t_f = felt surface temperature
V = velocity of sheet in direction z
W_τ = dimensionless evaporation quantity = $\alpha \lambda w/X k t_b$
w = quantity evaporated
X = thickness of sheet
x = distance through thickness of sheet
y = coordinate direction or distance in cross direction
y_a = mole fraction water vapor in air
y_0, y_1 = mole fraction water vapor in air saturated at surface temperature of sheet
z = distance in direction of sheet travel

Greek Letters

α = thermal diffusivity = $k/\rho c$
θ = time
λ = latent heat of evaporation
τ = dimensionless time parameter = $\alpha\theta/X^2$
ρ = density

Subscripts

a = air
s = cylinder surface
f = felt

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Second Virial Coefficients of the Acetonitrile-Acetaldehyde System

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The low-pressure compressibilities of acetonitrile, acetaldehyde, and their mixtures were measured in the temperature range 40° to 100°C. From these data second virial coefficients were determined for the pure components and for the mixture. The absolute value of the coefficient B_{12}, characteristic of interaction between dissimilar molecules, was considerably larger than that for B_{11} or B_{22}, which are characteristic of interactions between similar molecules. As a result it was not possible to predict the properties of the mixture with only data for the pure components. Calculations based on the Stockmayer potential and with conventional mixing rules gave seriously incorrect results for the second virial coefficient B_{12}.

The data were interpreted with the aid of an association theory. Dimerization equilibrium constants and enthalpies and entropies of formation were computed for the pure-component dimers and for the complex. The heat of formation for the complex was significantly larger than that for the dimers; comparison with energy terms calculated from electrostatic theory suggest that the structure of the complex is different from that of the pure-component dimers.

Volumetric properties of gases and gas mixtures are of practical interest, since they provide the basic data required for the calculation of thermodynamic functions such as may be required in separations or other chemical engineering operations. In addition such properties are a valuable source of information in obtaining quantitative data on intermolecular forces. While many experimental studies have been made on the properties of nonpolar gases and their mixtures, limited information is available for polar gases, and studies on gas mixtures containing two or more polar components are very scarce. It is these mixtures however which because of strong intermolecular forces exhibit very large deviations from ideal behavior. These deviations may be sufficiently high to invalidate seriously the ideal-gas assumption even at rather low pressures. In addition the nature of polar-polar interactions is often so specific that the forces between two dissimilar molecules is no simple average of the forces acting between molecules of the same species; in polar gas mixtures therefore the Lewis fugacity rule is usually most unreliable. As a contribution to understanding the thermodynamic properties of polar substances this work presents results on the volumetric behavior of two highly polar gases and their mixtures. Data are reported on the low-pressure compressibility of the acetoni-

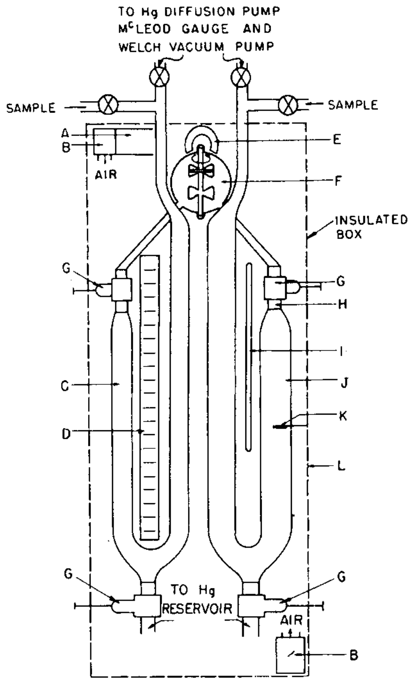

Fig. 1. *P-V-T-y* apparatus: *A* = heater duct, *B* = circulation blower, *C* = 0.50000-in. U tube, *D* = standard meter bar, *E* = magnet, *F* = mixing chamber, *G* = hoke bellows valve, *H* = Kovar-pyrex graded glass seal, *I* = thermometer, *J* = 0.75000-in. U tube, *K* = thermistor.

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TABLE 1. SECOND VIRIAL COEFFICIENTS FOR THE ACETONITRILE-ACETALDEHYDE SYSTEM
ml./mole

T, °C.	$-B_{11}$ (Acetonitrile)	$-B_{22}$ (Acetaldehyde)	$-B_{12}$
40.0	5,250 ± 100	944 ± 20	8,710 ± 150
60.0	3,620 ± 40	765 ± 20	6,170 ± 150
80.1	2,610 ± 40	633 ± 20	3,450 ± 150
100.4	1,930 ± 40	533 ± 20	2,390 ± 150

trile-acetaldehyde system in the temperature range 40° to 100°C.

EXPERIMENTAL

The volumetric properties of the pure gases and their mixtures were measured in a thermostated PVT apparatus shown schematically in Figure 1. The essential parts of this apparatus are two U tubes (one for each gas) and a mixing chamber. The U tubes are partially filled with mercury; the sample is on one side of this tube and the other side is evacuated. The pressure and volume of the sample are changed isothermally by raising or lowering the mercury level.

The two U tubes were made of Pyrex glass with inside diameters of ½ and ¾ in. respectively. The diameters were not the same in order that the different surface-to-volume ratios of the two tubes might be used to detect possible adsorption of the polar gas molecules onto the glass. (No evidence of significant adsorption was found in this work.) In both cases the outside leg (containing the sample) was fabricated from precision-bore tubing to eliminate tedious volume calibrations by displacement with mercury.

Ordinary glass, high-vacuum valves could not be used in the U tubes because of the contaminating effect of stopcock grease. Therefore metal valves were used for sealing off the upper end of the sample tubes and for allowing mercury to flow into the bottom of the U tubes.

On top of the valves attached to the sample legs of the U tubes were glass seals leading to capillary tubing which in turn led to a common mixing chamber.

For the gas mixture runs a known amount of each gas was displaced with mercury into the previously evacuated mixing chamber. Measurements of the pressure-volume relationships prior to and after the displacement enabled very accurate calculation of the gas-mixture composition.

Measurements of pressure and volume were made with a cathetometer. The pressure range investigated was 20 to 350 mm. Hg. To obtain very accurate readings a meter bar (calibrated by the National Bureau of Standards) was placed inside the insulated box between the two U tubes; this bar was used for coarse readings, fine readings being taken with the vernier on the cathetometer. Details of the procedure and the apparatus are presented elsewhere (3).

The apparatus was calibrated with argon which has a virial coefficient of zero at 320°K. (5).

Acetaldehyde and acetonitrile were obtained in spectroscopic grade. Traces of water were removed with previously activated Drierite. Both of the polar substances were distilled under dry nitrogen, and the central cuts were transferred to sample tubes. Dissolved nitrogen was removed by alternate freezing and melting under vacuum.

DATA REDUCTION

Details of converting the mercury-height readings to pressure and volume data are presented elsewhere (3). In the calculations allowance was made for the temperature coefficients of expansion of glass and mercury.

The data were fitted graphically to the virial equation

$$PV = nRT + nBP \qquad (1)$$

At the prevailing experimental conditions virial coefficients higher than the second need not be included. By plotting the pressure-volume product at constant temperature against the pressure the number of moles in the sample is determined from the intercept and the second virial coefficient from the slope.

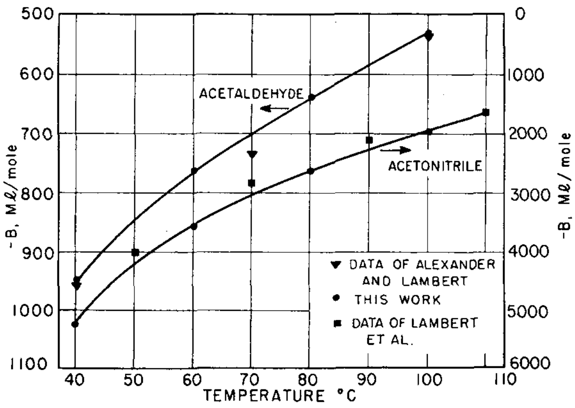

Fig. 2. Second virial coefficients for acetonitrile and acetaldehyde.

RESULTS

The second virial coefficients of the acetonitrile-acetaldehyde system are given in Table 1 which also includes an estimate of the errors. The second virial coefficients of the pure components compare very favorably with those reported by Alexander and Lambert (1) and by Lambert, Roberts, Rowlinson, and Wilkinson (7). A comparison of new and previously published results for the pure components is given in Figure 2.

Figure 3 presents the second virial coefficients as a function of composition. The lines are computed parabolas (based on the values of B_{12} as indicated) according to the theoretical equation

$$B(\text{mixture}) = y_1^2 B_{11} + 2y_1y_2B_{12} + y_2^2 B_{22} \qquad (2)$$

Equation (2) is a rigorous result (4, 5, 8) from the statistical mechanics of real gases which interprets the second virial coefficient as being a term characteristic of the interaction between two molecules. Thus B_{11} is a term characterizing interactions between two molecules of species 1; B_{22} characterizes interactions between two molecules of species 2, and B_{12} is characteristic of interactions between the dissimilar molecules. Table 1 indicates that at any temperature the value for B_{12} is no simple function of B_{11} and B_{22}. In fact the very large (absolute) values for B_{12} show that for the temperature range 40° to 100°C. the interaction between two dissimilar molecules is always greater than that corresponding to the interaction of two similar molecules of either of the two species. Hence any simple mixing rule aiming to predict B_{12} from known values of B_{11} and B_{22} must fail for this system.

PREDICTION BY STOCKMAYER POTENTIAL

A theoretical method for computing second virial coefficients of polar gases

TABLE 2. PREDICTION OF B_{12} WITH THE STOCKMAYER POTENTIAL*

	$-B_{12}$ ml./mole	
T, °C.	Stockmayer	Experimental
40.0	2,000	8,705
60.0	1,540	6,166
80.1	1,272	3,452
100.4	772	2,393

* Parameters for pure components are taken from reference 5. Parameters for the mixture are obtained from Equations (3), (4), and (5).

has been presented by Stockmayer (*13, 16*) who expresses the potential energy of two polar molecules by summing the contributions from dispersion, induction, and polar forces. His method results in the expression of a reduced second virial coefficient as a function of reduced temperature and reduced dipole moment; the necessary characterizing parameters are the dipole moment, a collision diameter, and a characteristic energy. These parameters characterizing the interactions for pure acetonitrile and for pure acetaldehyde have been computed from previously reported second virial coefficient data (*1, 7*) for the pure components. To find characterizing parameters for the interaction between acetonitrile and acetaldehyde the following commonly recommended mixing rules were used:

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \qquad (3)$$

$$\epsilon_{12} = \sqrt{\epsilon_{11}\,\epsilon_{22}} \qquad (4)$$

$$t^*_{12} = \frac{\mu_1\mu_2}{\sqrt{8}\,\epsilon_{12}\sigma^3_{12}} \qquad (5)$$

Using the characterizing parameters as computed by Equations (3), (4), and (5) one could then calculate values of B_{12} for the acetonitrile-acetaldehyde system by the Stockmayer method. The results, shown in Table 2, compare very poorly with the experimental values; at all temperatures studied the observed interaction between the dissimilar molecules is much larger than predicted.* This result indicates that the intermolecular forces operating between acetonitrile and acetaldehyde are in some sense qualitatively different from those operating in either pure component. A possible explanation of this qualitative difference is provided by interpreting the deviations from ideal behavior in terms of dimerization, or complex formation.

THERMODYNAMICS OF DIMERIZATION

The second virial coefficients of polar molecules tend to be significantly lower than those for nonpolar molecules. Large negative second virial coefficients are due to strong forces of attraction, and it therefore has been frequently suggested that the large deviations from ideal behavior of polar gases are due to the formation of dimers. Consider the dimerization equilibrium $2A \rightleftarrows A_2$. A dimerization equilibrium constant can be defined by

$$K_{p(AA)} = \frac{p_{A_2}}{p_A{}^2}$$

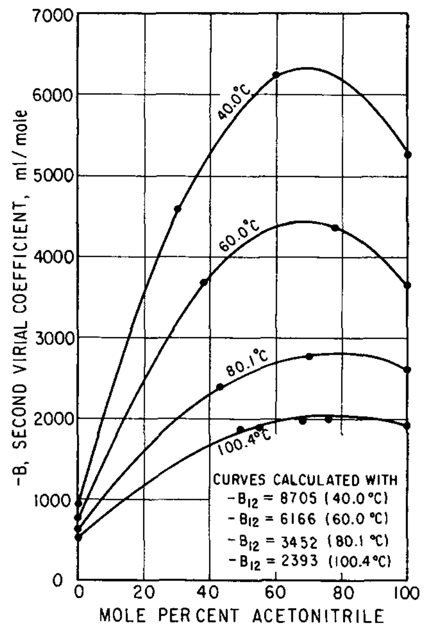

Fig. 3. Second virial coefficients for the acetonitrile-acetaldehyde system.

It is possible to relate the dimerization equilibrium constant to the excess second virial coefficient, that is to that part of the observed second virial coefficient which is in excess of what the second virial coefficient would be in the absence of polar forces. The observed second virial coefficient is divided into two parts: one corresponding to the contribution of nonpolar forces and the other corresponding to the contribution of polar (dimerization) forces. Thus

$$B_{AA}\,(\text{observed}) = B^h{}_{AA} + B^D{}_{AA} \quad (6)$$

The nonpolar contribution may be found from the properties of the polar molecule's homomorph (*2*) as estimated from reliable correlations for second virial coefficients of nonpolar substances (*10, 11, 12*); the polar contribution is then found by difference from Equation (6). It can be shown (*7, 14*) that provided the degree of dimerization is small the dimerization equilibrium constant is given by

$$B^D{}_{AA} = -RT\,K_{p(AA)} \qquad (7)^*$$

Similarly for the dimerization of component *B*

$$B^D{}_{BB} = -RT\,K_{p(BB)} \qquad (8)$$

and for the formation of a complex *AB*

$$B^D{}_{AB} = -RT\,K_{p(AB)} \qquad (9)$$

There is some arbitrariness in the calculation of B^h. Lambert uses the Berthelot equation, but in view of the results of Pitzer and Curl (*11*) showing the important effect of the acentric factor on second virial coefficients (especially at low reduced temperature) it appears to be better to use the more recent correlations (*11, 12*). The homomorph for acetonitrile and for acetaldehyde is propane.

Calculated values of B^h, B^D, and K_p are shown in Table 3. Also shown are the enthalpy and entropy of dimer formation in the standard state; these were computed from the equation

$$\Delta S^\circ = \frac{\Delta H^\circ}{T} + R\ln K_p \qquad (10)$$

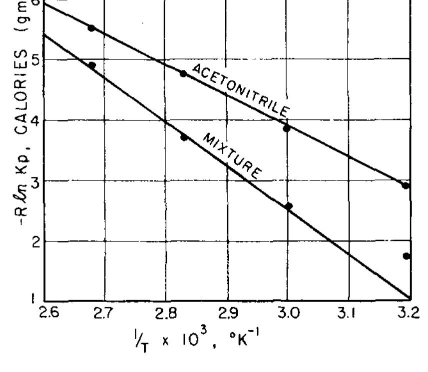

Fig. 4. Equilibrium constant vs. reciprocal temperature.

Figure 4 shows the variation of the logarithm of the equilibrium constant with reciprocal temperature. Good straight lines are obtained with the exception of the point corresponding to the complex at 40°C. This is not surprising since at 40°C. the degree of complex formation ($K_p = 0.4153$) is so large that about 10% of all the molecules are in the associated state. Under these conditions Equation (9) is no longer strictly valid, since interactions between dimers and monomers [which are neglected in Equations (7), (8), and (9)] are no longer negligible.

The absolute value of the enthalpy of formation of the complex is significantly higher than that of either of the pure-component dimers. This can be explained in terms of possible structures of the two dimers and of the complex. The observed values of the enthalpy of dimer (or complex) formation may be compared with calculations based on electrostatic theory. A dimer (or complex) between two polar molecules may be formed in either of two ways; the two molecules may line up parallel to one another or be joined end to end. The energies of formation for these two structures are $\Delta U = -\mu^2/r^3$ and $\Delta U = -2\mu^2/r^3$ respectively.

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*Barker and Smith have recently re-evaluated the data for acetonitrile and have arrived at an *Chem.*, 13, 171 (1960)]. The new parameters alternate set of Stockmeyer parameters [*Aust. J.* however do not significantly change the computed values for B_{12}.

* The equilibrium constant used by Lambert (*7*) is that for dimer decomposition and hence is the reciprocal of that used in this work.

Table 3. Thermodynamic Properties of the Acetonitrile-Acetaldehyde System

Substance	T, °C.	$-B^h$, ml./mole	$-B^D$, ml./mole	K_p, atm.$^{-1}$	$-\Delta H°$, cal./mole	$-\Delta S°$, cal./mole, °K
Acetonitrile	40.0	747	4503	0.2306	5110	19.25
	60.0	641	2975	0.1433		
	80.1	461	2049	0.09308		
	100.4	497	1428	0.06139		
Acetaldehyde	40.0	485	459	0.02351	3960	20.07
	60.0	424	341	0.01642		
	80.1	373	260	0.01181		
	100.4	333	200	0.008598		
Mixture (complex)	40.0	596	8109	0.4153	7250	24.3
	60.0	516	5650	0.2721		
	80.1	454	2998	0.1568		
	100.4	403	1990	0.08555		

Table 4. Calculated and Observed Heats of Formation

Dimer or complex	Parameters in electrostatic equations		Heats of formation, cal./mole		
	μ Debyes	r Angstroms	Calc'd parallel	Calc'd end-to-end	Observed
Acetonitrile-acetonitrile	3.5	3.10	—5280(1)	—10560	—5110
Acetaldehyde-acetaldehyde	2.7	3.20	—3380	—6760	—3960
Acetonitrile-acetaldehyde(2)	3.08	3.15	—4125	—8250	—7250

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[1] This value was misprinted in Lambert's article; the value calculated from his data is −5280, not −6280.

[2] μ is the geometric mean and r is the arithmetic mean of the pure-component values.

Values of r can be calculated from van der Waals radii of atoms and bond angles as given by Pauling (9). Table 4 shows the calculated and observed values of the enthalpy (or energy) of formation. (In these calculations there is no significant difference between ΔU and $\Delta H°$.) Since the calculated values of ΔU are based on formulas corresponding to ideal dipoles, the numbers in Table 4 should not be taken too seriously; however, they strongly suggest that both acetonitrile and acetaldehyde form dimers of the first type rather than the second. The observed value for the complex however appears to lie closer to that corresponding to the second, suggesting that the structure of the complex may be qualitatively different from that of the pure-component dimers.

An alternate interpretation is that the complex is formed by hydrogen bonding between the active hydrogen in the aldehyde and the nitrogen in the nitrile. Hydrogen bonding may also account for dimerization in the nitrile. Unfortunately no data are available on the strength of the nitrile-hydrogen bond. The data in Table 4 however suggest that this bond is considerably stronger than the carbonyl oxygen-hydrogen bond which is found in the acetaldehyde dimer.

The dimerization interpretation offers a suitable framework for correlating the volumetric properties of polar gases and their mixtures. To be useful however it is necessary that the structure of the complex as well as that of the dimers must be known to enable a quantitative prediction of the energy of interaction. In addition it is necessary to make an estimate of the entropy of association; a rough model for making this estimate has been proposed by Rowlinson (13), but there is good reason to believe (15) that the entropy and enthalpy of dimerization are closely related and it appears (6) that these two quantities may be related empirically. As more experimental information on the thermodynamics of dimer (and complex) formation becomes available, it should become possible to make good estimates of the second virial coefficients of polar gases and their mixtures.

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NOTATION

B = second virial coefficient
B^h = nonpolar (homomorph) contribution to second virial coefficient
B^D = polar (dimerization) contribution to second virial coefficient
$\Delta H°$ = standard enthalpy of formation
k = Boltzmann constant
K_p = equilibrium constant
n = number of moles
p = partial pressure
P = total pressure
r = distance of separation between two molecules
R = gas constant
$\Delta S°$ = standard entropy of formation
t^* = reduced dipole moment = $\mu^2/\sqrt{8}\,\epsilon\,\sigma^3$
T = temperature
ΔU = energy of formation
V = total volume
y = mole fraction
ϵ = characteristic energy parameter
μ = dipole moment
σ = characteristic distance parameter

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