# IMPORTANCE OF THE REAL BEHAVIOUR OF THE VAPOUR PHASE FOR THE EVALUATION OF VAPOUR–LIQUID EQUILIBRIUM DATA*

By

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## Introduction

The advent of computer methods for the description and calculation of vapour–liquid equilibria permits to consider factors, neglected earlier in order to simplify calculations, and to replace the earlier coarse approximations by more exact relationships. In the following it will be investigated how the real behaviour of the vapour phase affects the description of vapour–liquid equilibrium conditions.

The virial equation has been used as equation of the state of vapour phase. Our work consisted of the following steps:

1. Selection of an apparatus suitable for measuring the $P$-$v$-$T$ data of organic solvents.
2. By statistically analyzing the sources of error and the results, partly, development of a measurement method of adequate precision, and partly, information concerning the accuracy of each data, needed for processing the results.
3. Determination of $P$-$v$-$T$ data of a few solvents, then of solvent mixtures, and calculation of their second virial coefficients.
4. Designation of solvent mixtures, in the case of which the real behaviour of the vapour phase must be taken into consideration.

## Determination of the virial coefficients

Various empirical and semi-empirical equations of state have been used [1] for processing and calculating the $P$-$v$-$T$ data of gases and vapours, e.g. the van der Waals, the Benedict—Webb—Rubin, etc. equations, as well as the so-called virial equation of the form

$$Pv = nRT + nBP + nCP^2 \ldots \tag{1}$$

where the second virial coefficient $B$ expresses the interaction of two, the third virial coefficient $C$ of three, etc. molecules.
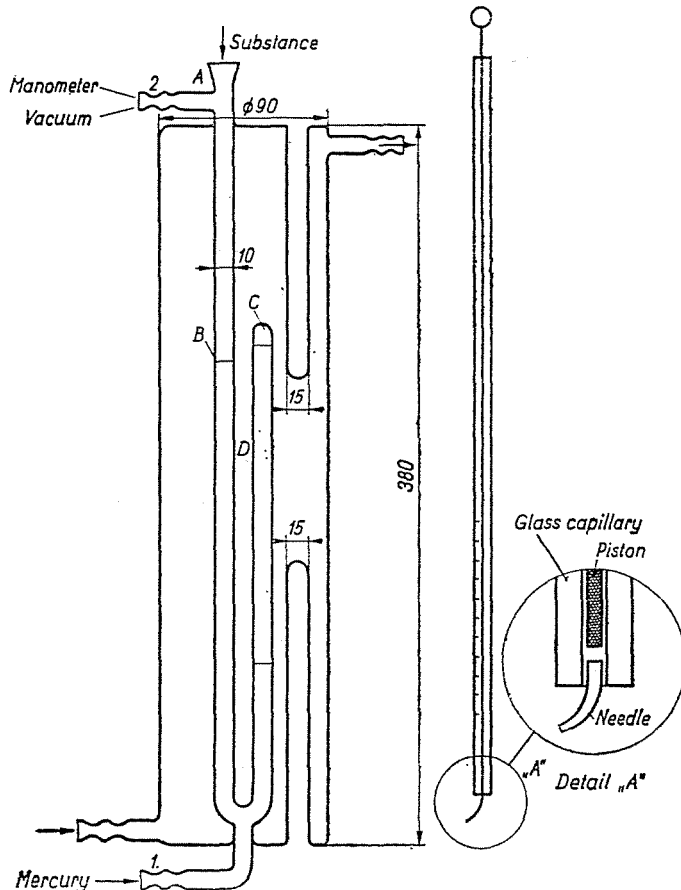
*Fig. 1.* Test apparatus and syringe

For gases and vapours not associating at a pressure of about 1 atmosphere, it is generally sufficient to take the first two right-hand side terms into consideration.

To determine the coefficients of the virial equation, such as the second virial coefficient, $P$-$v$-$T$ data are needed. Measurements have been carried out in a Boyle's apparatus [2, 3] (Fig. 1). The test substance is introduced into the closed end of the tube, where it is sealed by mercury from air. Mercury level was read in the two branches of the J-tube by means of a cathetometer and on the manometer connected to the apparatus, and pressure was calculated in knowledge of the atmospheric pressure. The volume of the closed part belonging to different mercury levels has been determined by calibration.

In knowledge of the results, the mole number $n$ and the second virial coefficient $B$ can be calculated by means of Eq. (1).

The initial trial measurements were of poor reproducibility, inducing us to find the coarse errors of the measurement method, such as:

1. Air got into the closed tube of the apparatus, of a volume determined as the difference of the pressure measured in condensed state and of the calculated tension, taken into consideration for correction.
2. The volume of the mercury meniscus enters into the calculation of vapour volume, also in calibration. For this, both the bottom and the top of the meniscus have to be read (Fig. 2).



$$D = \left(\tfrac{1}{2}h\right)^2 / l + l$$
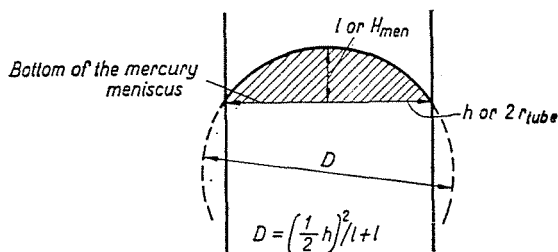
Calculation of the diameter of
the circle belonging to the circular segment
the sphere belonging to the calotte

*Fig. 2.* The mercury meniscus

3. During a set of measurements, atmospheric pressure varies. A change by 1 torr may alter the second virial coefficient by 6 to 8%. Its effect was eliminated by reading the atmopheric pressure for each measurement.
4. In calculating the pressure, mercury depression must be taken into consideration.

The improvements applied to the procedure were the following: (see Fig. 1). The open end of the apparatus and pipe connection② were closed with rubber stoppers. Through the silicone rubber tube, slipped over connection①, the J-tube was completely filled with purified mercury. Next, the mercury container was placed under vacuum, air captured between the mercury and the glass wall was sucked out, the silicone rubber tube closed with a spring clip, and the apparatus was set in measuring position. With a syringe pushed through the rubber stopper, pressure was equalized in the J-tube, the rubber stopper was removed, and the mercury level adjusted to about the marking B, by draining the mercury back into the mercury container. Next, the test substance was filled into the apparatus, by means of the syringe seen in Fig. 1. The "piston rod" was a stainless steel wire. The bent needle at the end of the syringe was introduced until the "bend" of the J-tube, and the needed quantity of substance was fed into the apparatus. Since an organic solvent is lighter than mercury, it rose to the closed end of the J-tube.

After having fed the test substance into the apparatus, the mantle of the apparatus was connected with the thermostat and the desired temperature was adjusted. The manometer and the vacuum pump were connected by a rubber tube to connection②. The vertical position of the apparatus was checked by the distance of markings C and D. At the beginning of the measurement, the pressure in the apparatus was adjusted to 200 to 300 torr by means of the vacuum pump, while during the measurement, pressure was increased by means of the syringe pushed through the upper rubber stopper.

Measurement data needed for calculating the second virial coefficient.

1. At each measurement point:
   a) the bottom and the top of the mercury meniscus in both stems of the apparatus,
   b) the mercury levels in the two branches of manometer,
   c) atmospheric pressure, and
   d) the temperature of the apparatus.
2. Once in a measurement series:
   a) ambient temperature,
   b) the height of marking C.

According to our experiences, these latter did not change within a measurement series, or better, a change by 0.5 °C of the external temperature did not affect the measurement results.

## Calibration and evaluation of measurement

*Calibration*

$$v(h) = \frac{m}{\varrho_{Hg,t}} - v_{men} \tag{2}$$

where   $v\ (h)$   the volume of the tube up to height $h$ (the volume is assigned to the bottom of the meniscus, since it is more accurate to read than its top) [cm$^3$];

$m$       the mass of the mercury weighed in [g];

$\varrho_{Hg,t}$   the density of mercury at the temperature of measurement [g/cm$^3$]; and

$v_{men}$   the volume of the meniscus [cm$^3$].

The height of the mercury meniscus depends on the diameter of the tube and on the capillary constant, dependent in turn on the purity of mercury, on the acting pressure, and on the material characteristics of the glass tube. In knowledge of these data, the volume of the mercury meniscus can be exactly calculated from complicated mathematical relationships [4]. To eliminate calculations, volumes of the meniscus as a function of the tube radius

and the height of the meniscus have been tabulated [5]. The available tables are, however, either related to smaller tube radii as the ours or were inaccurate. Therefore the volume of the meniscus was calculated by assuming it to be a regular calotte, so that: [6]

$$v_{men} = \pi \cdot H_{men}^2 \cdot \left[ R_G - \frac{H_{men}}{3} \right] \qquad (3)$$

where $H_{men}$ height of the meniscus [cm], and
$R_G$ radius of the sphere affected by the "calotte" [cm]

$R_G$ is expressed by: [6]

$$R_G = [r_{tube}^2/H_{men} + H_{men}]/2 \qquad (4)$$

where $r_{tube}$ is the radius of the tube [cm].

Owing to the variable-cross section of the tube, the volume was approximated by a quadratic equation with three constants, using the method of least squares. Also equations of higher powers have been applied, without, however, a significant decrease of the residual variance [7].

Calibrations at different temperatures were found to differ less than by the error of measurement, so that the relationship obtained at 70 °C was used throughout.

*Volumetry*

From the calibration discussed above, for the mercury level reading:

$$v = -2.07502 \cdot 10^{-1} + 8.72671 \cdot 10^{-1} h + 5.78359 \cdot 10^{-4} h^2 - v_{men} \ [cm^3]$$

$$(5)$$

$v_{men}$ is calculated as above.

*Pressure determination*

Calculation procedure: (see Fig. 3)

$$P = P_{int} + \Delta P_{corr} \ [torr] \qquad (6)$$

$$P_{int} = P_B - \Delta P_{man} \ [torr] \qquad (7)$$

where $P_{int}$ pressure in the open branch of the apparatus [torr];
$\Delta P_{corr}$ corrected mercury level difference in the apparatus [torr];
$\Delta P_{man}$ corrected pressure difference, read on the U-tube mercury manometer connected to the apparatus [torr]; and
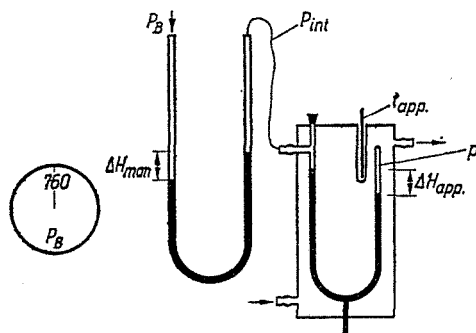$\Delta P_B$ atmospheric pressure [torr].

*Fig. 3.* Calculation of pressure

Atmospheric pressure has been determined with an aneroid barometer with a reading accuracy of 0.1 to 0.2 torr. Temperatures in the manometer and in the apparatus being different, the pressure has been calculated from the level difference readings by applying temperature correction:

$$\Delta P_{\text{corr}} = \Delta P_{\text{meas}}/[1 + \alpha \cdot t + \beta \cdot t^2] \tag{8}$$

where

$\Delta P_{\text{meas}}$  mercury level difference reading [mm];
$\Delta P_{\text{corr}}$  corrected pressure [mm];
$t$  test temperature [°C];
$\alpha, \beta$  thermal expansion coefficients of mercury, suggested by [8] as
$\alpha = 0.18182 \cdot 10^{-3}$ [1/°C]
$\beta = 0.0078 \cdot 10^{-6}$ [1/°C].

Pressure values in the apparatus have been corrected also for depression [9]. Depression values have been tabulated as a function of the tube radius and the height of the meniscus.

*Error analysis*

By comparing the standard deviation of the "measured" $P \cdot v$ product with its uncertainty estimable from the inherent errors of measurement by the error propagation law, it becomes clear

— whether all the substantial sources of error are known and taken into consideration;
— whether weighing is to be applied in the $Pv$-$P$ regression;
— where the method has to be refined in a further development.

In the case of a functional relationship $z = f(x, y)$, the uncertainty of

variable $z$, calculated from readings $x$ and $y$, is given by the relationship (error propagation law) [10]:

$$\text{Var}\,[z] = \left(\frac{\partial f}{\partial x}\right)^2 \text{Var}\,[x] + \left(\frac{\partial f}{\partial y}\right)^2 \text{Var}\,[y]\,, \qquad (9)$$

where Var means the variance.

Thus, the variance of the values of product $Pv$ is:

$$\text{Var}\,[(Pv)]_i = \left(\frac{\partial Pv}{\partial v}\right)_i^2 \text{Var}\,[v_i] + \left(\frac{\partial Pv}{\partial P}\right)_i^2 \text{Var}\,[P_i]\,. \qquad (10)$$

Assessment of the variance of the measured pressure and volume by composing the corrected empirical variance of the elementary measurements according to the law of error propagation is therefore needed.

By way of example, let us investigate in detail, how the uncertainty of *calibration* is composed from the random errors of the direct readings. The uncertainty of the calibration relationship is composed of two parts: of the measurement errors (variations) of the dependent ($v$) and of the independent ($h$) variables:

$$s_{v(h)}^2 = s_v^2 + \left(\frac{\partial v}{\partial h}\right)^2 s_h^2\,. \qquad (11)$$

Standard deviation of *volumetry*:
   1. Inaccuracy of weighing
      a) Inaccuracy of the balance: on our balance, the third decimal digit is still accurate:

$$3s = 10^{-3}\,[\text{g}]\,; \quad s^2 \simeq 10^{-7}\,[\text{g}^2]\,.$$

   b) Mercury losses: at the introduction of mercury; repeated sucking up into and pressed out of the syringe; from the difference in the syringe weights

$$s^2 \simeq 3 \cdot 10^{-4}\,[\text{g}^2]\,.$$

Their effect on the uncertainty of volumetry:

$$s_v^2 = \left(\frac{\partial v}{\partial m}\right)^2 \cdot s_m^2 = \left(\frac{1}{\varrho_{\text{Hg},t}}\right)^2 \cdot s_m^2 = \frac{1}{13{,}5^2} \cdot 3 \cdot 10^{-4} = 1{,}6 \cdot 10^{-6}\,[\text{cm}^6]\,.$$

   2. Variation of the density of mercury upon temperature variation: variation of the thermostated temperature was found to be $s_t^2 = 10^{-3}$

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[°C]; from the temperature dependence of the density of mercury [6]:

$$\frac{\partial \varrho_{Hg,t}}{\partial t} \simeq 2{,}4 \cdot 10^{-3} \ [\text{g/cm}^3 \, ^\circ\text{C}]$$

Resultant volume error:

$$s_v^2 = \left(\frac{\partial v}{\partial \varrho_{Hg,t}}\right)^2 \cdot \left(\frac{\partial \varrho_{Hg,t}}{\partial t}\right)^2 \cdot s_t^2 = \left(-\frac{A \cdot h}{13{,}5^2}\right)^2 \cdot \left(\frac{\partial \varrho_{Hg,t}}{\partial t}\right)^2 s_t^2 =$$

$$= \frac{0{,}8^2 \cdot h^2}{13{,}5^2} \cdot 2{,}4^2 \cdot 10^{-6} = 2 \cdot 10^{-11} \cdot h^2 \, [\text{cm}^6],$$

where $A$ is the cross section of the tube.

3. Error of meniscus correction

a) Inaccurate reading of the bottom and top of the meniscus:

$$s_v^2 = \left(\frac{\partial v_{men}}{\partial H_{men}}\right)^2 s_l^2, \qquad \text{where } s_l^2 = s_{Hg,\,bottom}^2 + s_{Hg,\,top}^2;$$

the value of the first is $7 \cdot 10^{-7}$ cm², that of the latter from repeated readings $4.6 \cdot 10^{-6}$. Thus, $s^2 = 5.3 \cdot 10^{-6}$ [cm²]. From the formula $v_{men} = \pi \cdot H^2_{men} \, [R - H_{men}/3]$ of the spherical calotte, with averages $H_{men} = 0.158$ cm and $R = 0.688$ cm,

$$\left(\frac{\partial v_{men}}{\partial H_{men}}\right) = 0{,}6 \, [\text{cm}^2] \qquad s_v^2 = 1{,}9 \cdot 10^{-6} \, [\text{cm}^6].$$

b) A possible deviation from the calotte form, being an unidirectional deviation, does not contribute to the random error, and causes no standard deviation.

In calibration, the estimated variance of volumetry is a total of

$$s_v^2 = 3.5 \cdot 10^{-6} + 2 \cdot 10^{-11} \, h^2 \ [\text{cm}^6].$$

According to Eq. (11), also the effect of the inaccuracy of height measurement must be taken into consideration.

a) Uncertainty of the mercury level reading, from repeated readings of an adjusted mercury level:

$$s^2 = 7 \cdot 10^{-7} \ [\text{cm}^2].$$

b) Inaccuracy of the reading of basic marking $C$ of the apparatus:

$$s^2 = 2.6 \cdot 10^{-6} \ [\text{cm}^2].$$

c) Imperfect verticality of the apparatus. Spaced at about 17 cm, marks have been scratched on the closed leg of the J-tube. The apparatus has been adjusted, until the distance between the two markings assumed its maximum, where the position was closest to vertical. Then, the skewness of the apparatus is due to the error in reading the basic markings, such as: $s^2 = 2s_{\text{basic marking}}^2$ throughout the tube length. For some length $h$:

$$s^2 = k^2 \cdot 2 \cdot s_{\text{basic marking}}^2 = 2.4 \cdot 10^{-8} \cdot h^2 \ [\text{cm}^2]$$

as

$$k = \frac{h\,[\text{cm}]}{17}.$$

Sum of errors caused by height measurement inaccuracies:

$$\left(\frac{\partial v}{\partial h}\right)^2 \cdot s_h^2 = A^2 \cdot s_h^2 = 0.8^2\ [7 \cdot 10^{-7} + 2.6 \cdot 10^{-5} +$$

$$+ 2.4 \cdot 10^{-8}\,h^2] = 2.2 \cdot 10^{-6} + 1.7 \cdot 10^{-8} \cdot h^2$$

Under consideration of the errors discussed, the estimated variance of calibration is:

$$s_{v(h)}^2 = 5.7 \cdot 10^{-6} + 1.7 \cdot 10^{-8}\,h^2 \ [\text{cm}^6].$$

Again in view of the sources of error, the estimated empirical variances of volume and pressure readings are:

$$s_v^2 = 7.8 \cdot 10^{-6} + 4.5 \cdot 10^{-8}\,h^2 \ [\text{cm}^6] \tag{12}$$

$$s_p^2 = 5.3 \cdot 10^{-5} + \Delta h_{\text{man}}^2 \cdot 1.8182 \cdot 10^{-9} \ [\text{cm}^2]. \tag{13}$$

According to Eq. (10):

$$s_{Pv}^2 = v_i^2 \cdot 5.3 \cdot 10^{-5} + P_i^2(7.8 \cdot 10^{-6} + 4.5 \cdot 10^{-8}\,h^2). \ [\text{cm}^8] \tag{14}$$

Table I, calculated with Eq. (14) leads to the following conclusions:
a) uncertainty of $Pv$ values is of the same order throughout the measurement range, making weighted regression useless;
b) the measurement in Table I is affected by the residual mean square

$$s^2 = \frac{\sum[(Pv)_{i,\,\text{meas.}} - (Pv)_{i,\,\text{calc.}}]^2}{n-2} = 0{,}0691, \tag{15}$$

of the same order of magnitude as the $s_{Pv}^2$ values calculated according to the law of error propagation (last column of the table): thus, the substantial sources of error can be stated to have been accounted for.

On the basis of these calculations, the uncertainty of the mole number

**Table I**

| P, cm Hg | $v$ cm² | H cm | $P^2 s_v^2$ | $V^2 s_P^2$ | $s_{Pv}^2$ |
|---|---|---|---|---|---|
| 58.832 | 15.005 | 18.7 | $8.15 \cdot 10^{-2}$ | $1.19 \cdot 10^{-2}$ | 0.0934 |
| 59.721 | 14.766 | 18.4 | 8.22 | 1.16 | 0.0938 |
| 61.921 | 14.224 | 17.8 | 8.46 | 1.07 | 0.0953 |
| 62.878 | 14.002 | 17.5 | 8.53 | 1.04 | 0.0957 |
| 79.281 | 11.014 | 13.8 | $1.03 \cdot 10^{-1}$ | $6.43 \cdot 10^{-3}$ | 0.1093 |
| 79.853 | 10.928 | 13.7 | 1.04 | 6.33 | 0.1098 |
| 80.472 | 10.837 | 13.6 | 1.04 | 6.22 | 0.1102 |
| 80.789 | 10.793 | 13.5 | 1.04 | 6.17 | 0.1106 |

and of the second virial coefficient can also be estimated. In the case of un-weighted regression [7] the variance of the parameters of a straight line

$$y = a + bx \tag{16}$$

is

$$\mathrm{Var}\,[a] = \frac{\mathrm{Var}\,[y]}{m} + \frac{\bar{x}^2\,\mathrm{Var}\,[y]}{\sum(x_i - \bar{x})^2} \tag{17}$$

$$\mathrm{Var}\,]b] = \frac{\mathrm{Var}\,[y]}{\sum(x_i - \bar{x})^2} \tag{18}$$

where $m$ is the number of measurement data.

Relationships (17) and (18) show the variance of the measured values to be the smaller, the greater the single $x_i$ values are spaced from $\bar{x}$ (i.e. the $P_i$ values from $\bar{P}$). Therefore, after having developed the method, measurements were performed at the two ends of the pressure range.

From the relationship $n = a/RT$ (provided $RT = $ const.):

$$\mathrm{Var}\,[n] = \left(\frac{\partial n}{\partial a}\right)^2 \mathrm{Var}\,[a] = \left(\frac{1}{RT}\right)^2 \mathrm{Var}\,[a] = $$
$$= \left(\frac{1}{RT}\right)^2 \left\{ \frac{\mathrm{Var}\,[Pv]}{m} + \frac{\bar{P}^2\,\mathrm{Var}\,[Pv]}{\sum(P_i - \bar{P})^2} \right\} \tag{19}$$

and from $B = b/n$

$$\mathrm{Var}\,[B] = \left(\frac{\partial B}{\partial b}\right)^2 \mathrm{Var}\,[b[ + \left(\frac{\partial B}{\partial n}\right)^2 \mathrm{Var}\,[n] = \frac{1}{n^2}\,\mathrm{Var}\,[b] + $$
$$+ \frac{B^2}{n^2}\,\mathrm{Var}\,[n] = \frac{1}{n^2}\,\frac{\mathrm{Var}\,[Pv]}{\sum(P_i - \bar{P})^2} + \frac{B^2}{n^2}\,\frac{1}{(RT)^2} \left\{ \frac{\mathrm{Var}\,[Pv]}{m} + \right.$$
$$\left. + \frac{\bar{P}^2\,\mathrm{Var}\,[Pv]}{\sum(P_i - \bar{P})^2} \right\}. \tag{20}$$

*P-v-T data of pure components*

The following solvents have been used in the measurements: methyl alcohol, ethyl alcohol, benzene, carbon tetrachloride and acetonitrile.

The purity of the solvents has been checked on the basis of the refractive index and by gas chromatography. The virial coefficients of each substance have been determined from several measurement series. Measurements were carried out at three temperatures, 70, 80 and 90 °C. The lower temperature limit was determined by the fact that below 70 °C, solvent vapours in test condense already at a very low pressure; on the other hand, above 90 °C, thermostating with water was not feasible. Results are shown in Figs 4 to 8.
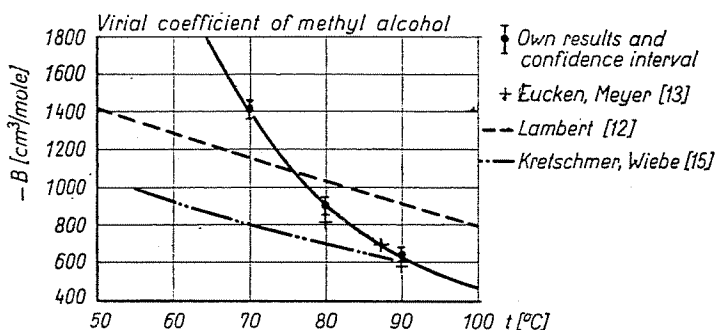
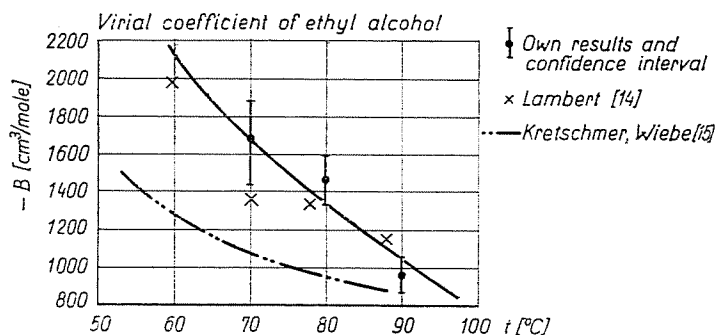*Fig. 4.* Comparison of own results and literature data

*Fig. 5.* Comparison of own results and literature data

From the *P-v-T* data, mole numbers and second virial coefficients have been computed by the method of least squares [7]. The standard deviation of the virial coefficient has been calculated according to Eq. (20). From the table of Student's distributions [11], the confidence interval at a 95%
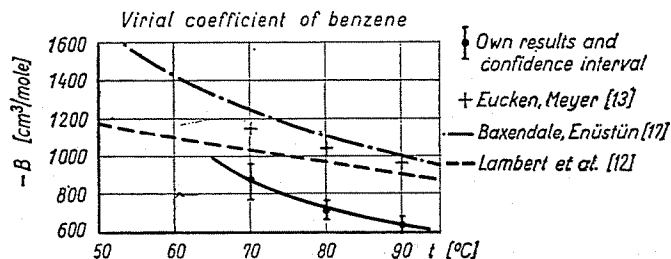
*Fig. 6.* Comparison of own results and literature data
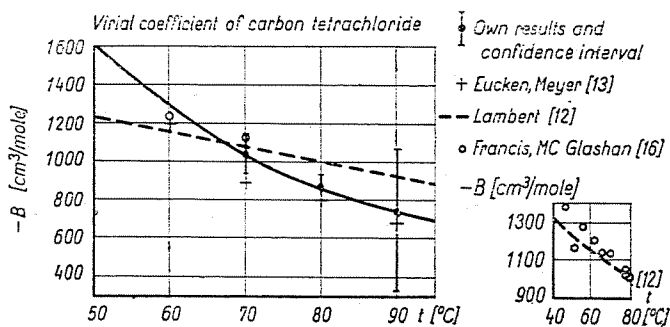


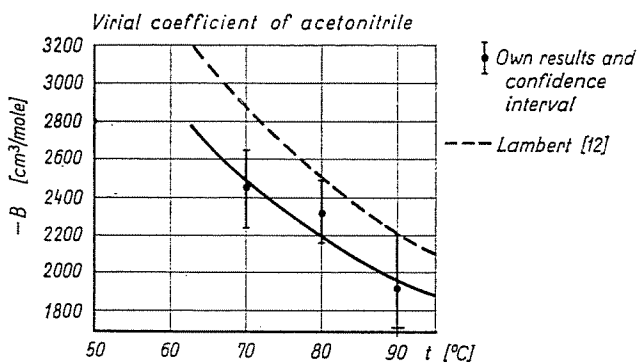*Fig. 7.* Comparison of own results and literature data



*Fig. 8.* Comparison of own results and literature data

probability level of the second virial coefficient has been determined:

$$B \pm t \cdot s_B, \tag{21}$$

where

    $t$    is the value of Student's $t$-distribution at a 95% probability level, and

    $s_B$  the empirical standard deviation of the virial coefficient.

Table II and Fig. 7 show the uncertainty of the virial coefficient of carbon tetrachloride, determined at 90 °C, to be rather high. According to Lambert et al. [12], above 80 °C no determination of the virial coefficient could be made since carbon tetrachloride vapours attacked mercury. This finding explains

### Table II

| Substance | 70 °C | | | 80 °C | | | 90 °C | | |
|---|---|---|---|---|---|---|---|---|---|
| | $B$ | $\pm ts_B$ | % | $B$ | $\pm ts_B$ | % | $B$ | $\pm ts_B$ | % |
| Methyl alcohol | −1412 | 56 | 4 | − 898 | 55 | 6 | − 633 | 46 | 7 |
| Ethyl alcohol | −1685 | 240 | 15 | −1456 | 130 | 9 | − 945 | 90 | 10 |
| Benzene | − 868 | 95 | 11 | − 716 | 57 | 8 | − 637 | 41 | 7 |
| Carbon tetra-chloride | −1042 | 102 | 10 | − 868 | 65 | 8 | − 730 | 355 | 48 |
| Acetonitrile | −2450 | 210 | 10 | −2320 | 166 | 7 | −1929 | 280 | 12 |

the inaccuracy of our measurements. Comparison of our results with the published ones [12 to 17] (Figs 4 to 8), permits the following statements to be made:

a) The second virial coefficients of methyl alcohol at 80 and 90 °C agree well with those by Eucken and Meyer [13], and at 80 °C also with those by Lambert et al. [12]. Values for 70 °C are also acceptable.

b) Values for ethyl alcohol are in good agreement with those by Lambert [14], and in poor agreement with those by Kretschmer and Wiebe [15].

c) Our own measurements on benzene gave for the second virial coefficients by 20 to 30% lower values than the published ones [12, 13, 16].

d) In the case of carbon tetrachloride, the second virial coefficient could only be determined at 90 °C with a high uncertainty, but results at 70 and 80 °C were in good agreement with the publications [12, 13, 17].

e) Only Lambert et al. [12] referred to results for acetonitrile. These are within the 95% confidence limit of our results.

Thus, in general, our own results are either in good agreement with published values, or they do not deviate by more than the data by various authors from each other.

The temperature dependence of the second virial coefficient is usually described according to Berthelot's equation

$$B = \frac{9}{128} \frac{RT_{cr}}{P_{cr}} \left( 1 - \frac{6 T_{cr}^2}{T^2} \right) = L - M/T^2 \qquad (22)$$

as a function of $\dfrac{1}{T^2}$.

Also our results have been processed in this way (Table III). Because of the narrow temperature range, these equations are only valid for interpolation, but are unsuitable for extrapolation.

## Table III

Temperature dependence of the second virial coefficients

| | |
|---|---|
| Methyl alcohol | $B = 5923.6 - 8.597 \cdot 10^8/T^2$ |
| Ethyl alcohol | $B = 4639 - 7.449 \cdot 10^8/T^2$ |
| Benzene | $B = 1317.7 - 2.563 \cdot 10^8/T^2$ |
| Carbon tetrachloride | $B = 1879.7 - 3.435 \cdot 10^8/T^2$ |
| Acetonitrile | $B = 2331.4 - 5.683 \cdot 10^8/T^2$ |

Berthelot's equation is suitable only for estimating the second virial coefficient of apolar compounds alone. From among the tested polar compounds, acetonitrile and methyl alcohol exhibited the following relationships [p. 281 in 14]:
Acetonitrile:

$$B/V_{cr} = 0.664 - 0.246 \, \exp \, (2.650 \, T_{cr}/T) \tag{23}$$

Methyl alcohol:

$$B/V_{cr} = 0.406 - 0.140 \, \exp \, (2.840 \, T_{cr}/T) \tag{24}$$

Values calculated in this way:

| | 70 °C | 80 °C | 90 °C |
|---|---|---|---|
| acetonitrile | −2705 | −2450 | −2220 |
| methyl alcohol | −1100 | − 975 | − 870 |

show a fairly good agreement with our results.
(The necessary critical data are found in [18])

## *Second virial coefficient of vapour mixtures*

The vapour–liquid equilibrium of real systems is described by:

$$\gamma_i x_i p_i^\circ = z_i y_i P \tag{25}$$

where $\gamma$ is the activity coefficient, and
$z$ the vapour correction factor.
The concentrations in the liquid and in the vapour phases $x$ and $y$ and the overall pressure of the system $P$ are quantities accessible to direct measurement. The vapour pressure of the pure liquid $p^\circ$ can be measured, or calculated from measurements, e.g. with Antoine's equation:

$$\log p^\circ = A - \frac{B}{C + t} \tag{26}$$

where $A$, $B$ and $C$ are constants of the Antoine equation.

However, the activity coefficient describing the non-ideal behaviour, and the vapour correction factor cannot be measured directly, neither can they be determined separately from Eq. (25). Rather far away from the critical state (at atmospheric or lower pressure), the vapour phase is characterized by a relatively low density, i.e. the molecules are spaced apart and interact much less than the molecules of the liquid of considerably higher density. Therefore it is a usual simplification to consider the non-ideal behaviour of the vapour–liquid system in the liquid phase, and the vapour phase as an ideal mixture of ideal gases. This simplification ($z_i = 1$) permits to calculate the activity coefficient from Eq. (25) (actually, the $\gamma_i/z_i$ value). The concentration dependence of the calculated activity coefficient is generally described by semi-empirical equations, such as Wilson's equation [19]. Its constants can be calculated from data measured at equilibrium:

$$\ln \gamma_k = - \ln \sum_{j=1}^{N} x_j + 1 - \sum_{i=1}^{N} \frac{x_i \varLambda_{ik}}{\sum_{j=1}^{N} x_j \varLambda_{ij}} \qquad (27)$$

where $\varLambda$ refers to constants of the Wilson equation. Wilson's equation is advantageous by fairly approximating the equilibrium of multicomponent systems using binary measurement results [20].

In several systems, the non-ideal behaviour is characteristic mainly of the liquid phase, but precise calculations often require the vapour correction factor to be taken into consideration.

Making use of the second virial coefficient, the vapour correction factor can be written as [21]:

$$z_i = \exp \left[ \frac{(B_{ii} - V_i) - (P - p_i)}{RT} + \frac{2 y_j^2 \delta_{ij} P}{RT} \right] \qquad (28)$$

where:

$$\delta_{ij} = \frac{2 B_{ij} - B_{ii} - B_{jj}}{2} . \qquad (29)$$

$B_{ij}$ is the so-called cross-coefficient for the interaction of two different molecules, of a value:

$$B_{ij} = \frac{B_e - y_i^2 B_{ii} + y_j^2 B_{jj}}{2 y_i y_j} \qquad (30)$$

provided the composition of the vapour mixture ($y_i$, $y_j$), the virial coefficients of the pure substances ($B_{ii}$, $B_{jj}$), and the second virial coefficient of the mixture ($B_e$) are known.

Our results were applied to determine the second virial coefficiens of the binary mixtures formed by ethanol, benzene and acetonitrile solvents. Apparatus and method were the same as those applied for determining the second virial coefficients of the pure substances. The mixtures were proportioned by weight, and the composition was checked by the refractive index.
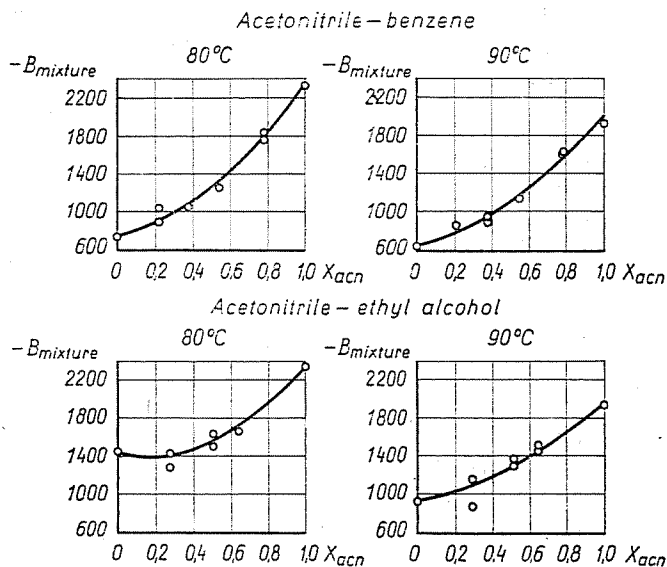
Acetonitrile — benzene



Acetonitrile — ethyl alcohol



*Fig. 9.* Concentration dependence of the second virial coefficient of mixtures

The second virial coefficients of the ethyl alcohol — benzene, acetonitrile — benzene and ethyl alcohol–acetonitrile binary mixtures have been measured, for which no published values were found. Solvent pairs ethyl alcohol — benzene; acetonitrile–benzene and ethyl alcohol–acetonitrile were tested in one, four and three compositions, respectively. One mixture was tested in five series at identical temperature and composition. The mole number and virial coefficient values (axis intersection and slope), calculated from each series, were compared in $F$-tests [11]. In the case of positive results, the data of the five series have been processed together. If the calculated $F$

Table IV

|  | 70 °C | 80 °C | 90 °C |
|---|---|---|---|
| Acetonitrile–ethanol | —1618 | —1126 | —1120 |
| Ethanol–benzene | —1339 | —1026 | — 980 |
| Acetonitrile–benzene | — | —1071 | — 987 |

value was higher than the critical one, that series which increased highly the $F$ value has been omitted, and the other series have been processed together.

Measured virial coefficients have been plotted *vs.* concentration (Fig. 9).

In knowledge of the second virial coefficients of the pure components, the cross-coefficients have been calculated from the second virial coefficients of the mixtures (Table IV).

*Impact of the exact description of the vapour phase on vapour–liquid equilibrium calculations*

Isobar data [24], molar ratios $x$ in the liquid phase and $y$ in the vapour phase, temperature $t$, further the Antoine constants of the substances and overall pressure $P$ were known. For each measurement point, tension was calculated by means of Antoine's equation. Vapour phase was described in three ways:

a) The vapour correction factor $z$ was taken as unit.

b) On the basis of thermodynamical relationships, the vapour correction factor $z$ was calculated by means of the second virial coefficients of the pure substances: $\delta_{ij} = 0$.

c) The vapour correction factor $z$ was calculated with the second virial and the cross-coefficients (Eq. 28).

The Wilson equation was fitted to the vapour–liquid equilibrium data, minimizing the sum of the squares, of the deviations of the measured and calculated vapour mole fraction values. Calculating the vapour correction factor $z$ by methods $b$ and $c$ gave a somewhat closer agreement between the measured and calculated $y$ values than by method $a$ under assumption $z = 1$.

The difference between the measured and calculated $y$ values can also be attributed to the inadequate description of the conditions by Wilson's equation. Therefore, the role of vapour correction has also been tested by thermodynamic consistency, calculating the value of integral

$$I = \int_{x_1=0}^{x_1=1} \log \frac{\gamma_1}{\gamma_2} \, dx_1 . \tag{31}$$

No evaluable deviation was found between $I$ values obtained with each of the three described modes of calculating $z$ (Figs 10, 11, 12). Thus, in the tested binary systems, no exact calculation of the vapour correction factor $z$ is necessary.

In these systems, benzene is an apolar molecule, while ethyl alcohol and acetonitrile are polar. Their behaviour is expected to substantially differ from the ideal. Nevertheless, the real behaviour of the vapour phase has little
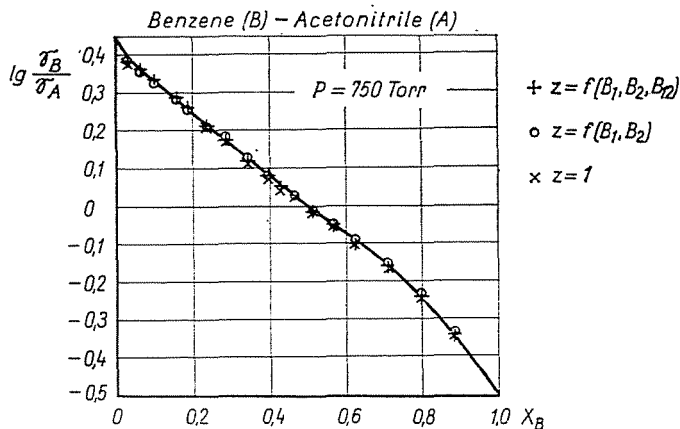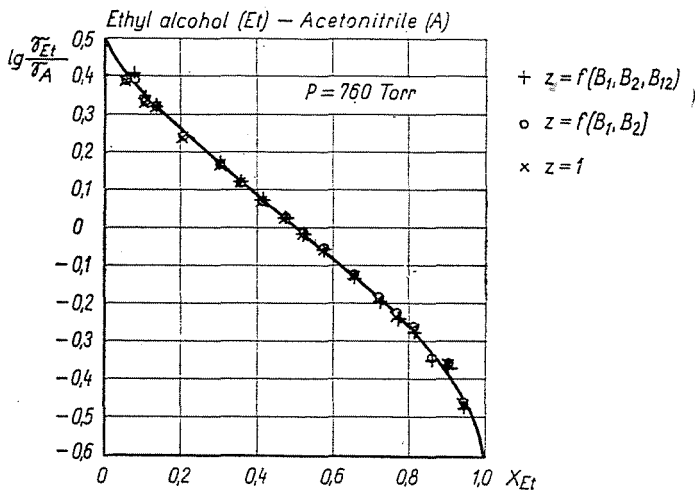
Fig. 10. Testing of the thermodynamic consistency



Fig. 11. Thermodynamical checking

importance for the vapour–liquid equilibrium. Namely, the interaction between the molecules strongly asserts itself in the liquid phase, the value of the activity coefficient differs considerably from unity, compared to it the interaction within the vapour phase is negligible.

Therefore, subsequent investigations using published results referred to systems with activity coefficients near unity, more affected by the nonideal behaviour of the vapour phase. Two systems of this kind have been selected: carbon tetrachloride–benzene [22] and acetonitrile–nitromethane [23].

The carbon tetrachloride–benzene system exhibits in the liquid phase a similar to ideal behaviour, in the vapour phase a behaviour similar to that
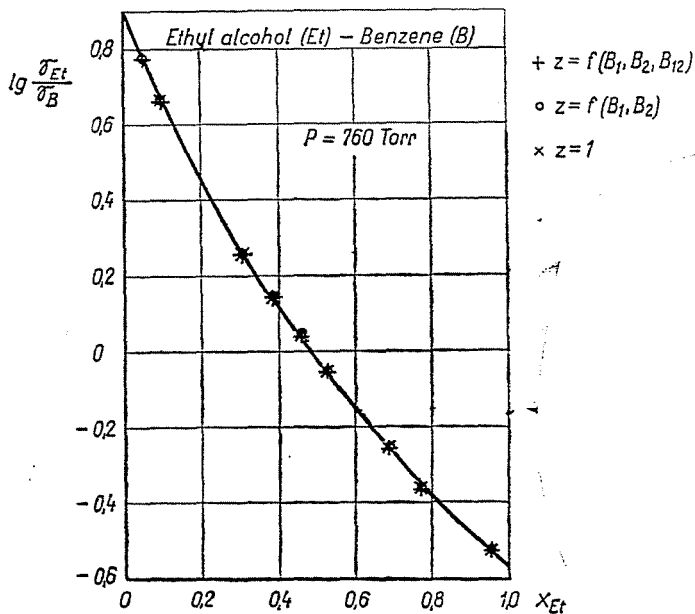
*Fig. 12.* Thermodynamical checking

of the ideal mixture of ideal gases (Table V), making the calculation of the vapour correction factor meaningless. On the other hand, the vapour correction factor of the acetonitrile–nitromethane system is important to calculate (Table VI). Forces acting between the molecules of different and of identical types are similar in magnitude (criterion of ideal mixtures), so that the value of the activity coefficient is near to unity.

**Table V**

Testing the thermodynamic consistency of a carbon
tetrachloride–benzene mixture

| $x1$ | $y1$ | $\left[\log \dfrac{\gamma_1}{\gamma_2}\right]_{z=1}$ | $\left[\log \dfrac{\gamma_1}{\gamma_2}\right]_{z=f(B_1, B_2)}$ |
|---|---|---|---|
| 0.1428 | 0.1666 | 0.028 | 0.029 |
| 0.2394 | 0.2702 | 0.019 | 0.021 |
| 0.3791 | 0.4105 | 0.006 | 0.007 |
| 0.4930 | 0.5204 | — 0.004 | — 0.002 |
| 0.4939 | 0.5215 | — 0.003 | — 0.002 |
| 0.6224 | 0.6411 | — 0.017 | — 0.015 |
| 0.7624 | 0.7719 | — 0.028 | — 0.027 |
| 0.8750 | 0.8780 | — 0.039 | — 0.038 |

J. LUKÁCS et al.

## Table VI

Testing the thermodynamic consistency
of an acetonitrile–nitromethane mixture

| $x1$ | $y1$ | $\left[\log \dfrac{\gamma_1}{\gamma_2}\right]_{z=1}$ | $\left[\log \dfrac{\gamma_1}{\gamma_2}\right]_{z=f(B_1,\ B_2)}$ |
|---|---|---|---|
| 0.0951 | 0.1741 | −0.01268 | 0.00052 |
| 0.1940 | 0.3255 | −0.01287 | 0.00001 |
| 0.2930 | 0.4539 | −0.01273 | −0.00018 |
| 0.3939 | 0.5638 | −0.01284 | −0.00063 |
| 0.4614 | 0.6325 | −0.01198 | 0.00000 |
| 0.5001 | 0.6674 | −0.01268 | −0.00083 |
| 0.6051 | 0.7548 | −0.01200 | −0.00050 |
| 0.8055 | 0.8925 | −0.01292 | −0.00210 |
| 0.9025 | 0.9488 | −0.01351 | −0.00304 |
| 0.9486 | 0.9737 | −0.01262 | −0.00231 |

On the other hand, owing to the interaction of the strongly polar molecules, the vapour phase of either the pure components, or in that of the mixture cannot be considered as an ideal gas, while being a nearly ideal mixture. Therefore, the value of the vapour correction factor differs from unity. Calculating the activity coefficients with both correction factors $z = 1$ and $z = f(B)$ shows the exact calculation of the vapour correction factor of this system to be of importance. For this system, calculation of integral (31) was needless. Namely, the ratio of activity coefficients calculated by assuming $z = 1$ is throughout of negative sign, while $z = f(B)$ yields initially positive values. Thus, without plotting and graphical integration it can be established that the latter values give better results. This is proved also by the fact that vapour composition values measured and calculated with Wilson's equation differ less if the vapour correction factor is taken into consideration.

It can be established, therefore, that at about 1 atmosphere, the calculated vapour–liquid equilibria of mixtures

1. with activity coefficient values substantially differing from one,
2. with activity coefficient values close to one, but with apolar molecules, are little influenced by the value of the virial coefficient.

On the other hand, for mixtures with activity coefficients near to one, but where the vapour phase cannot be considered as an ideal mixture of ideal gases due to the polarity and to the strong interaction of the molecules, the vapour correction has to be taken into consideration in equilibrium calculations and in testing the thermodynamic consistency of vapour–liquid equilibrium data. We wish to mention here that our investigations did not involve systems

of components strongly associating in the vapour phase, where the real behaviour of the vapour phase must be taken into consideration, irrespective of the behaviour of the liquid phase.

For details of measurements and calculations see [25].

## Summary

Vapour–liquid equilibrium calculations often ignore the non-ideal behaviour of the vapour phase. In this paper, the justification of neglect is investigated on measured $P$-$v$-$T$ data of pure organic solvents and their binary mixtures, and on published data. Except for systems containing components strongly associating in the vapour phase, vapour correction was found to be essential only for activity coefficient values in the liquid phase close to unity, and for polar molecules.

$P$-$v$-$T$ data were determined in a Boyle's apparatus. Mathematical statistical methods have been used to establish and develop the test method and to evaluate the results.

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