *Thermophysical Properties of*

Carbon Dioxide, Collet's Ltd., London (1968).

Watson, M. Q., "The Interaction Second Virial Coefficient for the He-CO_2 System between 230 and 300 K," M.S. Thesis, Texas A&M University, (1978).

Young, J. G., "Interaction Second Virial Coefficient for the He-CO_2 System between 250 and 300 K," M.S. Thesis, Texas A&M University, College Station, (1978).

Zaalishvili, S. D., "Second Virial Coefficients for Gas Solutions," *Zhur. Fiz. Khim.*, 30, 1981 (1956).

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A Thermodynamic Approach to Multicomponent Distillation System Synthesis

This paper shows a synthesis method of multicomponent distillation systems with heat integration based on the available energy concept. With this method, the problem of synthesizing the heat integrated distillation systems in which there are heat source and sink streams supplied from other processes can be solved so as to minimize the process utilities. Moreover, since the system synthesis is executed in the $(1 - T_0/T)$ vs. Q diagram, it is possible to visibly represent the physical meanings of the computing process.

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SCOPE

Distillation systems are widely employed as the main separation process because such systems have the ability to separate various kinds of mixtures into their components and are easy to operate. However, the associated energy consumption is much larger than that of other separation systems (Fitzmorris and Mah, 1980) and it is consequently very important and necessary to carry out the synthesis of distillation systems paying particular attention to saving energy.

Considering the synthesis problem of a heat-integrated distillation system, we are facing two subproblems: (1) the selection of a separation sequence, and (2) the determination of a heat exchanger network around the distillation system (Rathore et al., 1974a). The proposed approach methods are classified into two techniques: a mathematical approach and a thermodynamic approach. Rathore et al. (1974) presented a synthesis method for determining the optimal sequence and operating conditions; first investigate all possibilities of condenser-reboiler matches for every subsystem and then combine the suitable subproblems by using dynamic programming in order to minimize the total cost. But as there is the feedback information for the relationship between two synthesis subproblems, the dynamic programming generates an infeasible solution. Also, this method forces users to spend an excessive amount of computation time for all the possible heat matches of subproblems. On the other hand, Umeda et al. (1979) presented an evolutionary approach method for heat-integrated system design based on the available energy concept. This method can advance the heat recovery around distillation systems using heat pumps and multi-effect as well as intermediate-boilers and coolers. But it cannot systematically generate a distillation sequence.

When saving energy in chemical processes, engineers analyze energy flows of units in the systems and then synthesize or modify the systems using the information from the analysis. So, engineers need a method to treat both of the analysis and design problems iteratively. From this point of view, since distillation systems are parts of the whole process systems, engineers may reconsider the design conditions for heat integration from the total system. For example, a mathematical method can derive the optimal distillation sequence, but advancing the heat recovery for preheating feed streams and cooling product streams needs a very different method.

The available energy concept is very powerful in the analysis of energy flows and thermodynamic efficiencies for chemical units. Many researchers have thermodynamically analyzed various kinds of distillation systems, multi-effect systems and distillation systems with heat pumps, intermediate-boilers and coolers (Freshwater, 1951; Null, 1976; Mah, 1977, 1979; Naka, 1980). But, there is a few studies for the application of the concept to the synthesis problems such as heat exchanger networks

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