Second Virial Coefficient of Methanol

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A Burnett apparatus was used to obtain low-pressure, compressibility factor data for methanol vapor at temperatures from 25° to 200° C. at 25° intervals. Second virial coefficients from graphical extrapolation of these data corrected for adsorption are presented, with excellent agreement with the earlier work of Kretschmer and Wiebe and of Russell and Maass. Stockmayer force constants and association parameters computed from the second virial coefficients are also given.

LOW-PRESSURE compressibility measurements resulting in values of the second virial coefficient over the temperature range 25° to 400° C. have been reported by various investigators (*2, 3, 5, 8, 9, 10, 12, 20, 26*). Data at pressures considerably above atmospheric have been reported by Ramsay and Young (*18*), Lashakov (*13*), Petty and Smith (*17*), Zubarev and Bagdonas (*30*), and Finkelstein and Stiel (*4*).

EXPERIMENTAL

Apparatus. A Burnett apparatus described earlier by Anderson et al. (*1*) was recalibrated with helium of 99.99$^+$ mole % purity prior to this investigation (*11*). The maximum estimated errors in the temperature and pressure measurements were 0.01° C. and 0.0070 p.s.i., respectively, with corresponding precision of 0.0025° C. and 0.0017 p.s.i. With multiple runs at 100°, 150°, and 200° C., the pressure ratio P_i/P_{i+1} was fitted as a linear function of P_i by least squares regression analysis. The intercept at $P_i = 0$ provided the following values of the apparatus constant, N: 1.432481 at 100° C., 1.432470 at 150° C., and 1.432480 at 200° C. An average value of $N = 1.432477$ was used in all subsequent computations for methanol, with a maximum probable error of 0.0018% at the 99% confidence level. Extrapolation of $(Z - 1)P$ *vs.* P to zero pressure at each temperature provides Berlin second virial coefficients, B_p,

$$Z = 1 + B_pP + C_pP^2 + \cdots\cdots \tag{1}$$

which were converted to the Leiden second virial coefficients, B_v,

$$Z = 1 + \frac{B_v}{V} + \frac{C_v}{V^2} + \cdots\cdots \tag{2}$$

of Table I for helium by multiplication by RT. The maximum error limits of the present values in Table I reflect a maximum uncertainty of about 0.02% in the zero pressure limit of P_iN^i and the compressibility factor at the maximum pressure of 200 p.s.i.a. Since the compressibility factor for helium at 100° C., for example, is about 1.0050, a 4% uncertainty in the second virial coefficient results if only this pressure point were used to determine B_p. The remaining $\sim$ 0.6% uncertainty at 100° C. given by Table I is the result of extrapolation of $(Z - 1)/P$ to zero pressure.

Table I. Second Virial Coefficients of Helium

Temp., ° C.	B_v, Ml. per Gram-Mole	Ref.
100	11.36 ± 0.52	This work
	11.31	(*22*)
	10.78	(*7*)
	11.35	(*14*)
	11.38	(*6*)
	11.41	(*21*)
	11.15	(*25*)
	11.30	(*27*)
150	10.76 ± 0.63	This work
	11.07	(*14*)
	11.33	(*16*)
	11.17	(*1*)
200	10.16 ± 0.48	This work
	10.20	(*22*)
	9.56	(*7*)
	10.48	(*6*)
	10.49	(*21*)
	10.14	(*27*)
	10.98	(*24*)

Purity of Methanol. Methanol reported by the supplier to be 99.95 mole % purity was used. Gas chromatographic analysis by a competitor after the investigation revealed the following impurities: water, 0.10%; ethanol, 0.095%; methyl formate, 0.001%; *sec*-butanol, 0.002%; isobutanol, 0.002%.

METHANOL RESULTS

At least three runs were made for each isotherm except 175° C. (two runs) and 200° C. (one run), where slight decomposition of the sample occurred, as also cited by Kell and McLaurin (*8*). Graphs of P_i/P_{i+1} *vs.* P_i gave extrapolated values at zero pressure below the helium average result of $N = 1.432477$. The difference was greatest at 25° C. and steadily diminished until negligible at 200° C., as in a previous study of acetone (*1*); this shift of N was considered due to adsorption of the gas molecules to the walls of the stainless steel cell, and the data were corrected using the Langmuir model. As adsorption was comparatively weak with methanol, the assumption that $1 >> bP$ was adequate for all tempera-

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Table II. Second Virial Coefficients of Methanol

Temp., ° C.	$-B_p$, Atm.$^{-1}$	$-B_v$ (Exptl.), Ml. per Gram-Mole	$-B_v$ (Calcd.), Ml. per Gram-Mole
25	0.08481 ± 0.00425	2075 ± 104	2087
50	0.04469 ± 0.00200	1185 ± 53	1220
75	0.02580 ± 0.00105	737 ± 30	786
100	0.01747 ± 0.00062	535 ± 19	561
125	0.01264 ± 0.00046	413 ± 15	399
150	0.00924 ± 0.00029	321 ± 10	305
175	0.00682 ± 0.00022	251 ± 8	241
200	0.00476 ± 0.00015	185 ± 6	196

tures where b is the temperature-dependent Langmuir adsorption constant. Both raw Burnett data (P_i sequence) and smoothed, adsorption-corrected compressibility factor results have been deposited with the American Society for Information Science.

Second Virial Coefficients. Extrapolation of $(Z - 1)/P$ *vs.* P to zero pressure provides the Berlin second virial coefficients B_p of Table II; multiplication of these values by RT yields the Leiden second virial coefficients, B_v. Figure 1 shows a comparison of these values with those of prior investigations; the agreement with the work of Kretschmer and Wiebe (40° to 120° C.) and the work of Russell and Maass (75° to 200° C.) is particularly good.

The error limits placed on the virial coefficients of Table II were determined as follows. With a maximum error of ±0.01° C. in the temperature measurement and ±0.0070 p.s.i. at the highest pressure measurement, the direct error in the compressibility factor due to temperature and pressure measurement was estimated at 0.025% or less. Uncertainty in the apparatus constant due to elastic deformation of the cell with pressure was less than 0.001%. As with helium, the apparatus constant was considered accurate to 0.0018%. Propagation of this error in determination of compressibility factors from $\lim_{P_i \to 0} P_i N^i = \left(\frac{P_0}{Z_0}\right)$ leads to an estimate of 0.05% at the highest pressure of each isotherm. An additional error of 0.02% in Z was added for extrapolation from the lowest pressure point to zero pressure. Although this extrapolation covers only 2 to 3 p.s.i., considerable curvature occurs at the lower temperatures for methanol, unlike helium. Summation of the above errors yields 0.10% maximum uncertainty in the compressibility factor. At 25° C., the direct corresponding error in B_p is about 3%, to which ~ 2% extrapolation error for $\lim_{P \to 0} (Z - 1)/P$ should be added. As the temperature increases, the curvature of $(Z - 1)/P$ *vs.* P decreases, and the extrapolation error is less than 0.5% at 200° C. Hence, the error limits of Table II decrease from ~ 5% at 25° C. to ~ 3% at 200° C. The values of Kretschmer and Wiebe and of Russell and Maass fall within these limits.

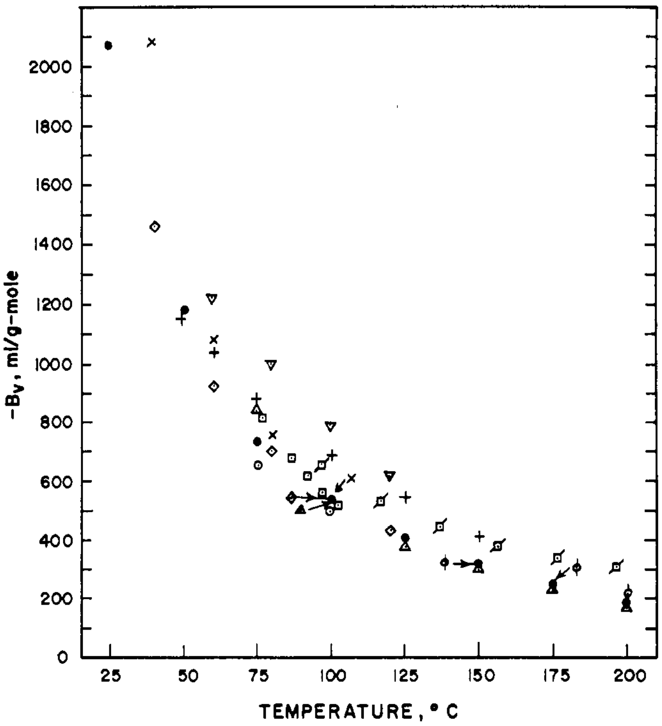

Figure 1. Second virial coefficients of methanol

● This work
⊡ (3)
△ (20)
▽ (12)
⊙ (26)
⊡ (5)
◇ (10)
× (9)
+ (2)
⌽ (8)

Stockmayer Force Constants. Information regarding the intermolecular forces between methanol molecules was derived from the experimental Leiden second virial coefficients by use of the Stockmayer 12-6-3 potential energy model (*23*). A digital computer program was developed to search the two-dimensional domain of the Stockmayer force constants, ε/k and σ, for the pair of constants that would provide the minimum standard error of estimate of $B_v(T)$.

With recent values (*28*) of the gas constant, R, and the Avogadro constant, $\tilde{N}$, the following force constants were obtained for methanol with a dipole moment value of $\mu = 1.69\ D$: $(\varepsilon/k) = 245.93°$ K.; $\sigma = 2.3754$ A., and $b_0 = \left(\frac{2}{3}\right) \cdot \pi \tilde{N} \sigma^3 = 16.906$ ml. per gram-mole. Table II shows this pair of force constants to provide a reasonable fit of $B_v(T)$, although calculated values are outside the error limits of Table II for a number of temperatures. Comparison of present Stockmayer force constants with literature values calculated from other $B_v(T)$ data and also from gas viscosity data by Monchick and Mason (*15*) is given in Table III.

Association. The Woolley model (*29*), a virial equation of state derived from the equilibrium constants for the formation of molecular clusters, was used to relate the second virial coefficient results to the equilibrium constants for dimerization, K_2. The result is simply $K_2 = -B_p$. A graph of log K_2 *vs.* $(1/T)$ yields $(-\Delta H_2/R)$ as the slope and $(\Delta S_2/R)$ as the intercept. The values obtained were $\Delta H_2 = -4.3$ kcal. per gram-mole and $\Delta S_2 = -24.9$ cal. per gram-mole ° K.

Table III. Stockmayer Force Constants of Methanol

t^*	ε/k, ° K.	σ, A.	Ref.
2.22	245.93	2.3754	This work
0.8	630	2.40	(*19*)
0.7	670	2.48	(*5*)
0.35	417	3.69	(*15*)

NOMENCLATURE

B_p = Berlin second virial coefficient, atm.$^{-1}$
B_v = Leiden second virial coefficient, ml. per gram-mole
b = Langmuir adsorption constant, atm.$^{-1}$
C_p = Berlin third virial coefficient, atm.$^{-2}$
C_v = Leiden third virial coefficient (ml. per gram-mole)^2
ΔH_2 = enthalpy of dimerization, kcal. per gram-mole
K_2 = equilibrium constant for dimerization, atm.$^{-1}$
N = Burnett apparatus constant
$\tilde{N}$ = Avogadro number, 6.02252 gram-mole^{-1}
P = pressure, atm. or p.s.i.a.
R = gas constant, 82.05606 ml.-atm. per gram-mole-° K.
ΔS_2 = entropy of dimerization, cal. per gram-mole-° K.
T = temperature, ° K.
t^* = Stockmayer polarity constant, $\mu^2/8^{1/2}\ \epsilon\sigma^3$
V = volume, ml. per gram-mole
Z = compressibility factor, PV/RT

Greek

ϵ/k = Stockmayer minimum potential energy parameter, ° K.
μ = dipole moment, debyes
σ = Stockmayer collision diameter, A.

Subscripts

i = integer indicating number of Burnett expansion

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