

TWIXT CUP AND LIP: DO EQUATION-OF-STATE MEASUREMENTS REALLY TELL US
ANYTHING USEFUL ABOUT INTERMOLECULAR FORCES?

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Abstract - The development of a method for the direct inversion of second virial coefficient data to obtain information about the intermolecular potential allows us to establish criteria for the significance of measurements of the equation of state. Precise virial coefficient measurements show evidence of systematic errors caused by adsorption; mixing methods for determining excess second virial coefficients are also susceptible to adsorption errors. If the range of applicability of volumetric techniques is limited by adsorption, other methods must be found that allow the important low-temperature region to be investigated. In principle, acoustic and calorimetric (isothermal Joule-Thomson and heat-of-mixing) methods for determining second virial coefficients can be used at low temperatures. The limitations of these methods and the problem of extracting the virial coefficients from the primary data are discussed.

INTRODUCTION

The relatively small number of posters submitted to this section suggests a lack of research activity in the properties of gases and gaseous mixtures. A brief search through the past four years of Chemical Abstracts turned up about 200 papers relating to equations of state; the field is not moribund but neither is it flourishing.

In part, the low count of papers is attributable to the fact that equation-of-state measurements are difficult and that there are no commercial instruments with which they can be made routinely. If measurements are difficult, should they be made at all? If there are important questions that can be answered, can we make the measurements more easily? These are the questions that I will address.

INTERMOLECULAR FORCES AND THE EQUATION OF STATE

Like many other workers, I have stated in papers and proposals that the primary goal in studies of the equations of state of gases is to learn about intermolecular forces. I submit that, with very few exceptions, most of the work in the field, mine included, has told us very little about interactions between molecules. Let us examine my contention. What might we expect from studies of equations of state?

Following Keller and Zumino (1,2), one is accustomed to argue that at best measurements of the second virial coefficient $B(T)$ alone could provide us with no more information about the intermolecular potential $U(r)$ than its repulsive branch and its width as a function of its depth. The proof of this statement rests on the demonstration that $B(T)$ is essentially the Laplace transform of $\Delta = r_L^3 - r_R^3$, where r_L and r_R are the left- and right-hand turning points of the potential:

$$B(T) = \frac{2\pi N \exp(-\epsilon/kT)}{3kT} \int_0^\infty \Delta \exp(-\phi/kT) d\phi \quad (1)$$

Here ϵ is the depth of the potential and $\phi = U(r) + \epsilon$.

Recently, however, Smith and coworkers (3,4,5) have shown that the Keller and Zumino proof, while formally correct, probably does not rule out the direct inversion of second virial coefficient data. They have developed an inversion procedure whose success appears to rest on the conditions that the potential is analytic and that it must be continuous at the point at which $U(r) = 0$.

The basis of the inversion is the postulation of a one-to-one relation between a characteristic length $\tilde{r}(T)$, which can be derived from the experimental properties of the second virial

coefficient at some temperature T , and $U(\tilde{r})$, the value of the intermolecular potential at a separation \tilde{r} :

$$U(\tilde{r}) = G(T^*)kT \quad (2)$$

where $G(T^*)$ is called the inversion function; the reduced temperature T^* is, as usual, kT/ϵ .

Experience has shown that \tilde{r} is best defined as

$$\tilde{r} = \left(\frac{B + T \frac{dB}{dT}}{2\pi N/3} \right)^{1/3} \quad (3)$$

The inversion function is determined by an iterative procedure. A first approximation $G(U_0, T^*)$ is obtained by calculating values of $B + T(dB/dT)$ from an approximate potential U_0 . The approximate function is then combined with the experimental virial coefficient data to obtain a second approximation to the potential

$$U_1(\tilde{r}) = G(U_0, T^*)kT \quad (4)$$

This potential is then used to evaluate an inversion function $G(U_1, T^*)$, from which a better approximation to $U(\tilde{r})$ can be obtained. (Of course, since the calculation of $B(T)$ requires integration over r , it is necessary to extrapolate U_1 outside the range for which \tilde{r} can be calculated. The extrapolation can be accomplished with an approximate potential function adjusted to join smoothly to U_1 .) The procedure is repeated until some measure of convergence is satisfied. Suitable criteria might be the degree to which the values of $B + T(dB/dT)$ calculated from the potential match the experimental values or the extent to which successive estimates of $U(\tilde{r})$ agree.

The inversion procedure has been tested on data simulated from known potential energy functions (3,4) and has proved successful, as shown in Fig. 1. (Also successful was a "blind-fold" challenge (5), in which the potential used to generate the data was revealed only after the inversion.)

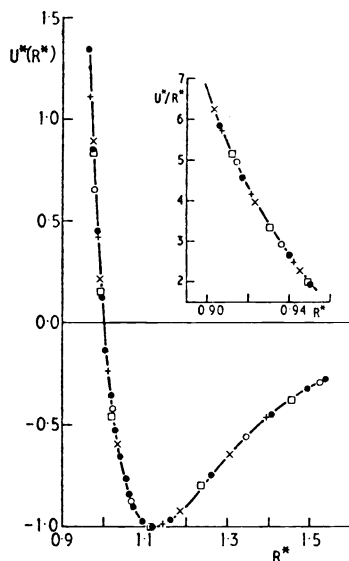


Fig. 1. Inversion of pseudoexperimental second virial coefficient data. The line represents the Lennard-Jones 12-6 potential used to generate the data; the points represent the potential obtained by inversion. Each symbol type corresponds to a different initial approximate potential. (From Ref. 3.)

Real data for argon have also been inverted (4). Values of B in the temperature range 90-700 K were employed and the inversion procedure was carried out for a number of different potential energy functions and a wide range of values of ϵ/k . A fairly sharp minimum in the rms deviation of the calculated second virial coefficients from the input data was found

for $\epsilon/k = 150 \pm 5 \text{ K}$ and the corresponding collision diameter σ was 0.334 nm. These values are close to the best estimates (6) for argon, $\epsilon/k = 142.5 \pm 1.0 \text{ K}$ and $\sigma = 0.335 \text{ nm}$, which have been obtained from analyses of a combination of properties. The difference may be indicative of systematic errors in some of the virial coefficient measurements.

Smith and Tindell(7) have recently made the first efforts at applying the inversion procedure to effective spherical potentials that are consistent with virial coefficients calculated for an anisotropic model potential. In the same spirit, let us use an approximate inversion function as a general guide to the design of virial coefficient measurements for the relatively simple polyatomic molecules that are of interest to many chemists. What measurements must be performed if we are to increase our knowledge of the intermolecular potentials for such molecules?

With an approximate inversion function obtained from a Lennard-Jones 12-6 potential, we find that virial coefficient data in the range $T^* = 0.6$ to $T^* = 4$ could define the potential between $r^* = r/\sigma = 1.7$ and $r^* = 0.9$. (For comparison, recall that $r^* = 1.12$ at the potential minimum.) If we assume $\epsilon/k = 250 \text{ K}$, a value typical of many hydrocarbons, this T^* range corresponds to 850 K. The normal boiling point lies roughly at $T^* = 0.9$, which corresponds to $r^* = 1.3$.

Clearly, only measurements over a very large temperature range and to temperatures below the normal boiling point will serve to define the potential. Although less ambitious studies may produce useful data, they will tell us little about intermolecular forces. In the next section we will examine the constraints that these requirements impose.

EXPERIMENTAL PROCEDURES AND EXPERIMENTAL PROBLEMS

A large number of ingenious techniques for measuring virial coefficients by essentially volumetric methods continue to be developed. These include "two-bulb" (8), "three-bulb" (9), "four-bulb" (10,11) and even "five-bulb" (12) apparatuses, each bulb increment allowing some parameter or apparatus constant to be determined without calibration. All of the methods require the precise measurement of the pressure within a bulb or of the pressure difference between bulbs. It is surprising how difficult such measurements can be.

Bell and Dunlop (13) have recently reported their experiences with the calibration of a quartz spiral pressure gauge that has a sensitivity exceeding one part in 10^5 . Similar observations that were made in our laboratory (14) are summarized in the calibration curve, Fig. 2, which shows the apparatus constant as a function of the pressure. (The digital output of the gauge must be multiplied by the apparatus constant to obtain the pressure.) Our gauge had a range

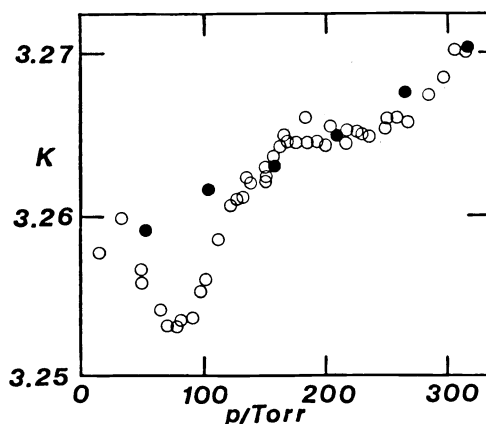


Fig. 2. Apparatus constant K as a function of pressure for a quartz spiral gauge. Full symbols represent the manufacturer's calibrations.

of 1000 torr and was calibrated by the manufacturer at 50-torr intervals; these calibrations are indicated by the full symbols. Subsequent calibrations by us on a much finer grid are represented by the open symbols. Had we simply interpolated smoothly between the original calibrations, we would have made errors as large as 0.2 torr.

Differential pressure measuring devices are also not immune to calibration problems. Ewing and Marsh (9) discovered that a sensitive pressure transducer, which according to the manufacturer's specifications has an accuracy independent of the total pressure, had a systematic error that varied by one percent over the pressure range 2 to 103 kPa. So acute is the calibration problem that a dual dead-weight gauge system has been constructed (15) specifically for the calibration of precision differential pressure gauges over a range of line pressures.

These pressure-measurement problems are typical of those that haunt the equation-of-state experimenter. They are systematic errors and are difficult to detect. The recent measurements on ethylene (16,17) shown in Fig. 3 are unusual in that four different volumetric studies agree, essentially within their precisions, over a wide temperature range. Systematic deviations, such as those for the one discordant study, are more often the rule.

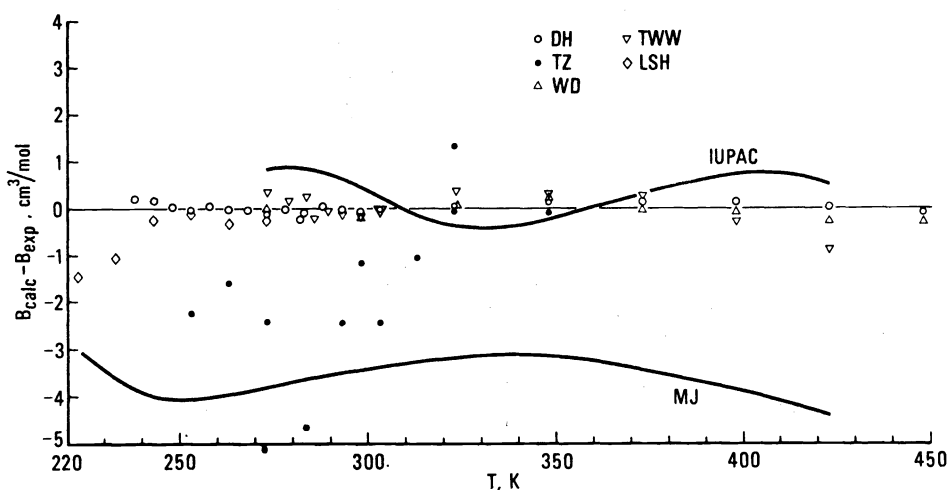


Fig. 3. Deviations of five sets of second virial coefficient data for ethylene from an empirical polynomial relation. The curved lines represent two other correlations. Note the systematic deviations at low temperatures of the measurements represented by diamonds. (From Ref. 16)

The most pernicious of systematic errors are those caused by adsorption. Such errors pose the most severe limitation on our ability to make measurements at the low temperatures necessary to define the attractive portion of the potential. The systematic deviation at low temperatures of the points labeled LSH in Fig. 3 is evidence of adsorption. That something is amiss was also indicated by apparent decreases in density observed in isochorically coupled Burnett expansion isotherms (18).

Dramatic effects of adsorption are seen in measurements of the pressure change on mixing gases at constant volume, a method used to determine interaction virial coefficients (19). Although the total pressure changes very little during the measurement, the partial pressure of each component is halved during the mixing process and the surface area available to each component is usually doubled. Measurements involving polar substances (20,21) are particularly susceptible to error.

The seriousness of the adsorption problem is illustrated in Fig. 4, which shows the uncertainty introduced by adsorption into measurements of the excess second virial coefficient $\mathcal{E} [= B_{12} - \frac{1}{2}(B_{11} + B_{22})]$ for benzene + cyclohexane (22). It has been assumed in the calculation that the adsorption isotherms can be represented by the BET equation, that the surface area is simply the geometric area, and that the adsorption isotherm of the mixture is a linear combination of the isotherms of the pure components. The calculations are therefore approximate and necessarily specific to the mixture and to the apparatus. As a measure of the magnitude of the errors, consider that over most of the temperature range shown the excess second virial coefficient is about $40 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

The primary experimental quantity, the pressure change developed on mixing, depends quadratically on the filling pressure p , hence it is desirable to work at high pressures. As a rule

of thumb, workers have avoided pressures greater than 80 percent of saturation ($p/p_0 = 0.8$) to forestall capillary condensation. Adherence to this simple rule clearly does not guarantee that the error due to adsorption is negligible.

Although adsorption corrections have been applied to measurements of ϵ (21,22), the tenuous character of the underlying assumptions leads me to question their validity. Since adsorption errors depend on the system studied and on the nature and cleanliness of the surfaces, nothing

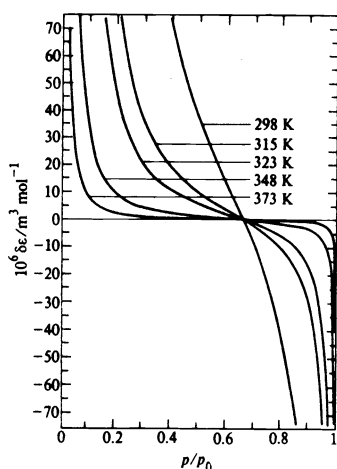


Fig. 4. Difference between true and apparent values of the excess second virial coefficient ϵ as a function of the degree of saturation, p/p_0 ; the lines represent different temperatures. Throughout most of this temperature range, ϵ is no larger than $40 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. (From Ref. 22)

short of an experimental determination of the amount of substance adsorbed will guarantee that volumetric measurements at low temperatures are free of systematic adsorption errors. The key to handling adsorption is to avoid it, and this means abandoning volumetric methods. Let us consider two alternatives.

ALTERNATIVE METHODS FOR DETERMINING THE EQUATION OF STATE

Measurements of the speed of sound

If a gas is placed in a cylinder of length L capped by transducers that can excite and detect longitudinal sound modes, the amplitude of the detected waves can be studied as a function of the excitation frequency. The frequencies f_n at which the detected amplitude passes through a maximum are given by

$$f_n = \frac{nc}{2L} \quad (5)$$

where c is the speed of sound in the gas and n is an integer identifying the mode. The dependence of the sound speed on both temperature and pressure can be expressed as a virial expansion

$$c^2(T,p) = \frac{\gamma_0 RT}{M} + A_1(T)p + A_2(T)p + \dots \quad (6)$$

in which $\gamma_0(T)$ is the specific heat ratio C_p/C_v in the zero pressure limit, M is the molecular weight, and A_1 and A_2 are acoustic virial coefficients. A_1 is related to the ordinary second virial coefficient through

$$A_1(T) = \frac{\gamma_0}{M} \left(2B + 2(\gamma_0 - 1)T \frac{dB}{dT} + \frac{(\gamma_0 - 1)^2}{\gamma_0} T^2 \frac{d^2B}{dT^2} \right) \quad (7)$$

Measurements of the speed of sound as a function of pressure and temperature can therefore give information about the equation of state and the ideal-gas heat capacity; indeed, two such studies (17,23) are reported at this conference.

The simple expression (5) must be corrected for frequency shifts associated with boundary-layer contributions to the acoustic admittances of the sides and ends of the resonator.

These corrections, which involve the transport properties and the specific heat ratio of the gas, are well understood. The relative size of the corrections $\Delta f/f$ is inversely proportional to $f^{1/2}$. In principle, then, errors can be minimized by working at high frequency. An obvious practical limit to the frequency is the time required for the internal degrees of freedom of a polyatomic molecule to come into equilibrium with the translational degrees of freedom. With few exceptions, notably diatomic molecules, the relaxation time at 1 atm is no longer than about $1 \mu\text{s}$, so measurements at frequencies up to 1 MHz would be unaffected. Less easy to evaluate are the systematic errors that result from the mixing of longitudinal and transverse sound modes that may occur when the acoustic wavelength is small compared to the resonator dimensions.

The amount of substance does not enter into either the basic equations or the correction terms, hence acoustic measurements might be expected to be unaffected by adsorption. Unfortunately, some recent studies by Mehl and Moldover (24) suggest that this is not the case. They interpret the sharp decrease in the speed of sound in nitrogen at low temperatures (Fig. 5) observed by Younglove and McCarthy (25) as a precondensation phenomenon.

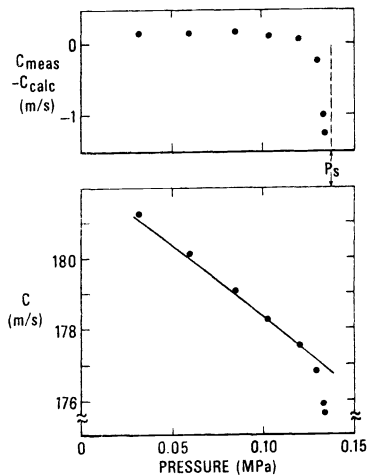


Fig. 5. Apparent speed of sound in nitrogen as a function of pressure at 80 K. The line in the lower curve was calculated from a correlation of the thermophysical properties of N_2 ; the upper curve shows the difference between the calculated and experimental values. P_s is the saturation pressure. (From Ref. 24)

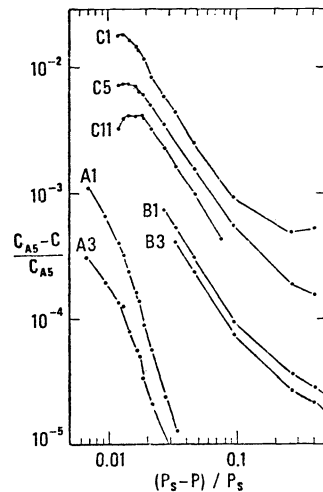


Fig. 6. Pressure dependence of the fractional deviations of the measured speed of sound in propane from measurements taken with the fifth mode of spherical resonator A. Measurements taken with the cylindrical resonator are labeled by C; those with the spherical resonators by A and B. The subscripts identify the mode. (From Ref. 24)

To test their hypothesis, Mehl and Moldover measured the speed of sound in propane with three resonators, two of which were spherical but of different diameter, while the third was cylindrical and similar in dimensions to the one used for the nitrogen study. The propane data exhibit an anomaly much like the one observed in nitrogen. As shown in Fig. 6, the anomaly is strongest at low frequency; it depends as well on the surface-to-volume ratio of the resonators and the finish of the resonator surface. A model for the acoustic admittance of a liquid film is in qualitative agreement with the observations.

Further measurements and analyses are required to determine if the acoustic method is applicable to low-temperature equation-of-state measurements. It is clear, however, that where adsorption is not a problem, reliable very high precision absolute measurements of the speed of sound can be made. Relative measurements (23,26), which are less sensitive to systematic errors and which avoid the determination of apparatus constants, may prove even more reliable.

It is no trivial matter, however, to extract the ordinary second virial coefficient from A_1 : the terms within the parentheses in Eqn. (7) are typically of the same magnitude and γ_0 is usually not accurately known. The obvious first step is to obtain A_1 and γ_0 from the pressure dependence of c^2 . This procedure is similar to that followed in dealing with ordinary p, V, T -data and in discussing it I have the opportunity of making a few general remarks about data analysis.

Twenty years ago, Scott and Dunlap (27) fitted experimental p, V -measurements on butane with both the pressure and density forms of the virial equation. The two methods of analysis led

to second virial coefficients whose standard deviations, as determined by the least-squares procedure, were about $5 \text{ cm}^3 \text{ mol}^{-1}$; the two values differed, however, by $30 \text{ cm}^3 \text{ mol}^{-1}$! They soon realized that the linear expressions they were using gave the *average* values of the slope of pV/nRT vs. n/V and pV/nRT vs. p/RT , while the second virial coefficients are defined as the *limiting* slopes at $n/V=0$ and $p/RT=0$. Even though the two isotherms appeared to be quite linear, it was only when terms in $(n/V)^2$ and $(p/RT)^2$ were included in the analysis that the values of B obtained from the two series agreed within their estimated uncertainties.

I raise this bit of "ancient history" because its lesson has sometimes been forgotten and also because it is possible to interpret the Scott-Dunlap observations in another way that illustrates an important feature of data analysis that is often overlooked -- the concept of covariance. To illustrate, I have fitted p,V -data for dichloromethane (28) along a single isotherm (349.53 K) by both linear and quadratic equations in the density. The results of the least-squares analyses are given in Table 1.

TABLE 1. Fit of $Z = pV/nRT = A + B(n/v) + C(n/V)^2$ for dichloromethane at 349.5 K

	<i>Linear</i>	<i>Quadratic</i>
σ	1.56×10^{-4}	0.36×10^{-4}
A	1.00024 ± 0.00009	0.99994 ± 0.00003
$B/\text{cm}^3 \text{ mol}^{-1}$	-570.8 ± 2.0	-541.2 ± 2.9
$C/10^5 \text{ cm}^6 \text{ mol}^{-2}$		-3.17 ± 0.30

The magnitude of the standard deviations of the parameters in the quadratic fit is determined by the scatter of the data, the number of observations, the range of densities and, if A, B , and C are not independent, the variations in the other parameters. Covariances σ_{ij} , which are easily obtained from the off-diagonal terms of the inverse matrix used to solve the least-squares normal equations, express the correlations between parameters i and j . The covariances and the standard deviations of the parameters σ_i and σ_j can be used to define a correlation coefficient ρ (29):

$$\rho = \frac{\sigma_{ij}^2}{\sigma_i \sigma_j} \quad (8)$$

The magnitude of ρ ranges between zero (no correlation) and one (complete correlation).

The correlation coefficient associated with B and C in the quadratic fit of the dichloromethane isotherm is -0.99 , the negative sign indicating that errors that cause B to be high will cause C to be low. In effect, the least-squares procedure has determined pairs of B 's and C 's that are consistent with the data, rather than with independent parameters. As a result of the high degree of correlation, some of the uncertainty in B must be associated with the uncertainty in C . We can therefore reduce the apparent uncertainty in B by fixing the value of C , say at zero. In doing so, we must also adjust B so that it is consistent with $C=0$. The adjustment can be calculated (29) from the change in C ($+3.17 \times 10^5$), the covariance, and the variance of C

$$\Delta B = \Delta C \left(\frac{\sigma_{BC}^2}{\sigma_C^2} \right) \quad (9)$$

We find $\Delta B = -29.7 \text{ cm}^3 \text{ mol}^{-1}$, so the adjusted value of B is $-570.9 \text{ cm}^3 \text{ mol}^{-1}$, the value obtained from the linear least-squares analysis.

The large difference between the second virial coefficients derived from the linear and quadratic fits may therefore be seen as resulting from the constraint of the highly correlated third virial coefficient. The standard deviations of the coefficients must not be interpreted as a measure of the precision of the coefficients as independent parameters.

Covariances must be considered in assessing errors in derived quantities. If a quantity y is a function of two variables α and β that are correlated, then the expression for the propagated error must include a term $2\sigma_{\alpha\beta}^2(\partial y/\partial\alpha)(\partial y/\partial\beta)$ in addition to the terms involving the variances of α and β . This is the case in the analysis of acoustic data, where [Eqn.(7)] $B = B(A_1, \gamma_0)$, if A_1 and γ_0 are both obtained from fitting c^2 as a function of p [Eqn.(6)].

The relation between the errors in c and the errors in A_1 and γ_0 is not obvious and will depend on the method of analysis. Mehl and Moldover (30) have treated Eqn. (7) as a differential equation for B and integrated it by estimating B and dB/dT at 273 K from the volumetric measurements of Douslin and Harrison (31). The differences between the virial coefficients derived from the acoustic data and those obtained volumetrically (31,32) are shown in Fig. 5. The deviations, which are systematic, reach $0.8 \text{ cm}^3 \text{ mol}^{-1}$ at the highest temperature.

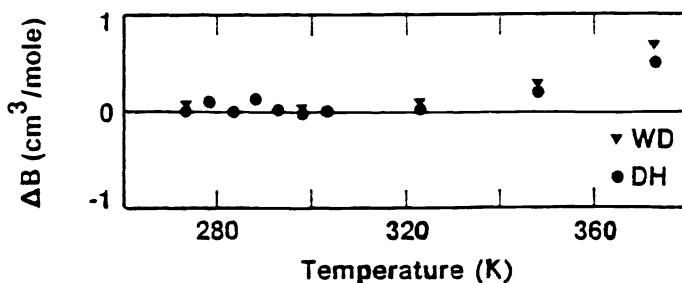


Fig. 7. Deviations of the data of Douslin and Harrison (31) and Waxman and Davis (32) from the virial coefficients calculated by integration of acoustic data. (From Ref. 30)

Ewing et al. (23) have adopted a different analysis procedure. They represent the second virial coefficient by a general polynomial

$$B(T) = \sum_{j=1}^k a_j T^{(5-j)/2} \quad (10)$$

which gives

$$A_1(T) = \sum_{j=1}^k a_j Y_j T^{(5-j)/2} \quad (11)$$

with

$$Y_j = (\gamma_0/M)[2 + (\gamma_0 - 1)(5 - j) + (\gamma_0 - 1)^2(5 - j)(3 - j) / 4\gamma_0] \quad (12)$$

The coefficients a_j can be determined by fitting A_1 by least squares. This method of analysis is very sensitive to the polynomial chosen for B , which must represent satisfactorily both the first and second derivatives. It is not clear that this criterion can be met for data of high precision that extend over a large temperature range.

Flow calorimetric methods

In principle, measurements of the isothermal Joule-Thomson coefficient can be employed to determine the equation of state of pure substances and direct measurements of the enthalpy of mixing can yield interaction virial coefficients. The feasibility of such methods has long been recognized, but it is only recently that reliable techniques for measurements at low reduced temperatures have been developed, chiefly by Wormald and coworkers.

The chief advantage of flow calorimetric methods for equation-of-state studies is the freedom from errors caused by adsorption. Flow methods may also be advantageous at high temperatures, where decomposition can be a problem. Two basic components comprise the apparatus: (1) a system for establishing steady flows at fixed pressures and (2) a calorimeter. The success of an experiment rests on the attention paid to detail in its design.

When the substances being studied are gaseous, flow control is easy; the generation of a steady flow of vapor by the evaporation of liquid is more difficult. Controlled flows of vapor have been produced by injecting liquid from a calibrated metering pump into a flash vaporizer (33,34) but a simpler system (35) that utilizes a refluxing liquid as the vapor source is equally effective (Fig. 8).

Detailed descriptions of highly refined calorimeter designs can be found in the literature (33-37). An innovation in heat-of-mixing calorimetry, the differential flow calorimeter (38), may be singled out. The twin calorimeter, which is shown schematically in Fig. 8, has

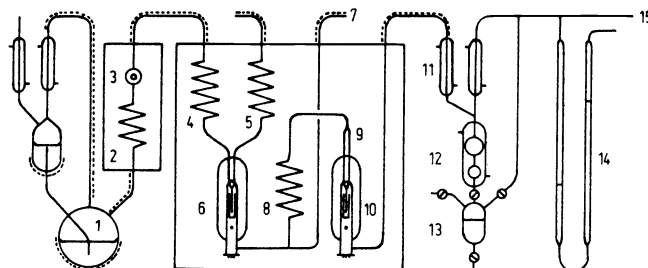


Fig. 8. Schematic diagram of a flow system and differential calorimeter. The condensers and flask to the left of the boiler (1) are a system that automatically degases the liquid. Throttle valve (3), which controls the flow rate, and heat exchanger (2) are in a thermostatted bath. A similar boiler and flow-control system are provided for the second component. Heat exchangers (4), (5) and (8) are in the main thermostat with the calorimeters (6) and (10). After flowing through heat exchanger (8), the stream is split at (9) before it enters the second calorimeter. A manometer connected at (7) can be used to measure the pressure in the calorimeter. The mixture leaving the calorimeter is condensed at (11) and can be collected and measured in bulbs (12) before it is drained into (13). The outlet pressure is measured on manometer (14). (From Ref. 35)

the important advantage that systematic errors caused by the Joule-Thomson effect are cancelled out. An additional advantage of the second calorimeter (35) is that it allows exothermic enthalpies of mixing to be determined: The components are mixed in the first calorimeter and the temperature rise is sensed. The mixture is restored to the thermostat temperature by a heat exchange coil and power is supplied to the heater of the second calorimeter until the temperature rise matches that in the first calorimeter. If the thermocouples used to sense the temperature in the two calorimeters are connected in opposition, this condition is indicated by a null.

Joule-Thomson measurements have been performed on benzene and cyclohexane (33,34,39), and the normal alkanes hexane, heptane, and octane (40) at reduced temperatures as low as 0.6. The strongly adsorbed compounds acetone and chloroform (36) have also been studied. Many heats of mixing have now been investigated, including low-pressure studies of systems as "unpleasant" as water + chloroform (41), dimethyl ether + chloroform (42), and acetone + chloroform (35,43) and several mixtures involving water (44,45).

For a Joule-Thomson calorimeter, the power ϕ required to maintain isothermal conditions may be written (36):

$$\phi = f \Delta p \left[\left(B - T \frac{dB}{dT} \right) + \left(C' - T \frac{dC'}{dT} \right) p \right] \quad (13)$$

where f is the flow rate, Δp is the pressure drop across the calorimeter, p is the mean pressure and $C' = (C - B^2)/RT$. The first term in parentheses is the zero-pressure isothermal Joule-Thomson coefficient ϕ .

At low density, H^E the heat of mixing for a binary vapor mixture is given by (35):

$$H^E = x(1-x)p(2\phi_{12} - \phi_{11} - \phi_{22}) - \frac{p^2}{RT} [B_m \phi_m - (1-x)B_{11}\phi_{11} - xB_{22}\phi_{22}] \quad (14)$$

The mole fraction of the second component is represented by x and the subscripts 11, 22, m , and 12 identify respectively the pure component, mixture, and interaction virial coefficients and Joule-Thomson coefficients. An alternative expression for the first term in (14) shows the relation of H^E to the excess second virial coefficient:

$$H^E = x(1-x)p \left(\mathcal{E} - T \frac{d\mathcal{E}}{dT} \right) \quad (15)$$

The direct analysis of both types of calorimetric measurement is seen to be similar to that required for acoustic data. Measurements made as a function of pressure must be extrapolated to the zero-pressure limit and the resulting quantities, here the intercepts, must be integrated to obtain the desired parameters, B and ϵ . Thus, additional information is necessary to fix at least one limit of the integration.

In an alternative procedure, Joule-Thomson data (36) are combined with measurements of the zero-pressure limit of the pressure derivative of the heat capacity,

$$\lim_{p \rightarrow 0} T \left(\frac{\partial C_p}{\partial p} \right)_T = - T^2 \left(\frac{d^2 B}{dT^2} \right) \quad (16)$$

in order to determine by least-squares the coefficients in an empirical expression such as (10).

Here again, the success of the method rests on the suitability of the polynomial. In addition, it is necessary to establish relative weights for the various sets of data that are combined in the analysis, a task that is clearly not trivial.

Interaction virial coefficients can be extracted from H^E measurements only when either the pure-component virial coefficients or Joule-Thomson coefficients are known. If a specific potential or corresponding states correlation is assumed, the data can be used to test combining rules by which the parameters representing the unlike interaction are obtained from the parameters for the pure components (44). For example, if the arithmetic mean is assumed for the size parameter of a two-parameter potential, the energy parameter can be written $\epsilon_{12} = \xi(\epsilon_{11}\epsilon_{22})^{1/2}$ and ξ can be varied to bring the calculated H^E 's into accord with the measured values. Equilibrium constants and enthalpies of reaction for weak gas-phase complexes have also been extracted from H^E measurements (42).

The determination of interaction parameters, for use in the prediction of the properties of fluid mixtures, is still a motivating force for the measurement of interaction virial coefficients. Despite much searching, no generally applicable combining rules have been found. Diaz Peña et al. (46) have given a general formula for generating combining rules for a two-parameter potential

$$\epsilon_{12} = \frac{\langle \epsilon \sigma^6 \gamma \rangle_i}{\langle \sigma \rangle_j^6 \langle \gamma \rangle_k} \quad (17)$$

The subscripts i , j , and k specify the form of the mean indicated by the bracket and γ stands for additional substance-specific parameters, such as I , α^{-2} , χ^{-2} , or χ/α , where I , α , and χ are the ionization energy, polarizability, and diamagnetic susceptibility, respectively. Rules may then be defined by specifying γ and the type of mean (arithmetic, geometric, or harmonic) for each index. A total of 108 distinguishable rules is generated when $\gamma=1$ is allowed and the simple means for ϵ_{12} are also included.

The rules have been ranked by comparing experimental values of B_{12} for 73 nonpolar binary mixtures with those calculated from a Lennard-Jones 12-6 potential. Included in the sample were noble gases, diatomic and pseudospherical molecules, and hydrocarbons. Three statistical criteria were taken as figures of merit.

A rule previously proposed by Good and Hope (47) was the most successful. It corresponds to the relations

$$\left. \begin{aligned} \sigma_{12} &= (\sigma_{11}\sigma_{22})^{1/2} \\ \epsilon_{12} &= (\epsilon_{11}\epsilon_{22})^{1/2} F(\gamma) \\ F(\gamma) &= 2(I_1 I_2)^{1/2} / (I_1 + I_2) \end{aligned} \right\} \quad (18)$$

Eqns.(18) are only marginally better than several others, however, including the geometric mean of ϵ and the geometric mean of σ with $F(\gamma)=1$ and, at a slightly lower ranking, the familiar combination of the geometric and arithmetic means.

The rules were also tested with the Kihara spherical core potential, for which the combination rule for the third parameter a_{12} is specified as the arithmetic mean. The rankings of combination rules for this potential are less clear-cut and do not correspond to those for the Lennard-Jones potential. Diaz Peña et al. conclude that only rules that correspond to the arithmetic mean for the energy parameter are clearly inferior. For the rest, "none of the rules tested shows a clear advantage over the other rules in correlating experimental data for all of the systems or for groups of similar systems."

CONCLUSIONS

Definitive information about the intermolecular potential can be obtained from equation-of-state measurements that meet the criteria of high precision, freedom from systematic errors, and sufficient range. Very few measurements on polyatomic molecules come up to this standard, but they are feasible and should be pursued. An insensitivity to adsorption errors gives isothermal Joule-Thomson coefficient studies clear advantage over volumetric methods for measurements at low temperatures; acoustic measurements at intermediate frequencies may also be advantageous. Practical procedures for extracting virial coefficients from high-precision calorimetric and acoustic data must be developed, however.

It is neither necessary nor desirable, of course, to choose only one experimental method. The beautiful study of ethylene described at this meeting (17) is an example of the successful combination of several different experiments. It is likely, as well, that calorimetric or acoustic measurements are best analyzed by linking them to a few precise volumetric measurements at temperatures at which adsorption is clearly negligible. My discussion has, of course, been limited to the second virial coefficient; I see few alternatives to volumetric methods for the determination of higher virial coefficients.

I have focused primarily on the importance of measurements as they relate to microscopic interactions. There are certainly good practical reasons to perform limited, moderate-precision measurements. We should not delude ourselves, however, that we can learn very much from them about intermolecular forces. Most measurements of interaction virial coefficients fall into this category. They provide us with essential information about unlike interactions, but only in terms of the potentials assumed for the pure substances. Here again, extensive well conceived heat-of-mixing measurements in combination with volumetric measurements can lead to new insights. Studies of the excess heat capacity of gaseous mixtures (48) may also be helpful.

High-temperature studies might be considered as well. Matias et al. (49) have calculated the second virial coefficients of alkali metal vapors in the temperature range 1000 to 10,000 K. Stephenson (50) has shown that the softening of the molecular hard core at high temperatures is mirrored in the detailed behavior of C_p . The testing of these theoretical predictions provides a formidable challenge.

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