저온 고압에서 Ethylene Gas의 열역학적 상태 방정식 및 이에 따르는 Computer Program의 개발

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A Study on the Development of an Equation of State and its Computer Program for Ethylene Gas at Low Temperature and High Pressure.

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요 약

Ethylene gas의 $P-V-T$ 관계를 임계점 이하(9.5°C, 51 bar)에서 가장 잘 나타낼 수 있논 상태 방정식 및 이의 계수를 최근 발표된 실험 data를 이용해서 비선형 최소자승법에 의해 구하는 compruter program을 개발하였다. 본 연구에서는 243—297°K의 온도와 50 bar 미만의 범위에 있는 90개의 data point를 사용하여 수정된 Bender 방정식에 상기 비선형 최소 자승법에 의해 curve fitting하여 6-parameter및 10-parameter 방정식들의 계수를 구하였으며 이들로부터 계산된 밀도의 RMS deviation은 0.1%, Michels의 실험 data로부터의 RMS deviation은 0.15%로서 이들 방정식들이 상기 실험 범위내에서 0.15% 이내의 오차 한계내에서 사용될 수 있다.

Abstract

An equation of state, which can best represent the $P-V-T$ data ethylene gas below the cirtical point (9.5°C, 51 bar), and its coefficients were determined by means of the non-linear least-squares technique using recently published experimental data. A total of 90 data points, ranging 243—297° K temperature and below 50 bar pressure, were fitted to the modified Bender equation and the coefficients of the 6-parameter and 10-parameter equations were obtained. The RMS deviations of the calculated denities are 0.1% from the experimental data used in this curve fitting, and 0.15% from Michels data. Therefore these equations of state can be used within the experimental range with a probable error of ±0.15%.

1. Introduction

Ever since the discovery of ethylene by, among others, the Dutch chemists at the end of 18th century, the importance of ethylene in the field of chemistry as one of the basic chemical compounds has been ever increasing. Unlike methane, which is abundant in nature as the main constituent of natural gas, ethylene has to be manufactured artificially from other organic materials such as ethane, propane, alcohol, etc. Nevertheless its importance was firmly established early in the 20th century because of the versatility of its chemical reactions with other compounds due primarily to its unsaturated double bond. The use of ethylene on a tonnage scale as a raw material in synthetic organic chemistry dates from 1933 when the process of polymerization of ethylene into polyethylene was discovered in the Winnington Laboratories of ICI Ltd. by Gibson and Fawcett. [1]

Despite the importance, actual volumetric measurement data for ethylene and for its mixtures with other gases are quite rare in the literature mainly due, it is believed, to the difficulties associated with accurate pressure measurement in a low temperature system. Thus the work of Michels et al, [2,3,4] published more than two decades age, is still regarded as the most reliable data. Although there are some other sources of data published, in most cases, however, the data are believed to be less accurate than what was originally claimed.

For this reason both Angus[5] and Miller[1] have presented P-V-T data according to Michels work almost exclusively in their extensive compilations, 'IUPAC ETHYLENE TABLE', and 'Ethylene and Its Industrial Derivatives' respectively.

The experimental range of Michels work, however, extends only from 0°C upwards and for this reason the region below 0°C in the IUPAC table is left blank (see *Fig.* 1). In 1976 Lee[6] reported the results of experimental P-V-T measurements on ethylene in the temperature range 243—297°K upto 41 bar pressure and for the methane-ethylene system using Burnett type apparatus. [19]

Accurate determination of thermodynamic properties such as entropy, S, or Gibbs free energy, G, requires either as many data points as possible, or an accurate equation of state which can represent the data points within the experimental error.

Therefore many equations of state, both theoretical and empirical, have been proposed, such as van der Waals, [7] Redlich and Kwong, [8] and Benedict-Webb-Rubin or simply BWR equation, [9] etc. Among these the BWR equation is very complex (8 parameters), and therefore, it is laborious to solve such an equation. For this reason, despite its high accuracy, it has rarely been used until recently in the field of engineering. The difficulties, however, have been overcome by the use of computing machines which allow one to solve quite complex equations of state.

In general the most accurate equations are also the most complex, thus various equations with more parameters have been proposed. In 1963 Strobridge proposed a 16-coefficient equation, whose parameters for nitrogen from 63 to 300°K upto about 200 bar were determined by a least-squares curve fit. [10] In 1970 Bender

[11] modified and further extended it to a 20-coefficient equation which can be expressed as

$$P = \rho T \{ R + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 \\ + (G + H\rho^2)\rho^2 \exp(-a_{20}\rho^2) \} \quad (1)$$

whre, $B, C, \cdots H$ are expressed as functions of temperature containing a total of 19 coefficients. The 20 coefficients in Eq. 1 were determined for nitrogen, argon, oxygen[12] carbon dioxide and methane[13] for the whole fluid region from the experimental $P-V-T$ data. Steward and Jacobsen increased the number of parameters to 33 and determined them for nitrogen and oxygen by means of a least-squares curve fitting technique. [14]

Another important equation is the virial equation of state which is an expansion of the compressibility factor as an infinite series in powers of density.

$$Z = PV/RT = 1 + B\rho + C\rho^2 + D\rho^3 + \cdots \quad (2)$$

Statistical mechanical considerations show that the 2nd virial coefficient, B, is a function of the interaction between pairs of molecules, the 3rd virial coefficient, C, is a function of the interaction between three molecules, and so on. Thus the 2nd virial coefficient is one of the few macroscopic properties which can provide quantitative information on the intermolecular forces between a pair of molecules. [16,17]

Although a power series in density such as the virial equation can be used represent simultaneously both liquid and gas phases it has not been particularly successful in the past, hence the use of an exponential term in the $B-W-R$ and succeeding equations. Moreover it is believed that the statistical mechanical virial equation does not converge at high densities. [7]

From a practical point of view there is an important difference between the virial equation

and the modified $B-W-R$ equation (e. g. Bender equation) in that, in Eq. 1 the compressibility factor is expressed in terms of density as well as temperature, while in the virial equation the compressibility factor is expressed in terms only of density. It follows that the coefficients of the virial equation being functions of temperature can be fitted to $P-V-T$ data only for a given isotherms. This makes Eq. 1 particularly valuable when handling experimental $P-V-T$ results which contain only a limited number of data points on each isotherm.

As will be discussed below, not all the 20-coefficients in Eq. 1 are necessary in representing a restricted range of $P-V-T$ surface (i. e. gas phase only). In this work, therefore, the best form of an equation of state and their parameters are determined by modifying the Bender equation, Eq. 1, using the experimental $P-V-T$ data by means of the non-linear least-squares method.

2. P-V-T data

As was mentioned earlier, few PVT data of ethylene have been published. Above $0°C$ the principal data, which have been available for many years, are due to Michels and his co-workers of the van der Waals Laboratory. The data produced by the laboratory, however, are limited in temperature range from $0°C$ to $150°C$, although ranging widely in pressure, from 16 to 3042 bar. Michels, de Bruyter and Nissen published, in 1936, density measurements along isotherms from $0°C$ to $150°C$ at $25°C$ intervals measured at pressures from 16 to 274 bar. In 1942 Michels and Geldermans corrected the previous data due to inaccuracy of the thermometer used in their experiment. [3] There is a

group of 16 points from the Kammerlingh Onnes Laboratory in the range of 272—293°K and 22 —38 bar. [18] However Angus criticised the accuracy of the data due to lack of selfconsistency. [5] Butcher and Dadson reported the experimental 2nd and 3rd virial coefficients of ethylene by using a Burnett type apparatus in the range of 263—473°K. [20]
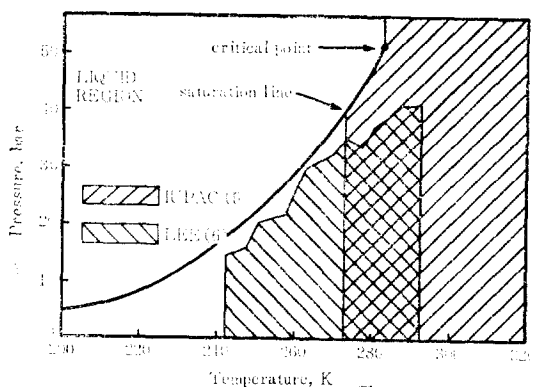

Fig. 1. The experimental range

In this paper, however, the authors dealt only with the virial coefficients and did not present actual experimental PVT data. Besides, the 2nd virial coefficient at $0°C(-161.4cc/gm$-mole) differs from that of Michels(-167.8)[21] and of Lee (-169.11).

In 1976 Lee reported a total of 90 data points along 12 isotherms from 243.7°K to 293°K at pressures from 3 to 41 bar. [6] These data are the most recent experimental values and to be considered most accurate (the maximum probable error in the compressibility factor was estimated as less than 0.001).

Thus, for the reasons given above, Lee's data were basically selected for the non-linear least-squares curve fit and the comparison was made between this work and that of Michels and co-workers at two temperatures, 0°C and 25°C.

3. The Non-Linear Least-Squares Procedure

The equation of state chosen for the curve fitting is the Bender equation,

$$P = \rho T \{ R + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 + (G + H\rho^2) \rho^2 \ \rho^2 \exp(-a_{20}\rho^2) \}$$

where $B = a_1 - a_2/T - a_3/T^2 - a_4/T^3 - a_5/T^4$

$C = a_6 + a_7/T + a_8/T^2$

$D = a_9 + a_{10}/T$

$E = a_{11} + a_{12}/T$

$F = a_{13}/T$

$G = a_{14}/T^3 + a_{15}/T^4 + a_{16}/T^5$

$H = a_{17}/T^3 + a_{18}/T^4 + a_{19}/T^5$

$a_1, a_2, \cdots\cdots a_{20}$ are parameters.

As a primary test the Bender equation was modified into a series of equations, each having different number of coefficients of 6, 9, 10 and 13. The exponential term, or correction term, of the equation was out of consideration, since this term was considered to be unnecessary in the gas phase alone. As will be seen, the 6-coefficient equation was good enough to represent all data points selected in this work. In order to compare the results from the different equation, 6 and 10-coefficient equations were chosen and the experimental data were treated accordingly.

The final forms of the two equations are,

$$P = \rho T \{ R + (a_1 - a_2/T - a_3/T^2)\rho + (a_4 + a_5/T)\rho^2 + a_6\rho^3 \} \qquad (3)$$

and

$$P = \rho T \{ R + (a_1 - a_2/T - a_3/T^2 - a_4/T^3)\rho + (a_5 + a_6/T + a_7/T^2)\rho^2 + (a_8 + a_9/T)\rho^3 + a_{10}\rho^4 \} \qquad (4)$$

The basic principle of the least-squares procedure is that the m parameters $a_1, a_1, \cdots a_m$ are

best fit to the equation of state when the objective function, S, which is defined as the sum of the weighted squares of the residuals, is a minimum with respect to the m least–squares parameters,

$$S=\sum_{j=1}^{n}\omega_j R_j{}^2 \tag{5}$$

where ω_j is a weighting factor which is defined as the reciprocal of the expected variance in the j'th residual,

$$\omega_j=1/\sigma_{R_j}^2 \tag{6}$$

and n is the number of data point.

The residual, R_j, is defined as the difference between an observed dependent variable, P_j, and its adjusted value, P_j'

$$R_j=P_j - P_j' \tag{7}$$

The adjusted value, P_j' is calculated from the equation of condition with m least–squares parameters,

$$f'(P_j', \rho_j, T_j, a_1, a_2, \cdots\cdots a_m)=0 \tag{8}$$

This is the general formulation of the least–squares problem as described by Deming.[22]

$\sigma_{R_j}^2$ in Eq. 6 is given by[23]

$$\sigma_{R_j}^2=\{YmS) \cdot P_j\}^2 \tag{9}$$

The root–mean–square deviation of the adjusted pressure calculated from the current values of a_k's is given by

$$YmS=\left\{\frac{\sum_j[(P_j'-P_j)/P_j]^2}{N}\right\}^{\frac{1}{2}} \tag{10}$$

Now the objective function, S, is to be minimised with respect to each of the m least squares parameters, $a_1, a_2, \cdots\cdots a_m$, thus

$$\frac{\partial S}{\partial a_k}=0 \quad\text{for}\quad k=1,2,\cdots\cdots m \tag{11}$$

By substituting Eq. 5 into Eq. 11, we obtain

$$\frac{\partial}{\partial a_k}(\sum_j\omega_j R_j{}^2)=2\sum_j\omega_j R_j\frac{\partial R_j}{\partial a_k}=0$$

or

$$\sum_j \omega_j R_j\frac{\partial R_j}{\partial a_k}=0 \tag{12}$$

for $k=1,2,\cdots\cdots m$ (m is 6 for Eq. 3, and 10 for Eq. 4).

This set of m equations are known as the normal equations and they are non–linear in the parameters. The non–linear normal equation, Eq. 12, can be linearized by means of the Gauss–Newton method of linearization. In this method it is assumed that there exist the approximated values of the parameters, a_k', such that

$$a_k'=a_k+\varDelta a_k \tag{13}$$

The residual, R_j, then may be expanded as a Taylor series about its value when S is a minimum,

$$R_j'(a_1', a_2', \cdots a_m')=R_j(a_1, a_2, \cdots a_m)+$$
$$\left(\varDelta a_1 \frac{\partial}{\partial a_1}+\varDelta a_2\frac{\partial}{\partial a_2}+\cdots \varDelta a_m\frac{\partial}{\partial a_m}\right)R_j+$$
$$\frac{1}{2!}\left(\varDelta a_1\frac{\partial}{\partial a_1}+\varDelta a_2\frac{\partial}{\partial a_2}+\cdots\varDelta a_m\frac{\partial}{\partial a_m}\right)^2$$
$$R_j+\cdots\cdots \tag{14}$$

By assuming $\varDelta a_k$ be small enough so that the terms higher than the first derivatives in Eq. 14 may be neglected,

$$R_j'(a_1', a_2', \cdots a_m')=R_j(a_1, a_2, \cdots a_m)+$$
$$\varDelta a_1\frac{\partial R_j}{\partial a_1}+\varDelta a_2\frac{\partial R_j}{\partial a_2}+\cdots\varDelta a_m\frac{\partial R_j}{\partial a_m} \tag{15}$$

or by rearranging Eq. 15 we obtain

$$R_j(a_1, a_2, \cdots a_m)=R_j'(a_1', a_2', \cdots a_m')$$
$$-\left\{\varDelta a_1\left(\frac{\partial R_j}{\partial a_1}\right)+\varDelta a_2\frac{\partial R_j}{\partial a_2}\right)+\cdots$$
$$\cdots\varDelta a_m\left(\frac{\partial R_j}{\partial a_m}\right)\right\} \tag{16}$$

This residual, which is now expressed in terms of the approximated values, a_k', is substituted into Eq. 12,

$$\sum_j\omega_j\left(\frac{\partial R_j}{\partial a_k}\right)\left\{R_j(a_1', a'_2, \cdots a_m')-\right.$$

$$\left(\varDelta a_1 \frac{\partial R_j}{\partial a_1} + \varDelta a_2 \frac{\partial R_j}{\partial a_2} + \cdots \varDelta a_m \frac{\partial R_j}{\partial a_m}\right)\} = 0 \tag{17}$$

Hence

$$\varDelta a_1 \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_k}\right)\left(\frac{\partial R_j}{\partial a_1}\right) + \varDelta a_2 \sum_j \omega_j$$

$$\left(\frac{\partial R_j}{\partial a_k}\right)\left(\frac{\partial R_j}{\partial a_2}\right) + \cdots \varDelta a_m \sum_j \omega_j$$

$$\left(\frac{\partial R_j}{\partial a_k}\right)\left(\frac{\partial R_j}{\partial a_m}\right)$$

$$= \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_k}\right) R_j'(a_1', a_2', \cdots a_m') \tag{18}$$

for $k = 1, 2, \cdots\cdots m$

In matxix notation, Eq. 18 are

$$\underline{X} \cdot \varDelta \underline{a} = \underline{Y} \tag{19}$$

whre

$$\underline{X} = \begin{vmatrix} \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_1}\right)\left(\frac{\partial R_j}{\partial a_1}\right) & \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_1}\right)\left(\frac{\partial R_j}{\partial a_2}\right) \\ \qquad\cdots\cdots \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_1}\right)\left(\frac{\partial R_j}{\partial a_m}\right) \\ \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_2}\right)\left(\frac{\partial R_j}{\partial a_1}\right) & \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_2}\right)\left(\frac{\partial R_j}{\partial a_2}\right) \\ \qquad\cdots\cdots \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_2}\right)\left(\frac{\partial R_j}{\partial a_m}\right) \\ \qquad\cdots\cdots\cdots\cdots \\ \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_m}\right)\left(\frac{\partial R_j}{\partial a_1}\right) & \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_m}\right)\left(\frac{\partial R_j}{\partial a_2}\right) \\ \qquad\cdots\cdots \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_m}\right)\left(\frac{\partial R_j}{\partial a_m}\right) \end{vmatrix}$$

thus $\underline{X}$ is $a(m \times m)$ square symmetric matrix and both $\underline{Y}$ aand $\varDelta \underline{a}$ are column vectors, i. e.

$$\underline{Y} = \begin{vmatrix} \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_1}\right) R_j'(a_1', a_2', \cdots a_m') \\ \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_2}\right) R_j'(a_1', a_2', \cdots a_m') \\ \sum_j \omega_j \left(\frac{\partial R_j}{\partial a_m}\right) R_j'(a_1', a_2', \cdots a_m) \end{vmatrix}$$

and

$$\varDelta a = \begin{vmatrix} \varDelta a_1 \\ \varDelta a_2 \\ \vdots \\ \varDelta a_m \end{vmatrix}$$

By multiplying both sides of Eq. 19 by the inverse mitrix of $\underline{X}$,

$$\underline{X}^{-1} \cdot \underline{X} \cdot \varDelta \underline{a} = \underline{X}^{-1} \cdot \underline{Y} \tag{20}$$

hence

$$\varDelta \underline{a} = \underline{X}^{-1} \cdot \underline{Y} \tag{21}$$

Eq. 21 is the solution to Eq. 19. After having calculated the solution of Eq. 21, the new approximation to a_k is given by

$$a_k = a_k' - \varDelta a_k \tag{22}$$

These new values of a_k are used in the calculation of R_j' in Eq. 16, and the solution of normal equation, Eq. 19. The iteration was continued until all the $\varDelta a_k$'s have converged to predetermined accuracies of each parameter.

4. Computation and Description of Computer Program

The computer program was written in FOR-TRAN IV language for use on the KIST CDC CYBER computer. Unlike the graphical method of data reduction, in the non-linear least-squares method, first approximated values of the least-squares parameters must be supplied before the iteration commences. These first supplied values must be near enough to the true values so that the condition for the convergence of this procedure(i. e. from Eq. 14 to Eq. 15) is not violated, otherwise the iteration normally does not converge or, sometimes converges to any false values.[24] In the case of the virial equation (Eq. 2) reasonably accurate virial coefficients for the initial values can be found in the literature [17]. In the case of the modified Bender equations no information was available as to the values of these coefficients.

The first approximated values were, therefore, determined from the experimental data and the equation of state. Thus from N points of data a set of N equations were established according to the equation chosen, for example,

$$P_k = \rho_k T_k \{R + (a_1 - a_2/T_k - a_3/T_k^2)\rho_k +$$

$$(a_4 + a_5/T_k)\rho_k^2 + a_\epsilon\rho_k^3\} \tag{23}$$

for $k = 1, 2, \cdots N$(for N is greater than 6 in this case). or

$$\left(\frac{P_1}{\rho_1 T_1 R} - 1\right)\frac{R}{\rho_1} = a_1 - a_2/T_1 - a_3/T_1^2$$
$$+ a_4\rho_1 + a_5\rho_1/T_1 + a_6\rho_1^2$$
$$\left(\frac{P_N}{\rho_N T_N R} - 1\right)\frac{R}{\rho_N} = a_1 - a_2/T_N$$
$$- a_3/T_2^N + a_4\rho_N + a_5\rho_N/T_N + a_\epsilon\rho_N^2 \tag{24}$$

Eq. 24 can be written in matrix notation

$$\begin{pmatrix} 1 & -1/T_1 & -1/T_1^2 & \rho_1 & \rho_1/T_1 & \rho_1^2 \\ 1 & -1/T_2 & -1/T_2^2 & \rho_3 & \rho_2/T_2 & \rho_2^2 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1 & -1/T_N & -1/T_N^2 & \rho_N & \rho_N/T_N & \rho_N^2 \end{pmatrix}$$
$$\begin{pmatrix} a_1 \\ a_2 \\ \cdot \\ a_6 \end{pmatrix} = \begin{pmatrix} (Z_1-1)\dfrac{R}{\rho_1} \\ (Z_2-1)\dfrac{R}{\rho_2} \\ \vdots \\ (Z_N-1)\dfrac{R}{\rho_N} \end{pmatrix} \tag{25}$$

or

$$\underline{X} \cdot \underline{A} = \underline{Y} \tag{26}$$

where $\underline{X}$ is a $(N \times 6)$ matrix and both $\underline{A}$ and $\underline{Y}$ are column matrices.

By assuming that all the PVT data in the matrices $\underline{X}$ and $\underline{Y}$ were 'exact', the solution of $\underline{A}$ in Eq. 26 is straightforward:

$$X^T \cdot X \cdot A = X^T \cdot Y \tag{27}$$

where X^T = transpose of matrix X, thus $(X^T \cdot X)$ becomes a (6×6) square matrix. From Eq. 27

$$(\underline{X}^T \cdot \underline{X})^{-1} \cdot (\underline{X}^T \cdot \underline{X}) \cdot \underline{A}$$
$$= (\underline{Y}^T \cdot \underline{Y})^{-1} \cdot (\underline{Y}^T \cdot \underline{Y}) \tag{28}$$

or

$$\underline{A} = (\underline{Y}^T \cdot \underline{X})^{-1} \cdot (\underline{X}^T \cdot \underline{Y}) \tag{29}$$

where $(\underline{X}^T \cdot \underline{X})^{-1}$ is an inverse matrix of $(\underline{X}^T \cdot \underline{X})$. The column matrix $\underline{A}$ was solved (for which a computer program was written) and the a's were supplied as the first approximate values of the least-squares parameters.

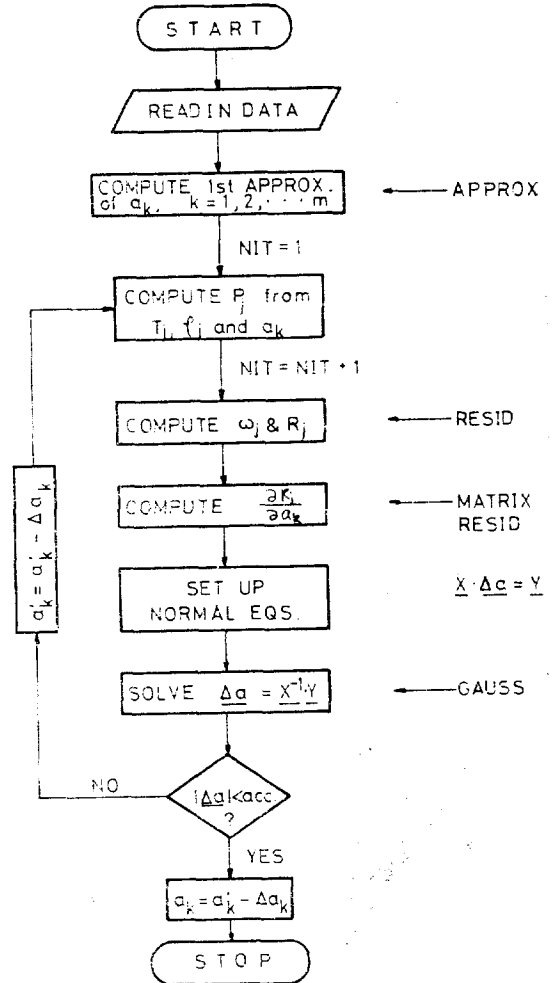In *Fig.* 2. the flow-chart for the computer

Fig. 2. Flow chart

program of this work is shown in connection with their relevant SUBROUTINEs at various parts of the main program.

Although the SI units are recommended, the pressure and density in actual computation are expressed in bar(=10^5N/sq. m) and gm-mole/cc (=10^3kg-mole/cu. m) due mainly to the inconveniently large number of pressure in SI unit and partly to convention.

The descriptions of main program and each subroutine are as follows.

In the main program, JWLEE, P_j, T_j, and

ρ_j are read in first. Then by calling APPROX the first approximated values of a_k' are calculated according to Eq. 29. After computing P_j' from T_j, ρ_j, and the a_k' using Eq. 3 or Eq. 4 subroutine RESID is called, in which the weighting factors, ω_j, is calculated by means of Eqs. 6, 9, and 10. The approximated residual, R_j', is calculated basically from Eq. 7 together with the equation of condition Eq. 3 or Eq. 4 using a_k' instead of a_k.

The elements of the matrices $\underline{X}$ and Y in Eq. 18 are calculated and stored by calling another subroutine MATRIX. The calculation of the partial derivatives in Eq. 16 is in principle impssible without knowing true residual R_j. The derivatives, $\frac{\partial R_j'}{\partial a_k}$ are therefore determined numerically by changing each value of a_k' b y0.001% in turn and recalling RESID. These are used as approximations to $\frac{\partial R_j}{\partial a_k}$. This approximation, however, is exact at the convergence point, that is, when $\Delta a_k = 0$.

The normal equations, Eq. 19, are then solved by calling GAUSS, which solves aset of simultaneous linear equations (upto 100 equations) by means of a Gauss-Jordan double-pivotal elimination. The calculated $\Delta a'_k$s by GAUSS were then compared with predetermined values of accuracies, e.g. $|\Delta a_1| < 10^{-1}$. When the $\Delta a'_k$s are larger than the accuacies, new approximated values were calculated according to Eq. 13 and suboutines RESID, MATRIX and GAUSS.

In the main program and the subroutines COMMON statement (labelled or unlabelled) was not used and all the informations were transferred between the main program JWLEE and relevant subroutines throug the 'argument lists' of subprograms so that each subprogram can be used by other users independent of the main program and of any other subprograms.

5. The Results

As was mentioned in section 3, all the 20 parameters in Bender equation (Eq. 1) were not needed to represent the PVT data within the range of this work (see $Fig. 1.$). Thus the number of the parameters of the original Bender equation was adjusted and the non-linear least-squares procedures showed that equations with 6 or more coefficients could represent within the experimental range of this work. 6 and 10-parameter equations, as examples, were therefore chosen and their least-squares parameters are presented in $Table$ 1.

With appropriate first approximated values(see section 4) the iteration of this procedure took normally 90 seconds (in CP time) for 6 coefficients and 130 seconds for 10 coefficients on CDC CYBER machine.

6. Discussion

From the point of view of the least-squares principle better equation necessarily gives smaller value of the objective function, S, given by Eq. 5. With parameters in $Table$ 1. the two equations gave similar values of the objective functions, i.e.

$$S_6 = 0.1223E - 05$$
$$S_{10} = 0.1151E - 05$$

Moreover the root-mean-square deviations of the calculated values of densities from those of experimental ones were, in both cases, less than 0.1%, which is within the experimental error of the data (0.15%).

In order to test the goodness of the Eq. 3 and Eq. 4 together with the parameters in $Table$ 1, the comparison was made between this work and that of Michels[3] at two isotherms 0°C and 25°C, by calculating the densities at Michels experimental pressures by Newton-Raphson iter

Table 1. The Least-Squares Parameters

	Eq. 3	Eq. 4
a(1)	$-.7281539658\,E+04$	$.9039078502\,E+05$
a(2)	$-.4313535711\,E+07$	$.7123659771\,E+08$
a(3)	$.1672398620\,E+10$	$-.1764207277\,E+11$
a(4)	$-.2668364218\,E+05$	$.1632640065\,E+13$
a(5)	$.1836241516\,E+09$	$-.7699390853\,E+07$
a(6)	$.1146379717\,E+08$	$.4539101816\,E+10$
a(7)		$-.6074464549\,E+12$
a(8)		$-.6888533651\,E+08$
a(9)		$.9471465598\,E+10$
a(10)		$.6392976579\,E+10$

ation method (for which a separate computer program, RHO, was written.) The results are listed in *Table* 2.

Table 2. shows that the maximum deviation at 0°C and 25°C are 0.05% and 0.1% respectively.

Thus from the reasons discussed above it can be concluded that the equation of state, either Eq. 3 or Eq. 4 together with the least-squares parameters presented in *Table* 1 can represent the $P-V-T$ data within the experimental range with errors less than 0.15% in compressibility factor.

Acknowledgement

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Table 2. *

0°C			25°C		
P_m	$\rho_m \times 1.000$	$\rho_b \times 1000$	P_m	$\rho_m \times 1000$	$\rho_b \times 1000$
16.7623	0.8560	0.8564	18.785	0.8559	0.8555
20.1766	1.0714	1.0715	22.785	1.0711	1.0702
23.2977	1.2864	1.2868	26.525	1.2864	1.2852
26.0739	1.4968	1.4973	29.933	1.4968	1.4953
28.7094	1.7184	1.7186	33.270	1.7180	1.7160
31.0450	1.9373	1.9376	36.323	1.9373	1.9348
33.0846	2.1521	2.1523	37.816	2.0509	2.0481
34.9196	2.3711	2.3709	39.1.2	2.1512	2.1496
			41.716	2.3711	2.3781

* The substripts m stands for Michels data and b stands for the modified Bender equation Eq. 4.
ρ=density, gm-mole/cc P=pressure, bar.

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