

ASSOCIATION AND AGGREGATION
OF MOLECULES IN THE VAPOUR PHASE. I.
SECOND VIRIAL COEFFICIENT OF METHANOL,
n-HEXANE AND THEIR MIXTURES AT 50°C

J. DĚDEK

*Department of Physical Chemistry,
Institute of Chemical Technology, Prague 6*

Received March 5th, 1970

A general procedure is proposed for calculating the second virial coefficient of a binary mixture in the presence of associating or aggregating components. The function φ ($0 < \varphi \leq 1$) is introduced which is a quantitative measure of both association and aggregation. In this case the second virial coefficient is defined as $B_p = V/(n^\circ\varphi) - RT/p$. The proposed method has been successfully applied to the description of the state behaviour of methanol-n-hexane mixture at 50°C.

Solution of many technological problems often necessitates the knowledge of state behaviour of gases and vapours. Modern state equations are based on microscopical approach to the interaction of forces between individual molecules. Using statistical mechanics, applied to the effect of these forces in gases, it is possible to derive relations for virial equations. The second virial coefficient includes interactions at most between pairs of molecules. In calculating this quantity by means of statistical mechanics dispersion and dipole forces are taken into account. In binary systems, containing both polar and non-polar components, interactions of induced dipoles are considered. There is a number of reviews in the literature¹⁻⁴, dealing with the calculation of state behaviour of gases and vapours.

However, when studying systems in which association or even aggregation of molecules can take place, it is found that the second virial coefficient can be expressed by the relation⁵⁻¹⁰

$$B_p = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}, \quad (1)$$

whereby

$$B_{11} = (B_{11})_{\text{phys.}} + (B_{11})_{\text{chem.}} \quad (2)$$

$$B_{22} = (B_{22})_{\text{phys.}} + (B_{22})_{\text{chem.}} \quad (3)$$

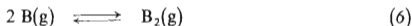
$$B_{12} = (B_{12})_{\text{phys.}} + (B_{12})_{\text{chem.}}, \quad (4)$$

where y_1 and y_2 are molar fractions of the components 1 and 2, respectively in the

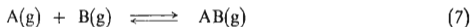
gaseous phase, B_{11} and B_{22} are second virial coefficients of components 1 and 2, and B_{12} is the cross virial coefficient. In the case of dimerization



or



and aggregation



both the second virial coefficients of pure components and the cross virial coefficient are equal to the sum of two contributions. The first of them ($(B_{11})_{\text{phys.}}$, $(B_{22})_{\text{phys.}}$ or $(B_{12})_{\text{phys.}}$) comprises deviations, caused by the presence of intermolecular forces, the second one ($(B_{11})_{\text{chem.}}$, $(B_{22})_{\text{chem.}}$ or $(B_{12})_{\text{chem.}}$) includes the formation of dimers or of a mixed aggregate. If we define the equilibrium constants (see⁶) for Eqs (5), (6), (7)

$$(K_p)_A = p_A^2/p_{A_2}, \quad (8)$$

$$(K_p)_B = p_B^2/p_{B_2}, \quad (9)$$

$$(K_p)_{AB} = p_A p_B/p_{AB}, \quad (10)$$

then, according to paper⁶

$$(B_{11})_{\text{chem.}} = -RT/(K_p)_A, \quad (11)$$

$$(B_{22})_{\text{chem.}} = -RT/(K_p)_B \quad (12)$$

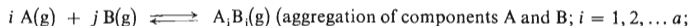
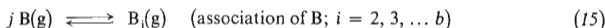
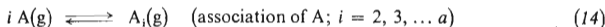
and

$$(B_{12})_{\text{chem.}} = -RT/(K_p)_{AB}. \quad (13)$$

It has been demonstrated theoretically¹¹ that relations (11)–(13) are limiting cases that can be applied only to not too high degrees of dimerization or aggregation.

THEORETICAL

Let us consider a binary gaseous mixture, containing components A and B. Association and aggregation in the gaseous phase can proceed according to three types of reactions



$$j = 1, 2, \dots, b) \quad (16)$$

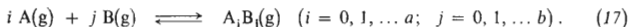
Eq. (14) represents a general description of association for component A, i.e. $i = 2$ means dimerization, $i = 3$ trimerization, etc. Actually, most frequently we find only dimerization. However, not all associates up to associate with $i = a$ must be present. So, e.g. for methanol some authors state that the vapour phase contains besides monomer also dimer and tetramer, but no trimer¹²⁻¹⁵. Recently, also the presence of trimer and octamer is assumed¹⁶.

TABLE I

Application of Chemical Equilibrium Principle to a Binary System with Association and Aggregation

Component	Number of mol of components before association and aggregation	Number of mol of components after association and aggregation have proceeded to equilibrium state
A ₂	—	$n_{2,0} = n_{1,0}^0 \xi_{2,0}/2$
A ₃	—	$n_{3,0} = n_{1,0}^0 \xi_{3,0}/3$
⋮	⋮	⋮
A _a	—	$n_{a,0} = n_{1,0}^0 \xi_{a,0}/a$
B ₂	—	$n_{0,2} = n_{0,1}^0 \xi_{0,2}/2$
B ₃	—	$n_{0,3} = n_{0,1}^0 \xi_{0,3}/3$
⋮	⋮	⋮
B _b	—	$n_{0,b} = n_{0,1}^0 \xi_{0,b}/b$
AB	—	$n_{1,1} = (n_{1,0}^0 + n_{0,1}^0) \xi_{1,1}/2$
A ₂ B	—	$n_{2,1} = (n_{1,0}^0 + n_{0,1}^0) \xi_{2,1}/3$
⋮	⋮	⋮
A _a B	—	$n_{a,1} = (n_{1,0}^0 + n_{0,1}^0) \xi_{a,1}/(a+1)$
⋮	⋮	⋮
A _i B _j	—	$n_{i,j} = (n_{1,0}^0 + n_{0,1}^0) \xi_{i,j}/(i+j)$
⋮	⋮	⋮
A _a B _b	—	$n_{a,b} = (n_{1,0}^0 + n_{0,1}^0) \xi_{a,b}/(a+b)$
A	$n_{1,0}^0$	$n_{1,0} = n_{1,0}^0 \left[1 - \sum_{i=2}^{i=a} \xi_{i,0} - \frac{1}{y_{1,0}^0} \left(\sum_{i=1}^{i=a} \sum_{j=1}^{j=b} \frac{i}{i+j} \xi_{i,j} \right) \right] = n_{1,0}^0 \varphi_A$
B	$n_{0,1}^0$	$n_{0,1} = n_{0,1}^0 \left[1 - \sum_{j=2}^{j=b} \xi_{0,j} - \frac{1}{y_{0,1}^0} \left(\sum_{i=1}^{i=a} \sum_{j=1}^{j=b} \frac{j}{i+j} \xi_{i,j} \right) \right] = n_{0,1}^0 \varphi_B$
		$n = (n_{1,0}^0 + n_{0,1}^0) \left[1 - y_{1,0}^0 \sum_{i=2}^{i=a} (1-1/i) \xi_{i,0} - y_{0,1}^0 \sum_{j=2}^{j=b} (1-1/j) \xi_{0,j} - \sum_{i=1}^{i=a} \sum_{j=1}^{j=b} \left(1 - \frac{1}{i+j} \right) \xi_{i,j} \right] = n^0 \varphi$

Eqs (14), (15) and (16) can summarily be described by the equation



This equation describes association in the case, when either $j = 0$ and simultaneously $2 \leq i \leq a$ (association of component A) or $i = 0$ and simultaneously $2 \leq j \leq b$ (association of component B). Aggregation takes place in all cases when $1 \leq i \leq a$ and simultaneously $1 \leq j \leq b$.

General principle of chemical equilibrium was applied to the system of Eqs (17) and the true thermodynamic equilibrium constant K_a was replaced by constant K_p . The results of this procedure are summarised in Table I. The initial number of moles was denoted $n_{1,0}^0$ for component A and $n_{0,1}^0$ for component B. In Table I equilibrium transformation degrees, $\xi_{i,j}$, are introduced for each respective association or aggregation equilibrium. The transformation degrees were chosen so that it holds

$$0 \leq \sum_{i=0}^{i=a} \sum_{j=0}^{j=b} \xi_{i,j} \leq 1 \quad (\xi_{0,0} = \xi_{1,0} = \xi_{0,1} \equiv 0), \quad (18)$$

has no physical meaning

wherein every $\xi_{i,j}$ has positive sign. These equilibrium transformation degrees can be calculated from the corresponding values of equilibrium constants $(K_p)_{i,j}$

$$(K_p)_{i,0} = \frac{p_{i,0}}{p_{1,0}^i} = \frac{n_{i,0}}{n_{1,0}^i} \left[\frac{p}{(n_{1,0}^0 + n_{0,1}^0) \varphi} \right]^{1-i} = \frac{\xi_{i,0}}{i \varphi_A^i} \left[\frac{y_{1,0}^0 p}{\varphi} \right]^{1-i}, \quad (19)$$

$$(i = 2, 3, \dots, a)$$

$$(K_p)_{0,j} = \frac{p_{0,j}}{p_{0,1}^j} = \frac{n_{0,j}}{n_{0,1}^j} \left[\frac{p}{(n_{1,0}^0 + n_{0,1}^0) \varphi} \right]^{1-j} = \frac{\xi_{0,j}}{j \varphi_B^j} \left[\frac{y_{0,1}^0 p}{\varphi} \right]^{1-j}, \quad (20)$$

$$(j = 2, 3, \dots, b)$$

$$(K_p)_{i,j} = \frac{n_{i,j}}{n_{1,0}^i n_{0,1}^j} \left[\frac{p}{(n_{1,0}^0 + n_{0,1}^0) \varphi} \right]^{1-i-j} =$$

$$\frac{\xi_{i,j}}{(i+j) (y_{1,0}^0 \varphi_A)^i (y_{0,1}^0 \varphi_B)^j} \left[\frac{p}{\varphi} \right]^{1-i-j} \quad (21)$$

$$(i = 1, 2, \dots, a; j = 1, 2, \dots, b).$$

Functions φ_A , φ_B and φ represent an abbreviated form of expressing the coefficient

of equilibrium number of moles of components A and B and of the total number of moles of all components; they also are included in Table I.

The usual procedure is to process the experimental values, obtained by means of some apparatus, by correlating them in the form of second virial coefficient equation

$$pV = n^0(RT + B_p p), \quad (22)$$

where n^0 is the number of moles of the gas under study or of gaseous mixture. All the other quantities have their usual meaning. In the case of association and aggregation in a binary gaseous mixture Eq. (22) has to be replaced by

$$pV = n^0 \varphi(RT + B_p p). \quad (23)$$

Eq. (23) comprises the change of number of moles with respect to association and aggregation which is not negligible (n^0 in Eq. (23) is constant, contrary to its meaning in Eq. (22)). In relations (19)–(21) ideal behaviour of the gaseous mixture is assumed. Function φ depends on total pressure p , on the initial composition of the gaseous mixture $y_{1,0}^0 = n_{1,0}^0 / (n_{1,0}^0 + n_{0,1}^0)$, (i.e. on the initial mol fraction of component 1 before association and aggregation) as well as on the values of all association and aggregation constants.

The condition that relation (23) could be applied for processing the measured values of behaviour of state is to know the values of association and aggregation constants in advance. These, however, are usually not available. Nevertheless, Eq. (23) can be used for the above mentioned procedure. For this purpose it has to be transformed into linear regression form for $1/n^0$ and B_p and the function

$$\sum_{m=1}^{m=n} \left\{ \left[\frac{1}{n^0} \left(\frac{V_m}{\varphi_m} \right) - B_p \right] - \frac{RT}{p_m} \right\}^2 \quad (24)$$

is minimized. At the same time the validity of Eqs (19)–(21) for association and aggregation equilibrium constants is required. Practical calculations result in solving a rather complicated system of non-linear equations.

EXPERIMENTAL

Volume Compression Apparatus for Measuring the Behaviour of State

A compression chamber (Fig. 1) was designed for the measurement of the behaviour of state, consisting of a glass burette, the so-called piezometer P. The piezometer is composed of five glass spheres having the volumes 53.42, 54.91, 53.41, 55.16 and 53.20 ml calibrated by means of mercury within the accuracy of ± 0.005 ml. Besides, the measuring part consists of a volume capacity V, a freezing

trap CT and a differential manometer with a check valve U. A molybdenum tip is sealed into the manometer to make possible to adjust repeatedly constant volume of the apparatus. Both piezometer P and manometer U are equipped with small mercury reservoirs R_1 and R_2 with glass frittes and controlling device. This allows rough and fine regulation of pressure in points P_1 and P_2 , so that the mercury level can be adjusted exactly to the gauge mark in the piezometer and precisely 0.1 mm under the molybdenum tip in the differential manometer. The whole device is placed in a thermostat, maintained at constant temperature within $\pm 0.02^\circ\text{C}$. Thermostated parts of the apparatus are drawn in Fig. 1 inside the dashed rectangle. Differential manometer U is joined through a cock K to a large mercury manometer M and to a 7-l glass reservoir R. Both the manometer and the reservoir are kept at room temperature. The pressure of gas or vapour under study is the sum of pressure readings of both manometers. The levels in the manometer were read off using precise kathetometer with the accuracy of ± 0.01 mm. The measured data on both manometers were corrected for gas or gaseous mixture pressure. The reproducibility of pressure measurements was ± 0.02 Torr.

The described apparatus is a modification of that used by Knoebel and Edmister²³ for investigations of behaviour of state. The difference is in the way of sampling, volume calibration and gas or gaseous mixture pressure measurement.

Measuring of the Dead Volume V_0 of the Apparatus

First of all we had to determine the dead volume V_0 of the apparatus, *i.e.* the volume between the highest gauge mark of the piezometer and the mercury level in manometer U. Calibration was carried out so that the apparatus was filled with air passing through a dried molecular sieve of the type 4A and then closed with mercury by means of differential manometer U and thermostated to 50°C . Afterwards the pressures were measured during compression from volume $V_0 + V_1 + V_2 + V_3 + V_4 + V_5$ gradually to V_0 , totalling 6 experimental values. For the described procedure it can be written

$$\sum_{i=0}^{i=j} V_i = nV_j, \quad (50^\circ\text{C}; p_j) \quad j = 0, 1, \dots, 5, \quad (25)$$

where V_0 is the volume of the dead part of the apparatus, $V_1, V_2 \dots V_5$ are the volumes of the piezometer spheres, n is the unknown number of moles of air closed in the apparatus, and V_j is molar volume of air at 50°C and at pressure p_j . Molar volume of air was calculated using equation of state for dry air¹⁷ in the form

$$z = \frac{pV}{RT} = 1 - 1.66 \cdot 10^{-7} p \text{ Torr} \quad (50^\circ\text{C}). \quad (26)$$

Eq. (26) affords 6 binding conditions for two constants: V_0 and n . Their values were found by minimization, after four calibration measurements: $(V_0)_1 = 218.201$ ml, $(V_0)_2 = 218.208$ ml, $(V_0)_3 = 218.201$ ml, and $(V_0)_4 = 218.195$ ml, *i.e.* average value $V_0 = 218.20$ ml.

Measuring of the Behaviour of State of Pure Substances

Behaviour of state of four samples of methanol and three n-hexane samples at 50°C was investigated. Methanol was a preparation of purity better than 99.99% (after drying on a 4A type

molecular sieve) and n-hexane was of purity better than 99.95%. Methanol (Lachema) was purified by double rectification on a 40-plate bubble cap column. n-Hexane was prepared by reaction of propyl bromide with sodium. The reaction product was rectified and the fraction of 99.95% purity was used for measurement.

TABLE II

$p - V - T$ Data for Methanol at 50°C

V , ml		p , Torr		
488.32	201.13	198.69	187.88	187.94
435.12	225.19	222.55	210.48	210.57
379.95	257.18	254.07	240.37	240.43
326.54	297.68	294.26	278.43	278.53
271.62	354.64	350.74	332.35	332.43

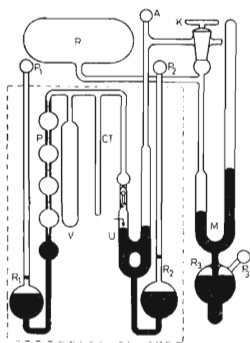


FIG. 1

Schematic Drawing of Volume Compression Apparatus for Measuring the Behaviour of State of Gases and Vapours

Description see Experimental.

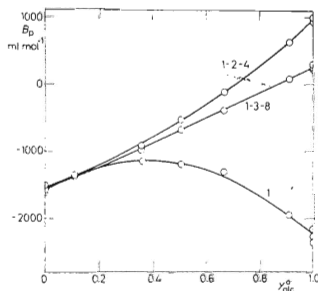


FIG. 2

Dependence of Second Virial Coefficient of Binary Gaseous Mixture Methanol — n-Hexane on Composition at 50°C

1 Without association, 1—2—4 association of the type monomer—dimer—tetramer, 1—3—8 association of the type monomer—trimer—octamer.

Both pure components, methanol and n-hexane were dried on an evacuated molecular sieve of the type 4A. Then a set of samples was prepared by condensing the dried and degassed liquids into thin-walled capillaries. Each capillary was cooled by liquid nitrogen and sealed cautiously. Then the capillaries were put one by one into the tube with the crushing device. The whole apparatus was exhausted to high vacuum (10^{-5} – 10^{-6} Torr), including the crushing device (in Fig. 1 this tube is not drawn; it is connected with the compression apparatus in point A, together with the vacuum station). After disconnecting the apparatus from the vacuum station the capillary was crushed by means of magnetic crusher. The sample was let to condense into the freezing trap which was cooled by liquid nitrogen. After about 15 min the apparatus was closed by means of differential manometer U, thermostating to 50°C was switched on and then 6 subsequent values of pressure were measured during gradual compression of vapours, by letting mercury into the piezometer and adjusting its level to the corresponding scale marks. Sometimes only 5 values could be measured, as with the last compression (to volume V_0) the saturated vapour tension was exceeded at the given conditions. The found values are summarized in Tables II and III.

Measuring of the Behaviour of State of Gaseous Mixture

A similar procedure was maintained as in the case of pure components. The only difference was in sampling: two weighed capillaries were crushed simultaneously, one of them containing methanol and the other one n-hexane. The inaccuracy of sampling was found to be -2 mg at maximum (*i.e.* the amount of sample, condensed into the compression part was at most by 2 mg less than that initially weighed). The measured values for 5 studied mixtures are presented in Table IV.

RESULTS

Data from Tables II–IV were processed on computers NE 803B and E 503 in three different ways. First the classical treatment was carried out assuming the absence of any associate. The calculation was performed by minimizing the equation obtained by substituting Eq. (1) into Eq. (22), using the orthogonalization¹⁸ procedure programmed in Algol. This computation procedure was applied in all cases of correlations in order to eliminate bad conditioning of the system matrix. The points, attained in this way, formed a curve denoted 1 in Fig. 2 (monomer) which complies with Eq. (1). Table V presents the found constants of Eq. (1).

Further the assumption was made that methanol forms dimers and tetramers in the vapour phase, as it was confirmed in several papers^{12–15}. If we denote methanol component A and n-hexane component B, we can write for this particular case of association

$$\varphi_A = 1 - \xi_{2,0} - \zeta_{4,0}, \quad (27)$$

$$\varphi_B = 1, \quad (28)$$

$$\varphi = 1 - y_{1,0}^0 \left(\frac{1}{2} \xi_{2,0} + \frac{3}{4} \zeta_{4,0} \right), \quad (29)$$

$$(K_p)_{2,0} = \frac{\xi_{2,0}}{2\varphi_A^2} \left[\frac{y_{1,0}^0 p}{\varphi} \right]^{-1}, \quad (30)$$

$$(K_p)_{4,0} = \frac{\xi_{4,0}}{4\varphi_A^4} \left[\frac{y_{1,0}^0 p}{\varphi} \right]^{-3} \quad (31)$$

The following procedure was chosen for practical solution: First the values of association constants $(K_p)_{2,0}$ and $(K_p)_{4,0}$ at 50°C were estimated according to literature data¹⁵. For this estimate all necessary values of function φ were calculated and the minimization of function (24) was performed for four measurements of the behaviour of state of methanol simultaneously. Then the computation algorithm performed automatically the approximation of the values of $(K_p)_{2,0}$ and $(K_p)_{4,0}$, till the accuracy of the constants was assured by four valid numerals and simultaneously the condition of minimum of function (24) as well as of the validity of relations (30) and (31) was satisfied. Association constants obtained in this way were used to calculate the cross virial coefficient from the values of state behaviour of mixtures, by minimizing Eq. (1). The points obtained were plotted into a curve, denoted in Fig. 2 1—2—4 (monomer — dimer — tetramer) which conforms with Eq. (1). Constants of Eq. (1) obtained for this case of association are summarized in Table V.

A similar procedure was employed for solving the case of association to trimer and octamer. On the basis of their recent results, Tucker and coworkers¹⁶ report that methanol associates in the vapour phase to form trimer and octamer. For this

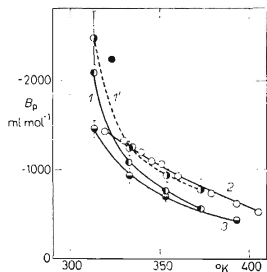


FIG. 3

Dependence of Second Virial Coefficient of Methanol on Temperature

1 Knoebel and Edminster²³ (± 30 ml mol⁻¹); 1' values from the paper of Knoebel²⁴ recalculated using the computer program for expansion series according to Eq. (1); 2 Lambert and coworkers⁵ (± 50 ml mol⁻¹); 3 Kretschmer and Wiebe¹³ (± 5 to ± 100 ml mol⁻¹). Full point was measured in the present work (± 45 ml mol⁻¹).

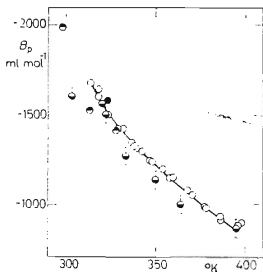


FIG. 4

Dependence of Second Virial Coefficient of n-Hexane on Temperature

○ McGlashan and Potter²⁵ (± 20 ml mol⁻¹); ● Bottomley and Reeves²⁶ (± 3 ml mol⁻¹); ⊙ Lambert and coworkers⁵ (± 50 ml mol⁻¹). ● This paper (± 25 ml mol⁻¹).

case of association it holds ($A = \text{methanol}$)

$$\varphi_A = 1 - \xi_{3,0} - \xi_{8,0}, \quad (32)$$

$$\varphi_B = 1, \quad (33)$$

$$\varphi = 1 - y_{1,0}^0 \left(\frac{3}{8} \xi_{3,0} + \frac{7}{8} \xi_{8,0} \right), \quad (34)$$

$$(K_p)_{3,0} = \frac{\xi_{3,0}}{3\varphi_A^3} \left[\frac{y_{1,0}^0 P}{\varphi} \right]^{-2}, \quad (35)$$

$$(K_p)_{8,0} = \frac{\xi_{8,0}}{8\varphi_A^8} \left[\frac{y_{1,0}^0 P}{\varphi} \right]^{-7}, \quad (36)$$

Practical solution was performed using the same computation procedure as in the preceding case. Again constants $(K_p)_{3,0}$ and $(K_p)_{8,0}$ were estimated from the literature data¹⁶. The values obtained were used to plot a curve, denoted in Fig. 2 1–3–8 (monomer–trimer–octamer), conforming with Eq. (1). Constants of this relation, together with association constants, are presented in Table V.

For the apparatus used in the present work it is possible to estimate the maximum error of the second virial coefficient δB_p . The value of this error is defined by

$$\begin{aligned} \delta B_p = & \left| \frac{\partial B_p}{\partial T} \delta T \right| + \left| \frac{\partial B_p}{\partial p} \delta p \right| + \left| \frac{\partial B_p}{\partial V} \delta V \right| + \left| \frac{\partial B_p}{\partial (n^0 \varphi)} \delta (n^0 \varphi) \right| \\ & + \left| \frac{\partial B_p}{\partial y_{1,0}^0} \delta y_{1,0}^0 \right| \end{aligned} \quad (37)$$

and is usually greater, as in practical cases a partial compensation of individual contributions in Eq. (37) can occur.

For solving Eq. (23) as to B_p we can write

$$B_p = V/n^0 \varphi - RT/p. \quad (38)$$

From Eq. (38) expressions for all partial derivatives can be obtained and then such measured data can be introduced which result in maximum numerical values of these derivatives,

$$\partial B_p / \partial T = -R/p = -416 \text{ ml mol}^{-1} \text{ deg}^{-1}, \quad (39)$$

$$\partial B_p / \partial p = RT/p^2 = 895 \text{ ml mol}^{-1} \text{ Torr}^{-1}, \quad (40)$$

$$\partial B_p / \partial V = 1 / (n^0 \varphi) = 292 \text{ mol}^{-1}, \quad (41)$$

$$\partial B_p / \partial (n^0 \varphi) = - (V / (n^0 \varphi)^2) = - 4.2 \cdot 10^7 \text{ ml mol}^{-2}, \quad (42)$$

$$\frac{\partial B_p}{\partial y_{1,0}^0} = \frac{\partial B_p}{\partial \varphi} \frac{\partial \varphi}{\partial y_{1,0}^0} = \frac{V}{n^0 \varphi^2} \sum_{i=2}^{i=a} (1 - 1/i) \xi_{i,0}, \quad (43)$$

$$= 2.1 \cdot 10^3 \text{ ml mol}^{-1} (1 - 2 - 4), \quad (43a)$$

$$= 9.1 \cdot 10^2 \text{ ml mol}^{-1} (1 - 3 - 8). \quad (43b)$$

It still remains to evaluate $\delta(n^0 \varphi)$ and $\delta y_{1,0}^0$. Let us assume that the error $\delta(n^0 \varphi)$ is caused only by adsorption on the apparatus walls. If we employ the data for metha-

TABLE III

$p - V - T$ Data for *n*-Hexane at 50°C

$V, \text{ ml}$		$p, \text{ Torr}$	
488.32	151.05	162.43	162.35
435.12	169.19	182.13	181.92
379.95	193.49	208.24	207.93
326.54	224.80	241.67	241.20
271.62	269.03	289.34	288.97
218.20	333.04	357.96	357.50

TABLE IV

$p - V - T$ Data for Methanol-*n*-Hexane Mixture at 50°C

$V, \text{ ml}$		$p, \text{ Torr}$			
488.32	180.07	243.64	298.67	223.05	186.26
435.12	201.84	272.98	334.56	249.97	208.72
379.95	230.73	311.08	382.10	285.68	238.49
326.54	267.82	362.14	443.03	331.47	276.56
271.62	320.66	432.58	529.77	396.62	330.63
218.20	396.88	536.44	653.79	490.18	407.18
y_A^0	0.113	0.361	0.508	0.670	0.912

mol adsorption on "Phoenix" glass at 52°C (see¹⁹) that were measured by means of a modified McLeod manometer²⁰, we obtain values ranging between $5.2 \cdot 10^{-10}$ (at 195 Torr) and $9.7 \cdot 10^{-10}$ (at 348 Torr) mol of adsorbed methanol on 1 cm^2

TABLE V

Survey of Results of Three Ways of Treatment

1 Without association, 1-2-4 association of the type monomer-dimer-tetramer, 1-3-8 association of the type monomer-trimer-octamer

Type of association	1	1-2-4	1-3-8
Association constants	—	$(K_p)_{2,0} = 7.43 \cdot 10^{-5} \text{ Torr}^{-1}$ $(K_p)_{4,0} = 1.77 \cdot 10^{-10} \text{ Torr}^{-3}$	$(K_p)_{3,0} = 1.18 \cdot 10^{-7} \text{ Torr}^{-2}$ $(K_p)_{8,0} = 5.73 \cdot 10^{-22} \text{ Torr}^{-7}$
B_{11} , ml mol ⁻¹	-2 226	944	257
B_{22} , ml mol ⁻¹	-1 574	-1 564	-1 569
B_{12} , ml mol ⁻¹	- 433	- 798	- 756
Standard deviation			
B_p , ml mol ⁻¹	± 46	± 24	± 25

TABLE VI

Survey of the Measured and Calculated Values of Second Virial Coefficient (ml mol⁻¹) for Methanol and n-Hexane at 50°C

Equation according to	Suitable for	(B_p)	
		methanol	n-Hexane
Berthelot's reduced equation ⁵	orientation	- 532	- 1 361
McGlashan and Potter ²¹	aliphatic hydrocarbons	—	- 1 512
Pitzer and Curl ²²	non-polar substances	—	- 1 447
Kreglewski ⁴	real gases	- 1 534	- 1 573
This paper (measured for monomer)		-2 226 ± 46	- 1 574 ± 46

of the glass surface. The volume compression apparatus described in the present paper had the surface about 550 cm², so that the error $\delta(n^0\varphi)$, caused by adsorption on glass, was 550 (9.7 - 5.2) · 10⁻¹⁰, i.e. 2.5 · 10⁻⁷ mol at maximum, under the assumption that the glass used ("Sial") has the same adsorption as the "Phoenix" glass.

In calculating the error $y_{1,0}^0$ we can write

$$\delta y_{1,0}^0 = \frac{\partial y_{1,0}^0}{\partial n_{1,0}^0} \delta n_{1,0}^0 + \frac{\partial y_{1,0}^0}{\partial n_{0,1}^0} \delta n_{0,1}^0, \quad (44a)$$

$$= \frac{1}{n^0} (1 - y_{1,0}^0) \delta n_{1,0}^0 - \frac{1}{n^0} y_{1,0}^0 \delta n_{0,1}^0, \quad (44b)$$

where $n^0 = n_{1,0}^0 + n_{0,1}^0$. Introducing for $n_{1,0}^0 = -0.002/32.05 = -6.25 \cdot 10^{-5}$, and for $n_{0,1}^0 = -0.002/86.17 = -2.3 \cdot 10^{-5}$ (maximum uncertainty -2 mg in sampling the components into the apparatus) and for $n^0 = 4.6 \cdot 10^{-3}$ mol (i.e. the most unfavourable case when $y_{1,0}^0 = 0.911$) we obtain $\delta y_{1,0}^0 = 3.3 \cdot 10^{-3}$.

Total maximum error δB_p is thus equal

$$\begin{aligned} \delta B_p = & |-416 \times 0.02| + |895 \times 0.02| + |292 \times 0.005| + |-4.2 \times 10^7 \times 2.5 \times 10^{-7}| \\ & + |2.1 \times 10^3 \times 3.3 \times 10^{-3}| = 45.1 \text{ ml mol}^{-1}. \end{aligned}$$

The greatest error is caused by inaccuracy in pressure measurement (17.9 ml mol⁻¹) and by adsorption on the glass of the apparatus (10.5 ml mol⁻¹). Adsorption of n-hexane on glass is much less as compared with methanol and therefore it need not be taken into account when calculating $\delta(n^0\varphi)$.

DISCUSSION

In Table VI and Figs 3 and 4 the values of second virial coefficients of both components are compared with the values that can be calculated according to equations taken from the literature. For hexane the agreement is excellent. The value of the second virial coefficient of methanol was found to deviate considerably in the case of classical treatment in which association is neglected. If, however, we use Eq. (2) and take $(B_{11})_{\text{phys}}$ equal -532 ml mol⁻¹ (according to Table VI, a value obtained from Berthelot's reduced equation) and using the value of $(B_{11})_{\text{chem}}$ calculated by substituting the value of $(K_p)_A = 1/(K_p)_{2,0}$ into Eq. (11), we obtain for the second virial coefficient of methanol at 50°C the value -2029 ml mol⁻¹.

For solving the minimum of function (24) or for minimizing Eq. (25) a standard computation procedure was employed¹⁸ which solves the general minimization problem for a linear regression form by means of orthogonalization process. This particular method has to be used, as in general minimization problems show ill-conditioned system matrices. When processing the measured values of the behaviour of state it is no more possible to calculate virial coefficients with sufficient accuracy unless calculation procedures are used suppressing the ill-conditionality²⁷. Also the Householder transformation²⁸⁻³⁰ can be used instead of orthogonalization in numerical processing of the linear regression form.

For example, when calculating the dead volume of the apparatus, V_0 , by minimizing Eq. (25) the following volumes were found for four dry air calibration measurements: 218.201, 218.208, 218.201 and 218.195 ml. If this problem is solved for the same measured values of pressure by means of the least squares method, without applying the orthogonalization procedure the volumes obtained are 218.148, 218.226, 218.189 and 218.239, when the numerical treatment was carried out on a NE 803 B computer with the accuracy of numerical representation corresponding to 8 valid decades.

We can sum up that the description of the behaviour of state of methanol-hexane mixture at 50°C requires two additional association constants, either for dimerization and tetramerization or for trimerization and octamerization, respectively. From the measurement of $p - V - T$ behaviour it cannot be decided which kind of association is taking place, however, it is possible to state that the models 1-2-4 and 1-3-8 are, as to the accuracy, practically equally suitable. Their final numerical values are summarized in Table V. From the work of Dunken and Winde¹⁵ only the value of $(K_p)_{2,0} = 2.2 \cdot 10^{-5} \text{ Torr}^{-1}$ at 50°C can be obtained by extrapolation for 50°C (from IR absorption of methanol vapours at 20, 25, 30, 35 and 40°C, whereby $(K_p)_{4,0}$ was not considered by the authors in quantitative treatment). Extrapolation of the values of association constants reported by Tucker and coworkers¹⁶ (from the measurement of $p - V - T$ behaviour at 15, 25 and 35°C) affords the following values for 50°C: $(K_p)_{3,0} = 1.12 \cdot 10^{-7} \text{ Torr}^{-2}$ and $(K_p)_{8,0} = 2.5 \cdot 10^{-22} \text{ Torr}^{-7}$.

The proposed solution for calculating the behaviour of state in the presence of associating components in a binary mixture constitutes a quite general procedure. Function φ is a quantitative measure of association. In the case studied the degree of association lay between 0.2% to 4.3% (*i.e.* function φ varied in the interval 0.998 to 0.957). It is not difficult to extend this problem analogously to a system of more than two components.

REFERENCES

1. Novák J. P.: Chem. listy 58, 1471 (1964).
2. Stiel L. J.: Ind. Eng. Chem. 60, 50 (1968).
3. Leland T. W. jr, Chappellear P. S.: Ind. Eng. Chem. 60, 16 (1968).
4. Kreglewski A.: J. Phys. Chem. 73, 608 (1969).

5. Lambert J. D., Roberts G. A. H., Rowlinson J. S., Wilkinson V. J.: Proc. Roy. Soc. (London) *A* 196, 113 (1949).
6. Lambert J. D., Clarke J. S., Duke J. F., Hicks C. L., Lawrence S. D., Morris D. M., Stone G. T.: Proc. Roy. Soc. (London) *A* 249, 414 (1959).
7. Cheh H. Y., O'Connell J. P., Prausnitz J. M.: Can. J. Chem. 44, 429 (1966).
8. O'Connell J. P., Prausnitz J. M.: Ind. Eng. Chem. Fundamentals 8, 453 (1969).
9. Rigby M., O'Connell J. P., Prausnitz J. M.: Ind. Eng. Chem. Fundamentals 8, 460 (1969).
10. Dantzler E. M., Knobler C. M.: J. Phys. Chem. 73, 1602 (1969).
11. Markuzin N. P.: Ž. Fiz. Chim. 39, 180 (1965).
12. Weltner W., Pitzer K. S.: J. Am. Chem. Soc. 73, 2606 (1951).
13. Kretschmer C. B., Wiebe R.: J. Am. Chem. Soc. 75, 2579 (1954).
14. Inskeep R. G., Kelliher J. M., McMahon P. E., Somers B. G.: J. Chem. Phys. 28, 1033 (1958).
15. Dunken H., Winde H.: Z. Chem. 7, 37 (1967).
16. Tucker E. E., Farnham S. B., Christian S. D.: J. Phys. Chem. 73, 3820 (1969).
17. Din F.: *Thermodynamic Functions of Gases*, Vol. 2, p. 49. Butterworths, London 1956.
18. Bauer F. L.: Numerische Mathematik 7, 338 (1965).
19. Bottomley G. A., Coopes I. H., Nyberg G. L., Spurling T. H.: Australian J. Chem. 18, 1105 (1965).
20. Bottomley G. A., Reeves C. G.: Trans. Faraday Soc. 53, 1455 (1957).
21. McGlashan M. L., Potter D. J. B.: Proc. Roy. Soc. (London) *A* 206, 448 (1951).
22. Pitzer K. S., Curl R. F. Jr.: J. Am. Chem. Soc. 79, 2369 (1957).
23. Knoebel D. H., Edmister W. C.: J. Chem. Eng. Data 13, 312 (1968).
24. Knoebel D. H.: *Thesis*. Oklahoma State University, Stillwater Oklahoma 1967.
25. McGlashan M. L., Potter D. J. B.: Proc. Roy. Soc. (London) *A* 267, 478 (1962).
26. Bottomley G. A., Reeves C. G.: J. Chem. Soc. 1958, 3794.
27. Hall K. R., Canfield F. B.: Physica 33, 481 (1967).
28. Golub G., Businger P.: Technical Report CS 12, 1964. Comp. Science Division, School of Humanities and Sciences, Stanford University, 1964.
29. Golub G.: Numerische Mathematik 7, 206 (1965).
30. Businger P., Golub G. H.: Numerische Mathematik 7, 269 (1965).

Translated by V. Čermáková.