CHAPTER IV

COMPUTATION OF EXCESS FUNCTIONS FROM VAPOUR PRESSURE
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In the earlier work (56) for the determination of excess free energy for a binary mixture, the composition in the liquid and the vapour phase along with the total vapour pressure were determined experimentally. This method is quite tedious. Recently (5,57) it has been realised that it is possible to calculate the excess free energy from the composition in the liquid phase and the total vapour pressure. This method, if used carefully is very convenient and the results obtained by this method compare well with the earlier more tedious methods, particularly when suitable correction for the non-idealities of the vapours is taken into account. The method described below is due to Barker (5). The excess free energy, \( g^E \), has been chosen as a function of \( x \) with one or more adjustable parameters. The method of least squares has been used while choosing the parameters in order to minimise the errors in the total pressure. The function \( g^E \) in terms of \( x \) and these parameters is usually written (58) in the form

\[
g^E = x_1 x_2 (a + b (x_1 - x_2) + c (x_1 - x_2)^2 + \ldots \ldots \ldots) \ldots (1)
\]

where \( x_1 \) and \( x_2 \) are the mole fractions of the two
components.

The equation obeys the condition that $g^E$ should be zero for the pure components and can be used to fit experimental data with any order of accuracy by choosing the suitable number of constants $a$, $b$, $c$ ... .

Thermodynamically $g^E$ is given by the equation

$$g^E = RT \left( x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \right) \quad \cdots \quad (2)$$

where $\gamma_1$ and $\gamma_2$ are the activity coefficients for components 1 and 2 and $R$ is the gas constant and $T$ is the temperature in °K.

The activity coefficients and chemical potentials are related by the equations (59)

$$\lambda_i^E = RT \ln \gamma_i$$

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where $\lambda_i^E$ and $\lambda_2^E$ are the changes in chemical potential in excess of the changes due to an ideal solution, $P$ is the total pressure, $P_1$ and $P_2$ are the vapour pressures of the components in pure form, $x$ and $y$ are the mole fractions in the liquid and vapour phases,
V₁ and V₂ are the liquid molar volumes, B₁₁ and B₂₂ are the second virial coefficients of the pure components and S₁₂ is given as

\[ S_{12} = 2B_{12} - B_{11} - B_{22} \]

where B₁₂ is the second virial coefficient in the mixed vapour.

From equations (3) it follows that

\[ P = \gamma_1 P_1' + \gamma_2 P_2' \]

\[ p_{1} = x_{1} P_{1} \exp \left( \left( V_{1} - B_{11} \right) \left( P - P_{1} \right) / RT \right) - P S_{12} y_{2}^{2} / RT \]  

\[ p_{2} = x_{2} P_{2} \exp \left( \left( V_{2} - B_{22} \right) \left( P - P_{2} \right) / RT \right) - P S_{12} y_{1}^{2} / RT \]

Here P₁' and P₂' are the values of the two partial pressures, if the solutions were ideal in the liquid phase and non-ideal in the vapour phase. B₁₂ has been assumed to be the arithmetic mean of B₁₁ and B₂₂ so that S₁₂ becomes zero and reduces the equation (5) and (6) to

\[ P_{1}' = x_{1} P_{1} \exp \left( \left( V_{1} - B_{11} \right) \left( P - P_{1} \right) / RT \right) \]

\[ P_{2}' = x_{2} P_{2} \exp \left( \left( V_{2} - B_{22} \right) \left( P - P_{2} \right) / RT \right) \]

On the basis of equation (1) the activity coefficients
can be written as

\[ \ln \gamma_i = A_1 + B_1 + C_{n1} + \ldots \ldots \ldots \ldots \) \ldots (9) \\
\ln \gamma_i = A_2 + B_2 + C_{n2} + \ldots \ldots \ldots \ldots \) \ldots (9) \\

where \( l_1 = x_2^2, m_1 = -x_2^2(1-4x_1), \) \\
\( n_1 = x_2^2(1-3x_1 + 12x_1^2), l_2 = x_1^2, \) \\
\( m_2 = x_1^2(1-4x_2), n_2 = x_1^2(1-3x_2 + 12x_2^2). \) \\

and \( A = a/RT, B = b/RT \) and \( C = c/RT \)

The constants \( A, B \) and \( C \) in equations (9) are determined by making successive approximations. In the beginning, it has been assumed that the solution behaves as a regular solution so that \( B \) and \( C \) become zero and if neglecting the corrections for the non-ideality in the vapour phase \( \gamma \) can be obtained from the equation

\[ A = 4 \ln \left( \frac{2P^*}{P_1 + P_2} \right) \]

where \( P^* \) is the vapour pressure of the binary mixture at 0.5 mole fraction read graphically. Hence by using equations (9) \( \gamma_i \) and \( \gamma_i \) can be calculated and from equations (7) and (8) \( p_1' \) and \( p_2' \) can be calculated. Knowing the values of \( \gamma_i, \gamma_i, p_1' \) and \( p_2' \), the total pressure \( P \) can be calculated by using the equation (4). Hence the residual pressure \( R \) is
given by the equation

\[ R = P_{\text{exp.}} - P_{\text{calc.}} \]

and the derivatives are given by

\[
\begin{align*}
\frac{dP}{dA} &= l_1 Y_1 p_1' + l_2 Y_2 p_2' \\
\frac{dP}{dB} &= m_1 Y_1 p_1' + m_2 Y_2 p_2' \\
\frac{dP}{dC} &= n_1 Y_1 p_1' + n_2 Y_2 p_2' 
\end{align*}
\]

The changes \$A$, \$B$ and \$C$ are made in the values of \$A$, \$B$ and \$C$ in order to reduce the residual pressures to zero by fitting the least squares in the equation

\[ (\frac{dP}{dA}) \delta A + (\frac{dP}{dB}) \delta B + (\frac{dP}{dC}) \delta C = R \quad \ldots (12) \]

\$A$, \$B$ and \$C$ can be determined by solving the equations

\[
\begin{align*}
\delta A &\leq (\frac{dP}{dA})^2 + \delta B \leq (\frac{dP}{dA})(\frac{dP}{dB}) \\
&\quad + \delta C \leq (\frac{dP}{dA})(\frac{dP}{dC}) = \varepsilon R(\frac{dP}{dA}) \\
\delta A &\leq (\frac{dP}{dA})(\frac{dP}{dB}) + \delta B \leq (\frac{dP}{dB})^2 \\
&\quad + \delta C \leq (\frac{dP}{dB})(\frac{dP}{dC}) = \varepsilon R(\frac{dP}{dB}) \quad \ldots (13) \\
\delta A &\leq (\frac{dP}{dA})(\frac{dP}{dC}) + \delta B \leq (\frac{dP}{dC})(\frac{dP}{dC}) \\
&\quad + \delta C \leq (\frac{dP}{dC})^2 = \varepsilon R(\frac{dP}{dC})
\end{align*}
\]

the summations are taken over all the experimental
points. The value of $\delta A$, $\delta B$ and $\delta C$ are added to the initial values of $A$, $B$ and $C$ and making use of these values, the residual pressures are again calculated and the process is repeated till no further improvement is obtained between $P_{\text{exp.}}$ and $P_{\text{calc.}}$. Making use of the final values of $V_1$ and $V_2$ or $A$, $B$ and $C$, $g^E$ can be calculated from equation (2) or equation (1). In the above calculations only three parameters $A$, $B$ and $C$ have been used and four parameters i.e., $A$, $B$, $C$ and $D$ were also tried but did not give any significant improvement in the results, hence it was decided to use only three parameters.

The values of $g^E$ at different temperatures can be used for calculation of $h^E$ and $s^E$. But the values of $h^E$ and $s^E$ thus obtained are usually one order of magnitude less accurate than the corresponding accuracy in $g^E$. In particular, if the value of $g^E$ is not too large the error is considerable. Therefore, it is preferable to obtain the value of $h^E$ from direct measurement. We found that with our data $h^E$ could be obtained with reasonable accuracy as compared with the direct measurements.

COMPUTATION: The calculations have been made on I. B. M. 1620 computer. The computer programme was
written in Fortran with Format. The programme had to be broken into three parts because the memory available in the computer was not sufficient. The programmes are given and discussed in appendix D. The sample calculations showing the variation of residual pressures with the change in the values of A, B and C for the system n-hexane/benzene at 94.0°C are given in Table III.
Table III

Variation in Residual Pressures with the change

in the Values of A, B and C.

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<th>Mole fraction $x_1$</th>
<th>Zeroth Iteration</th>
<th>First Iteration</th>
<th>Second Iteration</th>
<th>Third Iteration</th>
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