

with Diaion SK116 of 200 μm .⁸⁾ At a superficial velocity of 2.8×10^{-4} m/s, corresponding to $Re = 0.056$, the value of the longitudinal dispersion coefficient was found to be about 1×10^{-7} m²/s, which is five times the radial dispersion coefficients obtained in the present work. That value of the longitudinal dispersion coefficient may include the influences of irregular flow in the bed such as "fingering," "tilting," and "channeling" and of liquid mixing in the plugs attached to the column.

Acknowledgments

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Nomenclature

d_p	= diameter of particles	[m]
E_r	= effective radial dispersion coefficient	[m ² /s]
k	= experimental factor	[—]
Pe	= Peclet number, $\bar{u}d_p/E_r$	[—]
Re	= Reynolds number, $\bar{u}d_p/\nu$	[—]
u	= linear velocity in the void of the bed	[m/s]
\bar{u}	= superficial velocity	[m/s]
β_r, β_z	= factors	[—]

ε	= void fraction in a bed	[—]
θ	= time	[s]
ν	= kinematic viscosity	[m ² /s]

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SECOND VIRIAL COEFFICIENT OF GASEOUS METHANOL AT 150°C

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Key Words: Physical Property, Second Virial Coefficient, Methanol, PVT Relation, Gas Phase

Introduction

Studies of the second virial coefficients for multi-polar and/or associated components have been performed by many investigators. In particular, the second virial coefficient of methanol has been measured by several researchers because of its industrial importance. However, there are substantial discrepancies between published data,^{1,2,4,5)} which are divided into two groups in the plot of second virial coefficient of methanol against temperature.

In 1933 Newton-Dodge⁶⁾ pointed out the decom-

position of methanol at high temperatures. In the present study, the second virial coefficient of gaseous methanol at 150°C was determined by the Burnett method, taking the decomposition into consideration. Therefore, besides the measurement of pressures before and after each expansion, mole fractions of methanol and minor products from the decomposition of methanol were determined in the present study.

1. Experimental

Except for the Burnett vessels, the experimental apparatus and procedures were essentially the same as described in a previous paper.⁷⁾ Since the Burnett method was used only for obtaining the virial coef-

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ficient of methanol, the twin vessels used in the previous study were replaced by the two Burnett vessels (the volume ratio of the vessels is about 1:2). After pressure measurement was performed for the sample gas expanded in one of the Burnett vessels, the sample gas was introduced to the sample-preparation equipment where the sample was expanded to about 0.01 MPa at room temperature and recirculated for gas mixing.⁸⁾ It was assumed that the composition of the sample was not changed during the above procedures. The compositions of formaldehyde and carbon monoxide produced from the decomposition of methanol were analyzed by gas chromatography.

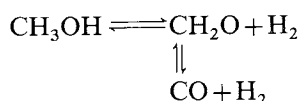
The temperature of an oil bath regulated within $\pm 0.001^\circ\text{C}$ was measured within an accuracy of $\pm 0.002^\circ\text{C}$ by a set of platinum resistance and Tinsley resistance thermometer bridge. The pressure of the sample gas was measured by an air-piston gage of Ruska Inst. Co., with a reproducibility better than ± 3 ppm.

Material

The methanol, obtained from Merck Co., was spectrograde and a small amount of impurities was detected by gas chromatography; the ratio of peak area was 1:20,000. This methanol was used in the experiments without further purification.

2. Results

Newton-Dodge⁶⁾ reported the chemical equilibrium between carbon monoxide, hydrogen, formaldehyde and methanol at high temperatures (200–250°C) and at 1 to 3 atmospheres pressure in the presence of a metal catalyst.



In the present study at 150°C the reactions were found from composition analysis by gas chromatography. The result of composition analysis is shown in Fig. 1. The mole fraction of hydrogen was calculated from the amounts of formaldehyde and carbon monoxide produced. The moles of methanol filled in the Burnett cell were estimated from the cell volume and the virial data of Kell-McLaurin.⁴⁾ From the amount of methanol and the composition of products, the total amount increased by the decomposition was evaluated at each pressure.

The Burnett data were analyzed by the reduction method based on the Berlin-form equation given as a power series in pressure. This is one of the methods described in a previous paper,³⁾ to which readers are referred for details.

In the plot of $(P_i - NP_{i+1})/P_i P_{i+1}$ against P_i the value of B is obtained from extrapolating to zero

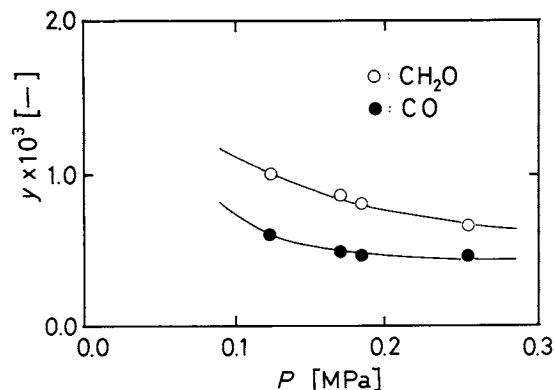


Fig. 1. Mole fractions of CH₂O and CO vs. pressure.

Table 1. Second virial coefficient of methanol at 423.15 K

	B [cm ³ ·mol ⁻¹]
Present study	-320 ± 5
Literature	
Kell-McLaurin ⁴⁾	-323 ± 2
	-318 ± 2
Kudchadker-Eubank ⁵⁾	-321 ± 10
Fox <i>et al.</i> ²⁾	-403^*
Bottomley-Spurling ¹⁾	-412

* Interpolated value.

pressure if special interactions between product-product and product-methanol are neglected.

The second virial coefficient evaluated from the extrapolation is -320 ± 5 cm³·mol⁻¹. The estimated error is quite large because the initial pressure was too low to obtain the accurate virial coefficient by the Burnett method.

In published investigations concerning the second virial coefficient of methanol, there are two different data series at high temperatures, as listed in Table 1.

The value reported by Bottomley-Spurling¹⁾ and Fox *et al.*²⁾* is about -400 cm³·mol⁻¹ at 150°C, which is ca. 100 cm³·mol⁻¹ smaller than our value.

Kell-McLaurin⁴⁾ measured the second virial coefficient of methanol at 150°C by use of equipment protected against decomposition of methanol. Their result agrees with the present one within experimental error. Kudchadker-Eubank⁵⁾ obtained a value of -321 ± 10 cm³·mol⁻¹ at 150°C from their Burnett data, though they took into consideration only the adsorption of methanol to the cell. Their value is also close to the present result.

Acknowledgment

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* The value of Fox *et al.* was evaluated by interpolation from the data at 402.0 and 424.2 K.

Nomenclature

B	= second virial coefficient in Leiden-form equation	$[\text{cm}^3 \cdot \text{mol}^{-1}]$
N	= apparatus constant	$[-]$
P	= pressure	$[\text{MPa}]$
y	= mole fraction	$[-]$

<Subscript>

i = i -th expansion

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BEHAVIOR OF POLYVINYL ALCOHOL ADDED AS A BINDER TO CLAYEY PARTICLES IN KNEADING AND DRYING OPERATIONS

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Key Words: Drying, Kneading, Polyvinyl Alcohol, Fine Clayey Particle, Adsorption, Critical Moisture Content, Transferred Amount

The author has been trying to reuse wasted fine clayey particles as carriers for pesticides by means of spray drying and other operations.⁵⁾ In these operations, polyvinyl alcohol (PVA) was added as a binder to the clayey particles in order to increase the strength of the agglomerates in the dry state.³⁾ However, as the behavior of PVA has not been exactly determined in kneading and drying operations,¹⁾ it is considered in this paper.

1. Experimental

Sample Talc having a median diameter of $7.9 \mu\text{m}$ was used as a sort of fine clayey particles. PVA having a degree of polymerization of about 500 and a degree of saponification of 86.5 to 89.0 was used as a binder.

Adsorption of PVA on talc particles The adsorption isotherm of PVA on talc was measured to find a plateau adsorption value. The adsorption equilibrium was confirmed to be roughly reached within 24 h. The initial and equilibrium concentrations of PVA in the solution were determined on the basis of the method developed by Zwick.⁶⁾

Drying characteristic of moist agglomerate and behavior of PVA in drying operation In order to make moist cylindrical agglomerates, distilled water or an aqueous solution of PVA was added to dried clayey particles. The wetted clayey particles were then kneaded and formed into cylindrical shapes $2\text{cm}\phi$ in diameter and 5 to 6 cm in length by means of an auger machine, the inside of which was kept in vacuum.

In measuring the drying rate on a moist cylindrical agglomerate without PVA, the side and one end of the agglomerate were wrapped two or three times with a polyethylene sheet 0.03 mm in thickness. The polyethylene sheet on the side was tightened with rubber bands in order to compel liquid flow in the axial direction. The drying characteristic of the agglomerate was measured by using a drying oven kept at $333 \pm 2 \text{ K}$.

After the moist agglomerate containing PVA was completely dried by the same procedure as above, the agglomerate was cut at 0.5 or 1.0 cm intervals from the drying surface. Then the dissolved amount of PVA was measured for every cut sample to determine the longitudinal distribution of dissolved PVA.

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