THE DETERMINATION OF EXCESS THERMODYNAMIC FUNCTIONS OF BINARY LIQUID MIXTURES

by

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Okungakhulumiyo akwehlul' umuntu.
- Sheleni Madlela Ndlovu.

Thermodynamics is an experimental science, not a branch of metaphysics.
- M. L. McGlashan.

I have started so I will finish.
- Magnus Magnusson.

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ABSTRACT

The work involved the determination of excess thermodynamic functions of binary liquid mixtures by experimental and theoretical means. Experimentally, excess Gibbs functions(G^E), and excess volumes(V^E) were determined. The theoretical work involved these functions as well as excess enthalpies(H^E).

G^E values were determined experimentally by the dew point—bubble point method(DPBP). The work involved development of a previously designed apparatus. A new procedure was realised and adopted. In the new procedure, fixed quantities of material were used for obtaining required dew point pressures and bubble point pressures. As a complementary part of measuring G^E, a computer program was developed. Two systems were subjected to experiment. One of them, benzene+cyclohexane, produced results which compared well with published data. The system benzene+hexane produced results which were a marked improvement on previous DPBP work. After a discussion of the results, improvements on apparatus design were suggested.

Excess volumes were meassured by batch dilatometry. Four systems were used for testing the procedure. Then measurements on binary systems that have not been measured previously were made.

Theoretical aspects of the work involved applying various theories of fluids to the prediction of excess functions. One group of these theories was based on the principle of corresponding states. Experimental data of a number of pure substances were analysed to produce some universal relations. The other group of theories was based on equations of state which are analytical in essence. The main new feature in this part of the work was the way in which various combining rules were used in conjunction with the different equations of state. Computer programs were developed so that a multiplicity of combinations was available for predicting excess functions.

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This thesis is the author's account of the research carried out under the supervision of Dr. D.T. Dixon. A part of Chapter 5 is based on unpublished work carried out by Dr. Dixon and Professor M.L. McGlashan whilst at the University of Reading.

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CHAPTER 1

INTRODUCTION AND OUTLINE

1.1 INTRODUCTION

The main parts of this work involved

(1) the development of the method of obtaining excess Gibbs functions from measured dew point pressures and bubble point pressures,

(2) the testing of various theories by applying them to the prediction of excess functions, and

(3) the measurement of excess volumes of mixing.

The dew point-bubble point(DPBP) method is unique in the following respect. The composition of a mixture need not, and is not, measured accurately prior to the measurement of the pressures. In all other methods for determining excess Gibbs functions, the compsitions of either the liquid phase or the vapour phase, or both, are measured in addition to the vapour pressures. In the DPBP method, compositions and G^E values are calculated from the measured vapour pressures. A subsidiary part of this work involved the development of a computer program for calculating G^E values from the pressures.

Various theories have been applied in the prediction of excess functions and their predictive capacities have been compared against experiment. The main points of this part of the work involved:

(a) discussing the principle of corresponding states of fluids and its extension to fluid mixtures,

(b) applying the Van der Waals equation of state and the Guggenheim equation of state to the prediction of excess functions,

(c) developing computer programs which were versatile enough to accommodate a number of combining rules, and

(d) comparing the performance of various theoretical combinations in their capacity to predict excess functions.

The measurement of excess volumes of mixing was almost incidental in nature. Small quantities of material were used throughout the series of measuements. The author has to confess that small quantities were used purely out of interest. However, results from the test systems compared well with published data and it was felt that the procedure was sound enough to be applied in the measurement of excess molar volumes of new binary systems.

1.2 OUTLINE

The DPBP work has been developed so that, for a given quantity of material, pressure and volume measurements can be taken right from being in the vapour phase to an extent whereby most of the material is in the liquid phase. Reasons for adopting this procedure whereby a fixed quantity of material is used are given in Section 3.6. The new procedure is described in detail in Section 3.7.3. Part of the DPBP work involved the development of a computer program for calculating G^E values and phase compositions from the measured pressures. An advancement on the previously existing program(F.A. Hewitt, Ph.D. Thesis, University of Keele,1976) involved the use of algebraic relations in order to evaluate partial derivatives which formed part of the analysis of the dew point and bubble point pressures. Previously, the partial derivatives were evaluated graphically. Although the algebraic approach may appear awkward at first glance(see Section 3.2), it is considered to be a better approach than the graphical one. The main drawback with the graphical approach is that one has to have an approximate idea about the nature of the pressure-composition phase diagram before calculations commence. From the current work, lack of knowledge of the phase diagram does not appear to be a drawback.

As indicated in Section 1.1, the prediction of excess functions of binary mixtures was based on

(a) the principle of corresponding states(p.c.s), and

(b) equations of state of the Van der Waals type.

In applying the p.c.s, critical temperatures, critical volumes and critical pressures were the bases for formulating the p.c.s theories. However, the universal functions that were developed were based on two parameters, say the reduced temperatures and the reduced pressures. The third parameter was involved in so far as there is a relation amongst the three properties. A new feature of the p.c.s work was the manner of evaluating the critical parameters of the hypothetical fluids. This new procedure was termed the "randomisation of the Van der Waals constants"(see Section 5.4.1). Previously, the quantitative description of hypothetical fluids was generally done via the use of a potential model, say the application of the Lennard-Jones 12-6 potential. Some of the previous approaches are also incorporated in the study.

It was realised that relations of the Van der Waals and the Guggenheim equations of state could expressed in a general relation. From this general relation, two equations of state were proposed. [More equations of state could be proposed from this general relation - see equation (6.6).] The four equations of state were then applied in the prediction of excess functions. Critical volumes and critical temperatures were the basis of the application of these equations of state.

An interesting feature of the work on prediction involved the incorporation of a number of combining rules for the purposes of evaluating cross-term parameters like T_{12}^{c}. This increased greatly the scope of prediction. As a result large quantities of calculated data could be obtained. In fact, the vastness of the data necessitated that, as a first step, the analysis of results was to be limited to mere comparisons amongst the various combinations that were available.

Work on excess volumes is described in Chapter 4. Nothing more need be said about it at this juncture.

The main computer programs which were used for various aspects of this work are listed in the appendices. All the programs are written in FORTRAN.

CHAPTER 2

METHODS FOR MEASUREMENT OF EXCESS GIBBS FUNCTIONS

2.1 INTRODUCTION

The measurement of the excess Gibbs function of a given binary mixture depends in the main on the determination of the mole fraction of component 2 in the liquid phase x, the mole fraction of component 2 in the vapour phase y, the vapour pressure of the co-existing liquid and vapour phases p_m, and the vapour pressures of the pure components, namely p_1^o and p_2^o. The quantities p_m, p_1^o and p_2^o are obtained at the same temperature.

In discussing methods for the experimental determination of excess Gibbs functions, it is customary to refer only to the quantities p_m, x and y. There are, however, other significant data. These include:

(a) V_1^o and V_2^o - the molar volumes of the pure liquids 1 and 2,
(b) B_{11} and B_{22} - the second virial coefficients, and
(c) B_{12} - the second virial coefficient associated with unlike interactions.

All these parameters are experimentally accessible quantities although it is seldom necessary to measure each of them every time excess Gibbs functions are to be determined experimentally. This is because data may be available through the literature. Whatever their source, the quantities in (a) to (c) above must be obtained or determined at T, the temperature at which the pressures p_m, p_1^o, and p_2^o are measured.

At this point it is appropriate to give relationships between the excess Gibbs function of a given binary mixture and the other measurable quantities that have been mentioned. When an external pressure p acts on a given binary system, it may be shown that(1)

$$\mu_1^E(T,p,x) = RT\ln\{p_m(1-y)/[p_1^o(1-x)]\} + (B_{11} - V_1^o)(p_m - p_1^o) + p_m\delta_{12}y^2 + (V_1 - V_1^o)(p - p_m) \quad \ldots (2.1)$$

and

$$\mu_2^E(T,p,x) = RT\ln\{p_m y/(p_2^o x)\} + (B_{22} - V_2^o)(p_m - p_2^o) + p_m\delta_{12}(1-y)^2 + (V_2 - V_2^o)(p - p_m) \quad \ldots (2.2)$$

where $\mu_1^E(T,p,x)$ and $\mu_2^E(T,p,x)$ are the excess chemical potentials for components 1 and 2, respectively, and V_1 and V_2 are the partial molar volumes. The quantity δ_{12} is given by

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \quad \ldots (2.3)$$

In the derivation of equations (2.1) and (2.2), two main assumptions are made:

(i) the vapour pressure of the mixture, p_m, is considered to be low enough so that, in the equation of state for the gas, higher virial coefficients than the second are neglected, and

(ii) $|p - p_m|$ is considered small enough so that it may be assumed that the partial molar volumes V_1 and V_2 in the liquid phase are independent of pressure.

The excess chemical potentials are related to the excess Gibbs function thus:

$$G_m^E(T,p,x) = (1-x)\mu_1^E(T,p,x) + x\mu_2^E(T,p,x) \quad \ldots (2.4)$$

where $G_m^E(T,p,x)$ is the excess molar Gibbs function. The combination of equation (2.4) with equations (2.1) and (2.2) leads to

$$\begin{aligned} G_m{}^E(T,p,x) = {} & (1-x)RT\ln\{p_m(1-y)/[p_1^o(1-x)]\} + xRT\ln[p_m y/(p_2^o x)] \\ & + (1-x)(B_{11} - V_1^o)(p_m - p_1^o) + x(B_{22} - V_2^o)(p_m - p_2^o) \\ & + p_m\delta_{12}\{(1-x)y^2 + x(1-y)^2\} \\ & + V_m{}^E(T,x).(p - p_m) \qquad \ldots (2.5) \end{aligned}$$

where $V_m{}^E(T,x)$, the excess molar volume, is given by

$$V_m{}^E(T,x) = (1-x)(V_1 - V_1^o) + x(V_2 - V_2^o) \quad \ldots (2.6)$$

If $\left|p - p_m\right| < 100$ kPa, the excess molar Gibbs function and the excess chemical potentials are effectively independent of pressure p. Hence equation (2.5) becomes

$$\begin{aligned} G_m{}^E(T,x) = {} & (1-x)RT\ln\{p_m(1-y)/[p_1^o(1-x)]\} + xRT\ln\{p_m y/(p_2^o x)\} \\ & + (1-x)(B_{11} - V_1^o)(p_m - p_1^o) + x(B_{22} - V_2^o)(p_m - p_2^o) \\ & + p_m\delta_{12}\{(1-x)y^2 + x(1-y)^2\} \qquad \ldots (2.7) \end{aligned}$$

The use of equation (2.7), having measured p_m, x and y, has been the usual method of determining excess molar Gibbs functions. However, from the phase rule, it is clear that it is an overdetermination to obtain experimentally all of the quantities p_m, x and y. A determination of p_m and either of the phase compositions is sufficient in furnishing the required thermodynamic information. The phase composition that is not obtained experimentally can be calculated through the use of the constant temperature-constant pressure Gibbs-Duhem equation of which equation (2.8) is one such form.

$$(1-x)d\ln f_1 + xd\ln f_2 = 0 \qquad \ldots (2.8)$$

where f_1 and f_2 are the activity coefficients for components 1 and 2, and are related to the excess chemical potentials thus:

$$RT\ln f_1(T,x) = \mu_1^E(T,x) \qquad \ldots (2.9)$$

$$RT\ln f_2(T,x) = \mu_2^E(T,x) \qquad \ldots (2.10)$$

Once the solution for the non-measured phase composition has been obtained, equation (2.7) may then be used to obtain values for $G_m^E(T,x)$.

An alternative approach to solving for the non-measured phase composition involves the use of a convenient analytical form for the variation of excess molar Gibbs functions with composition. An example of such an analytical form is the Redlich-Kister equation$^{(2)}$:

$$G_m^E(T,x)/RT = x(1-x)\sum_{j=1}^{\ell} A_j(1 - 2x)^{j-1} \qquad \ldots (2.11)$$

where ℓ is the number of A_j coefficients sufficient to give a good correlation between the data and the equation. Again the Gibbs-Duhem equation finds usage, for through using it, one obtains, from equation (2.4)

$$\partial G_m^E(T,x)/\partial x = -\mu_1^E(T,x) + \mu_2^E(T,x) \qquad \ldots (2.12)$$

The combination of equations (2.4) and (2.12) leads to

$$\mu_1^E(T,x) = G_m^E(T,x) - x\partial G_m^E(T,x)/\partial x \qquad \ldots (2.13)$$

$$\mu_2^E(T,x) = G_m^E(T,x) + (1-x)\partial G_m^E(T,x)/\partial x \qquad \ldots (2.14)$$

The combination of equation (2.11) with each of equations (2.13) and (2.14) yields

$$\mu_1{}^E(T,x)/RT = \sum_{j=1}^{\ell} A_j x^2(1 - 2x)^{j-2}\{2j(1-x) - 1\} \quad \ldots (2.15)$$

and,

$$\mu_2{}^E(T,x)/RT = \sum_{j=1}^{\ell} A_j (1-x)^2(1 - 2x)^{j-2}(1 - 2jx) \quad \ldots (2.16)$$

Equations (2.15) and (2.16) are then equated to equations (2.1) and (2.2), respectively - assuming non-dependence of excess chemical potentials on external pressure - to give

$$p_m = p_1^o\{(1-x)/(1-y)\}\exp\{\sum_{j=1}^{\ell} A_j x^2(1 - 2x)^{j-2}[2j(1-x) - 1] - [(B_{11} - V_1^o)(p_m - p_1^o) + p_m\delta_{12}y^2]/RT\} \quad \ldots (2.17)$$

and,

$$p_m = p_2^o(x/y)\exp\{\sum_{j=1}^{\ell} A_j(1-x)^2(1 - 2x)^{j-2}(1 - 2jx) - [(B_{22} - V_2^o)(p_m - p_2^o) + p_m\delta_{12}(1-y)^2]/RT\} \quad \ldots (2.18)$$

Thus if p_m and x, or p_m and y, are measured for n mixtures, then relations of the nature of equations (2.17) and (2.18) provide 2n equations in $n + \ell$ unknowns. A solution for the n unknown phase compositions and ℓ coefficients is possible if $n \geqslant \ell$.

The Redlich-Kister equation may not be a suitable form for the experimental data under consideration. In such an eventuality, it is advisable to adopt an analytical form which is compatible with the data. The Myers-Scott equation(3) and the Wilson equation(4), equations (2.19) and (2.20), respectively, may be such analytical forms.

$$G_m{}^E(T,x)/RT = x(1-x)\{1 - k(1 - 2x)\}\sum_{j=1}^{\ell} A_j(1 - 2x)^{j-1} \quad \ldots (2.19)$$

$$G_m^E(T,x)/RT = -(1-x)\ln(1-A_{21}x) - x\ln\{1-A_{12}(1-x)\} \quad \ldots (2.20)$$

A number of other analytical forms have been proposed. Hala, et al(5) discussed some of these equations. These equations include

(i) the Wohl equation,

(ii) the Scatchard-Hamer equation,

(iii) the van Laar equation, and

(iv) the Margules equation.

This group of equations has been used less frequently recently - at any rate on binary liquid mixtures involving non-polar or slightly polar molecules.

There is another approach in the determination of excess Gibbs functions. This method requires no measurement of either of the phase compositions. Instead, equilibrium vapour pressures at the dew point and the bubble point are measured. From this, and in combination with the use of a suitable analytical form, the phase compositions and the excess Gibbs functions are calculated. A detailed discussion of the method is given in Chapter 3.

2.2 METHODS

There are various methods for the determination of excess Gibbs functions of binary liquid mixtures. The methods may be classified as follows:

(i) dynamic methods, and

(ii) static methods.

There are other methods, for example those based on transpiration and chromatographic techniques, but they are not usually applied to organic liquids of interest in relation to this work. The following discussion is limited to those methods mentioned in (i) and (ii) above. The common feature in such methods is the measurement of vapour pressure under equilibrium conditions. In all such methods, therefore, good control and accurate measurement of temperature are essential requirements.

2.2.1 Dynamic methods

The use of recirculating stills or related modes of apparatus is a distinguishing feature in the determination of excess Gibbs functions by dynamic methods. Another feature is that p_m, x and y are determined experimentally, and relations of the type of equation (2.7) are then used for evaluating excess Gibbs functions.

There are various ways of introducing known amounts of the pure components into recirculating stills. The use of ampoules is one such technique. The liquid mixture is then boiled and the resulting vapour is condensed and trapped at some other point in the apparatus. The design of the apparatus is such that some of the trapped condensate flows back to the boiling liquid. The boiling-and-trapping process is continued until a steady state is considered to have been achieved. However, it is now known, and has been known for sometime, that the attainment of equilibrium via the use of recirculating stills is a notoriously difficult process. The experimenter hopes that the steady state situation is as near to the equilibrium position as possible(1,6). The vapour pressure is then measured. The composition of the trapped condensate, which in effect is the composition of the vapour phase, y, is determined by withdrawing some of the condensate and then obtaining some measurable physical quantity which can be related to composition. The material that is in the boiler section constitutes the liquid phase under steady state conditions. The composition x is determined in similar fashion to y.

Besides the difficulty of obtaining the true equilibrium state in recirculating stills, there are other difficulties which are inherent in dynamic methods. The boiling process of the mixture must be such that 'flash' boiling is avoided so that droplets, however small, of the boiling liquid are not entrained to the condensing region. There are also difficulties associated with analysis of the phase compositions. The relationship between the measurable physical quantity and composition must be well established. This may not be easy as, for example, there may be a temperature dependence in the physical quantity under consideration. There is also the difficulty of achieving a uniform temperature throughout the apparatus. However, careful design can minimise the effects of such problems. All being said and done, the main advantage with obtaining p_m, x and y is the ease of evaluating excess Gibbs functions from using equation (2.7). In addition, p_m, x and y information can be used for carrying out thermodynamic consistency tests. The common procedure for such tests involves the use of an integrated form of the Gibbs-Duhem equation(2,7). Care should be taken with regards to consistency tests based on the integrated form of the Gibbs-Duhem equation. Marsh(8) and McGlashan(1) point out the limitations of such consistency tests. However, given the experimental difficulties associated with the use of recirculating stills, such tests serve a purpose in indicating inconsistency.

There are a number of examples in the literature regarding vapour-liquid equilibria studies by use of recirculating stills. One of the earlier examples of high precision work involving the use of recirculating stills is that of Scatchard and co-workers(6). The design of the still was primarily for the purpose of minimising errors associated with the use of recirculating stills. The still was tested on the ethanol+trichloromethane system(9). The compositions of the mixtures were determined from density measurements. A further difficulty encountered was loss of material through the condenser. The consequences with regards to compositional changes, especially if the ratios of the vapour pressures of the pure components are high, cannot be overemphasised in the event of encountering material loss. However, under their operational conditions, the work was considered as satisfactory.

Scatchard, Wood and Mochel did a series of other experiments in which p_m, x and y were measured. The design of the apparatus was essentially an improvement of that in the earlier work(6). THe binary systems studied included tetrachloromethane+cyclohexane(10), benzene+ cyclohexane(11), benzene+tetrachloromethane(12), benzene+methanol(13), and methanol+tetrachloromethane(14). Quite apart from obtaining thermodynamic information on these systems, the data were used in deriving equations for the ternary system benzene+cyclohexane+tetrachloromethane(12).

Other research groups were also working on the determination of excess Gibbs functions using recirculating stills. Kretschmer, et al(15) obtained equilibria data on the binary system ethanol+2,2,4-trimethylpentane as part of a systematic study to determine some of the physical properties of ethanol+hydrocarbon systems. McGlashan, et al(16) obtained data for the tetrachloromethane+trichloromethane system. Their recirculating still was tested on the benzene+tetrachloromethane system, since this had been studied previously(12).

2.2.2 Static methods

There are a number of features which distinguish static methods from dynamic methods. The following is an outline of such distinguishing features.

(1) In general, p_m, x and y are measured when dealing with dynamic methods. In the case of static methods, p_m and the total composition are measured; x and y are then calculated. [In the rest this chapter, the symbol (p_m,x) will be used to indicate the measurement of vapour pressure and liquid phase composition. For the measurement of vapour pressure and vapour phase composition, (p_m,y) will be used.]

(2) In dynamic methods, p_m is measured after the attainment of steady state conditions between the material in the boiler section and the condensing region. In static methods, however, p_m is measured after the attainment of equilibrium between the liquid and vapour phases within the vapour pressure cell.

(3) Thorough degassing of the liquid components is of absolute importance when using static methods whereas it is of peripheral interest in the case of dynamic methods.

(4) In dynamic methods, the determination of the phase compositions requires prior analyses of the properties of mixtures of accurately known compositions. Such a procedure is avoided when determining excess Gibbs functions by static methods. The only necessary step is the initial measurement of amounts introduced into the vapour pressure cell.

(5) Generally, smaller amounts of liquid substances are needed, and much shorter times are required due to less cumbersome experimentation, when dealing with static methods than when dealing with dynamic methods.

(6) In the analysis of experimental data, calculations are easier when using dynamic methods than otherwise. However, the availability of powerful computers has eclipsed this advantage which dynamic methods have over static methods.

The work by Redlich and Kister(17) is an example of the earlier studies on equilibria of mixtures by static methods. A (p_m, x) method was employed. The apparatus was designed so that there was restriction of vapour space over the liquid. Thus the liquid phase composition under equilibrium conditions was considered to be the same as the initial composition. The calculation of activity coefficients was effected through the use of approximate forms of the Margules relations which are given by

$$\ln f_1 = Ax^2 \; ; \quad \ln f_2 = A(1-x)^2 \qquad \ldots (2.21)$$

where A is a constant.

The contribution by Barker(18) may be considered as the first detailed attempt for obtaining a procedure for the systematic analysis of thermodynamic data via static methods. The experimental work involved the measurement of vapour pressures and liquid phase compositions of given mixtures. The Redlich-Kister equation was adopted as an explicit form for the variation of excess molar Gibbs functions with composition. The method of calculation, which was developed for use with hand calculators, has been adopted for computers and is now used commonly.

Since the work by Barker(18), static methods have become more fashionable than dynamic methods as means of acquiring excess molar Gibbs functions. Marsh(8) has written a review which traces the development of experimental techniques associated with measurement of excess functions of organic liquids. A study of the literature shows that earlier studies involved mixtures in which one of the components is relatively involatile. Thus, under operating conditions, the vapour phase composition was taken to be virtually unity in mole fraction of the volatile component. An example is the work by McGlashan and Williamson(19) which involved equilibria studies of _n_-hexane+_n_-hexadecane by (p_m, x) measurements. Having measured initially the overall composition, they calculated the liquid phase compositions by making allowance for some _n_-hexane evaporating into the vapour space. In contrast, for situations where the volatilities of the components are somewhat similar, the work is more involved since - as is usually the case - both equilibrium phase compositions have to be calculated. For example, Scatchard and Satkiewicz(20) studied liquid-vapour equilibria of ethanol+cyclohexane mixtures using an apparatus designed by Scatchard, et al(21). Having measured initially the overall composition and having measured the equilibrium vapour pressure, they calculated, by an iterative method, both x and y. They adopted the Wilson equation(4) - equation (2.20) - as the analytical form for the dependence of excess molar Gibbs functions on composition.

Gaw and Swinton(22) - employing a differential manometer in which benzene was used as the standard - obtained excess molar Gibbs functions of mixtures of hexafluorobenzene+cyclohexane. They used a modified version of the Barker method to solve for x and y. The procedure involved using the predetermined overall composition as the initial value of x. The Barker method was then used to compute a value for y. The computed value was then used for furnishing a better value of x, making use of the knowledge of the volume of the apparatus covered by the vapour and allowance being made for non-ideal behaviour. The iterations were carried out until the values of x and y were self-consistent and did not change significantly with additional cycling.

At this point, it is appropriate to comment on some of the design aspects of manometers. Manometers may be of a nulling, a differential, or an absolute type. The drawback with nulling manometers is the tendency of the zero points to shift position. This necessitates the determination of the zero point for each pressure measurement(21). Differential manometers are feasible if the thermodynamic properties of the reference substance are well established. Thus in order to lessen experimental burden by dispensing with problems associated with the points just mentioned, it is desirable to use techniques in which the measurement of pressure is more or less direct. Manometers of the absolute type are useful in this respect.

In addition to the development of absolute manometers, there has been a number of improvements in other aspects of design of apparata for measurement of excess Gibbs functions. Marsh(23), in the study of the binary systems involving octamethylcyclotetrasiloxane (OMCTS) mixtures with benzene and with tetrachloromethane, designed an apparatus with a single "cut-off" manometer. An interesting feature of the design is the mounting of the vacuum section on a vertically moveable frame so that the manometer and the vapour pressure cell could be removed from the thermostat bath if the need arose. Harris and Dunlop(3) employed an apparatus with a mercury manometer as the pressure measuring device. In later stages of the project, a quartz spiral Bourdon gauge replaced the rather cumbersome mercury manometer. In the study of OMCTS+cyclohexane mixtures, Tomlins and Marsh(24) designed an apparatus which featured an automatic pressure controller as well as a capacitance manometer which was used as a null device to isolate the liquid and vapour phases. A precision mercury manometer was used for measuring the equilibrium vapour pressures. Another important feature was the incorporation of the continuous dilution technique for sample introduction. The entire composition range could be covered in two runs. The authors(24) compared the results from the continuous dilution technique with the results from the technique involving the measurement of overall compositions by use of ampoules. They concluded that the latter technique, although cumbersome, offers a small advantage in accuracy. In later research projects, improvements were made which resulted in only one run being necessary to cover the entire composition range(25),(26).

Young, et al(27) also designed an apparatus with piston injectors so that successive volumetric additions of one of the components could be made after each pressure measurement. A pressure transducer was used as a null device to isolate the equilibrium cell from the pressure gauge. The pressure in the cell was measured with a quartz Bourdon gauge. Improvements on the cell were made by Mentzer, et al(28). The most notable improvement involved the construction of the equilibrium cell from stainless steel, with the presence of a copper gasket for providing a leak-tight seal. Also, pure liquids were introduced through the sides of the cell, rather than through the top, to ensure good mixing. In some cases, however, earlier designs are still maintained. For example, Rubio, et al(29), in their study of benzene+n-pentadecane mixtures, used an apparatus based on the design by McGlashan and Williamson(19). The modification was that, in the later work(29), all valves and taps that could come into contact with the organic liquids were greaseless.

All the literature cited so far is connected with the determination of excess Gibbs functions via (p_m,x) methods. Compared to (p_m,x) methods, there have been fewer attempts at obtaining excess Gibbs functions by (p_m,y) methods. An example of a (p_m,y) method is the work by Christian, et al(30). They developed a technique for obtaining activity coefficients of components in liquid binary mixtures from measured total vapour pressures and vapour densities. Four systems were studied and a comparison of the results of one of the systems - namely, benzene+tetrachloromethane - with previously published results(12) indicated that the technique lacked high precision.

High precision work for the determination of excess molar Gibbs functions from (p_m,y) methods has been done by Brewster and McGlashan(31),(32). The earlier work(31) involved the development of the method, and it was tested by obtaining $G_m^E(T,x)$ values for benzene+cyclohexane at 313.15 K. Pressure was measured with the aid of a precision mercury manometer. The method involved determining dew pressures of gaseous binary mixtures of known compositions at temperature T. In outline, dew pressures were determined from sharp discontinuities which occurred along carefully measured pressure and volume readings. The other study involved the determination of excess molar Gibbs functions of binary mixtures formed from tetramethylmethane(CMe_4), tetramethylsilane($SiMe_4$), and tetramethylstannane($SnMe_4$)(32). There was lack of success, however, for the CMe_4 + $SnMe_4$ system. This is because the (p_m, y) method is unsuitable for mixtures consisting of components with high ratios in the vapour pressures of the pure components.

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CHAPTER 3

MEASUREMENT OF EXCESS MOLAR GIBBS FUNCTIONS: THE DEW POINT-BUBBLE POINT METHOD

3.1 INTRODUCTION

The dew point-bubble point method - which will be referred to as the DPBP method - is a special case of a static method. This method is unique in that no attempt is made whatsoever to measure accurately the composition of a given mixture. Instead, the dew point pressure P_d and the bubble point pressure P_b of a mixture are measured. The phase compositions are then calculated from these pressure measurements.

The DPBP method, the theory of which was advanced by Dixon and McGlashan(1), was verified experimentally by Dixon and Hewitt(2). In the present work, interest is centred on two areas. The first area is the development of an experimental procedure which eliminates some of the problems encountered in the earlier work(2),(3). The other point of interest concerns the computer program for analyzing the DPBP data. The present program differs from the previous one(3) in that algebraic relations are used in order to evaluate partial derivatives(see Section 3.2). Previously, the partial derivatives were evaluated numerically. Before presenting an account of these facets of the DPBP method, a summary of the theoretical aspects is given.

Consider a pressure-composition phase diagram of a binary system as indicated in Figure 3.1. The equilibrium vapour pressure of a given mixture is related to the phase compositions and other quantities as given by equations (2.17) and (2.18). Now, for a mixture of overall composition X with P_d and P_b as the dew point pressure and the bubble point pressure, respectively, there is a special relationship between the liquid phase and vapour phase compositions. It can be seen from Figure 3.1 that these special relationships are given by equations (3.1) to (3.3).

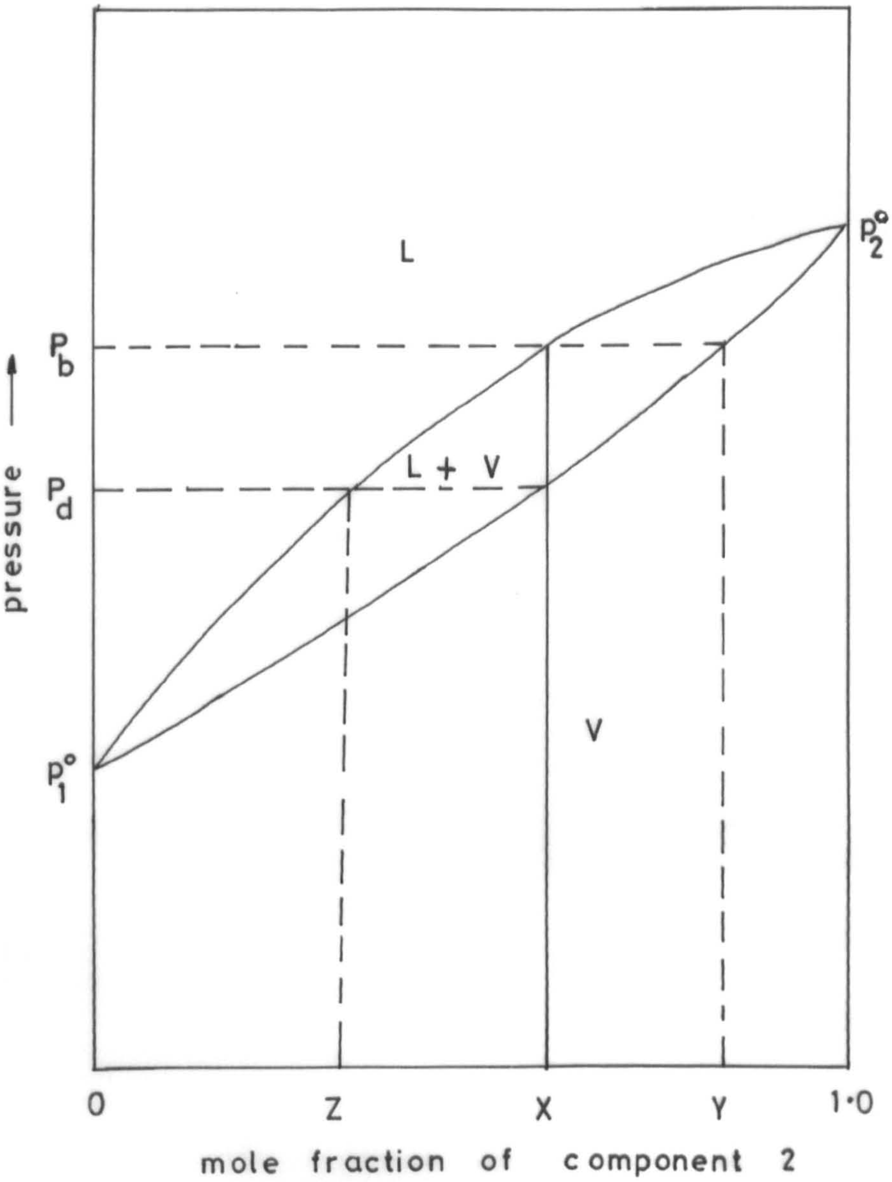


Figure 3.1 A pressure-composition phase diagram of a binary system. L and V represent the liquid and vapour phases, respectively. The other symbols are described in the text.

$$X = x_b = y_d \qquad \ldots (3.1)$$

$$Y = y_b \qquad \ldots (3.2)$$

$$Z = x_d \qquad \ldots (3.3)$$

In the above equations, x and y are the mole fractions of component 2 in the liquid phase and vapour phase, respectively, whereas the subscripts b and d refer to the bubble point and dew point, respectively. Relations given by equations (2.17) and (2.18) are then applied to bubble point and dew point conditions so that one has

$$P_b = p_1^o\{(1 - X)/(1 - Y)\}\exp\{\sum_{j=1}^{\ell} A_j X^2(1 - 2X)^{j-2}[2j(1 - X) - 1] - [(B_{11} - V_1^o)(P_b - p_1^o) + P_b\delta_{12}Y^2]/RT\} \qquad \ldots (3.4)$$

$$P_b = p_2^o(X/Y)\exp\{\sum_{j=1}^{\ell} A_j(1 - X)^2(1 - 2X)^{j-2}(1 - 2jX) - [(B_{22} - V_2^o)(P_b - p_2^o) + P_b\delta_{12}(1 - Y)^2]/RT\} \qquad \ldots (3.5)$$

$$P_d = p_1^o\{(1 - Z)/(1 - X)\}\exp\{\sum_{j=1}^{\ell} A_j Z^2(1 - 2Z)^{j-2}[2j(1 - Z) - 1] - [(B_{11} - V_1^o)(P_d - p_1^o) + P_d\delta_{12}X^2]/RT\} \qquad \ldots (3.6)$$

$$P_d = p_2^o(Z/X)\exp\{\sum_{j=1}^{\ell} A_j(1 - Z)^2(1 - 2Z)^{j-2}(1 - 2jZ) - [(B_{22} - V_2^o)(P_d - p_2^o) + P_d\delta_{12}(1 - X)^2]/RT\} \qquad \ldots (3.7)$$

Thus for a mixture whose P_d and P_b have been measured, there are 4 equations in which X, Y, Z and ℓ - the number of A_j coefficients - are unknowns. Therefore, if pressure measurements are carried out on n mixtures of a given binary system, then there are 4n equations in 3n + ℓ unknowns. A solution for the unknowns is possible if $n > \ell$. If the second virial coefficients are not known, then they may also be treated as parameters. Hence one may have 4n equations in 3n + ℓ + v unknowns, where v is the number of unknown virial coefficients, namely any of B_{11}, B_{22} and B_{12}.

3.2 COMPUTATION

The 4n equations in $3n + \ell + v$ unknowns are transcendental functions. Hence a numerical method which involves iteration is required. The method that was adopted involves the use of a non-linear least squares technique. The implementation of this procedure requires the formulation of partial derivatives of the vapour pressures with respect to the unknowns and then setting up an appropriate Jacobian matrix. Table 3.1 contains a listing of the partial derivatives that can be obtained from equations 3.4 to 3.7.[An explanation on the adopted nomenclature is given shortly.] Figure 3.2 is a representation of the Jacobian matrix.

TABLE 3.1 A listing of the various partial derivatives.

Group A	${}_1(\partial P_b/\partial X)$	${}_2(\partial P_b/\partial X)$	${}_1(\partial P_d/\partial Z)$	${}_2(\partial P_d/\partial Z)$
Group B	${}_1(\partial P_b/\partial Y)$	${}_2(\partial P_b/\partial Y)$	${}_1(\partial P_d/\partial X)$	${}_2(\partial P_d/\partial X)$
Group C	${}_1(\partial P_b/\partial A_j)$	${}_2(\partial P_b/\partial A_j)$	${}_1(\partial P_d/\partial A_j)$	${}_2(\partial P_d/\partial A_j)$
Group D	${}_1(\partial P_b/\partial B_{11})$	${}_2(\partial P_b/\partial B_{11})$	${}_1(\partial P_d/\partial B_{11})$	${}_2(\partial P_d/\partial B_{11})$
Group E	${}_1(\partial P_b/\partial B_{22})$	${}_2(\partial P_b/\partial B_{22})$	${}_1(\partial P_d/\partial B_{22})$	${}_2(\partial P_d/\partial B_{22})$
Group F	${}_1(\partial P_b/\partial B_{12})$	${}_2(\partial P_b/\partial B_{12})$	${}_1(\partial P_d/\partial B_{12})$	${}_2(\partial P_d/\partial B_{12})$

$$\left[\begin{array}{cccccccc}
{}^{1}_{1}\left(\frac{\partial P_b}{\partial X}\right) & {}^{1}_{1}\left(\frac{\partial P_b}{\partial Y}\right) & 0 & 0 & 0 & 0 & & {}^{1}_{1}\left(\frac{\partial P_b}{\partial A_1}\right) & {}^{1}_{1}\left(\frac{\partial P_b}{\partial A_2}\right) \\
{}^{1}_{2}\left(\frac{\partial P_b}{\partial X}\right) & {}^{1}_{2}\left(\frac{\partial P_b}{\partial Y}\right) & 0 & 0 & 0 & 0 & & {}^{1}_{2}\left(\frac{\partial P_b}{\partial A_1}\right) & {}^{1}_{2}\left(\frac{\partial P_b}{\partial A_2}\right) \\
{}^{1}_{1}\left(\frac{\partial P_d}{\partial X}\right) & 0 & {}^{1}_{1}\left(\frac{\partial P_d}{\partial Z}\right) & 0 & 0 & 0 & & {}^{1}_{1}\left(\frac{\partial P_d}{\partial A_1}\right) & {}^{1}_{1}\left(\frac{\partial P_d}{\partial A_2}\right) \\
{}^{1}_{2}\left(\frac{\partial P_d}{\partial X}\right) & 0 & {}^{1}_{2}\left(\frac{\partial P_d}{\partial Z}\right) & 0 & 0 & 0 & \Longrightarrow & {}^{1}_{2}\left(\frac{\partial P_d}{\partial A_1}\right) & {}^{1}_{2}\left(\frac{\partial P_d}{\partial A_2}\right) \\
0 & 0 & 0 & {}^{2}_{1}\left(\frac{\partial P_b}{\partial X}\right) & {}^{2}_{1}\left(\frac{\partial P_b}{\partial Y}\right) & 0 & & {}^{2}_{1}\left(\frac{\partial P_b}{\partial A_1}\right) & {}^{2}_{1}\left(\frac{\partial P_b}{\partial A_2}\right) \\
0 & 0 & 0 & {}^{2}_{2}\left(\frac{\partial P_b}{\partial X}\right) & {}^{2}_{2}\left(\frac{\partial P_b}{\partial Y}\right) & 0 & & {}^{2}_{2}\left(\frac{\partial P_b}{\partial A_1}\right) & {}^{2}_{2}\left(\frac{\partial P_b}{\partial A_2}\right) \\
0 & 0 & 0 & {}^{2}_{1}\left(\frac{\partial P_d}{\partial X}\right) & 0 & {}^{2}_{1}\left(\frac{\partial P_d}{\partial Z}\right) & & {}^{2}_{1}\left(\frac{\partial P_d}{\partial A_1}\right) & {}^{2}_{1}\left(\frac{\partial P_d}{\partial A_2}\right) \\
0 & 0 & 0 & {}^{2}_{2}\left(\frac{\partial P_d}{\partial X}\right) & 0 & {}^{2}_{2}\left(\frac{\partial P_d}{\partial Z}\right) & & {}^{2}_{2}\left(\frac{\partial P_d}{\partial A_1}\right) & {}^{2}_{2}\left(\frac{\partial P_d}{\partial A_2}\right) \\
 & & & \Big\Downarrow & & & & & \\
0 & 0 & 0 & 0 & 0 & 0 & \Longrightarrow & {}^{n}_{1}\left(\frac{\partial P_b}{\partial A_1}\right) & {}^{n}_{1}\left(\frac{\partial P_b}{\partial A_2}\right)
\end{array}\right]$$

Figure 3.2 Part of a Jacobian matrix representing a set of 4n equations in 3n + 2 unknowns. The partial derivatives for n = 2 are all laid out.

Before proceeding with the analysis, it is worthwhile explaining the nomenclature regarding the partial derivatives. The element ${}^{1}_{1}(\partial P_b/\partial X)$ is taken as an example. What is within the brackets is self-explanatory; it is the partial derivative of the bubble point pressure with respect to the mole fraction of the second component in the liquid phase. The 'superscript', namely 1, refers to the first pair of DPBP measurements. [The pairs are arranged in order of increasing values of mole fractions of the second component.] The 'subscript' 1 refers to the fact that the relationship under consideration relates P_b with the vapour pressure of component 1, p_1^o. It is quite clear, therefore, that the relations for ${}^{n}_{1}(\partial P_b/\partial X)$ - where n is any pair of the DPBP measurements - are similar in format. Thus, for convenience, n may be omitted when reference is made regarding relations for the various partial derivatives. This is exactly what was done when Table 3.1 was drawn up.

3.2.1 The generalisations of the partial derivatives

From Table 3.1, it can be appreciated that there is a large number of partial derivatives to be dealt with. It may be appreciated also that most of the expressions for the partial derivatives are rather involved. In order to write a compact computer program, it was necessary to classify the derivatives into groups so that general expressions could be used for representing derivatives whose relations are similar in structure. In fact, the initial step in classification is as indicated in Table 3.1. The classification into mentioned groups is based on differentiating the vapour pressures with respect to

A. liquid phase compositions,

B. vapour phase compositions,

C. Redlich-Kister coefficients,

D. second virial coefficient of component 1,

E. second virial coefficient of component 2, and

F. cross-term second virial coefficient.

The first phase of the generalisation within each of the groups is now presented.

Group A

It can be seen from equations (3.4) and (3.6) that the format for ${}_1(\partial P_b/\partial X)$ is the same as that of ${}_1(\partial P_d/\partial Z)$. The study of equations (3.5) and (3.7) reveals that the situation is similar for the pair ${}_2(\partial P_b/\partial X)$ and ${}_2(\partial P_d/\partial Z)$. Hence P_d and P_b can be represented by the general symbol p. The liquid phase compositions are also generalised so that x symbolises the liquid phase composition at either the dew point or the bubble point pressure. Similarly, the generalised symbol for the vapour phase compositions is y. Thus

$$ {}_1(\partial p/\partial x) = \phi_1.[-1/(1-x) + 2\sum_{j=1}^{\ell} A_j x(1-2x)^{j-3}\{2j - 1 - 2j(1+j)x(1-x)\}] \qquad \text{... (3.8)} $$

$$ \text{where } \phi_1 = pRT/\{RT + p(B_{11} - V_1^{o}) + p\delta_{12}y^2\} \qquad \text{... (3.8a)} $$

and

$$ {}_2(\partial p/\partial x) = \phi_2.[1/x - 2\sum_{j=1}^{\ell} A_j(1-x)(1-2x)^{j-3}\{2j - 1 - 2j(1+j)x(1-x)\}] \qquad \text{... (3.9)} $$

$$ \text{where } \phi_2 = pRT/\{RT + P(B_{22} - V_2^{o}) + p\delta_{12}(1-y)^2\} \qquad \text{... (3.9a)} $$

Group B

The relations for the pair of derivatives ${}_1(\partial P_b/\partial Y)$ and ${}_1(\partial P_d/\partial X)$ are identical in format. This is also the case with ${}_2(\partial P_b/\partial Y)$ and ${}_2(\partial P_d/\partial X)$. The symbols are generalised so that one has

$${}_1(\partial p/\partial y) = \phi_1.\{1/(1-y) - 2p\delta_{12}y/RT\} \qquad \ldots (3.10)$$

$${}_2(\partial p/\partial y) = \phi_2.\{-1/y + 2p\delta_{12}(1-y)/RT\} \qquad \ldots (3.11)$$

Group C

${}_k(\partial P_b/\partial A_j)$ and ${}_k(\partial P_d/\partial A_j)$, where k is either 1 or 2, have identical formats. Hence

$${}_1(\partial p/\partial A_j) = \phi_1.x^2(1 - 2x)^{j-2}[2j(1 - x) - 1] \qquad \ldots (3.12)$$

$${}_2(\partial p/\partial A_j) = \phi_2.(1 - x)^2(1 - 2x)^{j-2}(1 - 2jx) \qquad \ldots (3.13)$$

Group D

$${}_1(\partial p/\partial B_{11}) = p(py^2 - p + p_1^o)/\{RT + p(B_{11} - V_1^o) + p\delta_{12}y^2\} \qquad \ldots (3.14)$$

$${}_2(\partial p/\partial B_{11}) = p^2(1-y)^2/\{RT + p(B_{22} - V_2^o) + p\delta_{12}(1-y)^2\} \qquad \ldots (3.15)$$

Group E

$${}_1(\partial p/\partial B_{22}) = p^2y^2/\{RT + p(B_{11} - V_1^o) + p\delta_{12}y^2\} \qquad \ldots (3.16)$$

$${}_2(\partial p/\partial B_{22}) = p\{p(1-y)^2 - p + p_2^o\}/\{RT + p(B_{22} - V_2^o) + p\delta_{12}(1-y)^2\} \qquad \ldots (3.17)$$

Group F

$${}_1(\partial p/\partial B_{12}) = -2p^2y^2/\{RT + p(B_{11} - V_1^o) + p\delta_{12}y^2\} \qquad \ldots (3.18)$$

$${}_2(\partial p/\partial B_{12}) = -2p^2(1-y)^2/\{RT + p(B_{22} - V_2^o) + p\delta_{12}(1-y)^2\} \qquad \ldots (3.19)$$

The relations given by equations (3.14) to (3.19) have been written in full. That is, the terms ϕ_1 and ϕ_2, which are defined in equations (3.8a) and (3.9a), have not been used. This is an attempt at projecting the visual similarity, or otherwise, of the relations in question.

More general expressions could be obtained by further algebraic manipulation of the relations given by equations (3.8) to (3.19). Although the resulting relations may be manipulated further still, it is convenient to obtain expressions that bear resemblance to the expressions for the various differential coefficients. Also, there are other ways of generalising the expressions. The form of analysis that was adopted is now presented. The Group A relations serve as an example in illustrating how relations with common features could be reduced further.

A convenient starting point is the grouping or classification of terms with identical structures from within each of equations (3.8) and (3.9). A detailed study of those equations shows that three classes of factors or terms may be obtained. The classification is illustrated in Table 3.2.

Table 3.2 Classification of terms in equations (3.8) and (3.9).

	Terms from (3.8)	Terms from (3.9)
Class I	p; RT; δ_{12};	(as in equation (3.8)).
	$2\ \{A_j(1 - 2x)^{j-3}\{2j - 1 - 2j(1 + j)x(1 - x)\}$	
Class II	${}_1(\partial p/\partial x)$	${}_2(\partial p/\partial x)$
	$1/(1 - x)$	$1/x$
	$(B_{11} - V_1^o)$	$(B_{22} - V_2^o)$
Class III	y in $p\delta_{12}y^2$	$(1 - y)$ in $p\delta_{12}(1 - y)^2$
	x in $2\ \{A_jx\ldots\}$	$(1 - x)$ in $2\ \{A_j(1 - x)\ldots\}$

It can be seen from Table 3.2 that the terms in Class I are common to both equations. The terms in Class II are expressed as functions of the properties of one of the pure components whereas the Class III terms pertain to the properties of the other component. As an example, the expression $\{p(B_{11} - V_1^o) + p\delta_{12}y^2\}$ in equation (3.8) contains $(B_{11} - V_1^o)$ which clearly is a property of component 1; it also contains y which is the mole fraction of the second component. In the present analysis, therefore, $(B_{11} - V_1^o)$ is a class II factor whereas y is a class III factor. The corresponding situation in equation (3.9) is that $(B_{22} - V_2^o)$ is in class II and $(1 - y)$ is in class III. Having classified the terms, equations (3.8) and (3.9) are reduced into a general equation. In this general equation, the terms in class I are clearly common. The class II terms are generalised by a process of subscription so that they can fit either of the equations by adjusting the value of the subscript. Class III terms are rather awkward to deal with. Algebraic manipulation is required so that the resultant terms are then functions of the properties of the component under consideration. In other words, algebraic manipulation is required to convert class III terms into class II terms. This is accomplished by designating the liquid phase compositions as $(k - 1 - x)$ and the vapour phase compositions as $(k - 1 - y)$, where k is either 1 or 2. Examination shows that the phase compositions have negative values when $k = 1$. However, this apparent impediment is easily overcome. For the liquid phase compositions, the sign on the other terms in the expression is altered accordingly so that the effective sign on the compositions is positive. As far as the vapour phase compositions are concerned, the negative sign is superfluous since the terms are squared. It is also helpful to mention that the class II terms $1/(1 - x)$ and $1/x$ have been written in generalised form. This is given by $1/(k - 2 + x)$, where $k = 1$ or 2. From the foregoing information, the general relation from equations (3.8) and (3.9) is given by

$${}_k(\partial p/\partial x) = \phi_k.[1/(k-2+x) - 2\sum_{j=1}^{\ell} A_j(k-1-x)(1-2x)^{j-3}.\{2j-1-2j(1+j)x(1-x)\}]$$

... (3.20)

$$\text{where } \phi_k = pRT/\{RT + p(B_{kk} - V_k^o) + p\delta_{12}(k - 1 - y)^2\} \qquad \text{... (3.20a)}$$

Similar procedures are used to reduce the pairs of relations, as given by equations (3.10) to (3.19), to five other general equations. The pairs of equations under consideration lie within the groups as specified above. The exceptions are in groups D and E. In these groups, there is a 'cross-over' in that the form of equation (3.14) is similar to that of equation (3.17) whereas the forms of equations (3.15) and (3.16) are similar. The general relationships are now given.

From equations (3.10) and (3.11);

$${}_k(\partial p/\partial y) = \phi_k.[1/(2 - k - y) + \{2p\delta_{12}(k - 1 - y)/RT\}] \qquad \text{... (3.21)}$$

From equations (3.12) and (3.13);

$${}_k(\partial p/\partial A_j) = \phi_k.(k-1-x)^2(1-2x)^{j-2}\{2j(2-k) + 2k - 3 - 2jx\} \qquad \text{... (3.22)}$$

From equations (3.14) and (3.17);

$${}_k(\partial p/\partial B_{kk}) = p\{p(k-1-y)^2 - p + p_k^o\}/\{RT + p(B_{kk} - V_k^o) + p\delta_{12}(k-1-y)^2\}$$

... (3.23)

From equations (3.15) and (3.16);

$${}_k(\partial p/\partial B_{i\neq k}) = p^2(k-1-y)^2/\{RT + p(B_{kk} - V_k^o) + p\delta_{12}(k-1-y)^2\} \qquad \text{... (3.24)}$$

In equation (3.24), when $i = 1$, $k = 2$ and vice versa.

Finally, from equations (3.18) and (3.19), one obtains

$${}_k\partial p/\partial B_{12}) = -2p^2(k-1-y)^2/\{RT + p(B_{kk} - V_k^o) + p\delta_{12}(k-1-y)^2\} \qquad \text{... (3.25)}$$

Equations (3.20) to (3.25) are the generalised relations for the various partial derivatives. Each of them represents four specific relations. This is because, in each case, p could be either P_b or P_d and k has a value of 1 or 2. The computer programme contains algorithms for the generalised relations.

3.3 THE APPARATUS

The apparatus used in this work was an improved version of the one used by Dixon and Hewitt(2). It consisted mainly of a glass still part of which was maintained, during experimentation, in a temperature-regulated water bath. The following constitute what may be regarded as the main components of the still:

(1) the detachable reservoir DR,
(2) the storage reservoirs SR1 and SR2,
(3) the volume metering tubes VMT1 and VMT2,
(4) the gas-mixing vessel GMV, and
(5) the vapour pressure measurement system VPMS.

The pressure controlling system PCS and the vacuum pumping systems VPS1 and VPS2 are associated but essential parts of the still.

The largest structural alteration or improvement of the still involved the incorporation of the detachable reservoir DR(see Figure 3.3). Apart from carrying out initial degassing in it, DR served as a means of introducing material into the apparatus. Also, once material had been transferred to the required storage reservoir, DR could be detached and cleaned without interferring with the progress of an experiment. Another significant alteration to the design involved the storage reservoirs. Their shapes were altered from being tubular all along to being spherical at the bottom. This was an attempt at increasing the efficiency of degasing of the components by providing larger surface areas per unit volume for the components. In addition, molecular sieves were dispensed with. All the other changes - most of which involved the incorporation of more "Rotaflo" glass-to-polytetrafluoroethene taps - were concerned mainly with making the still safer and/or easier to operate. The increase in the number of "Rotaflo" taps provided more sections on the apparatus. Hence effects of structural damage, due to whatever circumstances, could be minimised. Such

Figure 3.3 The detachable reservoir.

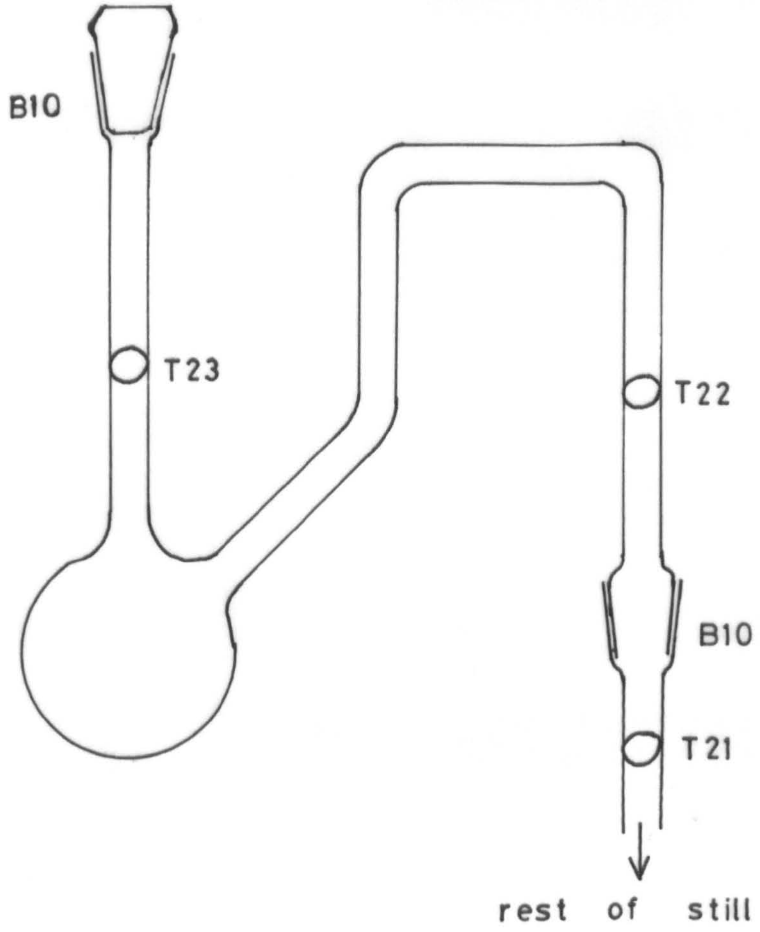
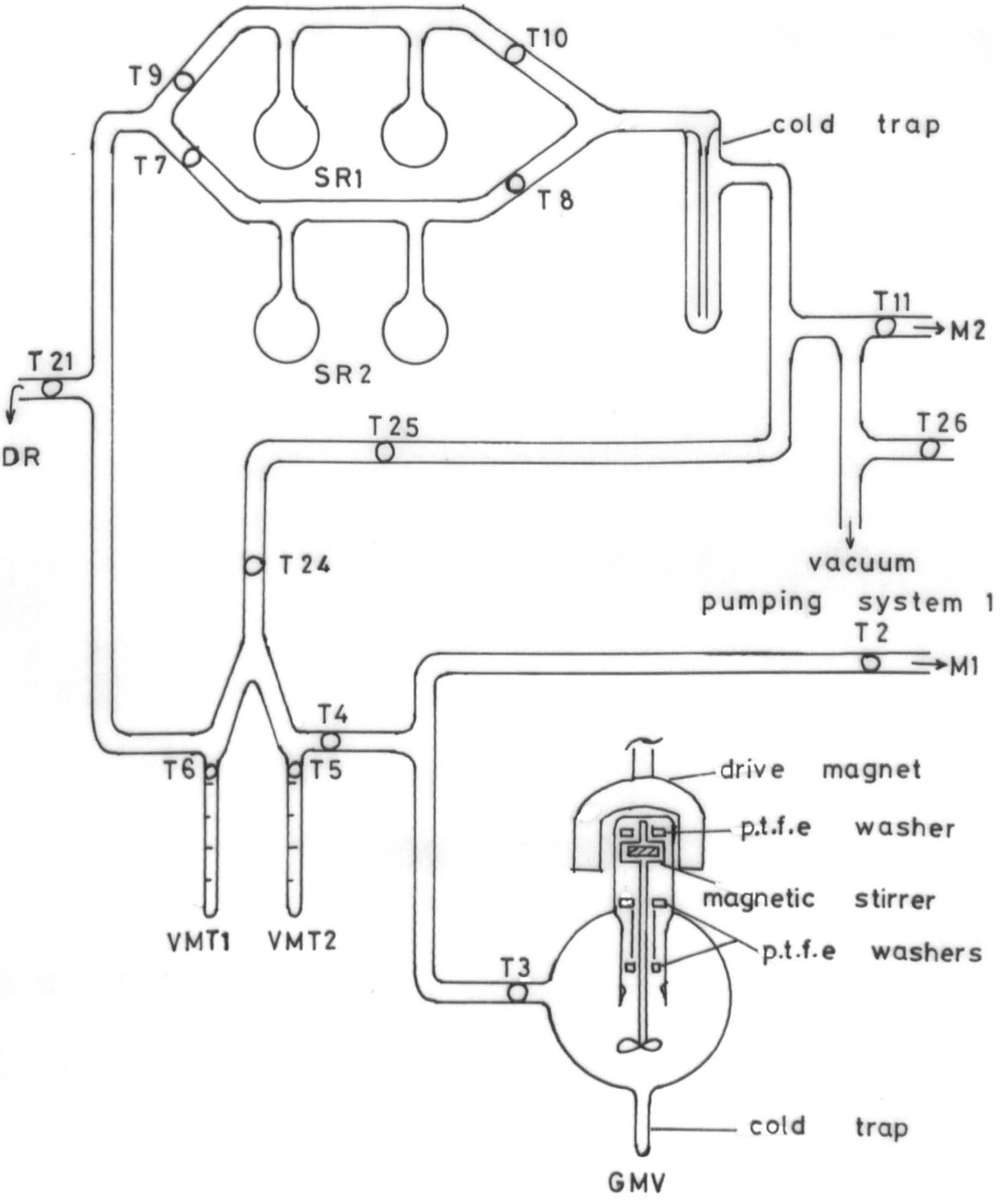


Figure 3.4 A diagram illustrating the arrangement of the storage reservoirs, volume-metering tubes and gas mixing vessel.



changes should not be viewed merely in terms of avoiding or minimising structural damage to the apparatus. In some respects, the changes had positive aspects about them. For example, the air-inlet bounded by "Rotaflo" tap T26(see Figure 3.4) was inserted to provide a means of allowing air into the apparatus without having to switch off the vacuum pumping system VPS1.

Each component of the still was used for implementing one or more of the following functions:

(1) degassing of liquid samples,
(2) storage of the degassed liquid samples,
(3) preparation of binary mixtures,
(4) measurement of vapour pressures, and
(5) 'cleaning' of the apparatus in readiness for subsequent experimental runs.

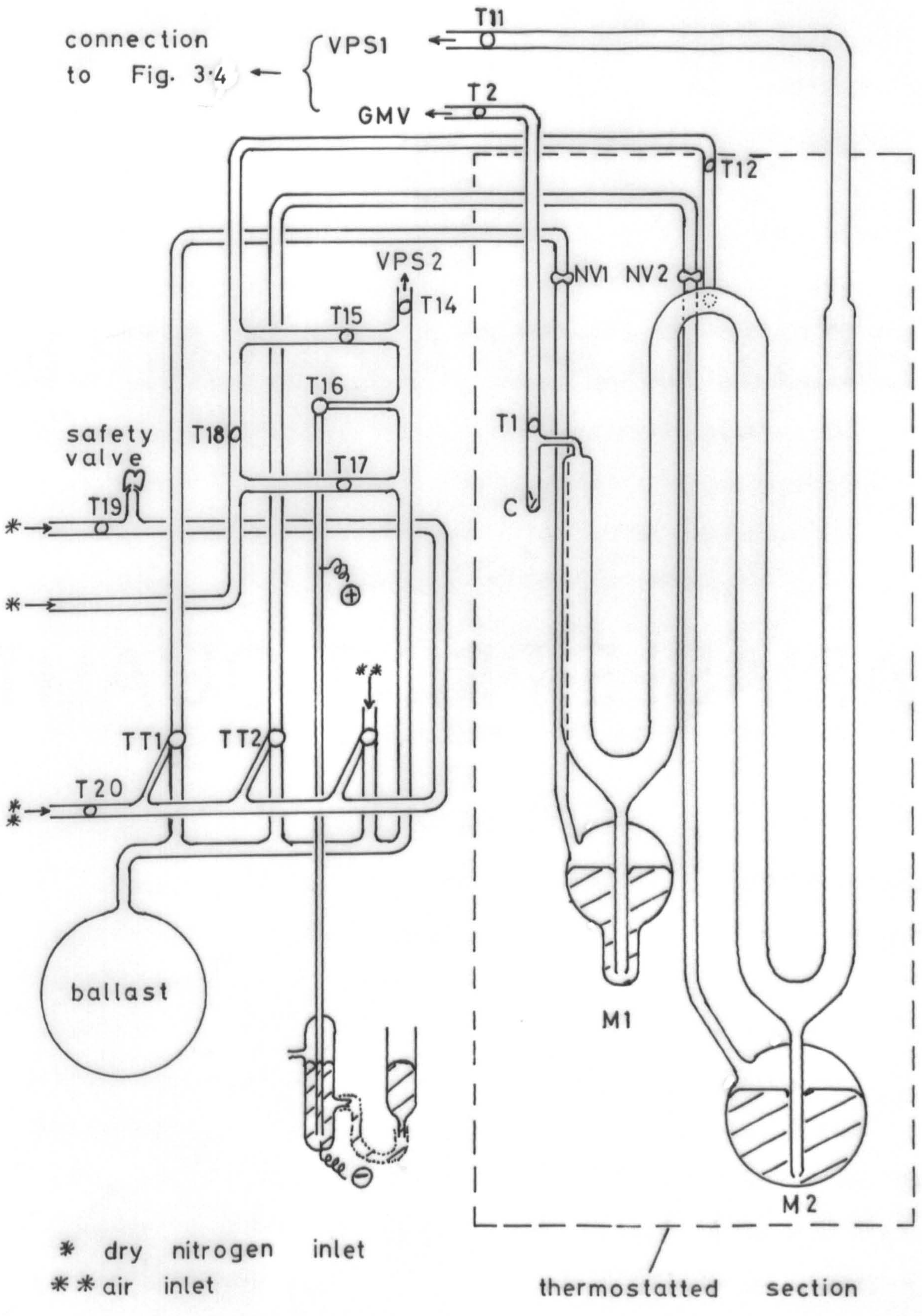
Table 3.3 is a summary of the various components and their associated functions. The functions are indicated by numbers identified above.

TABLE 3.3 Various components of the still and asociated functions.

Components	Functions
DR	1
SR1 and SR2	1,2
VMT1 and VMT2	1,3
GMV	3
VPMS	4
PCS	4
VPS1 and VPS2	5

The experimental details associated with the functioning of the various components are in Section 3.7. However, it is in order, at this juncture, to give structural descriptions of these components.

Figure 3.5 The pressure control system and the vapour pressure measuring system.



Reference to DR has been made already. Each of SR1 and SR2 comprised of two arms. This facility enabled thorough degassing by vacuum sublimation. The volume metering tubes VMT1 and VMT2, which were graduated to 10^{-2} cm^3, enabled the preparation of mixtures of approximately known compositions. The metered components were mixed in the gas-mixing vessel GMV. This comprised a bulb of ca. 930 cm^3 which was equipped with a magnetically driven propeller stirrer. Two manometers, M1 and M2, and the cell C(see Figure 3.5) constituted the vapour pressure measurement system VPMS. Each of the manometers was made of 20 mm precision bore tubing and a large bulb at the bottom which acted as a mercury reservoir. The smaller manometer, M1, was attached to C. The combination of cell C and any space above the mercury meniscus on the left-hand arm of M1 constituted the vapour pressure cell(VPC). The pressure controlling system PCS consisted of a gas ballast which was connected to the VPMS via two-way taps(TT1 and TT2) and needle valves(NV1 and NV2). Each of the vacuum pumping systems consisted of a diffusion pump and a rotary pump. Although "Rotaflo" taps T12 and T15 could serve as a way of connecting the two pumping systems, VPS1 and VPS2 were made to operate independent of each other. VPS2 served the PCS whilst VPS1 was arranged to serve the rest of the apparatus.

3.4 REGULATION AND MEASUREMENT OF TEMPERATURE

The vapour pressure measurement system was housed in a thermostatted tank, designed by Hewitt(3), in which the short-term control of temperature was well within ±0.002 K. The tank, of dimensions 1.2 m x 0.6 m x 0.6 m, consisted of a single-iron frame and bracing, as well as iron-plating and a 9.5 mm thick glass plate window. The iron-plating was coated with polyurethane paint. Stirring of the water was effected through four four-bladed propellers, of 10 cm diameter, which rotated at 300 rpm. The blades were designed so that they caused circulatory motion of tank water in a vertical mode. The tank was insulated with expanded polystyrene of 5 cm thickness. Further insulation was provided by placing polystyrene chips on top of the water.

Temperature control was by means of a mercury-toluene regulator. The regulator consisted of a long cylindrical copper tube which was attached to a head made of a combination of glass and metal(see Figure 3.6). The regulator was coupled to a diac-triac device. This device, which was combined with an adjustable switched power input, gave an adjustable constant power input to a maximum of 3 kW. The level of the power input was, to an extent, dependent on the amount of insulation provided. It was found convenient to use as low a power input as possible. This was determined by manipulating manually the control dials. Infrequently, it was found necessary to alter the controls during an experimental run. The circuit diagram of the electronic relay and power controller is illustrated in Figure 3.7. Temperature was measured with the aid of a Hewlett-Packard Model 2804A quartz thermometer. In order to record temperatures, the thermometer was connected to a Servo-scribe chart recorder.

A frequent, and quite unpredictable, problem was the sudden shift in temperature to an extent of 0.003 K at most. Since no reasonable explanation which could have accounted for the phenomenon was forthcoming, it was resolved eventually to obtain vapour pressure data even though this problem kept recurring. This necessitated the recording of vapour pressures as well as temperatures so that, in extreme cases, approximate temperature corrections could be made. However, approximate calculations indicated that the errors in the vapour pressures arising from this effect were ca. 3 Pa.

Figure 3.6 A diagram of the mercury-toluene regulator head.

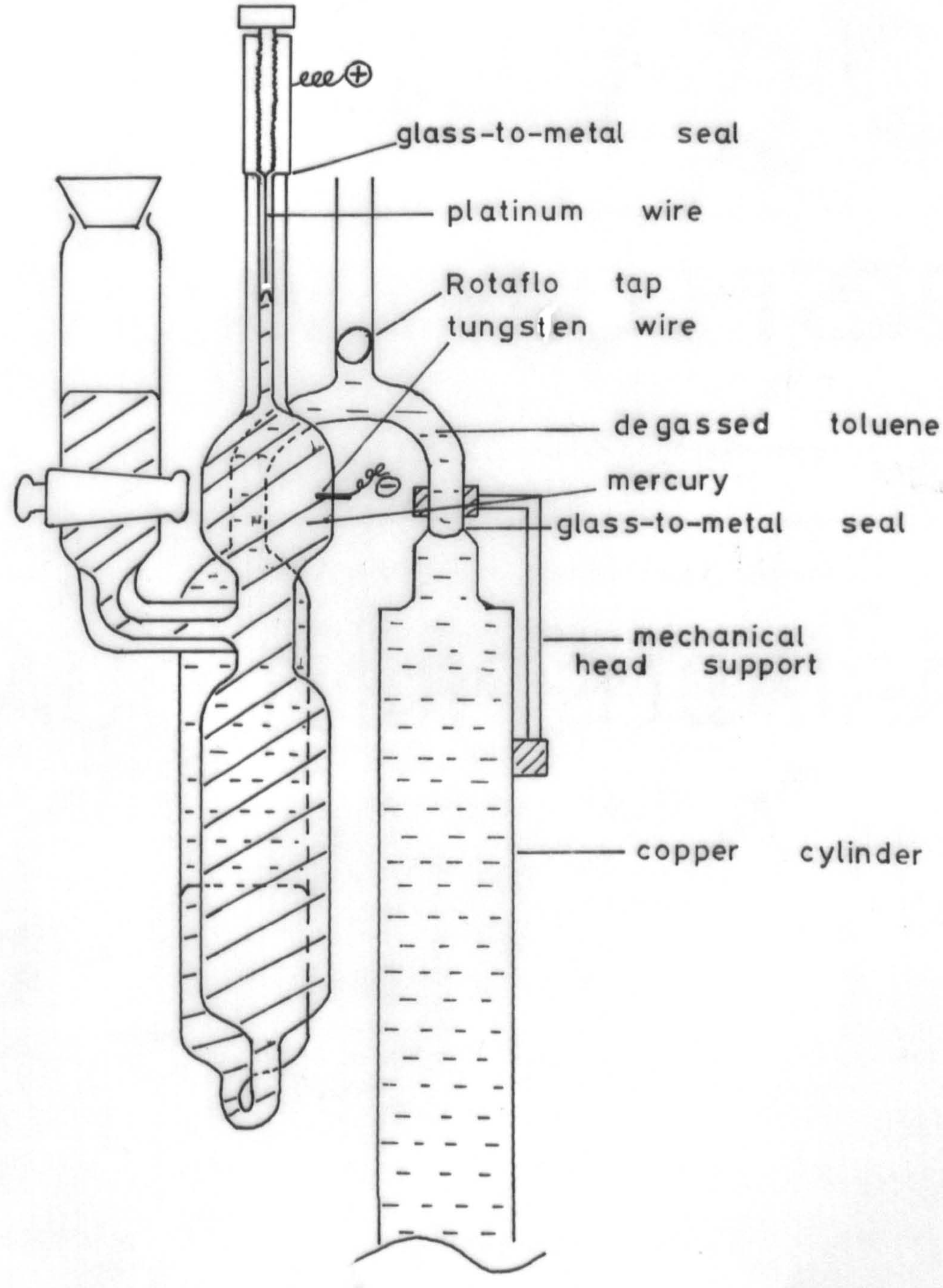
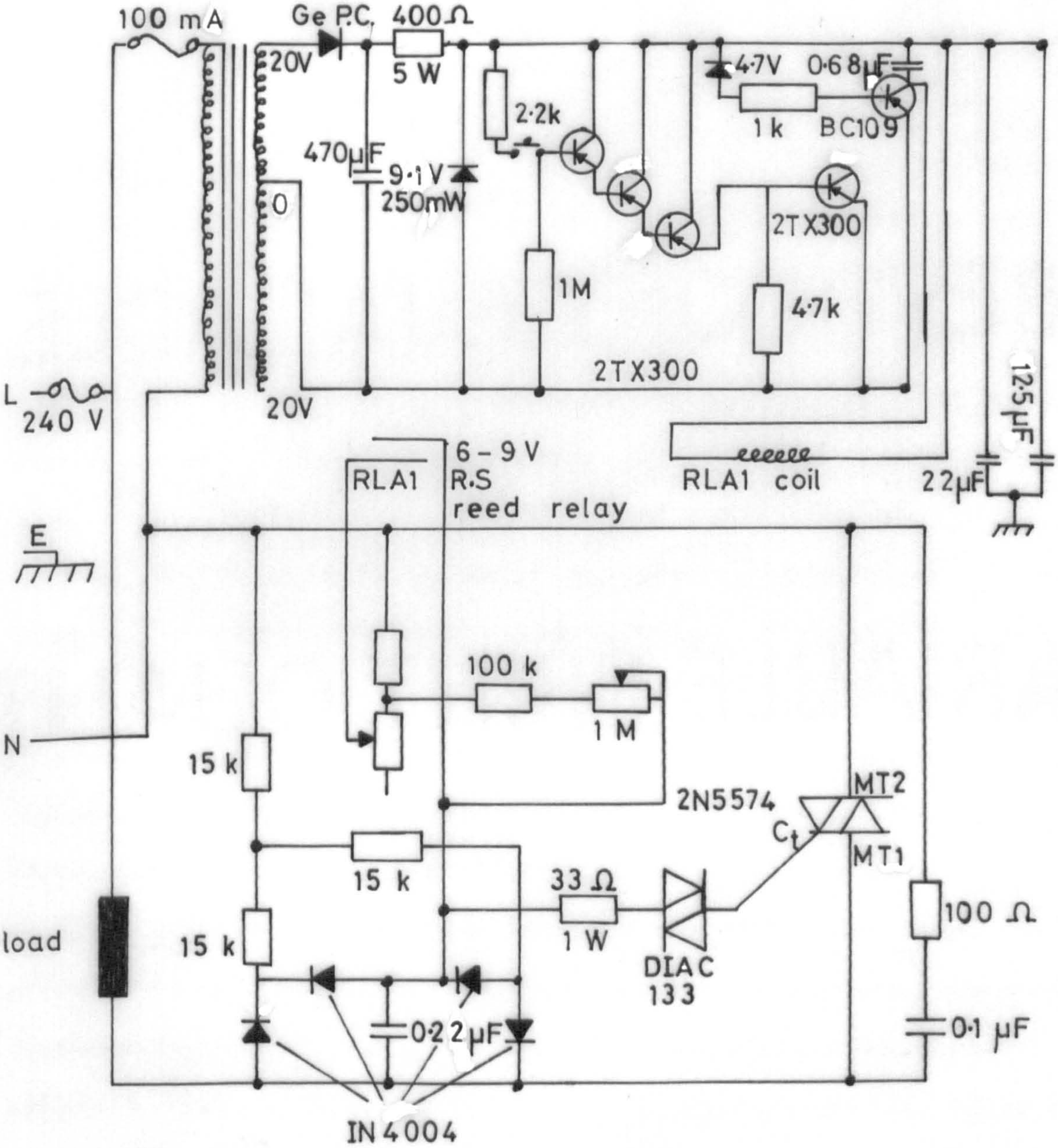


Figure 3.7 Circuit diagram of the electronic relay and power controller.



3.5 EXPERIMENTAL APPROACH IN THE PREVIOUS WORK

In the previous work(2),(3), the components were metered in the volume-metering tubes. The amounts were pre-calculated so that if both components had been transferred to the GMV, the resultant mixture would be in gaseous phase. However, instead of passing the metered amounts into the GMV, the samples were transferred directly into the "finger" of the vapour pressure cell. The level of mercury had been pre-arranged so that there was as little of the vapour space as the geometry of the cell would allow. The components were then thoroughly mixed with the aid of a magnetic stirrer. After about 30 minutes, the first of the pressure/volume readings was taken. Four or five more pressure/volume readings, at intervals of about 15 minutes, were taken. The bubble-point pressure of the mixture was then determined by plotting pressure against volume and then extrapolating the resulting line to obtain a pressure value at zero volume of the vapour phase.

The determination of the dew-point pressure then ensued. All of the material was transferred from the vapour pressure cell to the GMV. The gaseous mixture was then stirred for an hour. The manometer was set ready by raising the mercury to a desired level. After mixing, all the taps between the GMV and the manometer were opened so that some of the mixture vapour entered the vapour pressure cell. A series of compression pressure/volume readings was then taken until an approximate linear relationship between pressure and volume was obtained. Material was then condensed into the "finger". Simultaneously, the level of mercury was raised. A number of expansion pressure/volume readings was then taken. The dew-point pressure was the intersection of the compression series and the expansion series. For the benzene+cyclohexane system, the compression technique was employed in both the single-phase region and the two-phase region. This was because clear dew points could be obtained.

3.6 A CRITIQUE OF THE APPROACH IN THE PREVIOUS WORK

The principal point to note about the experimental approach in the previous work is that variable quantities of material were used for obtaining dew-point and bubble-point pressures. It is suggested that, in such a procedure, there are possibilities of compositional changes in moving from the dew point or to the bubble point pressure, or vice versa. Some of the factors that could give rise to compositional changes are presented.

If it is assumed that the components of the mixture retain in part some of their characteristics, then there may be variations in composition between the various sections of the apparatus since the diffusion coefficients of the components are likely to be different. Also, preferential transfer of one component over the other could be a function of the vapour pressures of the pure components. It is envisaged that this factor may be crucial in instances where there are relatively large differences in the vapour pressures of the components. An additional hazard associated with material transfer is condensation along connecting tubes. And since the adsorptivities on glass of the components may be different, mixture composition may be affected. McGlashan(4) suggested minimisation of the condensation problem by installing controlled heating systems along the connecting tubes. A similar heating system on the DPBP apparatus was, as now, not incorporated.

The above-mentioned factors should not be seen as operating in a mutually exclusive manner. Furthermore, they should not be taken to be exhaustive. As the design of the apparatus stands, there are no prospects of verifying experimentally the extent to which these factors affect changes in composition. Conjectures can only be made to account for the previous variable success on $G_m^E(T,x)$ determinations by the DPBP method. For example, at 313.15 K the vapour pressures of pure benzene and pure cyclohexane are quite similar whereas the vapour pressures of pure benzene and pure hexane are relatively disparate at 298.15 K. This may be a reason why the binary system benzene+cyclohexane produced satisfactory results whilst the binary system benzene+hexane gave results which were at variance with those of other workers(5),(6). Since the experimental verification of the effects by the above-mentioned, and any other, factors was outside the scope of this work, it was necessary to develop a procedure which minimises or eliminates the part played those factors. The procedure described in Section 3.7.3 is a step towards that goal.

3.7 EXPERIMENTAL

The main aspects regarding the measurement of excess molar Gibbs functions by the DPBP method are:

(1) preparation and storage of liquid samples,

(2) making up of mixtures, and

(3) measurement of dew-point and bubble-point pressures.

3.7.1 Preparation and storage of liquid samples

Pure liquids, which had been dried previously over phosphorus(V) oxide, were transferred into the detachable reservoir DR(see Fig.3.3). In this reservoir, initial degassing was carried out using the freeze-pump-thaw technique. After a satisfactory level of initial degassing, material was transferred to either of the double-limbed storage reservoirs SR1 and SR2. It was in these vessels that thorough degassing was carried out. This involved the use of liquid nitrogen as a means of producing a thermal gradient across the two limbs. Material was transferred across the thermal gradient. When all the material had turned to solid, a rotary pump was used to pump away the vapour above the solid phase. Occasionally, the freeze-pump-thaw technique was employed. During the pumping of the sublimed phase, a liquid nitrogen cold trap was provided. This was an attempt at isolating the sublimed material from any untoward volatile material within the apparatus.

From experience, it was observed that thorough degassing was accomplished by transferring some of the liquid sample from the storage vessels to the volume-metering tubes and then carrying out degassing within these tubes. Briefly, the degassing procedure within either VMT1 or VMT2 involved freezing the material with liquid nitrogen and pumping over the solid phase. On thawing, gas bubbles were invariably liberated. The freezing, pumping and thawing of the material was carried out repeatedly until there was no liberation of gases on thawing. To ensure thorough degassing, the cycle involving the non-appearance of bubbles was carried out at least three times. This was taken as a sign of sufficient degassing of material. Material treated in the above manner was then used for obtaining dew-point pressures and bubble-point pressures. Small differences between P_d and P_b values of the pure components were regarded as confirmation of sufficient degassing.

Cyclohexane was found to be a particularly difficult substance to degas. After having discounted the presence of impurity to account for large differences between P_d and P_b values, it was evident that a variation of the degassing procedure was necessary. The procedure that was eventually adopted involved cooling the cyclohexane within the VMT just sufficiently for it to remain transparent in the solid phase. Previously, it had been solidified until it had a white appearance. Using the procedure that was adopted eventually, it was observed that on thawing there were still gas bubbles that were being liberated. If the same sample was solified to whiteness, no bubbles were liberated on thawing. This effect was reproducible. It was evident that prolonged cooling resulted in co-dissolution during the thawing process. Using the other technique, the gases and cyclohexane separated according to their boiling points. As a result of this work on cyclohexane, the technique was extended to other substances.

3.7.2 Preparation of binary mixtures

The binary mixtures were prepared by transferring calculated amounts from the volume-metering tubes to the gas-mixing vessel. The quantity of material transferred was such that the mixture was in the vapour phase within the GMV. In order to determine the requisite amounts, the relation given by equation (3.26) could have been used.

$$pV = n\{RT + B(T)p\} \qquad \ldots (3.26)$$

In equation (3.26), p is about 85 per cent of the estimated dew-point pressure of a given mixture, V is the volume of the gas-mixing vessel, B(T) is the estimated second virial coefficient of the mixture, and n is the total amount of substance in the mixture. However, since p was an estimate, calculations were carried out on the basis that the mixture vapour behaved as an ideal gas. That is, the relation given by equation (3.27) was the basis for determining the amounts that were transferred into the GMV.

$$pV = nRT \qquad \ldots (3.27)$$

The application of the latter relation was further justified by the fact that n could not be obtained precisely. In preparing the mixtures, the overriding concern was that the material would be in vapour phase once it was in the GMV. It was important that approximate compositions of the mixtures were known. This was useful in that it facilitated the estimation of initial values of the compositions which were required for the iterative solutions for the unknown variables. The mixtures were then stirred within the GMV for at least four hours before measurements on dew-point pressures and bubble-point pressures were taken.

3.7.3 Measurement of dew point and bubble point pressures

Figure 3.8 is a schematic diagram of the apparatus for measuring dew point and bubble point pressures. After thorough evacuation of the apparatus, the following operations were carried out in order to measure the dew point and bubble point pressures:

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(3) the transfer of the metered components into the gas mixing vessel GMV,

(4) the adjustment of the mercury levels within either manometer M1 or both M1 and M2 before introducing material into the VPC,

(5) the transfer of some of the gaseous material from the GMV to VPC,

(6) the measurement of mercury heights within the arms of the manometers in order to obtain pressure/volume isotherms,

(7) the adjustment of mercury levels in order to obtain the bubble point pressure or the dew point pressure(depending on what had been measured initially),

(8) the pumping away of excess material as mercury heights measurements were taken, and

(9) the measurement of the liquid volume of the material whose dew point and bubble point pressure had been measured.

Determination of the volume of VPC

The volume of the vapour pressure cell VPC was determined by the nitrogen compression method. The technique involved the introduction of dry pure nitrogen into the VPC and obtaining a series of pressure/volume readings which were then analysed in order to give the volume of the cell.

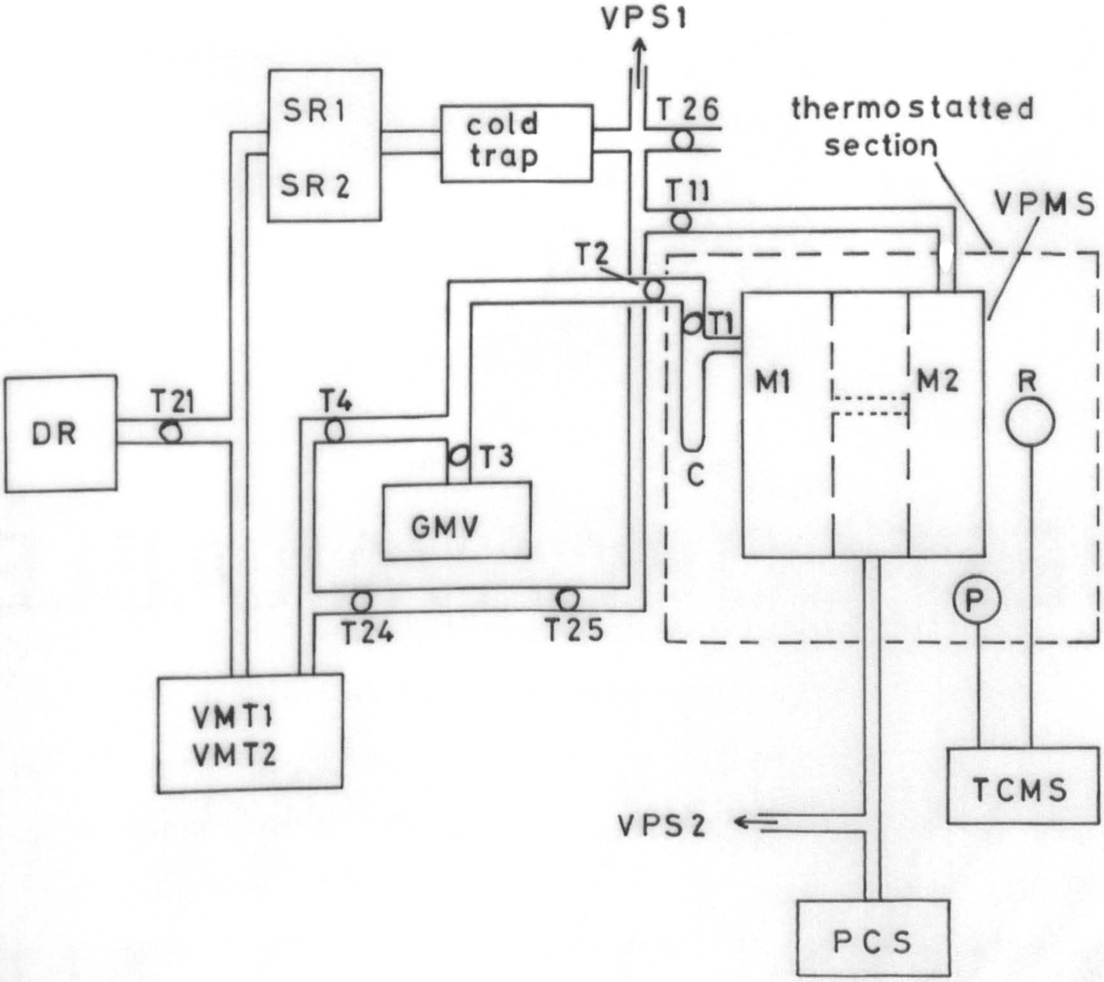

Figure 3.8 A schematic diagram of the apparatus for measuring dew point and bubble point pressures. TCMS is the temperature control and monitoring system. R and P are the regulator and thermometer probe, respectively. The other symbols are defined in the text.

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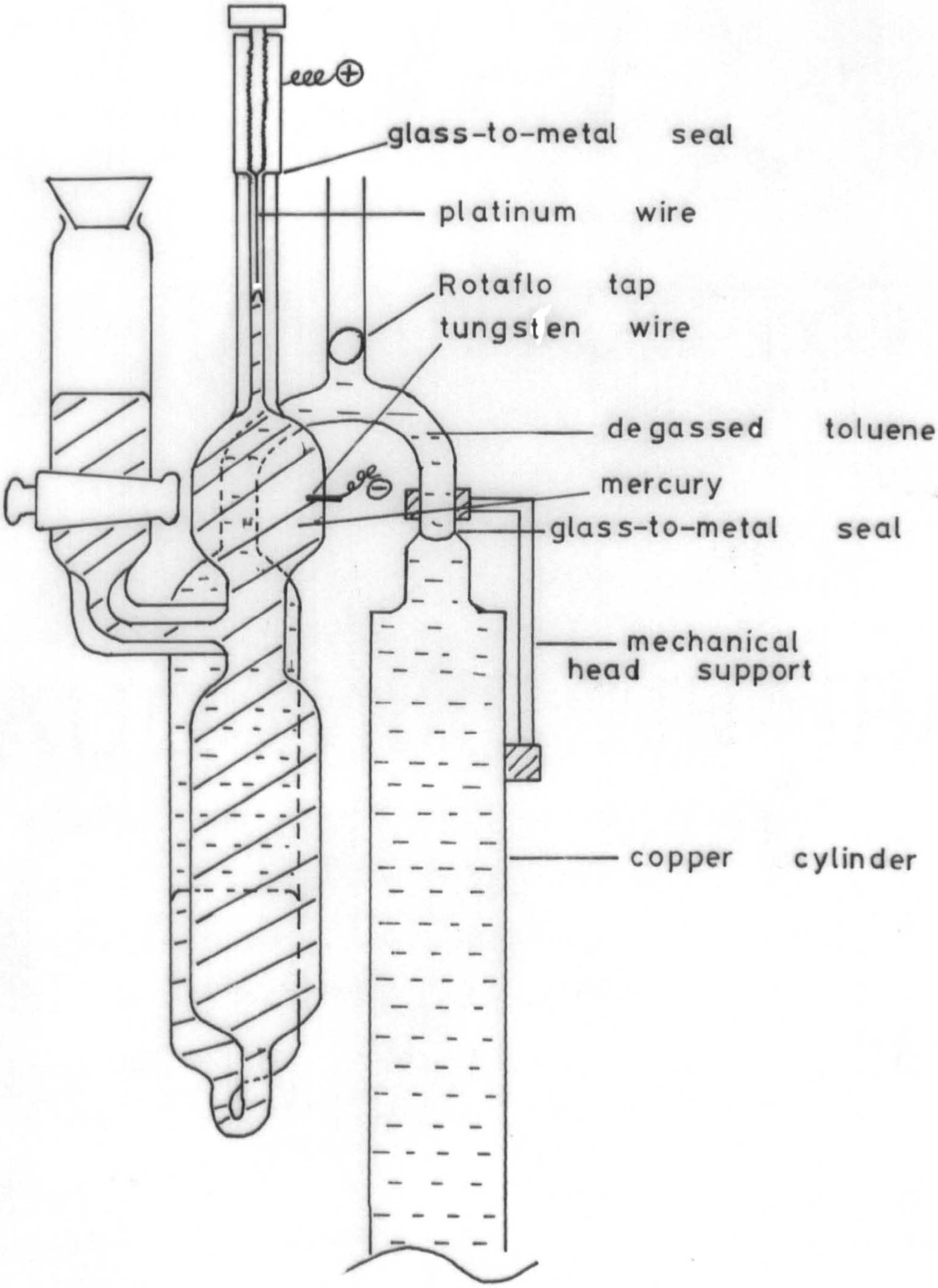

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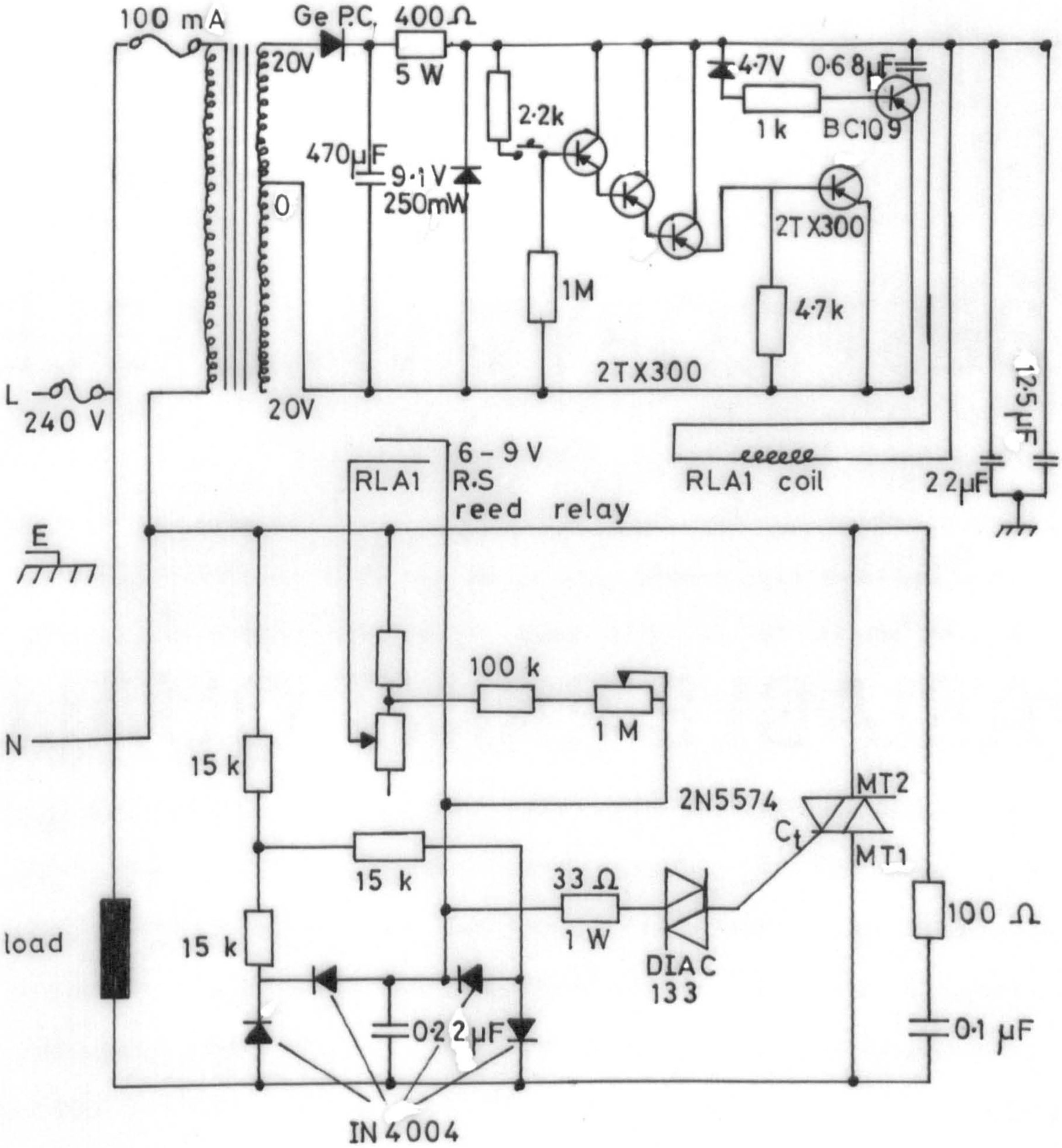

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(4) the adjustment of the mercury levels within either manometer M1 or both M1 and M2 before introducing material into the VPC,

(5) the transfer of some of the gaseous material from the GMV to VPC,

(6) the measurement of mercury heights within the arms of the manometers in order to obtain pressure/volume isotherms,

(7) the adjustment of mercury levels in order to obtain the bubble point pressure or the dew point pressure(depending on what had been measured initially),

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Determination of the volume of VPC

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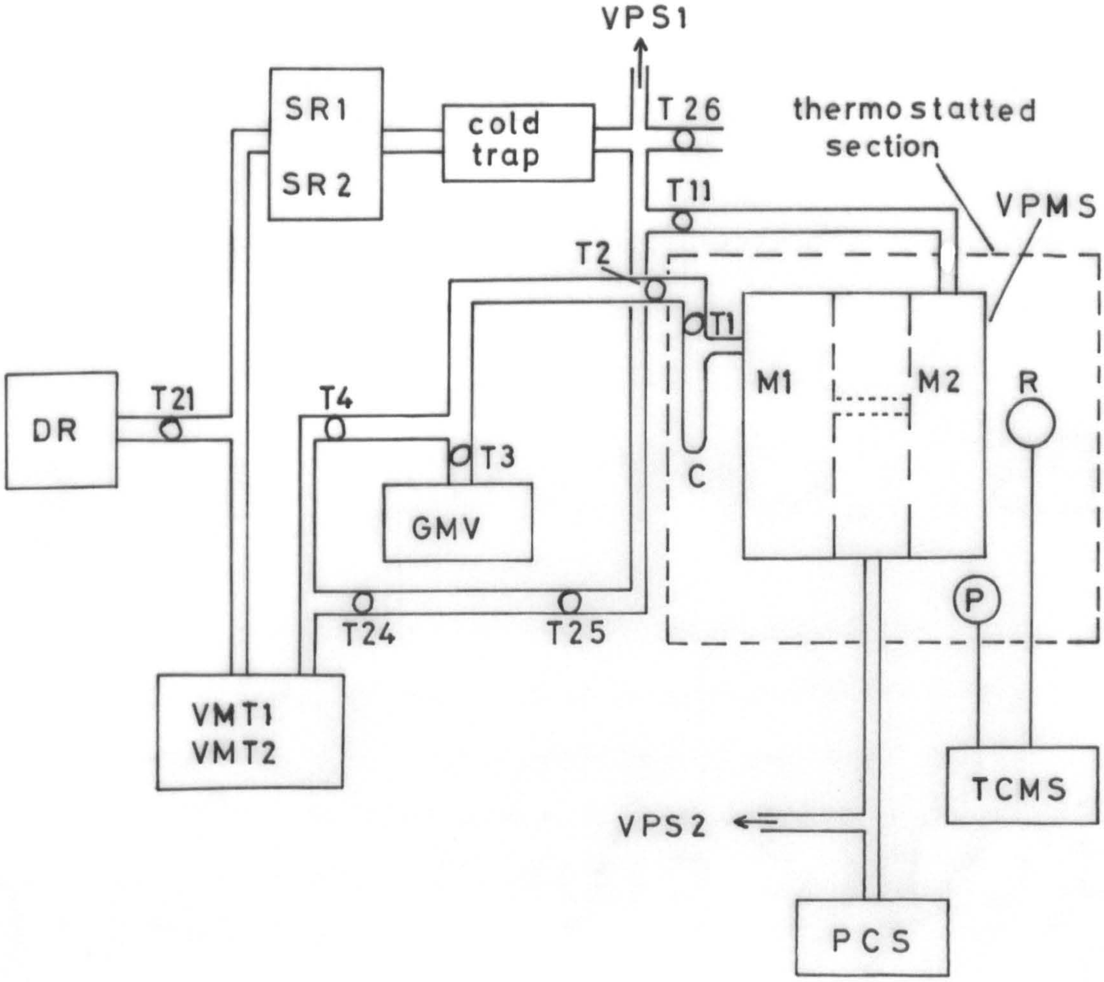


Figure 3.8 A schematic diagram of the apparatus for measuring dew point and bubble point pressures. TCMS is the temperature control and monitoring system. R and P are the regulator and thermometer probe, respectively. The other symbols are defined in the text.

Before carrying out the operation, all taps associated with the manometers were closed. Then after filling the ballast vessel with dry nitrogen, mercury was raised to about three-quarters of the way in the U-bend of manometer1(M1). In manometer 2(M2) mercury was raised to about halfway, generally, above the U-bend. By opening taps T15 and T12, some nitrogen was admitted into both arms of M1 and the left arm of M2. In order to ensure that this operation was carried out smoothly, the following steps were taken.

(a) Nitrogen was allowed into the section bounded by taps T15 and T12.

(b) With tap T15 closed, some nitrogen was allowed into the manometers by opening T12 cautiously.

(c) Whilst step (b) was carried out, the mercury level in the U-bend of M1 was maintained roughly using needle valve 1(NV1).

(d) The steps (a) to (c) were repeated until there was a reasonable height difference in the mercury levels in the arms of M2.

When sufficient nitrogen had been admitted into the manometers, the mercury levels in both manometers were raised slowly, using NV1 and NV2, to heights which permitted easy use of the cathetometer. The system was then left for an hour to allow for equilibration. By raising the mercury in M1, a series of compression pressure/volume readings were taken.

Measurement of components within VMT1 and/or VMT2

For components to be metered within VMT1 and/or VMT2, they had to be transferred from the storage reservoirs SR1 and SR2, respectively. To transfer material from SR1 to VMT1, the following steps were taken. Taps T4, T5 and T24 were closed and then taps T6 and T9 were opened. Then VMT1 was cooled with liquid nitrogen contained in a Dewar vessel. VMT1 was dipped in such a manner that the level of transferred and condensing material was always just above the level of the liquid nitrogen. When about

0.1 cm^3 of the material had been transferred, tap T9 was closed to isolate SR1. Tap T6 was closed and tap T24 was opened. After thawing, the material within VMT1 was degassed as described in Section 3.7.1. More material was transferred, in 0.1 cm^3 portions, and degassed until there was an excess of about 0.05 cm^3. Then, if necessary, further degassing was carried out.

The transfer of material from SR2 into VMT2 involved similar steps to those involved in the transfer from SR1 to VMT1. The difference was that, in the former case, taps T5 and T7 were manouvred in place of taps T6 and T9, respectively, and vice versa.

Transfer of components into the GMV

Before the transfer of pure components from VMT1 or VMT2 to GMV, taps T2 and T24 were closed. Depending on whether material was to be transferred from VMT1 or VMT2, tap T6 or T5 was opened as appropriate. Also, tap T4 was opened. The finger of GMV was then cooled with liquid nitrogen so that material condensed within the gas-mixing vessel. After ensuring that all the material had been transferred into GMV, tap T3 was closed and taps T2 and T24 were opened.

In the case of mixtures, the components were first mixed in one of volume-metering tubes before transfer into the GMV. For convenience, the more volatile component was transferred into the VMT holding the less volatile component. This process required that taps T4 and T24 be closed before the transfer across the volume-metering tubes. This transfer, although not necessary, was convenient in that one of the VMT's could be cleaned by evacuation in readiness for subsequent material transfer from the corresponding storage vessel. The mixture was then transferred to GMV using the same method as described for the transfer of pure components.

Pre-adjustment of mercury levels in M1 and/or M2

The transfer of material into VPC was preceded by the raising of the mercury levels within the arms of the manometers M1 and/or M2. Taps T12, T14 and T15, as well as two-way taps TT1 and TT2 and needle valves NV1 and NV2, were closed. Then dry nitrogen was passed into the ballast via tap T17. TT1 and TT2, and NV1 and NV2, were then opened in order to raise slowly the mercury levels within M1 and M2. In M1, mercury was raised to about 10 cm above the U-bend of the manometer whereas in M2, it was raised to about 55 cm. Taps T1, T2 and T11 were then closed. When the expected pressure values were sufficiently low, only M1 was used. In this case, the procedure was similar except that TT2 and NV2 were not opened.

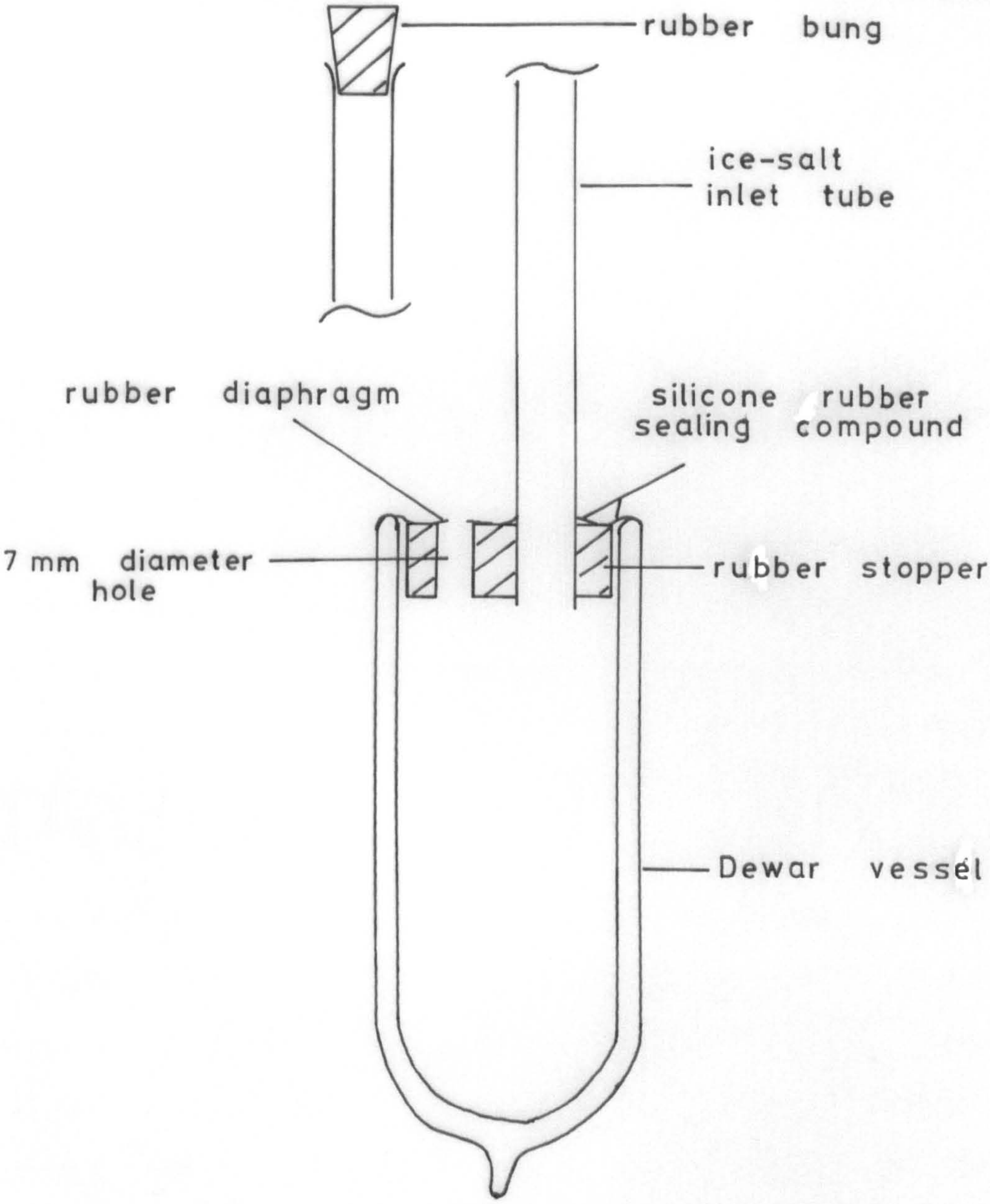
Transfer of material from GMV into VPC

The initial step in this transfer was the closure of tap T4. Taps T3 and T1 were then opened. Tap T2 was then opened slowly in order to lessen the mechanical shock due to the movement of mercury within M1. The magnetic stirrer in GMV was then switched on and the apparatus was left in this mode for at least an hour. Tap T1 was then closed and the excess material was pumped away via taps T4, T24 and T25.

Measurement of heights of the mercury levels

The measurement of heights of the mercury levels enabled one to obtain pressure/volume isotherms from which dew point pressures and bubble point pressures could be determined. Although it is of little or no consequence whether dew point pressures or bubble point pressures are measured first, it was found convenient to measure the latter first. In fact, in the earlier stages of the work, dew point pressures were measured first in some instances.

Figure 3.9 The submersible cold trap.



The measurement of bubble point pressures was accomplished thus. Using an ice-salt mixture contained in a vessel as shown in Figure 3.9, material within VPC was condensed in cell C(see Figure 3.5). Whilst this was proceeding, some nitrogen from the ballast was introduced into and contained within the section bounded by taps T12 and T15. As soon as the upward movement of mercury within the left arm of M1 could not be detected by eye, TT1 was closed temporarily and NV1 was opened cautiously. Immediately, tap T12 was opened cautiously. Often, it was necessary to adjust the mercury levels in M2 by temporary closure of TT2 and cautious opening of NV2. In order to introduce more nitrogen into the controlling system, the following steps were taken. The needle valves were closed as well as tap T12. The two-way taps TT1 and TT2, as well as T15, were opened and then re-closed. Then any of NV1, NV2, and T12 could be re-opened as required. When the mercury level approached the top end of the left arm of M1, NV2 and T12, if they were open, were closed. The vessel containing the ice-salt mixture was then slid down slowly. This was done in such a manner that the mercury level either was maintained or moved up slowly. The complete withdrawal of the ice-salt vessel was followed by the immediate closure of NV1. TT1 and TT2 were then opened, and closed, to allow more nitrogen within the sections bounded by the two-way taps and needle valves. Tap T15 was opened and then the nitrogen was pumped away. After at least 30 minutes, the first set of heights of the mercury levels in all arms of M1 and M2 were measured. A cathetometer, with a precision of 10^{-3} cm, was used for this purpose. The measurement of subsequent sets of heights was carried out after successive expansions of the volume of the vapour pressure cell. This was accomplished thus. Tap T15 was closed and then tap T12 was opened cautiously. Once the mercury level in the left arm of M1 had dropped to the required height, tap T12 was closed and tap T15 was opened. Then the liquid material in cell C was stirred. The stirring was accomplished by using a small hand magnet to move two glass-encapsulated wire pieces within C. After 30-40 minutes of re-equilibration, height measurements were taken.

Usually, five sets of pressure/volume readings were required.

Mercury levels within the manometers were adjusted so that dew point pressures could be determined. The procedure that was adopted eventually was regarded as the least cumbersome route towards the measurement of dew point pressures. Initially, an approximate height of the mercury level in the left arm of M1 at which all material vaporised was estimated. A number of approximate pressure/volume points were then taken to check this region experimentally. Once this was confirmed, detailed measurement of dew point pressures was embarked upon.

The mercury level was lowered such that all the material in VPC was in vapour phase. This was accomplished by any combination of the following steps:

(a) TT1 and NV1 were opened so that nitrogen was pumped away,

(b) TT2 and NV2 were opened to pump away the nitrogen, and

(c) T15 was opened and, after pumping away of nitrogen and re-closure of T15, T12 was opened cautiously.

As soon as mercury had reached the required level, the needle valves, T12 and T15 were closed. Nitrogen was then re-introduced into the ballast and TT1 and TT2 were then closed. After a period of equilibration, the first of the pressure/volume isotherms were measured. More of the isotherms were obtained, by compression, until the two-phase region was reached. Compression was achieved by use of NV1. Occasionally, it was necessary to open, and close, TT1 during this series of measurements. After reaching the two-phase region, nitrogen was pumped away from the ballast. The volume of VPC was re-expanded, using the procedure described above, until all the material was in vapour phase. Nitrogen was re-introduced into the ballast and an ice-salt mixture was used to move the mercury level in VPC to a height above the dew point height. Five or six pressure/volume points were then obtained by expansion in a fashion similar to the determination of the bubble point pressure.

Measurement of liquid volume of the material

The volume of the vapour pressure cell was expanded to ensure that all material was in the vapour phase. Also, it was found convenient to pump away, via T12 and T15, the nitrogen above the mercury levels in the right arm of M1 and the left arm of M2. With tap T24 closed, one of the volume-metering tubes was then cooled with liquid nitrogen and the material from the VPC was allowed to condense within the tube. The volume of the liquid material was thus obtained.

Determination of P_d and P_b from isotherms

Figure 3.10 is an example of a plot of pressure/volume readings which were used to determine the dew point pressure. The bubble point pressure example is illustrated in Figure 3.11. Although plotting the graphs manually would probably suffice in the accurate determination of P_d and P_b of a given component or mixture, it was found expedient to resort to mathematical anlyses. It was assumed that, in the regions of phase change, the relationships between pressure and volume were linear. Hence

$$p = a + bV \qquad \ldots (3.28)$$

where p is the pressure, V is the volume of VPC, and a and b are constants. Linear least-squares methods were used for evaluating a and b. When computing for P_b, the pressure/volume isotherm is extrapolated to a value of V when the volume of the vapour phase is zero.

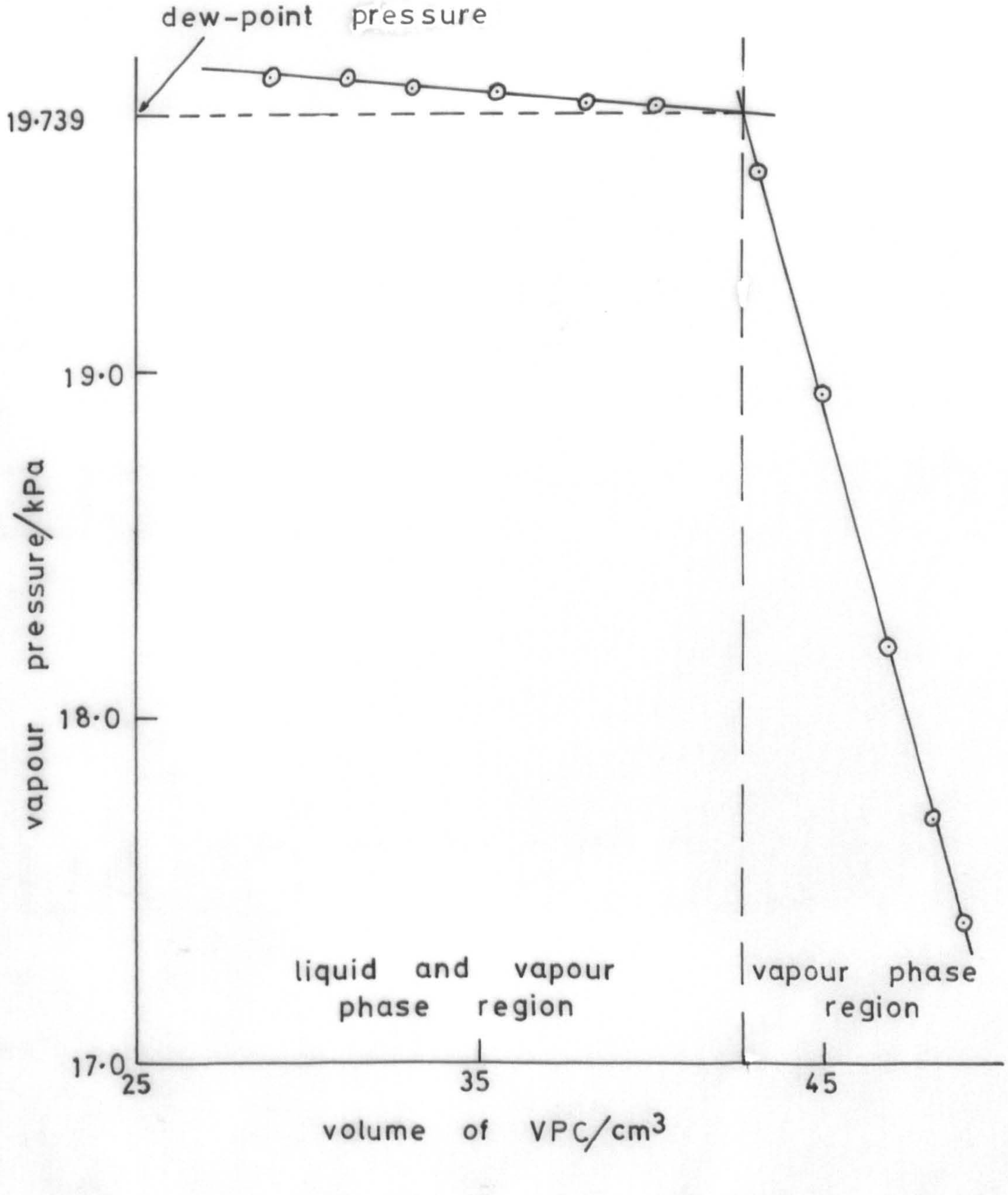


Figure 3.10 An example of the pressure/volume results for the determination of the dew point pressure of (1-x)-benzene + x-hexane at 298.25 K. The overall mole fraction of hexane was 0.7. Computation of results led to a value of 19739 Pa.

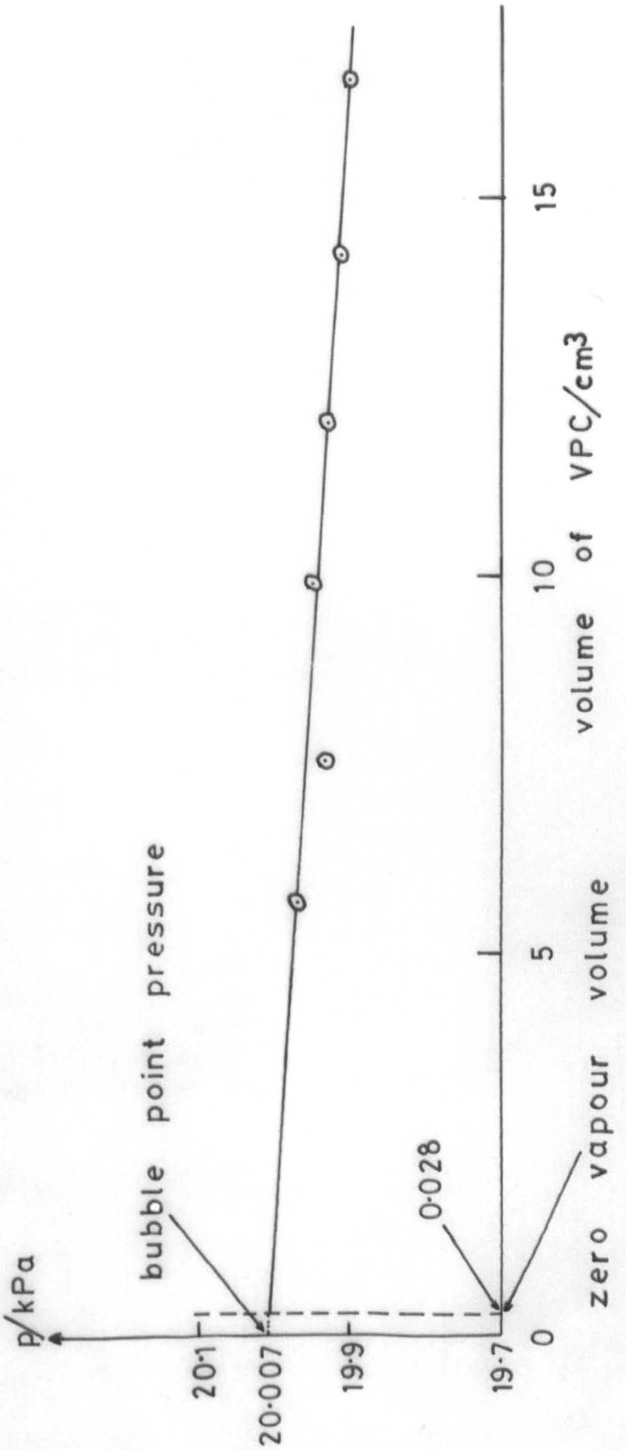


Figure 3.11 An example of the pressure/volume results for the determination of the bubble point pressure of benzene+hexane at 298.25 K. The overall mole fraction of hexane was 0.7. Computation of results led to a value of 20007 Pa.

3.8 RESULTS AND DISCUSSION

The DPBP apparatus was used for obtaining excess Gibbs functions of the binary systems

(a) (1-x)-benzene + x-cyclohexane, and

(b) (1-x)-benzene + x-hexane.

Both these systems were studied previously by the DPBP method(2),(3). The results of the first system were in good agreement with literature results(7). However, the results of the benzene+hexane system did not compare well with published data(5),(6). The systems were thus studied as a means of testing the new procedure as described in Section 3.7.3.

The materials were obtained commercially. Benzene was Research grade(BDH Chemicals Limited), with a stated purity of 99.9%. The cyclohexane was spectrograde reagent(Fisons). Gas chromatographic analyses of both reagents did not indicate significant levelsof impurity. The hexane sample used had a stated purity of 99%(Aldrich). The hexane was shaken, in the cold, with mercury to remove any traces of sulphur. As it did not discolour the mercury, it was decided that it was good enough to use without further purification. All these liquids were dried with phosphorus (V) oxide; the minimum drying duration was five days.

3.8.1 Benzene+cyclohexane

Dew point and bubble point pressures of this system were measured at 313.18 K. The vapour pressures of pure benzene and pure cyclohexane were found to be 24431 Pa and 24709 Pa, respectively. In analysing the dew point and the bubble point pressures, the following values of virial coefficients and liquid molar volumes were used(2):

$B_{11} = -1276 \text{ cm}^3 \text{ mol}^{-1}$, $B_{22} = -1456 \text{ cm}^3 \text{ mol}^{-1}$,

$B_{12} = -1324 \text{ cm}^3 \text{ mol}^{-1}$,

V_1^o = 91 cm^3 mol^{-1}, V_2^o = 111 cm^3 mol^{-1}.

The analysis was accomplished with the aid of a computer progam. The results are displayed in Tables 3.4 and 3.5. Table 3.4 gives the calculated compositions X, Y and Z(see equations 3.1 to 3.3). The Redlich-Kister equation obtained was

$$G^E/J\ mol^{-1} = 1204.44x(1 - x) \qquad \ldots\ (3.29)$$

This equation compared favourably with the work carried out previously in this laboratory(2). The equation produced a root-mean-square of the pressure residuals of 48 Pa. Although this was rather large, it was decided that the results were satisfactory. Furthermore, the results from the smoothed equation compare well with those from the work of Brewster and McGlashan(7). Table 3.6 shows the comparison between the two sets of results. Table 3.5 shows the pressure residuals for the three sets of dew point and bubble point pressure measurements.

Also shown in Table 3.4 are the four values of G^E associated with each mixture. XPXSGX represents the experimental G^E from P_b measurement and is calculated from equation (2.7) with $p_m = P_b$, x = X and y = Y. XPXSGZ is the corresponding G^E value for the dew point pressure. In this case p_m = P_d, x = Z and y = X. CAXSGX and CAXSGZ are the calculated G^E values form the bubble point and dew point, respectively. These are evaluated using equation (3.29) with x = X for bubble point and x = Z for the dew point.

The first dew point and bubble point set in Table 3.4 indicates that measurements were carried out at or very near the azeotrope. At this point, all values of G^E must be equivalent. The slight deviations, both in compositions and in G^E values, reflect the scatter of the results.

TABLE 3.4 Results of the binary system benzene+cyclohexane. The column headings are explained in the text.

Measurements were carried out at 313.18 K.

Redlich-Kister coefficient 1 = 0.46255

P_b / Pa	P_d / Pa	X	Y	Z	XPXSGX / J mol^{-1}	CAXSGX / J mol^{-1}	XPXSGZ / J mol^{-1}	CAXSGZ / J mol^{-1}
27528	27528	0.5953	0.5767	0.6187	287.6	290.2	285.8	284.1
27243	26977	0.7117	0.6726	0.7556	250.0	247.2	220.1	222.4
26931	26628	0.7689	0.7242	0.8148	214.5	214.0	181.3	181.7

Root-mean-square value of XPXSGX - CAXSGX = 2.7 J mol^{-1}

Root-mean-square value of XPXSGZ - CAXSGZ = 2.0 J mol^{-1}

Standard deviation of the pressures = 47.6 Pa

TABLE 3.5 Comparison of calculated pressure values using the results from analysing the measured dew-point and bubble-point pressures.

(1-x)-benzene + x-cyclohexane at 313.18 K.

Equation number	Calculated pressure/Pa	Presure residual/Pa
1	27550.4	-22.4
2	27558.5	-30.5
3	27515.4	12.6
4	27507.7	20.3
5	27225.7	17.3
6	27207.6	35.4
7	26986.4	-9.4
8	27005.9	-28.9
9	26929.1	19.9
10	26925.9	5.2
11	26629.5	-1.1
12	26633.2	-4.8

TABLE 3.6 A comparison between current results and those of Brewster and McGlashan(7) for the binary system (1-x)-benzene+x-cyclohexane. In both cases, smoothed equations were used to yield values of excess Gibbs functions at rounded mole fractions.

x	G^E/J mol^{-1}(current)	G^E/J mol^{-1}(literature)
0.1	108.4	114.4
0.2	192.7	199.2
0.3	252.9	256.8
0.4	289.1	289.0
0.5	301.1	297.2
0.6	289.1	282.6
0.7	252.9	245.6
0.8	192.7	186.4
0.9	108.4	104.8

3.8.2 Benzene+hexane

Dew point and bubble point pressures were measured at 298.25 K. The vapour pressures of pure benzene and pure hexane were found to be 12758 Pa and 20240 Pa, respectively. These values compared favourably with literature values (8). In analysing the measured pressures, the following values of virial coefficients and liquid molar volumes were used(5):

$B_{11} = -1490\ \text{cm}^3\ \text{mol}^{-1}$, $B_{22} = -1984\ \text{cm}^3\ \text{mol}^{-1}$,

$B_{12} = -1737\ \text{cm}^3\ \text{mol}^{-1}$,

$V_1 = 89.41\ \text{cm}^3\ \text{mol}^{-1}$, $V_2 = 131.61\ \text{cm}^3\ \text{mol}^{-1}$.

The results are displayed in Tables 3.7 and 3.8, with calculated compositions and G^E values in the former table; the latter table shows the pressure residuals. The notation used is identical to that described in Section 3.8.1.

The Redlich-Kister equation obtained was

$$G^E/\text{J mol}^{-1} = x(1-x)\{1565.38 + 90.8837(1-2x) - 130.138(1-2x)^2\} \quad ...(3.30)$$

The root-mean-square(RMS) values of the G^E residuals and pressure residuals are also in the tables. The RMS value of the pressure residuals is very much greater than most of the individual residuals. This is partly due to a limited number of the degrees of freedom. However, the RMS values of the G^E residuals, 1.2 J mol^{-1} in both cases, indicate that the results are internally consistent.

The comparison between current results and those of Murray and Martin(6) is shown in Table 3.9. Compared to the previous effort carried out in this laboratory(3), there is considerable improvement. The dependence of G^E on mole fraction is illustrated in Figure 3.12. The two plots are for current measurements and those of Murray and Martin(6).

TABLE 3.7 Results of the binary system benzene+hexane. The column headings are explained in the text. Measurements were carried at 298.25 K.

Redlich-Kister coefficient 1 = 0.63126
Redlich-Kister coefficient 2 = 0.03665
Redlich-Kister coefficient 3 = -0.05248

P_b Pa	P_d Pa	X	Y	Z	$\frac{\mathrm{XPXSGX}}{\mathrm{J\ mol^{-1}}}$	$\frac{\mathrm{CAXSGX}}{\mathrm{J\ mol^{-1}}}$	$\frac{\mathrm{XPXSGZ}}{\mathrm{J\ mol^{-1}}}$	$\frac{\mathrm{CAXSGZ}}{\mathrm{J\ mol^{-1}}}$
15895	14182	0.1547	0.3107	0.0626	205.3	204.8	89.5	90.7
17089	15093	0.2395	0.4107	0.1080	286.5	287.3	151.6	150.0
17912	15903	0.3126	0.4771	0.1560	341.1	339.8	204.5	206.2
19297	18202	0.5020	0.6088	0.3441	389.5	391.2	357.6	356.8
19824	19288	0.6069	0.6749	0.4985	369.2	367.4	390.6	391.4
20007	19739	0.6637	0.7117	0.5893	339.2	339.6	374.1	373.9
20163	20041	0.7181	0.7492	0.6731	303.8	303.9	334.1	334.1

Root-mean-square value of XPXSGX - CAXSGX = 1.2 J mol^{-1}

Root-mean-square value of XPXSGZ - CAXSGZ = 1.2 J mol^{-1}

Standard deviation of the pressures = 19.0 Pa

TABLE 3.8 Comparison of calculated pressure values using the results from analysing the measured dew-point and bubble-point pressures. (1-x)-benzene + x-hexane at 298.25 K.

Equation number	Calculated pressure/Pa	Presure residual/Pa
1	15893.6	1.4
2	15895.8	-0.8
3	14184.3	-2.3
4	14181.7	0.3
5	17096.7	-7.3
6	17095.3	-5.9
7	15080.6	12.7
8	15093.0	0.3
9	17901.6	10.4
10	17903.1	8.9
11	15917.0	-13.6
12	15907.2	-3.8
13	19306.6	-9.4
14	19312.5	-15.3
15	18194.1	7.8
16	18198.1	3.8
17	19815.5	8.5
18	19805.6	18.4
19	19294.2	-6.5
20	19293.5	-5.8
21	20010.0	-2.6
22	20012.9	-5.5
23	19737.7	1.1
24	19736.2	2.6
25	20163.9	-0.9
26	20165.0	-2.0
27	20041.0	0.1
28	20039.9	1.2

TABLE 3.9 A comparison between current results and those of Murray and Martin(6) for the binary system (1-x)-benzene+x-hexane. In both cases, smoothed equations were used to yield values of excess Gibbs functions at rounded mole fractions.

x	G^E/J mol^{-1}(current)	G^E/J mol^{-1}(literature)
0.1	139.9	164.5
0.2	251.7	278.8
0.3	332.0	349.9
0.4	378.8	383.4
0.5	391.3	384.2
0.6	370.1	355.9
0.7	316.7	301.5
0.8	234.2	223.1
0.9	126.8	122.3

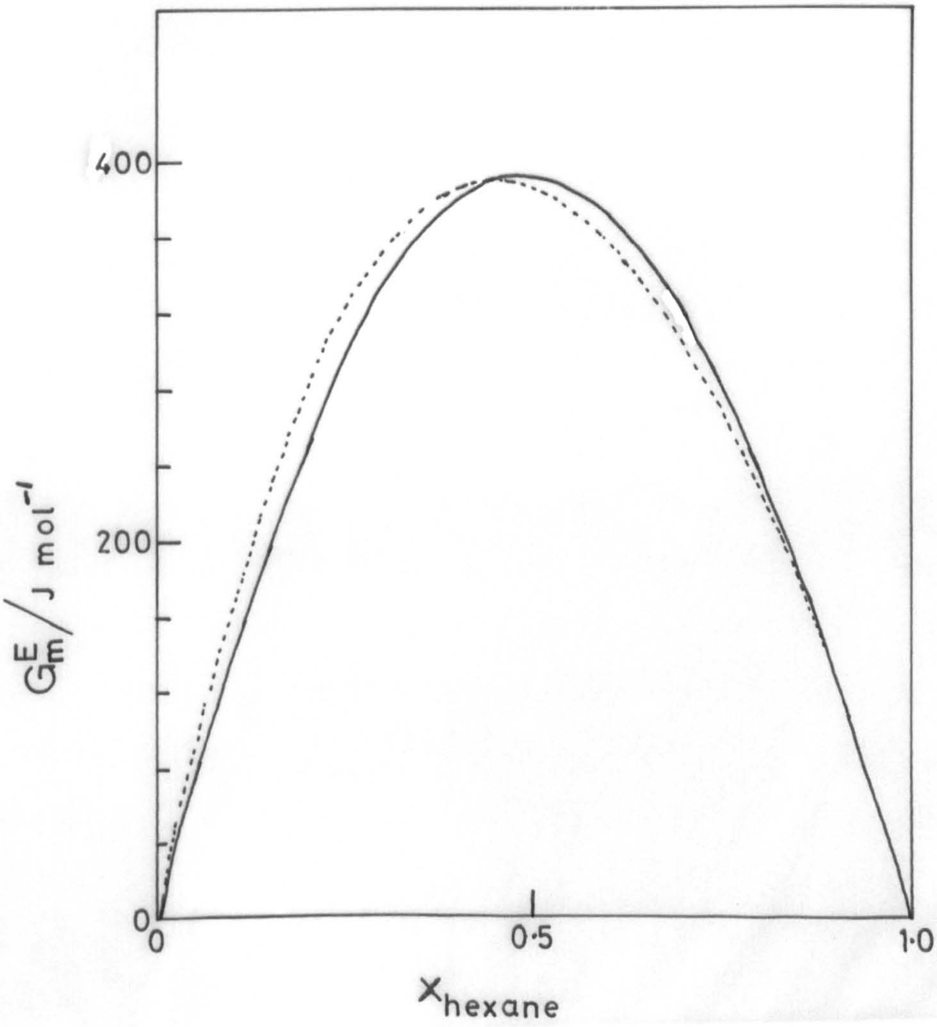


Figure 3.12 Excess Gibbs functions as a function of composition for the binary system benzene+hexane. The full line represents the results from this work(at 298.25 K). The dotted line represents the work of Murray and Martin(at 298.15 K)(6).

3.8.3 Discussion

Having decided on the current procedure for the DPBP method, the work on benzene+cyclohexane was purely diagnostic. The real test lay with the benzene+hexane system. The results of this system indicate that there is still room for improvement. The likely causes for the difference in the results are now discussed and suggestions for further work are given in Section 3.9.

In the current work, gravitational condensation was observed in both systems. That is, some of the liquid material in cell C vaporised and condensed on top of the mercury meniscus in the left arm of manometer M1(see Figure 3.5). This phenomenon was observed even when bubble point pressures were being measured. That is, even when the mercury meniscus was near the top of the left arm of M1, condensation occurred. Given that the total quantity of material used for each run was of the order of 0·03 cm^3(liquid phase), it is likely that pressure values were affected. In addition, the situation could not be rectified quantitatively, say by developing relevant mathematical relations, since it was not easy to measure the actual volumes of the liquid material in both parts of the apparatus. In contrast, the other research groups used larger quatities of material. Any condensation that may have occurred would have had minimal effect on pressure values. This is because vapour compositions would have changed only very slightly.

A recurring problem was related to the difficulty of thorough degassing of liquid samples. This difficulty was solved eventually(see Section 3.7.1). In fact, it was discovered after prolonged experimentation that about 0.3 cm^3 of liquid within a VMT was the maximum quantity that could be degassed successfully. Thus at high mole fractions of one of the components, degassing had to carried out in a stepwise fashion. However, the pressure/volume isotherms for P_b measurements indicated that trace amounts of air had minimal effect.

3.9 SUGGESTIONS FOR FURTHER WORK

From the discussion, it can be seen that the results are not sufficiently accurate yet they are not entirely hopeless. With such a state of affairs, it is not unreasonable to suggest ways that may improve results. It is thought that results are not sufficiently accurate due mainly to deficiencies associated with the design of the vapour pressure cell(VPC). The present design is somewhat difficult to improve on for the following reasons.

(1) There are large volume changes associated with converting a fixed quantity of material from being entirely in the liquid phase to being entirely in the vapour phase, or vice versa. Even if the presence of mercury allows room for manouvrability in altering the volume of VPC, the total permissible volume is still not large enough to work with larger quantities of material.

(2) The measurement of P_b requires that the vapour space in between above the surface of the liquid phase in C and the top of the mercury meniscus in the left arm of M1 must be as small as possible. This is because it is necessary to minimise the extrapolation of the pressure/volume isotherms to zero vapour volumes. However, there are structural distortions above certain levels of the left arm of M1. These distortions are a result of glass-blowing work of C to the rest of the manometer. This is a constraint on the reduction of the vapour space.
It is suggested, therefore, that improvements on VPC design can take place along the following lines. A cylindrical form of the vapour pressure cell is suggested. At the base of this cylinder, there would be a "finger" into which, under suitable conditions, liquid phase material would be lodged. The volume of the VPC would be altered by use of a piston with a leak-proof piston washer.[Details regarding materials for constructing this section of the apparatus can only be sorted out at the time of construction.]
Material, in vapour form, would be introduced near to the top end of the cylinder.

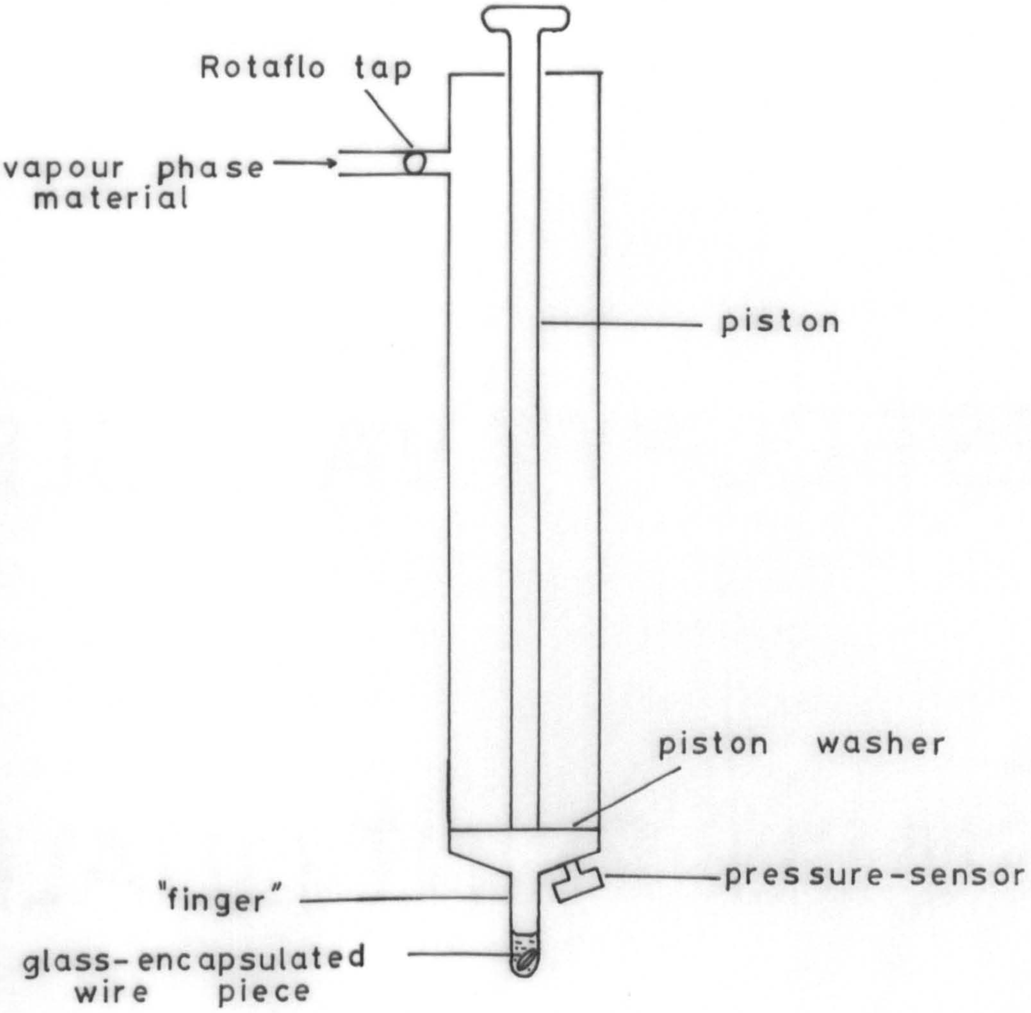


Figure 3.13 A diagram of the suggested vapour pressure cell.

Figure 3.13 is a diagram of the suggested vapour pressure cell. Material would be introduced into VPC with the piston washer just above the inlet at the side. Pressure/volume measurements would then be obtained by compression. Pressure would be measured with the aid of a pressure-sensoring device such as a pressure transducer. The pressure device would be located near to the base of VPC. It should be noted from Figure 3.13 that the base wall of the VPC would have a slight slope. This would ensure that, on compression, all of the liquid material would collect in the "finger". Liquid material would be stirred by moving the glass-encapsulated iron piece with an external magnet.

The initial difficulty with the suggested design would be the calibration of volume of VPC. However, this would be compensated for with the relative ease of measuring pressures. Also, it should be realised that the suggested design would not eliminate shortcomoings associated with the use of small quantities of material and extrapolations to zero vapour volumes. However, problems related to gravitational condensation would be eliminated entirely.

As for the rest of the DPBP apparatus, it is not visualised presently that design improvement would necessarily lead to improved results. Any changes would have to be related to personal tendencies. On a general note, it may be desirable to redesign the storage section so that one could circumvent stepwise degassing when quantities greater than 0.3 cm^3 are required. This could be done, for example, by having more volume-metering tubes.

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CHAPTER 4

MEASUREMENT OF SOME EXCESS VOLUMES OF MIXING

4.1 DESIGN FEATURES

The main design features in connection with this work are:

(a) the dilatometer,

(b) the preparation and storage of liquid samples, and

(c) temperature control.

4.1.1 The dilatometer

A batch-type dilatometer of similar design to the one used by Hewitt(1) was employed in the determination of excess volumes of mixing. The only modification was the length of the precision bore capillary stem which, in this case, was shorter. Figure 4.1 is a diagram of the assembly.

The diameter of the capillary bore was specified by the manufacturers to be 0.086 cm. The radius of the capillary bore was calibrated by determining changes in the heights of the mercury meniscus levels which corresponded with given changes in mass of mercury. In this determination, a thimble-shaped attachment (see Figure 4.1) replaced the dilatometer body. This attachment was designed to have as low an internal volume as possible. This was an attempt at reducing the weight of the whole calibration assembly. The following is an outline of the procedure that was adopted in determining the radius of the capillary bore.

(1) The apparatus was weighed when empty.

(2) Mercury was introduced into the apparatus and the mass of mercury, m_1, was obtained.

(3) The assembly was left to equilibrate for at least an hour after which

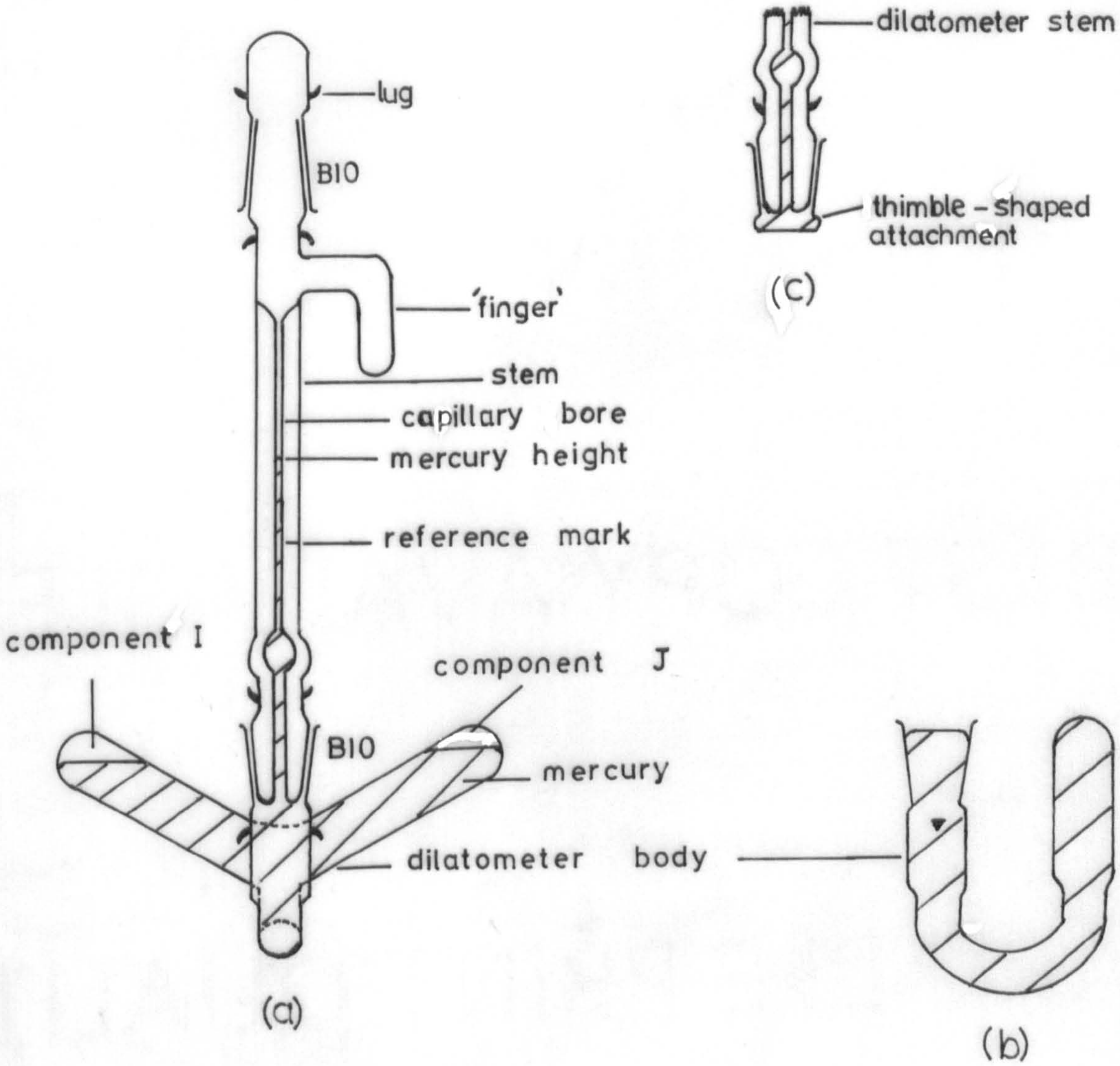


Figure 4.1 (a) Assembly of the dilatometer. (b) Side view of dilatometer body before filling with liquid component. (c) Arrangement for determining radius of capillary bore of stem.

the mercury meniscus level relative to a reference point was determined. This was designated as h_1.

(4) Using a syringe with a fine needle attached to it, some of the mercury was removed from the capillary bore. The assembly was weighed again. Thus m_2, the mass of mercury left in the apparatus, was obtained.

(5) Height h_2 was obtained by repeating step (3).

(6) The radius of the capillary bore was thus calculated from mass changes and corresponding height changes.

(7) Steps (2) to (6) were repeated a number of times and the mean value of the radius was obtained.

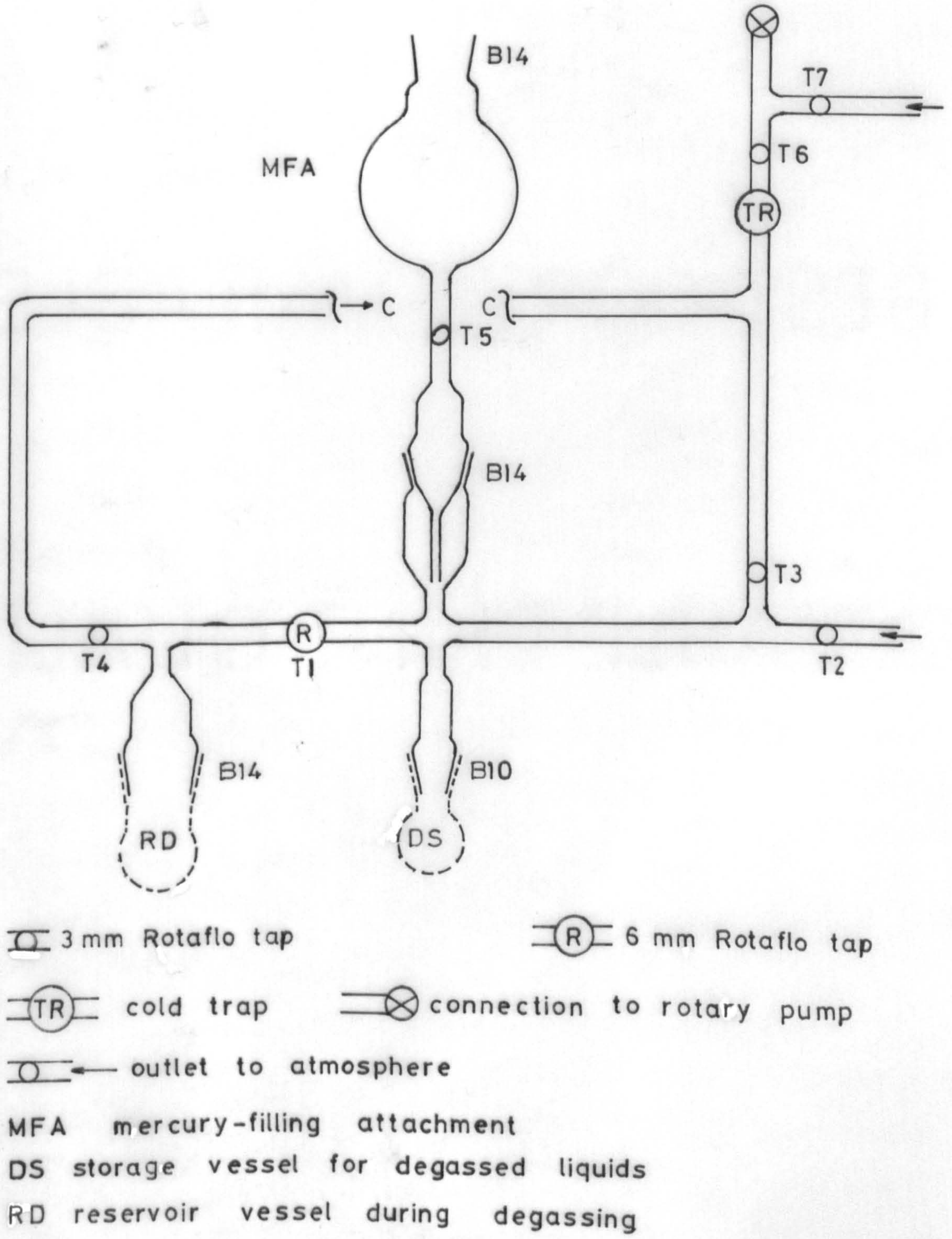
From the experimental determination, the radius of the capillary bore was found to be 0.0428 cm, with a standard deviation of 0.0001 cm. This method of determining the radius was also found to be an effective way of checking the uniformity of the capillary bore along the stem. Mention must be made of the fact that none of the determinations were treated with allowance for volume changes due to compressibility as successive height changes were not large enough to distinguish between compressibility effects and the experimental margin of error arising from determinations of height changes.

4.1.2 Sample preparation and storage

Figure 4.2 is a diagram of the apparatus for degassing of the liquid samples. The same apparatus was used for filling evacuated dilatometer bodies with mercury. Samples were obtained at purity levels such that further purification was deemed unnecessary.(See Section 4.2.2 for details.)

Before undergoing degassing, samples were dried by contacting with anhydrous phosphorus pentoxide for at least a week. Portions of the liquid samples were then transferred, under dry nitrogen conditions, to oven-dried round-bottomed flasks with B14 sockets. The flasks were then attached to point RD as depicted in Figure 4.2. The storage vessel, of a special form, was attached to point DS. The original design by Hewitt(1) was found to be

Figure 4.2 Diagram of the liquid degassing and mercury-filling rig.



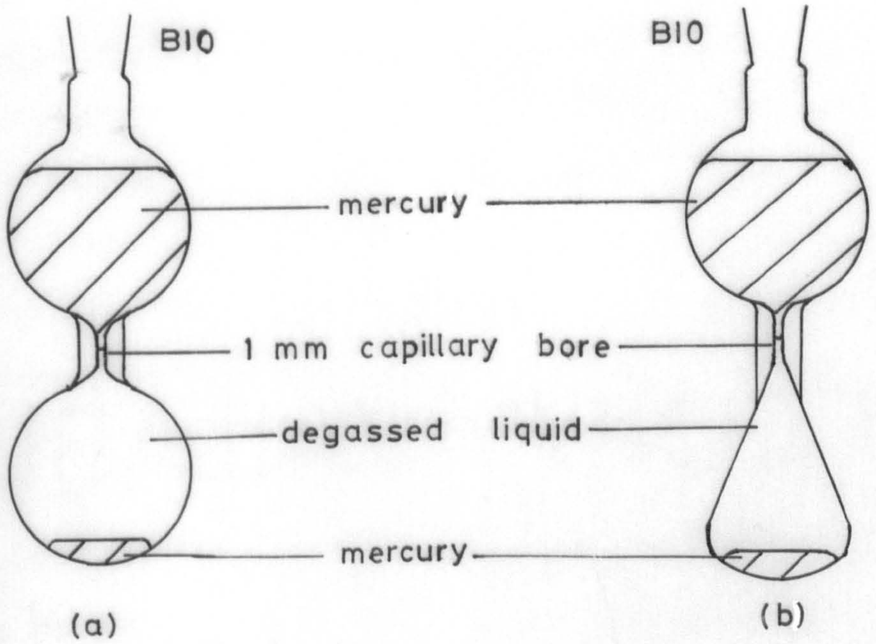


Figure 4.3 The storage vessels. Model (a) was used by Hewitt(1). Model (b) is the modified version.

inappropriate especially when small quantities of material were available. Hence it was modified so that the lower bulb was tappered at the top. The comparison in the designs is indicated in Figure 4.3.

Using liquid nitrogen as a way of effecting a thermal gradient, some of the liquid was passed from point RD across tap T1 to point DS, where the liquid was thoroughly degassed using the freeze-pump-thaw procedure. In the meantime, the freeze-pump-thaw procedure was carried out on the bulk sample at point RD, tap T4 being used as the exit. Then more of the liquid was passed from RD to DS, the accumulating sample being thoroughly degassed at DS. The process was repeated many times until the required amount of liquid had been accumulated in the storage vessel. The degassed sample was then sandwiched between layers of mercury as shown in Figure 4.3.

The procedure described above was not appropriate for liquids of relatively high boiling points because the transfer across the established thermal gradients was not fast enough, unless if the liquids were heated at point RD. The alternative procedure involved having all of the liquid in the storage vessel. The degassing was then accomplished by the usual freeze-pump-thaw technique. In latter stages of the work all samples were treated in this manner. The exception was tetramethylsilane, for it was more efficient to degas it using the method of collecting minor portions at a time.

4.1.3 Temperature control and measurement

The experiments involving the measurement of excess volumes of mixing were carried out in a thermostatted water bath with a short-term control in temperature of within ±0.001 K. The thermostatted system consisted of a cylindrical tank of 40 cm diameter and 34 cm height. It was surrounded with expanded polystyrene of 5 cm thickness, with a layer of polystyrene chips covering the top section. A stirrer, which operated continuously, was employed. Agitation of the water was enhanced by attaching a baffle which was positioned in such a way that it acted counter to the rotation of the

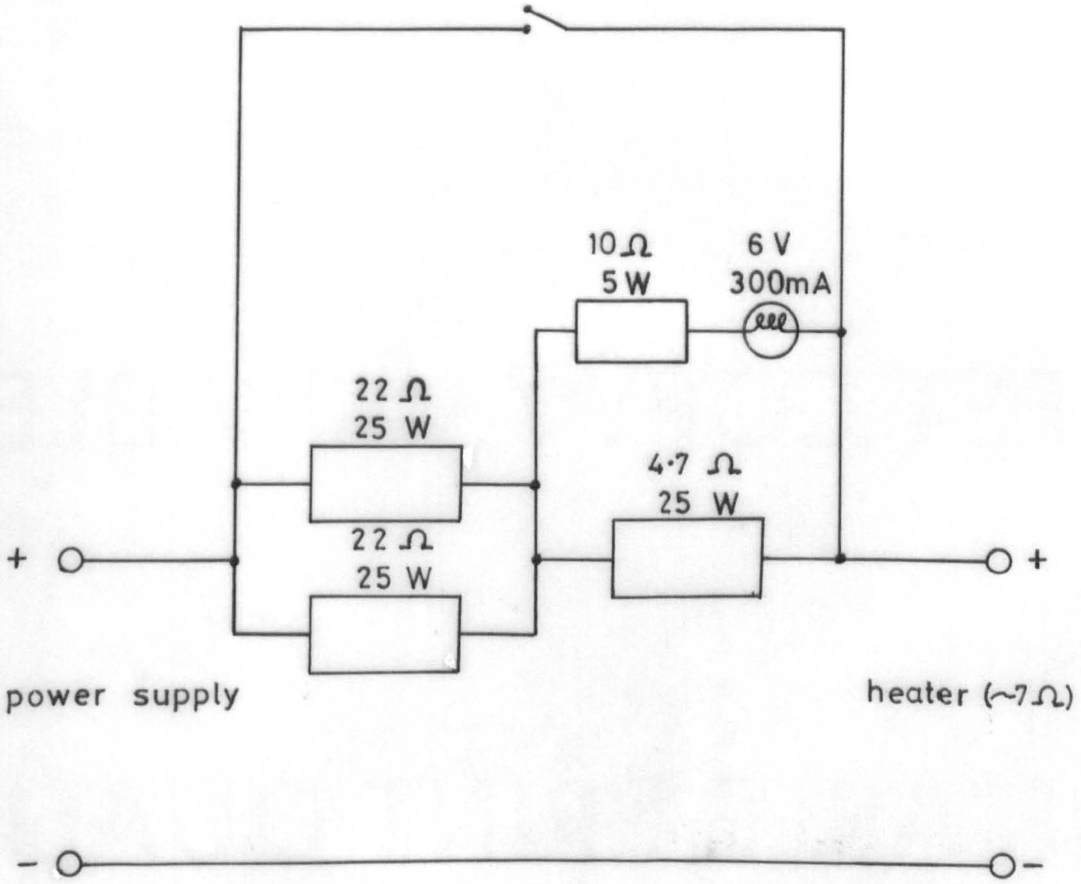
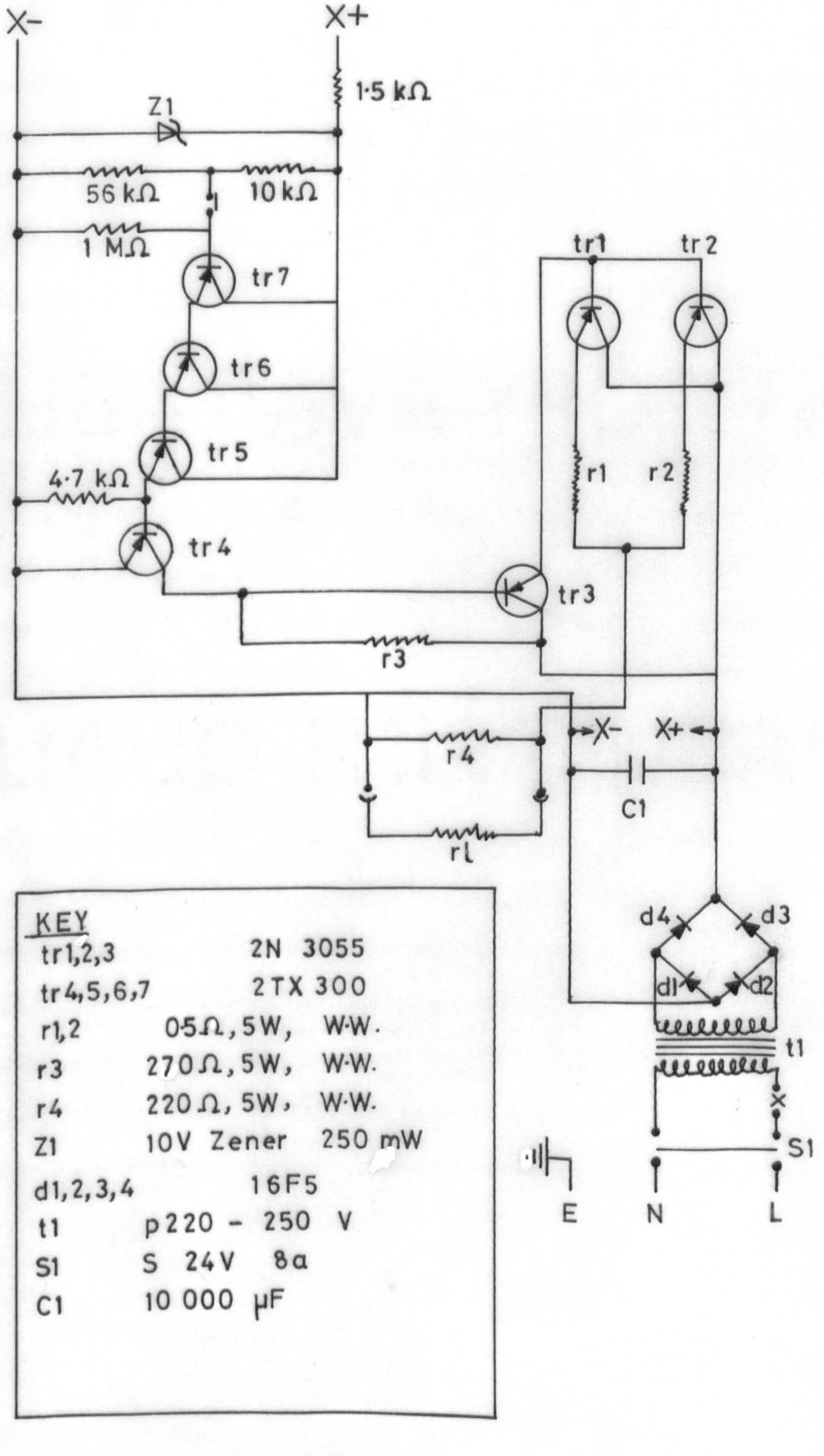


Figure 4.4 A circuit diagram of the electronic relay for controlling a 7.1 ohm heater(dropper resistor). All 25 watt resistors were mounted on heat sink.

Figure 4.5 A circuit diagram of the electronic relay for controlling a 22 ohm heater.



KEY

tr1,2,3	2N 3055
tr4,5,6,7	2TX 300
r1,2	0·5Ω, 5W, W·W.
r3	270Ω, 5W, W·W.
r4	220Ω, 5W, W·W.
Z1	10V Zener 250 mW
d1,2,3,4	16F5
t1	p220 - 250 V
S1	S 24V 8a
C1	10 000 μF

stirrer. A tap-water cooling coil was also installed. It was used when ambient temperatures were within one Kelvin of the temperature at which the excess volumes were being determined. For fine temperature control, the heating device consisted of Nichrome wire supported on glass tubing and protected with insulating varnish. The resistance of the heater was 7.1 ohm. Fig. 4.4 is a circuit diagram of the electronic relay for controlling the heater. In fact, this was a dropper resistor. The original design catered for a heater with a resistance of 22 ohm. Figure 4.5 is a circuit diagram of the electronic relay for the original design(1). However, the original relay was retained because the corresponding heater proved to be convenient as a booster heater. The 7.1 ohm heater, as well as the dropper resistor, would then replace the booster heater so that fine temperature control could be achieved. The regulation of temperature was achieved with the use of a mercury-toluene regulator. Figure 4.6 is a schematic diagram of the arrangement of the apparatus for the regulation of temperature. After considerable experimentation, it was found that temperature regulation was improved by the almost total immersion of the regulator in the thermostatted bath. In the short term, temperature control improved from ±0.0025 K to well within ±0.001 K. In the long term, the control improved from ±0.010 K to ±0.005 K. The temperature was measured with the use of a Hewlett-Packard Model 2804 A quartz thermometer. In order to record temperatures the thermometer was connected to a Servo-scribe chart recorder. This arrangement was convenient in that the experimenter obtained a quick visual image of the level of control, as well as a permanent record of temperature over an extended period. The quartz thermometer was calibrated regularly against a standard platinum resistance thermometer.

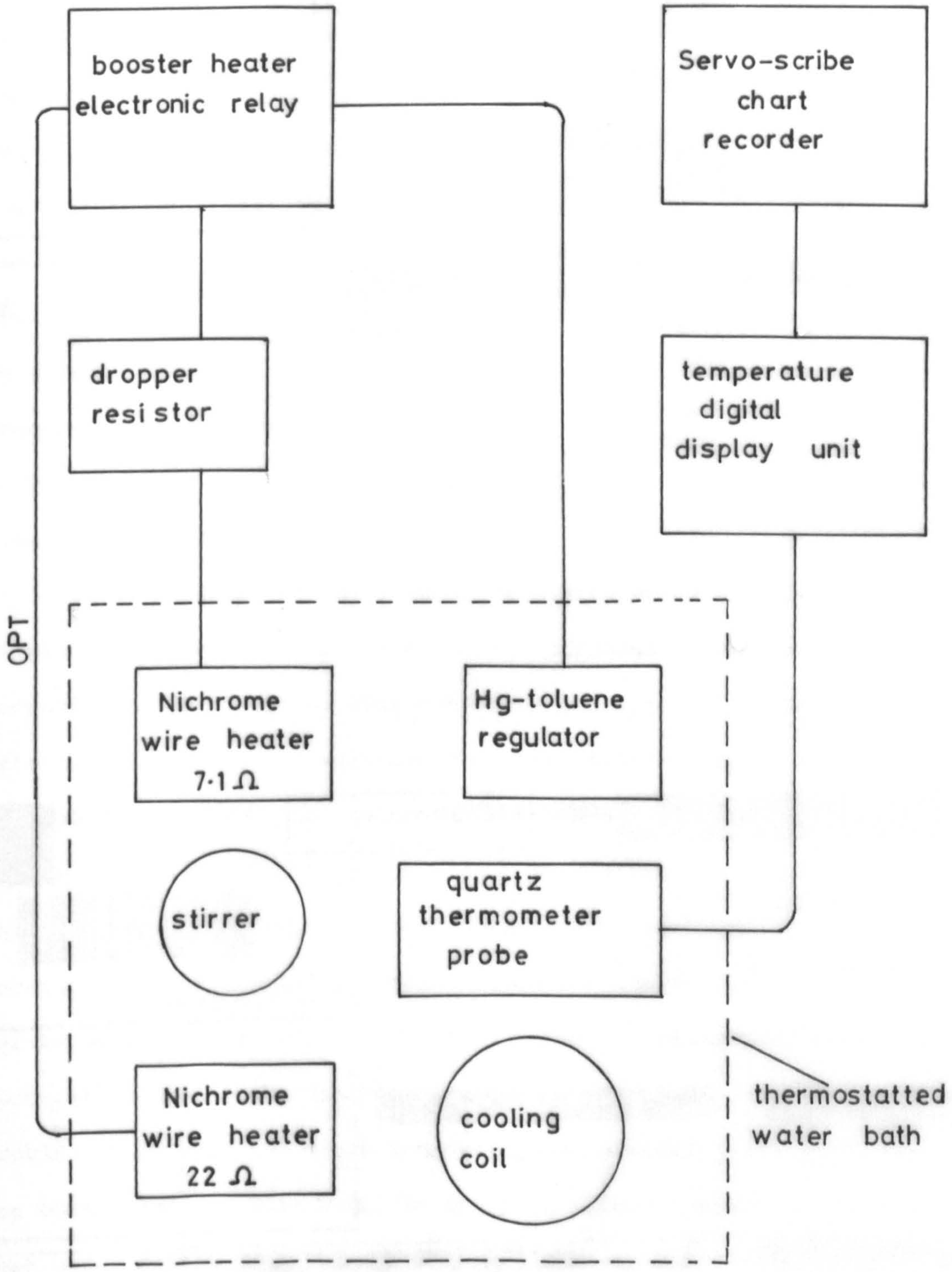


Figure 4.6 A schematic diagram of the arrangement of the apparatus for regulation of temperature. Route OPT was used optionally for rapid increase of bath temperature.

4.2 MEASUREMENT OF EXCESS VOLUMES OF MIXING

The experimental procedure for the determination of excess volumes of mixing is in the main similar to the method that was adopted in an earlier work in this laboratory(1),(2). However, due to the fact that the quantities used were rather smaller than those used in the earlier work, there were variations in procedure in some features. For example, the measuring of amounts of the components was by weight rather than, as was the case in the earlier work, by volume. A number of binary systems on which work has been done previously were used as test cases before proceeding to new systems.

4.2.1 Experimental procedure

In determining excess volumes of mixing by batch dilatometry, two simple procedures are available for the purposes of measuring the compositions of mixtures. They are measurement by weight or by volume. After initial tests, it was concluded that measurement by weight was more reliable and easier than measurement by volume. A number of disadvantages are immediately apparent in the method of determining compositions by volume. The relationships between temperature and volume of pure substances have to be known precisely. Even if such information is available, it is fairly difficult, if not impossible, to have an exact knowledge of the temperature during the transfer of material from one vessel to another. The problem of knowing the exact temperature of materials and measuring volumes was compounded, in this work, by the fact that materials and apparatus were kept under different conditions. The micrometer syringes and associated apparatus were kept at ambient temperatures whereas tetramethylsilane was kept in the cold room. Furthermore, initial attempts at measuring amounts by volume were exposed as totally unreliable especially with regard to tetramethylsilane. When tetramethylsilane was transferred from a micrometer syringe to a dilatometer, it was observed that as the syringe piston was pushed down, however slowly, some of the liquid was moving up the walls of the syringe shaft. Even if this process could be lessened by 'pre-washing'* the syringe with tetramethylsilane, it was fairly difficult to eliminate it completely. [*'Pre-washing' is a technique which involves wetting the whole of the syringe with a small quantity of liquid and then expelling excess liquid before refilling it.] Experimental evidence for the process by which some of the tetramethylsilane moved up the shaft as the piston was pushed down was borne out by simple density measurements which furnished results that did not correlate with those in the literature(3); the density values were always lower than the published values. The effect was less marked for other pure substances. Besides, there were small but significant variations in density values even in situations where due care had been taken by 'pre-washing' the syringes. Coupled with problems of temperature control, it was decided that the weighing method was superior to the volumetric method.

A Model 62 FM Oertling balance, with a pan capacity of 200 grams, was used for weighing. Small flat wooden blocks with clips fastened to them were used as supports for holding dilatometer bodies securely on the balance pans. The components were transferred to the different arms of the mercury-filled dilatometer body with the aid of syringe needles attached to the micrometer syringes. The needles were bent accordingly so that, prior to mixing, a given component would always be lodged into one arm of the dilatometer body. In order to withdraw liquid components successfully from the storage vessels, pieces of glass tubing of an appropriate length and with capillary bore were used as conduits for facilitating the insertion of the bent but flexible needles.

For a given binary mixture, some considerations were taken into account when deciding the amounts of material to be used. Based on one or more test measurements, the amounts were calculated so that the change in height of the mercury meniscus levels accompanying a mixing process would be less than 1 cm. However, caution is essential. Small changes in height accompanying a mixing process are not desirable because the significance of errors increases with decreasing height changes. Although the radius of the capillary bore of the dilatometer stem was determined along most of the stem, it was preferable that changes in height of the mercury meniscus levels were made to occur on a particular section of the stem. A section of about 2.5 cm in length was used; this gave enough room for flexibility. There were advantages to be gained by adopting this procedure. Corrections for effects due to compressibility could be, and were, ignored. Errors due to, in principle and possibly in practice, inherent minute variations of the radius with sections of the capillary bore were thus lessened in a systematic manner.

After transferring the required amounts of pure components into the dilatometer body, the dilatometer stem was fitted into the greaseless ground joint and held tightly in place using springs hooked on lugs (see Figure 4.1). The level of mercury in the dilatometer was such that there was allowance for the expansion of mercury which invariably occurred as the dilatometer was placed into the thermostat bath. Before securing the springs on lugs, some thick grease was smeared onto the crevices of the ground joints so that water was kept out of the dilatometer. For binary mixtures in which tetramethylsilane is one of the components, some pure tetramethylsilane was placed in the 'finger' at the top of the dilatometer stem. This was found to be useful in preventing tetramethylsilane from 'bubbling' during an experimental run. The precaution was definitely worthwhile in situations where minor amounts of tetramethylsilane were injected into the dilatometer body. The assembled dilatometer was then placed into the thermostat bath and allowed to reach thermal equilibrium.

Using a cathetometer of 10^{-3} cm precision, the difference in height between the level of top of the mercury meniscus and the reference mark was measured and termed h_b. The room temperature reading T_b was obtained as h_b was being measured. The dilatometer was then taken out of the thermostat bath and mixing was carried out manually before replacing the dilatometer into the thermostat bath. After thermal equilibrium had been attained, h_a, the difference in height between the new mercury meniscus level and the reference mark, was measured. Concurrently, the room temperature T_a was obtained. Thus the height change accompanying a mixing process, Δh, is given by the relation

$$\Delta h = h_a\{1 + \alpha(T_a - 293.15\ \mathrm{K})\} - h_b\{1 + \alpha(T_b - 293.15\ \mathrm{K})\} \qquad \ldots\ (4.1)$$

where α is the coefficient of thermal expansion of the cathetometer. T_a and T_b are the room temperatures after and before mixing, respectively. The excess molar volume of mixing, $V_m{}^E$, is obtained using the relation

$$V_m{}^E = \pi r^2 \Delta h / n_t \qquad \ldots\ (4.2)$$

where n_t is the total amount of substance involved in the mixing.

4.2.2 Test systems

It has already been stated(see Chapter 1) that the quantities of material used in this work are rather minute in comparison with those used by other workers. Hence it was necessary to test the feasibility of using the technique in the production of precise and accurate results. The testing was accomplished by carrying out a study on four binary mixtures. For the selected systems, measurements on excess volumes of mixing have been carried out by other workers. The selected systems are:

(1) benzene + cyclohexane,

(2) tetramethylsilane + cyclohexane,

(3) cyclooctane + cyclopentane, and

(4) cycloheptane + cyclopentane.

For all the systems, the excess volumes were determined at 298.15 K.

Benzene+cyclohexane is a recommended system for testing new experimental arrangements designed for furnishing data on excess volumes of mixing$^{(4)}$. In the present study on this system, the determination of mole fractions of the components was, as in the previous study in this laboratory(1),(2), by accurate measurements of volumes of the pure components. For all the other mixtures, the measurement of mass was used as a basis for determining amounts. The advantages of relying on the measurement of mass, instead of volume, for the determination of amounts are discussed in Section 4.2.1. The study on tetramethylsilane+cyclohexane was important in that two variations from the work by Dixon and Hewitt(2), namely the quantities used and the manner of determining amounts of substance, were introduced. The cyclooctane+cyclopentane and the cycloheptane+cyclopentane mixtures were selected for study because:

(a) there was a need to compare the results of this study with those obtained by a different technique, and

(b) the components that make up the mixtures were to be used in new studies on tetramethylsilane mixtures.

The mentioned cycloalkane binary systems have been studied using dilution dilatometry(5),(6).

All the substances were obtained commercially. Besides drying over anhydrous phosphorus pentoxide and degassing, no further purification was carried out. Analysis by gas chromatographic techniques was carried out on benzene and the cycloalkanes. In all these substances, impurity levels were considered as insignificant. Tetramethylsilane, of spectroscopic grade and purity levels quoted to be greater than 99.8 per cent, was not subjected to any analysis.

For each of the binary systems, the data on excess molar volumes of mixing as functions of composition were fitted into an equation - known as the Redlich-Kister equation(7) - of the type

$$V_m^E\{x(1-x)\}^{-1}/\mathrm{cm}^3\ \mathrm{mol}^{-1} = \sum_{j=1}^{\ell} A_j(1-2x)^{j-1} \quad \ldots\ (4.3)$$

where V_m^E is the excess molar volume of mixing, x is the mole fraction of the second component, A_j is the j^{th} coefficient, and ℓ is the number of Redlich-Kister coefficients required to obtain a good fit from a linear least squares analysis of the experimental data. The level of scatter of the data is indicated by σ which is defined as

$$\sigma/\mathrm{cm}^3\ \mathrm{mol}^{-1} = \{\sum_{i=1}^{n} (\delta V_m^E)_i^2/(n-\ell)\}^{1/2} \quad \ldots\ (4.4)$$

where i is the i^{th} observation at a given composition and n is the number of observations. Equation (4.5) gives the definition of δV_m^E for each observation.

$$\delta V_m^E = V_m^E(\mathrm{expt}) - V_m^E(\mathrm{calc}) \quad \ldots\ (4.5)$$

V_m^E(expt) and V_m^E(calc) are, respectively, the experimental values and those values calculated from the fitting equation.

The results, including comparison with published data, are summarised in Tables 4.1 to 4.3. Table 4.1 depicts the results from the present work. Experimental values of the excess molar volumes of mixing and calculated values obtained by employing equations of the form of equation (4.3), as well as differences between the two sets of values, are shown as functions of the experimentally determined mole fractions. Table 4.2 is a summary of the Redlich-Kister coefficients and σ values for particular binary systems. Included in the table are the corresponding data from published work. The coefficients tabulated in Table 4.2 are then used in relations of the nature of equation (4.3) in order to obtain smoothed values for excess volumes of mixing as functions of composition. The result of such calculations is displayed in Table 4.3, and it may be seen that there is favourable agreement between this work and that of other workers. The level of agreement was considered good enough for the technique to be employed in determining excess volumes for systems that have not been studied before.

TABLE 4.1 Excess molar volumes of mixing as functions of composition. Test systems.

x	V_m^E(expt)/cm^3 mol^{-1}	V_m^E(calc)/cm^3 mol^{-1}	δV_m^E/cm^3 mol^{-1}
(1-x)-benzene + x-cyclohexane at 298.15 K			
0.4718	0.6400	0.6398	0.0002
0.6493	0.5921	0.5947	-0.0026
0.7117	0.5423	0.5390	0.0033
0.8045	0.4159	0.4168	-0.0009
(1-x)-tetramethylsilane + x-cyclohexane at 298.15 K			
0.1955	-0.7512	-0.7512	0.0000
0.4840	-1.0936	-1.0938	0.0002
0.5953	-1.0294	-1.0290	-0.0004
0.6976	-0.8844	-0.8845	0.0001
(1-x)-cyclooctane + x-cyclopentane at 298.15 K			
0.4058	-0.2556	-0.2568	0.0012
0.5030	-0.2862	-0.2835	-0.0027
0.6340	-0.2853	-0.2873	0.0020
0.6345	-0.2876	-0.2872	-0.0004
0.7027	-0.2708	-0.2712	0.0004
0.8041	-0.2200	-0.2196	-0.0004
(1-x)-cycloheptane + x-cyclopentane at 298.15 K			
0.2399	-0.0632	-0.0624	-0.0008
0.3097	-0.0766	-0.0791	0.0025
0.3956	-0.0988	-0.0965	-0.0023
0.4897	-0.1090	-0.1098	0.0008

TABLE 4.2 A_j coefficients and σ values for the test systems at 298.15 K.

System	Reference	A_1	A_2	A_3	A_4	σ
(1)	(a)	2.5744	-0.1240			0.0030
(1)	(b)	2.5730	-0.1105			0.0030
(2)	(a)	-4.3626	-0.5281	-0.2506		0.0005
(2)	(b)	-4.3778	-0.5444			0.0040
(3)	(a)	-1.1316	0.3708	-0.0987		0.0021
(3)	(c)	-1.131	0.434	0.016	0.019	
(4)	(a)	-0.4431	0.1872	0.0131		0.0036
(4)	(d)	-0.4519	0.2089	0.0223		

Key to Table 4.2:

(1) (1-x)-benzene + x-cyclohexane

(2) (1-x)-tetramethylsilane + x-cyclohexane

(3) (1-x)-cyclooctane + x-cyclopentane

(4) (1-x)-cycloheptane + x-cyclopentane

(a) this work

(b) Dixon and Hewitt(2)

(c) Ewing, et al(5)

(d) Ewing and Marsh(6)

TABLE 4.3 Comparison of results from this work with those of other workers.

x	V_m^E(this work)/cm^3 mol^{-1}	V_m^E(literature)/cm^3 mol^{-1}
(1-x)-benzene + x-cyclohexane at 298.15 K(2)		
0.4718	0.6398	0.6397
0.6493	0.5947	0.5934
0.7117	0.5390	0.5375
0.8045	0.4168	0.4153
(1-x)-tetramethylsilane + x-cyclohexane at 298.15 K(2)		
0.1955	-0.7512	-0.7407
0.4840	-1.0938	-1.0977
0.5953	-1.0290	-1.0297
0.6976	-0.8845	-0.8781
(1-x)-cyclooctane + x-cyclopentane at 298.15 K(5)		
0.4058	-0.2568	-0.2528
0.5030	-0.2835	-0.2834
0.6340	-0.2873	-0.2893
0.6345	-0.2872	-0.2892
0.7027	-0.2712	-0.2728
0.8041	-0.2198	-0.2196
(1-x)-cycloheptane + cyclopentane at 298.15 K(6)		
0.2399	-0.0624	-0.0615
0.3097	-0.0791	-0.0789
0.3956	-0.0965	-0.0974
0.4897	-0.1098	-0.1118

__NOTE:__ The numbers - in parentheses - placed against each system refer to the cited literature.

4.2.3 New binary systems

As part of a continuing effort in providing thermodynamic information on binary liquid mixtures, excess volumes of mixing were determined for the following systems:

(1) tetramethylsilane + cyclopentane,

(2) tetramethylsilane + cycloheptane, and

(3) tetramethylsilane + cyclooctane.

The measurements were carried out at 298.15 K. Tables 4.4 and 4.5 are a summary of the results. In the former table, experimental values for excess molar volumes and the excess molar volume values calculated from fitting equations are displayed. In addition, the deviations between the two sets of values are indicated. Table 4.5 shows the coefficients of equations of the type of equation (4.3) which give good fits to the experimental data. Also, σ values are given. The analyses, by the method of linear least squares, were carried out without weighting of the data. The results are also given in diagrammatic form in Figure 4.7.

An exploratory study was also carried out on the binary system (1-x)-tetramethylstannane + x-cyclohexane at 298.15 K. The results are given in Table 4.6. A linear least squares analysis gave the relation given by equation (4.6), with 0.0076 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ as the standard deviation of the results.

$$V_m^E\{x(1-x)\}^{-1}/\mathrm{cm}^3\ \mathrm{mol}^{-1} = 0.1581 - 0.0170(1 - 2x) \qquad \ldots (4.6)$$

TABLE 4.4 Excess molar volumes of mixing as functions of composition.

New binary systems.

x	V_m^E(expt)/cm^3 mol^{-1}	V_m^E(calc)/cm^3 mol^{-1}	δV_m^E/cm^3 mol^{-1}
(1-x)-tetramethylsilane + x-cyclopentane at 298.15 K			
0.1947	-0.5695	-0.5708	0.0013
0.2963	-0.7691	-0.7665	-0.0026
0.3999	-0.8888	-0.8897	0.0009
0.5052	-0.9342	-0.9329	-0.0013
0.7009	-0.7862	-0.7887	0.0025
0.8054	-0.5912	-0.5907	-0.0005
0.8825	-0.3912	-0.3908	-0.0004
(1-x)-tetramethylsilane + x-cycloheptane at 298.15 K			
0.2913	-1.5623	-1.5587	-0.0036
0.3954	-1.7292	-1.7372	0.0080
0.5012	-1.7463	-1.7477	0.0014
0.5876	-1.6506	-1.6419	-0.0087
0.6873	-1.4024	-1.4049	0.0025
0.7931	-1.0325	-1.0330	0.0005
(1-x)-tetramethylsilane + x-cyclooctane at 298.15 K			
0.2025	-1.6587	-1.6615	0.0028
0.3093	-2.1127	-2.0996	-0.0131
0.3605	-2.2020	-2.2092	0.0072
0.4440	-2.2586	-2.2628	0.0042
0.5098	-2.2116	-2.2092	-0.0024
0.5824	-2.0586	-2.0669	0.0083
0.6945	-1.7184	-1.7078	-0.0106
0.7848	-1.3123	-1.3158	0.0035

TABLE 4.5 A_j coefficients and σ values for the new systems(298.15 K).

System	A_1	A_2	A_3	A_4	$\sigma/cm^3\ mol^{-1}$
(1)	-3.7311	0.1054	0.0708		0.0021
(2)	-6.9940	-1.2736	-0.1403		0.0073
(3)	-8.8881	-2.4524	-0.3907	0.9360	0.0106

KEY TO TABLE 4.5:

(1) (1-x)-tetramethylsilane + x-cyclopentane

(2) (1-x)-tetramethylsilane + x-cycloheptane

(3) (1-x)-tetramethylsilane + x-cyclooctane

TABLE 4.6 Excess molar volumes of mixing.

(1-x)-tetramethylstannane + x-cyclohexane at 298.15 K.

x	$V_m^E(expt)/cm^3\ mol^{-1}$	$V_m^E(calc)/cm^3\ mol^{-1}$	$\delta V_m^E/cm^3\ mol^{-1}$
0.4865	0.0332	0.0394	-0.0062
0.4981	0.0471	0.0395	0.0076
0.6038	0.0349	0.0387	-0.0038
0.6354	0.0400	0.0377	0.0023

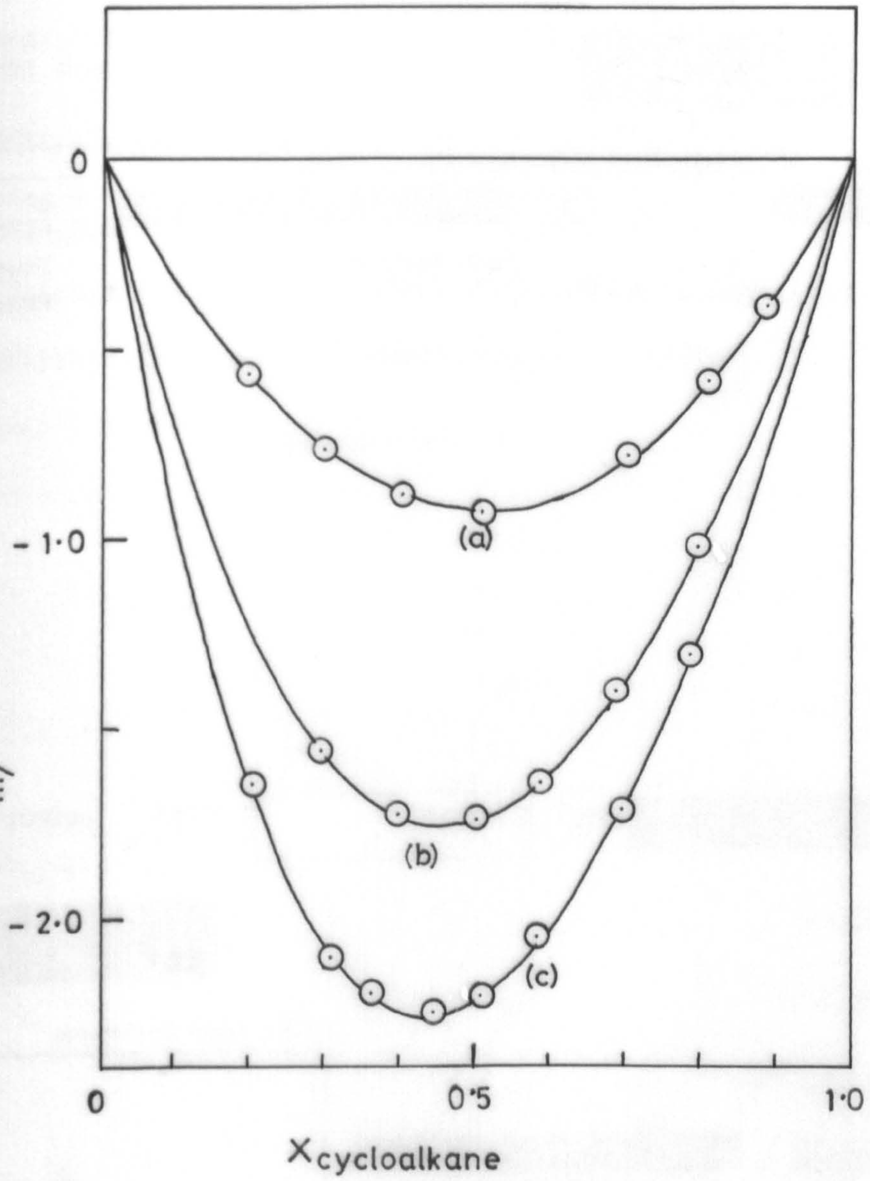


Figure 4.7 Excess molar volumes of mixing of (1-x)-tetramethylsilane + x-cycloalkane as a function of composition at 298.15 K. The cycloalkanes in mixtures (a), (b) and (c) are cyclopentane, cycloheptane and cyclooctane, respectively.

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CHAPTER 5

PREDICTION OF EXCESS FUNCTIONS:
THE PRINCIPLE OF CORRESPONDING STATES

5.1 BASIS OF THE THEORY

The foundations of the form of the principle of corresponding states, as used in this work, are based on formulations by Pitzer(1). In its most general sense, the principle of corresponding states(p.c.s) as thus formulated states that thermodynamic properties of fluids are universal functions of the reduced pressure, the reduced volume and the reduced temperature. The reduced parameters are defined thus:

$P^r = P/P^c$ ... (5.1)

$V^r = V/V^c$ ... (5.2)

$T^r = T/T^c$ ... (5.3)

where P, V, and T are the pressure, molar volume, and temperature, respectively. The superscripts c and r refer to the critical parameters and reduced parameters, respectively.

The assumptions for the p.c.s were enunciated by Pitzer(1), and they were subsequently discussed by Guggenheim(2). These may be summarised as follows:

(1) Classical statistical mechanics are employed.

(2) Molecules are considered to be spherically symmetrical, either actually or by virtue of rapid and free rotation.

(3) Intramolecular vibrations are considered similar whether the

material is in the vapour state or is in the liquid state.

(4) The potential energy of an assembly of molecules is taken to be a function only of the various intermolecular distances.

(5) The potential energy of a pair of molecules is given by

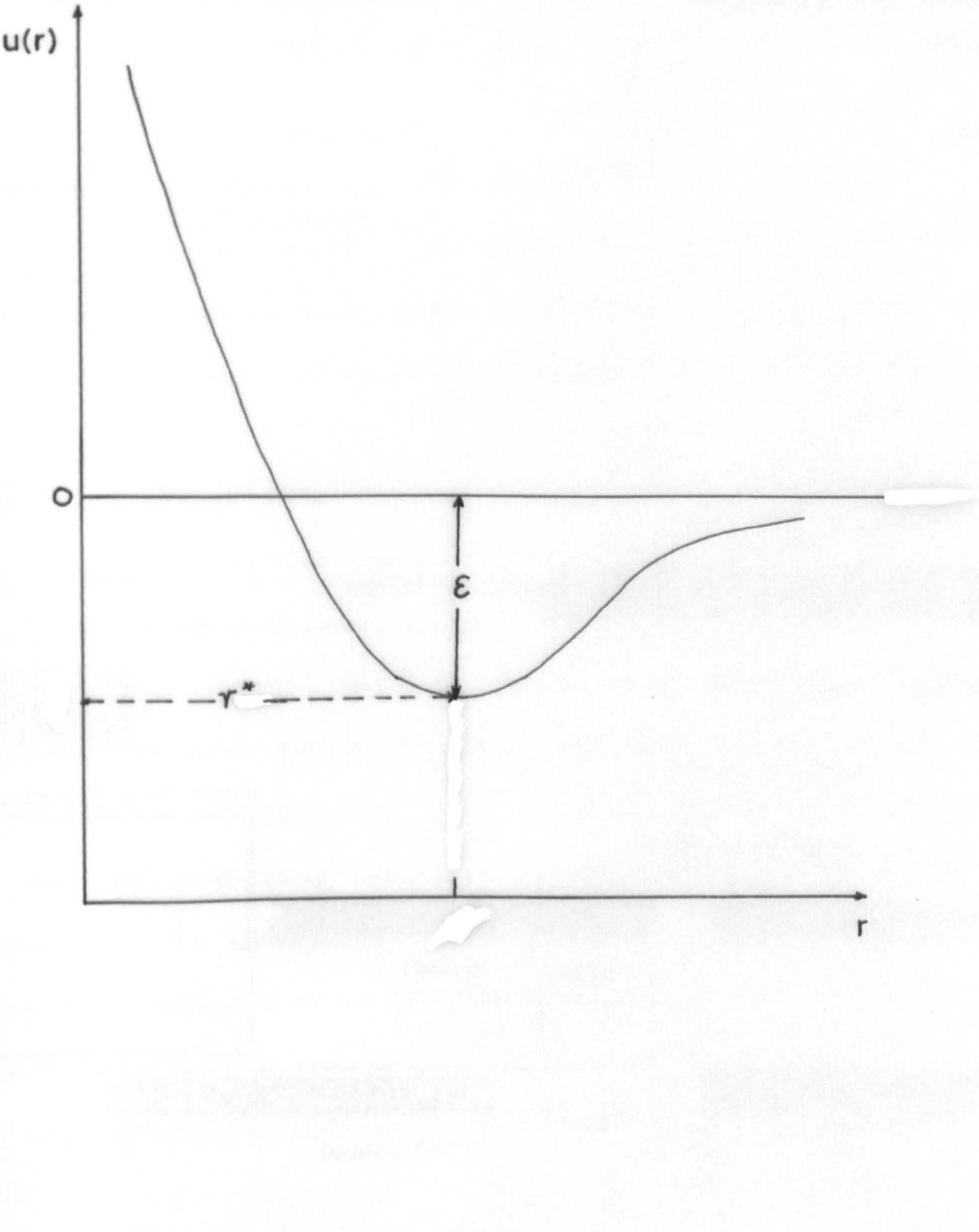
$$u(r)/\varepsilon = \phi(r/r^*) \qquad \ldots (5.4)$$

where ϕ is a universal function for all the substances which belong to a set that obeys the principle of corresponding states, r is the intermolecular separation, u(r) is the potential energy as a function of r, and ε and r^* are the energy and intermolecular separation co-ordinates at the minimum of u(r) and are characteristic of the substance. Figure 5.1 is a representation of the relation given by equation (5.4).

The soundness of any theory is the extent to which it holds when tested against experimental evidence. The p.c.s has been applied both to pure fluids(2) and to fluid mixtures(3). In the former work(2), properties such as the critical compressibility factor, the second virial virial coefficient, the Boyle point, and the coefficient of thermal expansion of a liquid - to name a few - were studied. It was shown that argon, krypton, and xenon follow the principle to a high degree of accuracy. Accuracy was less pronounced in the case of neon. Nitrogen, oxygen, carbon monoxide and methane were shown to follow the p.c.s with fair accuracy as liquids and as vapours, but not as solids.[Discussion on the application of the p.c.s to solids is beyond the scope of this work.] In the work by Guggenheim and McGlashan(3), the principle was extended for use in the calculation of second virial coefficients for gaseous mixtures. The agreement between calculated and experimental values was nearly always to within 1 cm^3 mol^{-1}.

In the light of this success, the present work extends the p.c.s to the evaluation of excess volumes, excess enthalpies, and excess Gibbs functions of some liquid binary mixtures. The objective is to calculate excess functions from a knowledge of the critical parameters of the pure

Figure 5.1 Potential energy as a function of intermolecular separation.



fluids. It is argued that if experimental thermodynamic quantities of pure substances adjudged to belong to a set can be represented by universal functions of which the reduced parameters are variables, then the corresponding thermodynamic quantities of the mixtures of that set can be represented by the same universal functions. A study on the use of the p.c.s as an evaluation procedure for excess functions of liquid mixtures involving neopentane, tetramethylsilane, and tetramethylstannane was carried out by Dixon(4). However, the work was hampered by a lack of data on critical parameters of the pure substances.

5.2 THE APPLICATION OF THE P.C.S TO PURE FLUIDS

The main assumption regarding the principle of corresponding states is that any substance which is a member of a given set must meet the condition given by equation (5.4). Thus if substances α and β belong to a set, then

$$u_{\alpha\alpha}(r)/\varepsilon_{\alpha\alpha} = \phi(r/r^*_{\alpha\alpha})$$

$$u_{\beta\beta}(r)/\varepsilon_{\beta\beta} = \phi(r/r^*_{\beta\beta}) \qquad \ldots (5.5)$$

The pair-interaction energies for such substances are said to be conformal. ϕ is a universal function for the set of substances. Its exact nature need not be known; the main requirement is its universality. Assuming that the condition demanded by equation (5.5) is met, the partition function Q for any substance of a set consisting of N molecules occupying a volume V at temperature T is, taking α as as example, given by(5)

$$Q_\alpha(T,V,N) = (2\pi m_\alpha kT/h^2)^{3N/2}.(V^N/N!)\{j_\alpha(T)\}^N.\{\Omega(kT/\varepsilon_{\alpha\alpha}, V/[N(r^*_{\alpha\alpha})^3])\}^N \qquad \ldots (5.6)$$

where k is the Boltzmann constant, h is the Planck's constant, m_α is the mass of a molecule α, and j_α is the partition function for the intermolecular degrees of freedom and is taken to be independent of V/N. Ω is a universal function for all the substances of the set. The term $\Omega(kT/\varepsilon_{\alpha\alpha}, V/[N(r^*_{\alpha\alpha})^3])$ allows for interactions between molecules. Since the terms $(2\pi m_\alpha kT/h^2)^{3N/2}$ and $\{j_\alpha(T)\}^N$ are functions of temperature, they shall, for convenience, be replaced by a composite term $\{f_\alpha(T)\}^N$. Also, if N is sufficiently large, then, by Stirling's approximation, $1/N! = (N^{-1}e)^N$. Then equation (5.6) becomes

$$Q_\alpha(T,V,N) = \{f_\alpha(T)VN^{-1}e\}^N.\{\Omega(kT/\varepsilon_{\alpha\alpha}, V/[N(r^*_{\alpha\alpha})^3])\}^N \qquad \ldots (5.7)$$

The parameters $\varepsilon_{\alpha\alpha}$ and $r^*_{\alpha\alpha}$ are related to the critical quantities thus(6).

$$\varepsilon_{\alpha\alpha}/kT^c_\alpha = a_T \qquad \ldots (5.8)$$

$$L(r^*_{\alpha\alpha})^3/V^c_\alpha = a_V \qquad \ldots (5.9)$$

$$\varepsilon_{\alpha\alpha}/\left(P^c_\alpha . r^{*\,3}_{\alpha\alpha}\right) = a_P \qquad \ldots (5.10)$$

where L is the Avogadro number, and a_T, a_V, and a_P are universal constants. From equations (5.8) to (5.10), it follows that

$$P^c_\alpha V^c_\alpha/RT^c_\alpha = a_Z \qquad \ldots (5.11)$$

where R is the universal gas constant, and a_Z is the universal compressibility factor. It can be shown, from equation (5.7) and in combination with equations (5.8) and (5.9), that

$$P_\alpha V_\alpha/RT_\alpha = \phi_1(T_\alpha{}^r, V_\alpha{}^r) \qquad \ldots (5.12)$$

From equations (5.11) and (5.12), it follows that

$$\phi_2(P_\alpha{}^r, V_\alpha{}^r, T_\alpha{}^r) = 0 \qquad \ldots (5.13)$$

Equation (5.13) is thus an expression which states that ϕ_2 is a universal function for all the members of a set obeying the p.c.s. This universal function contains as variables the reduced pressure, the reduced volume, and the reduced temperature. The equation is known as the reduced equation of state.

In addition to those consequences that have been discussed, namely equations (5.8) to (5.13), there are a number of other consequences of the principle of corresponding states. No derivation of these consequences shall be given; they will only be listed. The listing reflects, in large measure, the usefulness of such consequences for the purposes of evaluating excess molar volumes, excess molar enthalpies and excess molar Gibbs functions. The list is as follows:

$$P_\alpha{}^\sigma/P_\alpha^c = \phi_3(T_\alpha{}^r) \qquad \ldots (5.14)$$

$$B_{\alpha\alpha}/V_\alpha^c = \phi_4(T_\alpha{}^r) \qquad \ldots (5.15)$$

$$V_\alpha{}^{l\sigma}/V_\alpha^c = \phi_5(T_\alpha{}^r) \qquad \ldots (5.16)$$

$$V_\alpha{}^{g\sigma}/V_\alpha^c = \phi_6(T_\alpha{}^r) \qquad \ldots (5.17)$$

$$\Delta_e H_\alpha/RT = \phi_7(T_\alpha{}^r) \qquad \ldots (5.18)$$

where, $P_\alpha{}^\sigma$ is the saturated vapour pressure of the liquid;

$B_{\alpha\alpha}$ is the second virial coefficient of the gas;

$V_\alpha{}^{l\sigma}$ is the molar volume of the orthobaric liquid;

$V_\alpha{}^{g\sigma}$ is the molar volume of the gas phase at pressure $P_\alpha{}^\sigma$;

and, $\Delta_e H_\alpha$ is the molar enthalpy of evaporation.

Other consequences of the p.c.s are manifested in what are known as residual functions. It is from these residual functions that excess functions are derived. Thus it is important to dwell on the experimental determination of residual functions, as well as expressing such functions in terms of universal functions for which reduced parameters are variables.

5.2.1 RESIDUAL FUNCTIONS

A residual function is defined as the excess of a thermodynamic function for a pure fluid over that for the fluid behaving as a perfect gas at the same temperature and volume, or at the same temperature and pressure. Mathematically, the definition for the value of a residual function is given by$^{(7)}$

$$X^{res}(T,V) = -\int_V^\infty [(\partial X/\partial V)_T - (\partial X/\partial V)_T{}^{pg}]\,dV$$

$$X^{res}(T,P) = \int_0^P [(\partial X/\partial P)_T - (\partial X/\partial P)_T{}^{pg}]\,dP \qquad \ldots (5.19)$$

where X is a given thermodynamic quantity. The discussion is devoted to temperature-pressure relationships as this is the domain in which most of experimental thermodynamics takes place. Since interest in this work involves the experimental and theoretical determination of thermodynamic functions of binary mixtures in the liquid phase, we shall use the relation given by equation (5.20) as the definition for residual functions.

$$X^{res}(T,P) = X^{l}(T,P) - X^{pg}(T,P) \qquad \ldots (5.20)$$

X may be the molar Gibbs function, the molar enthalpy, or the molar volume, and the superscripts l and pg refer to liquid phase and perfect gas, respectively. The expansion of the right-hand-side of equation (5.20) affords a pathway for the experimental determination of residual molar Gibbs functions or residual molar enthalpies. Thus

$$\begin{aligned} X^{res}(T,P) = {} & \{X^{l}(T,P) - X^{l}(T,P^{\sigma})\} + \{X^{l}(T,P^{\sigma}) - X^{g}(T,P^{\sigma})\} \\ & + \{X^{g}(T,P^{\sigma}) - X^{pg}(T,P^{\sigma})\} + \{X^{pg}(T,P^{\sigma}) - X^{pg}(T,P)\} \end{aligned} \qquad \ldots (5.21)$$

where the superscripts σ and g refer to the orthobaric and the gas states, respectively. Before writing out the formulae for $G^{res}(T,P)$ and $H^{res}(T,P)$, a relation for the equation of state of a gas is required. This is given by

$$pV^{g} = RT + B(T)p + \ldots \qquad \ldots (5.22)$$

where p is the pressure of the gas of molar volume V^{g}. B(T) is the second virial coefficient and is a function of temperature only. In equation (5.22), terms higher than the second have been neglected on the assumption that values of p are not appreciably greater than 10^5 Pa. From equations (5.21) and (5.22), it can be shown that the residual molar Gibbs function is given by

$$G^{res}(T,P)/RT = \int_{P^{\sigma}}^{P}(V^{l}/RT)dP + \{B(T)P^{\sigma}/RT + \ldots\} + \ln(P^{\sigma}/P) \qquad \ldots (5.23)$$

Now, if P is not very much greater than 10^5 Pa, then V^{l} may be assumed to be equal to $V^{l\sigma}$ with little loss of accuracy in subsequent calculations. Thus the integration in equation (5.23) may be carried out, so that one obtains

$$G^{res}(T,P)/RT = PV^{1\sigma}/RT \; - \; P^{\sigma}V^{1\sigma}/RT \; + \; BP^{\sigma}/RT \; + \; \ldots \; + \; \ln(P^{\sigma}/P) \qquad \ldots (5.24)$$

where it is to be understood that B is in fact B(T). The residual molar enthalpy may be shown to be

$$H^{res}(T,P)/RT = \int_{P^{\sigma}}^{P}[(V^{1} - T\partial V^{1}/\partial T)/RT]\,dP \; - \; \Delta_{e}H(T,P^{\sigma})/RT$$
$$+ \; \{(B - T\partial B/\partial T)(P^{\sigma}/RT) + \ldots\} \qquad \ldots (5.25)$$

Similar assumptions to those used in obtaining equation (5.24) are used. Hence,

$$H^{res}(T,P)/RT = P(V^{1} - T\partial V^{1}/\partial T)^{\sigma}/RT \; - \; P^{\sigma}(V^{1} - T\partial V^{1}/\partial T)^{\sigma}/RT$$
$$- \; \Delta_{e}H(T,P^{\sigma})/RT \; + \; \{(B - T\partial B/\partial T)(P^{\sigma}/RT) + \ldots\} \qquad \ldots (5.26)$$

Anticipating that there may be a dearth of data for $\Delta_{e}H(T,P^{\sigma})$, especially with respect to measurements at various temperatures, it is best to use the Clapeyron relation. $\Delta_{e}H(T,P^{\sigma})$ is thus replaced by $T(V^{g\sigma} - V^{1\sigma})\partial P^{\sigma}/\partial T$ and equation (5.26) becomes

$$H^{res}(T,P)/RT = P(V^{1} - T\partial V^{1}/\partial T)^{\sigma}/RT \; - \; P^{\sigma}(V^{1} - T\partial V^{1}/\partial T)^{\sigma}/RT$$
$$- \; T\partial \ln P^{\sigma}/\partial T \; - \; (B/R)\partial P^{\sigma}/\partial T \; + \; (V^{1\sigma}/R)\partial P^{\sigma}/\partial T$$
$$+ \; P^{\sigma}(B - T\partial B/\partial T)/RT \qquad \ldots (5.27)$$

The formula for the residual molar volume is obtained directly from equation (5.20). This is given by equation (5.28).

$$V^{res}(T,P) = V^{l} - RT/P \qquad \ldots (5.28)$$

Equations (5.24), (5.27), and (5.28) give relations for the experimental determination of residual molar Gibbs functions, residual molar enthalpies, and residual molar volumes, respectively. Now, the objective is to attempt the application of the principle of corresponding states so that the residual functions may be expressed in terms of experimentally established forms for given universal functions. A study of the terms appearing on the right-hand sides of equations (5.24), (5.27), and (5.28) indicates that the use of the universal functions $\phi_3(T^r)$, $\phi_4(T^r)$, and $\phi_5(T^r)$ as defined in equations (5.14) to (5.16), is probably the best choice in the application of p.c.s to the residual functions under consideration. Before doing so, it is instructive to show that the residual functions may be expressed in terms of universal functions of the reduced parameters. That is, they are consequences of the principle of corresponding states. Relating statistical mechanics and thermodynamics, one has

$$A = - kT\ln Q \qquad \ldots (5.29)$$

where A is the Helmholtz function and Q is the partition function. Hence, from equation (5.7), one obtains

$$A^{res}(T,V)/RT = \phi_8(T^r, V^r) \qquad \ldots (5.30)$$

The reduced parameters T^r and V^r have replaced the terms kT/ε and $V/(Nr^{*3})$ via the use of relations (5.8) and (5.9), respectively. From thermodynamic relations and in combination with equation (5.13), it can be deduced that

$$G^{res}(T,P)/RT = \phi_9(T^r,\ P^r) \qquad \ldots\ (5.31)$$

$$H^{res}(T,P)/RT = \phi_{10}(T^r,\ P^r) \qquad \ldots\ (5.32)$$

$$PV^{res}(T,P)/RT = \phi_{11}(T^r,\ P^r) \qquad \ldots\ (5.33)$$

Finally, for substance α belonging to a set, the residual functions in terms of the universal functions $\phi_3(T^r)$, $\phi_4(T^r)$, and $\phi_5(T^r)$, are expressed to obtain:

(a) from equation (5.24)

$$\begin{aligned} G_\alpha^{res}(T,P)/RT &= \phi_9(T_\alpha^r,\ P_\alpha^r) \\ &= \ln(P_\alpha^\sigma/P_\alpha^c) + a_Z.(T_\alpha^c/T).(P_\alpha^\sigma/P_\alpha^c).\{(B_{\alpha\alpha}/V_\alpha^c) - (V_\alpha^{1\sigma}/\ V_\alpha^c)\} \\ &\qquad + a_Z.(T_\alpha^c/T).(P/P_\alpha^c).(V_\alpha^{1\sigma}/V_\alpha) - \ln(P/P_\alpha^c) \\ &= \ln\phi_3 + a_Z.(T_\alpha^c/T).\phi_3.(\phi_4 - \phi_5) + \\ &\qquad a_Z.(T_\alpha^c/T).(P/P_\alpha^c).\phi_5 - \ln(P/P_\alpha^c) \end{aligned} \qquad \ldots\ (5.34)$$

(b) from equation (5.27)

$$\begin{aligned} H_\alpha^{res}(T,P)/RT &= \phi_{10}(T_\alpha^r,\ P_\alpha^r) \\ &= -(T/T_\alpha^c).(\partial\ln\phi_3/\partial T_\alpha^r) - a_Z.\phi_3.(\phi_4 - \phi_5).(\partial\ln\phi_3/\partial T_\alpha^r) \\ &\qquad + a_Z.(T_\alpha^c/T).\phi_3.(\phi_4 - \phi_5) - a_Z.\phi_3.\{\partial(\phi_4 - \phi_5)/\partial T_\alpha^r\} \\ &\qquad + a_Z.(T_\alpha^c/T).(P/P_\alpha^c).\{\phi_5 - (T/T_\alpha^c).(\partial\phi_5/\partial T_\alpha^r)\} \end{aligned} \qquad \ldots\ (5.35)$$

and, (c) from equation (5.28)

$$V_\alpha^{res}(T,P) = V_\alpha^c.\phi_5 - RT/P \qquad \ldots (5.36)$$

In equations (5.34) to (5.36), a_Z is as defined by equation (5.11), and, for the sake of clarity of presentation, it is to be understood that the universal functions ϕ_3, ϕ_4, and ϕ_5 are functions of the reduced temperature. Equation (5.35) can be obtained alternatively by applying the Gibbs-Helmholtz relation on equation (5.34). That is

$$\begin{aligned} H_\alpha^{res}(T,P)/RT &= - T.\partial\{G_\alpha^{res}(T,P)/RT\}/\partial T \\ &= - T_\alpha^r.\partial\{G_\alpha^{res}(T,P)/RT\}/\partial T_\alpha^r \qquad \ldots (5.37) \end{aligned}$$

5.3 THE EXTENSION OF THE P.C.S TO LIQUID MIXTURES

Let α, β, ... be substances that belong to a set which obeys the principle of corresponding states. It has been seen that one of the assumptions of the p.c.s is the conformality of pair-interaction energies for like pairs. In order to extend the p.c.s to liquid mixtures, a further assumption is required; the pair-interaction energies for unlike pairs are assumed to be conformal. That is, they are of the same form as equation (5.4). Thus, for a binary mixture made up of substances α and β, we have

$$u_{\alpha\beta}(r)/\varepsilon_{\alpha\beta} = \phi(r/r^*_{\alpha\beta}) \qquad \ldots (5.38)$$

Thus the universal function ϕ is the same whether like or unlike interactions are considered. Hence relations given by equations (5.39) to (5.42) are obtained.

$$\varepsilon_{\alpha\beta}/kT^c_{\alpha\beta} = a_T \qquad \ldots (5.39)$$

$$L(r^*_{\alpha\beta})^3/V^c_{\alpha\beta} = a_V \qquad \ldots (5.40)$$

$$\varepsilon_{\alpha\beta}/P^c_{\alpha\beta}\cdot r^{*\,3}_{\alpha\beta} = a_P \qquad \ldots (5.41)$$

$$P^c_{\alpha\beta}V^c_{\alpha\beta}/RT^c_{\alpha\beta} = a_Z \qquad \ldots (5.42)$$

It would be ideal if the cross-term critical parameters were obtained from experiment. However, there are only a few systems for which such data, or some of such data, are available. Hence there is a need for developing theoretical means of evaluating $T^c_{\alpha\beta}$, $V^c_{\alpha\beta}$, and $P^c_{\alpha\beta}$. They are evaluated through what are known as combining rules. Amongst the earliest pronouncements on such rules are the Lorentz-Berthelot combining rules(8). These rules state that

$$\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta})^{(1/2)} \qquad \ldots (5.43)$$

$$r^*_{\alpha\beta} = (r^*_{\alpha\alpha} + r^*_{\beta\beta})/2 \qquad \ldots (5.44)$$

Thus $\varepsilon_{\alpha\beta}$, the pair-interaction energy associated with unlike interactions, is a geometric mean of the pair-interaction energies for like interactions whereas $r_{\alpha\beta}$, the intermolecular separation parameter, is an arithmetic mean. Equation (5.43) is a good approximation for systems in which the major contribution to $\varepsilon_{\alpha\beta}$ is due to central forces of the type known as London dispersion forces(9). Equation (5.44) holds if molecules of substances α and β are considered to be, or behave as, spheres with diameters proportional to $r^*_{\alpha\alpha}$ and $r^*_{\beta\beta}$, respectively. Assuming that the conditions as specified by equations (5.43) and (5.44) hold, then the appropriate combination of these equations with equations (5.8) to (5.11) yields the critical parameters for unlike interactions.

$$T^{c}_{\alpha\beta} = (T^{c}_{\alpha}T^{c}_{\beta})^{(1/2)} \qquad \ldots (5.45)$$

$$V^{c}_{\alpha\beta} = [(V^{c}_{\alpha})^{(1/3)} + (V^{c}_{\beta})^{(1/3)}]^{3}/8 \quad \ldots (5.46)$$

$$P^{c}_{\alpha\beta} = 8(T^{c}_{\alpha}T^{c}_{\beta})^{1/2}[(T^{c}_{\alpha}/P^{c}_{\alpha})^{1/3} + (T^{c}_{\beta}/P^{c}_{\beta})^{1/3}]^{-3} \qquad \ldots (5.47)$$

However, it may be appreciated that only a few substances, if any, will satisfy the requirements for the application of the Lorentz-Berthelot rules. Hence a number of other combining rules have been proposed(see Section 5.6).

In this work, excess functions are determined by relating residual functions of mixtures to residual functions of the pure components. [It will be seen how this is done in Sections 5.4 and 5.5.] However, the computation of residual functions of mixtures requires that theories concerning the nature of liquid mixtures be formulated. Various theories have been proposed. This work will be restricted to what are known as "one-fluid" and "two-fluid" theories$^{(10)}$.

5.4 THE "ONE-FLUID" THEORY OF MIXTURES

In this theory, the mixture is treated as though it were a pure fluid ψ which is conformal with the pure substances α and β, especially as far as residual functions are concerned. This pure fluid is hypothetical. Since ψ is conformal with α, β, and any other members belonging to a set, then

$$u_{\psi\psi}(r)/\varepsilon_{\psi\psi} = \phi(r/r^{*}_{\psi\psi}) \qquad \ldots (5.48)$$

where $u_{\psi\psi}(r)$ is the pair-interaction energy of the hypothetical fluid, and $\varepsilon_{\psi\psi}$ and $r^{*}_{\psi\psi}$ are the molecular parameters of the hypothetical fluid. Now, if T^{c}_{ψ}, V^{c}_{ψ} and P^{c}_{ψ} are the critical parameters of the hypothetical fluid, then

$$\varepsilon_{\psi\psi}/kT^{c}_{\psi} = a_T \qquad \ldots (5.49)$$

$$L(r^{*}_{\psi\psi})^3/V^{c}_{\psi} = a_V \qquad \ldots (5.50)$$

$$\varepsilon_{\psi\psi}/P^{c}_{\psi}.r^{*}_{\psi\psi}{}^3 = a_P \qquad \ldots (5.51)$$

$$P^{c}_{\psi}V^{c}_{\psi}/RT^{c}_{\psi} = a_Z \qquad \ldots (5.52)$$

The consequence of this is that

$$\phi_2(P_{\psi}{}^{r},\ V_{\psi}{}^{r},\ T_{\psi}{}^{r}) = 0 \qquad \ldots (5.53)$$

Thus the same universal functions for the pure component residual properties are used for obtaining corresponding residual properties of the hypothetical fluid. Excess functions are then obtained using the relations:

$$G_m^E(T,P,x)/RT = G_\psi^{res}(T,P)/RT - (1-x)G_\alpha^{res}(T,P)/RT - xG_\beta^{res}(T,P)/RT$$
$$= \phi_9(T_\psi^r, P_\psi^r) - (1-x)\phi_9(T_\alpha^r, P_\alpha^r) - x\phi_9(T_\beta^r, P_\beta^r) \quad \ldots (5.54)$$

$$H_m^E(T,P,x)/RT = \phi_{10}(T_\psi^r, P_\psi^r) - (1-x)\phi_{10}(T_\alpha^r, P_\alpha^r) - x\phi_{10}(T_\beta^r, P_\beta^r) \quad \ldots (5.55)$$

$$V_m^E(T,P,x) = V_\psi^c.\phi_5(T_\psi^r) - (1-x)V_\alpha^c.\phi_5(T_\alpha^r) - xV_\beta^c.\phi_5(T_\beta^r) \quad \ldots (5.56)$$

where $G_m^E(T,P,x)$, $H_m^E(T,P,x)$ and $V_m^E(T,P,x)$ are the excess molar Gibbs function, the excess molar enthalpy and the excess molar volume, respectively, and x is the mole fraction of β.

It may be seen from equations (5.54) to (5.56) that if the three excess functions are known at a given composition, then there are three equations in three unknowns. The unknowns are T_ψ^c, P_ψ^c and V_ψ^c. Hence a solution for the critical parameters of the hypothetical fluid exists. Thus an immediate check can be made between theory and experiment. This may be done by using the relation $P_\psi^c V_\psi^c/RT_\psi^c$ - the critical quantities being a result of the simultaneous solution of equations (5.54) to (5.56) - and comparing the result to a_Z. However, interest in this work is centred on the determination of excess functions of mixtures from a knowledge only of the properties of the pure substances. To that end it is necessary to make assumptions regarding the critical parameters of the hypothetical fluid. The assumptions relate the critical parameters of the hypothetical fluid to the critical parameters of the pure substances as well as compositions of the mixture.

5.4.1 Formulae for P_ψ^c, V_ψ^c and T_ψ^c

A model known as the random mixing approximation(11) will be used for the evaluation of P_ψ^c, V_ψ^c and T_ψ^c. In using this model, two approaches are adopted. The first approach is the traditional one in which random mixing is assumed for the purposes of calculating the pair potential for the hypothetical fluid. We refer to this approach as the randomisation of the pair potentials, and abbreviate it as RPP.

According to the RPP approach, therefore,

$$u_{\psi\psi}(r) = (1-x)^2 u_{\alpha\alpha}(r) \ + \ 2x(1-x)u_{\alpha\beta}(r) \ + \ x^2 u_{\beta\beta}(r) \qquad \ldots (5.57)$$

Equation (5.57), in combination with appropriate relations of the type of equation (5.5), leads to

$$\begin{aligned} \varepsilon_{\psi\psi}.\phi(r/r^*_{\psi\psi}) = (1-x)^2 \varepsilon_{\alpha\alpha}.\phi(r/r^*_{\alpha\alpha}) \ + \ 2x(1-x)\varepsilon_{\alpha\beta}.\phi(r/r^*_{\alpha\beta}) \\ + \ x^2 \varepsilon_{\beta\beta}.\phi(r/r^*_{\beta\beta}) \qquad \ldots (5.58) \end{aligned}$$

Brown(12) has shown that $\phi(r/r^*)$ is consistent with a mathematical function popularly known as the Lennard-Jones(13) n-m potential. This n-m potential is given by

$$\phi(r/r^*) = \{m/(n-m)\}.(r^*/r)^n \ + \ \{n/(m-n)\}.(r^*/r)^m \qquad \ldots (5.59)$$

Using relations given by equations (5.8) to (5.11) in combination with equations (5.58) and (5.59), one obtains, after equating coefficients and taking the roots,

$$V_\psi^c = [A1N]^{3/(n-m)}.[A1M]^{3/(m-n)} \qquad \ldots (5.60)$$

$$T_\psi^c = [A1N]^{m/(m-n)}.[A1M]^{n/(n-m)} \qquad \ldots (5.61)$$

$$P_\psi^c = [AP1N]^{(3+m)/(m-n)}.[AP1M]^{(3+n)/(n-m)} \qquad \ldots (5.62)$$

where

$$A1N = (1-x)^2 T_\alpha^c (V_\alpha^c)^{n/3} + 2x(1-x) T_{\alpha\beta}^c (V_{\alpha\beta}^c)^{n/3} + x^2 T_\beta^c (V_\beta^c)^{n/3}$$

$$A1M = (1-x)^2 T_\alpha^c (V_\alpha^c)^{m/3} + 2x(1-x) T_{\alpha\beta}^c (V_{\alpha\beta}^c)^{m/3} + x^2 T_\beta^c (V_\beta^c)^{m/3}$$

$$AP1N = (1-x)^2 (T_\alpha^c)^{(3+n)/3} (P_\alpha^c)^{-n/3} + 2x(1-x) (T_{\alpha\beta}^c)^{(3+n)/3} (P_{\alpha\beta}^c)^{-n/3} + x^2 (T_\beta^c)^{(3+n)/3} (P_\beta^c)^{-n/3}$$

and AP1M is a relation whose structure is identical to that of AP1N; the difference is that n, wherever it appears, is replaced by m. Equations (5.60) to (5.62) represent relations for critical parameters of the hypothetical fluid in terms of critical parameters of the pure substances, taking composition into account. There is now enough information to enable one to calculate excess functions from a knowledge only of the critical parameters of the pure fluids. [A summary of the procedure for calculating excess functions using the principle of corresponding states is given in Section 5.7.] However, calculations by Dixon$^{(4)}$ and from this work show that when values for n and m (the Lennard-Jones indices) are raised, and/or when values for n/m ratios increase, values for the excess functions increase. This is even more of the case when the ratios of the critical volumes of the components become larger. For example, when the widely used Lennard-Jones 12-6 potential is applied, for the calculation of excess functions of the neopentane+TMS system, where TMS is tetramethylsilane, there are large discrepancies between calculated and experimental results. There is improvement when, say, the 6-4 potential is used.

Evidently, one of the ways of improving the predictive capacity of the p.c.s method involves finding a general relation which effectively reduces the n-m values, or ratios thereof, in equations relating P^c_ψ, V^c_ψ and T^c_ψ with critical parameters of the pure fluids. In view of this, we propose to use the van der Waals prescription as a basis for relating P^c_ψ, V^c_ψ, and T^c_ψ with the critical parameters of the pure fluids. This procedure, which we call the randomisation of the van der Waals constants(RVC), gives the following relations:

$$T^c_\psi V^c_\psi = (1-x)^2 T^c_\alpha V^c_\alpha + 2x(1-x) T^c_{\alpha\beta} V^c_{\alpha\beta} + x^2 T^c_\beta V^c_\beta \qquad \ldots (5.63)$$

$$V^c_\psi = (1-x)^2 V^c_\alpha + 2x(1-x) V^c_{\alpha\beta} + x^2 V^c_\beta \qquad \ldots (5.64)$$

The formula for T^c_ψ is obtained by combining equations (5.63) and (5.64).

$$\begin{aligned} T^c_\psi = {} & [(1-x)^2 T^c_\alpha V^c_\alpha + 2x(1-x) T^c_{\alpha\beta} V^c_{\alpha\beta} + x^2 T^c_\beta V^c_\beta] \\ & \times [(1-x)^2 V^c_\alpha + 2x(1-x) V^c_{\alpha\beta} + x^2 V^c_\beta]^{-1} \end{aligned} \qquad \ldots (5.65)$$

P^c_ψ is evaluated by making use of the relation given by equation (5.52) so that one has

$$P^c_\psi = a_Z . RT^c_\psi / V^c_\psi \qquad \ldots (5.66)$$

5.5 THE "TWO-FLUID" THEORY OF MIXTURES

In this theory, as far as residual properties are concerned, the mixture is regarded as though it consists of two fluids each conformal with one another, and each conformal with both of the pure components α and β. The two hypothetical fluids, $\psi\alpha$ and $\psi\beta$, are in the same proportions as α and β are. Then the pair-interaction energies, $u_{\psi\alpha}(r)$ and $u_{\psi\beta}(r)$, are given by

$$u_{\psi\alpha}(r)/\varepsilon_{\psi\alpha} = \phi(r/r^{*}_{\psi\alpha}) \qquad \ldots (5.67)$$

$$u_{\psi\beta}(r)/\varepsilon_{\psi\beta} = \phi(r/r^{*}_{\psi\beta}) \qquad \ldots (5.68)$$

The parameters $\varepsilon_{\psi\alpha}$, $\varepsilon_{\psi\beta}$, $r^{*}_{\psi\alpha}$ and $r^{*}_{\psi\beta}$ are related to the critical properties of the hypothetical fluids thus:

$$\varepsilon_{\psi\alpha}/kT^{c}_{\psi\alpha} = \varepsilon_{\psi\beta}/kT^{c}_{\psi\beta} = a_T \qquad \ldots (5.69)$$

$$L(r^{*}_{\psi\alpha})^3/V^{c}_{\psi\alpha} = L(r^{*}_{\psi\beta})^3/V^{c}_{\psi\beta} = a_V \qquad \ldots (5.70)$$

$$\varepsilon_{\psi\alpha}/(P^{c}_{\psi\alpha}\cdot r^{*3}_{\psi\alpha}) = \varepsilon_{\psi\beta}/(P^{c}_{\psi\beta}\cdot r^{*3}_{\psi\beta}) = a_P \qquad \ldots (5.71)$$

$$P^{c}_{\psi\alpha}V^{c}_{\psi\alpha}/RT^{c}_{\psi\alpha} = P^{c}_{\psi\beta}V^{c}_{\psi\beta}/RT^{c}_{\psi\beta} = a_Z \qquad \ldots (5.72)$$

where $V^{c}_{\psi\alpha}$, $V^{c}_{\psi\beta}$, $P^{c}_{\psi\alpha}$, $P^{c}_{\psi\beta}$, $T^{c}_{\psi\alpha}$ and $T^{c}_{\psi\beta}$ are critical properties of the hypothetical fluids. Thus residual properties of the hypothetical fluids may be calculated using relations of the types given by equations (5.34) to (5.36). Consequently, excess functions are evaluated using relations given by equations (5.73) to (5.75).

$$\begin{aligned} G_m^{E}(T,P,x)/RT = {} & (1-x)[\phi_9(T_{\psi\alpha}{}^{r}, P_{\psi\alpha}{}^{r}) - \phi_9(T_\alpha{}^{r}, P_\alpha{}^{r})] \\ & + x[\phi_9(T_{\psi\beta}{}^{r}, P_{\psi\beta}{}^{r}) - \phi_9(T_\beta{}^{r}, P_\beta{}^{r})] \qquad \ldots (5.73) \end{aligned}$$

$$\begin{aligned} H_m^{E}(T,P,x)/RT = {} & (1-x)[\phi_{10}(T_{\psi\alpha}{}^{r}, P_{\psi\alpha}{}^{r}) - \phi_{10}(T_\alpha{}^{r}, P_\alpha{}^{r})] \\ & + x[\phi_{10}(T_{\psi\beta}{}^{r}, P_{\psi\beta}{}^{r}) - \phi_{10}(T_\beta{}^{r}, P_\beta{}^{r})] \qquad \ldots (5.74) \end{aligned}$$

$$\begin{aligned} V_m^{E}(T,P,x) = {} & (1-x)[V^{c}_{\psi\alpha}\cdot\phi_5(T_{\psi\alpha}{}^{r}) - V^{c}_{\alpha}\cdot\phi_5(T_\alpha{}^{r})] \\ & + x[V^{c}_{\psi\beta}\cdot\phi_5(T_{\psi\beta}{}^{r}) - V^{c}_{\beta}\cdot\phi_5(T_\beta{}^{r})] \qquad \ldots (5.75) \end{aligned}$$

However, before evaluating excess functions, relations for $V^c_{\psi\alpha}$, $V^c_{\psi\beta}$, $T^c_{\psi\alpha}$, $T^c_{\psi\beta}$, $P^c_{\psi\alpha}$ and $P^c_{\psi\beta}$ in terms of the corresponding critical quantities of the pure components, as well as mixture composition, are required. Certain assumptions have to be made. These assumptions relate to the manner in which a real mixture, made of pure liquids α and β, has to be viewed in terms of the two hypothetical fluids ψα and ψβ. A cell model is adopted. Each hypothetical fluid is envisaged as a cell containing a central molecule of either α or β, and the environment around the central molecule is taken to be random.

Just as in the case for the "one-fluid" model, two approaches are used. Thus according to the RPP approach, one obtains

$$u_{\psi\alpha}(r) = (1-x)u_{\alpha\alpha}(r) + xu_{\alpha\beta}(r) \qquad \ldots (5.76)$$

$$u_{\psi\beta}(r) = (1-x)u_{\alpha\beta}(r) + xu_{\beta\beta}(r) \qquad \ldots (5.77)$$

From the RPP approach, relations for the critical parameters of the two hypothetical fluids in terms of critical parameters of α and β are obtained. These are given by equations (5.78) to (5.83):

$$V^c_{\psi\alpha} = [AN]^{3/(n-m)}.[AM]^{3/(m-n)} \qquad \ldots (5.78)$$

$$V^c_{\psi\beta} = [BN]^{3/(n-m)}.[BM]^{3/(m-n)} \qquad \ldots (5.79)$$

$$T^c_{\psi\alpha} = [AN]^{m/(m-n)}.[AM]^{n/(n-m)} \qquad \ldots (5.80)$$

$$T^c_{\psi\beta} = [BN]^{m/(m-n)}.[BM]^{n/(n-m)} \qquad \ldots (5.81)$$

$$P^c_{\psi\alpha} = [APN]^{(3+m)/(m-n)}.[APM]^{(3+n)/(n-m)} \qquad \ldots (5.82)$$

$$P^c_{\psi\beta} = [BPN]^{(3+m)/(m-n)}.[BPM]^{(3+n)/(n-m)} \qquad \ldots (5.83)$$

where

$$AN = (1-x)T^c_\alpha(V^c_\alpha)^{n/3} + xT^c_{\alpha\beta}(V^c_{\alpha\beta})^{n/3}$$

$$BN = (1-x)T^c_{\alpha\beta}(V^c_{\alpha\beta})^{n/3} + xT^c_\beta(V^c_\beta)^{n/3}$$

$$APN = (1-x)(T^c_\alpha)^{(3+n)/3}(P^c_\alpha)^{-n/3} + x(T^c_{\alpha\beta})^{(3+n)/3}(P^c_{\alpha\beta})^{-n/3}$$

$$BPN = (1-x)(T^c_{\alpha\beta})^{(3+n)/3}(P^c_{\alpha\beta})^{-n/3} + x(T^c_\beta)^{(3+n)/3}(P^c_\beta)^{-n/3}$$

The relations for AM, BM, APM, and BPM are similar in structure to the relations for AN, BN, APN, and BPN, respectively. The differences are due to the fact that, in each of the relations, n is replaced by m. The picture is completed by giving relations obtained via the RVC approach.

$$V^c_{\psi\alpha} = (1-x)V^c_\alpha + xV^c_{\alpha\beta} \qquad \ldots (5.84)$$

$$V^c_{\psi\beta} = (1-x)V^c_{\alpha\beta} + xV^c_\beta \qquad \ldots (5.85)$$

$$T^c_{\psi\alpha} = [(1-x)T^c_\alpha V^c_\alpha + xT^c_{\alpha\beta}V^c_{\alpha\beta}].[(1-x)V^c_\alpha + xV^c_{\alpha\beta}]^{-1} \qquad \ldots (5.86)$$

$$T^c_{\psi\beta} = [(1-x)T^c_{\alpha\beta}V^c_{\alpha\beta} + xT^c_\beta V^c_\beta].[(1-x)V^c_{\alpha\beta} + xV^c_\beta]^{-1} \qquad \ldots (5.87)$$

$$P^c_{\psi\alpha} = a_Z.RT^c_{\psi\alpha}/V^c_{\psi\alpha} \qquad \ldots (5.88)$$

$$P^{c}_{\psi\beta} = a_Z.RT^{c}_{\psi\beta}/V^{c}_{\psi\beta} \qquad \ldots (5.89)$$

5.6 THE USE OF VARIOUS COMBINING RULES

It has been mentioned earlier that the application of the Lorentz-Berthelot rules could not conceivably cover all types of molecules. In order to account for variation in molecular behaviour, various combining rules have been proposed. Some of these were selected and applied in this work.

However, in some cases, different workers have necessarily used different sets of variables. In this work, we have reduced the various relations[for the combining rules] to approximations that are, as far as possible, functions of identical sets of variables. [We shall see shortly that the final expressions are given in terms of critical temperatures and/or critical volumes.] The reasons for adopting this approach are two-fold, mainly. Firstly, there is a scarcity of experimental data regarding the various parameters that are used in the various combining rules. Secondly, it is considered advisable to assess the results of calculations which are based on as few variations of data input as possible. Of course, we do not claim that the expressions used as a result of approximations give superior results. Nor do we presume that other parameters - those that are neglected - have little or no effect on values of excess functions. It is just that, in the first instance, we are limitting the number of variables in order to facilitate comparisons between various calculating procedures. Also, the selected combining rules affect directly only the evaluation of $T^{c}_{\alpha\beta}$. That is, whereas $V^{c}_{\alpha\beta}$ will be furnished from equation (5.46) only, there are a number of relations which are used for the evaluation of $T^{c}_{\alpha\beta}$. $P^{c}_{\alpha\beta}$, if required, is evaluated from the relation

$$P^{c}_{\alpha\beta} = a_Z . RT^{c}_{\alpha\beta}/V^{c}_{\alpha\beta} \qquad \ldots (5.90)$$

where a_Z is input as a datum in the calculations.

The following, with the accompanying relations, is the selected list of the combining rules that are used in this study.

Hudson-McCoubrey(14):

$$\varepsilon_{\alpha\beta} = (\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta})^{1/2} . \left\{\frac{2^6(r^*_{\alpha\alpha} . r^*_{\beta\beta})^3}{(r^*_{\alpha\alpha} + r^*_{\beta\beta})^6}\right\} . \left\{\frac{2(I_\alpha I_\beta)^{1/2}}{I_\alpha + I_\beta}\right\} \qquad \ldots (5.91)$$

where I_α and I_β are the ionisation potentials of α and β, respectively. The p.c.s is applied so that the quantities ε and r^* are replaced by critical parameters. Equation (5.91) thus becomes

$$T^{c}_{\alpha\beta} = (T^{c}_{\alpha}T^{c}_{\beta})^{1/2)} \left\{2^6 v^{c}_{\alpha}v^{c}_{\beta}/[(v^{c}_{\alpha})^{1/3} + (v^{c}_{\beta})^{1/3}]^6\right\} 2(I_\alpha I_\beta)^{1/2}/(I_\alpha + I_\beta) \qquad \ldots (5.92)$$

In the absence of data for ionisation potentials, the assumption that $I_\alpha \approx I_\beta$ is made. The application of this assumption in combination with equation (5.46) gives

$$T^{c}_{\alpha\beta} = (T^{c}_{\alpha}T^{c}_{\beta})^{1/2} \left\{V^{c}_{\alpha}V^{c}_{\beta}/(V^{c}_{\alpha\beta})^2\right\} \qquad \ldots (5.93)$$

Equation (5.93) is thus taken to be the Hudson-McCoubrey combining rule.

Wormald and co-workers(15):

$$T^c_{\alpha\beta} = (T^c_\alpha T^c_\beta)^{1/2}\left\{(V^c_\alpha V^c_\beta)^{1/2}/V^c_{\alpha\beta}\right\} \qquad \ldots (5.94)$$

<u>Kirkwood-Muller</u>(16):

The Kirkwood-Muller rules for evaluating $\varepsilon_{\alpha\beta}$ are given by the relation

$$\varepsilon_{\alpha\beta} = \frac{2\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}}{\chi_\alpha\chi_\beta}\left[\left\{\frac{\varepsilon_{\alpha\alpha}(r^*_{\alpha\alpha})^6}{\chi_\alpha^{\,2}}\right\} + \left\{\frac{\varepsilon_{\beta\beta}(r^*_{\beta\beta})^6}{\chi_\beta^{\,2}}\right\}\right]^{-1}\left\{\frac{2r^*_{\alpha\alpha}r^*_{\beta\beta}}{r^*_{\alpha\alpha} + r^*_{\beta\beta}}\right\}^6 \qquad \ldots (5.95)$$

where χ_α and χ_β are the diamagnetic susceptibilities of α and β, respectively. In a work involving the study of second virial coefficients of argon and krypton and of mixtures of these substances, Fender and Halsey(16) simplified the Kirkwood-Muller rules by assuming that $r_{\alpha\alpha} = r_{\beta\beta}$ and $\chi_\alpha = \chi_\beta$. This gives rise to the expression

$$\varepsilon_{\alpha\beta} = 2\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}/(\varepsilon_{\alpha\alpha} + \varepsilon_{\beta\beta}) \qquad \ldots (5.96)$$

In our proposal, we only assume that $\chi_\alpha = \chi_\beta$. Hence we obtain

$$\varepsilon_{\alpha\beta} = 2\varepsilon_{\alpha\alpha}\varepsilon_{\beta\beta}[\varepsilon_{\alpha\alpha}(r^*_{\alpha\alpha})^6 + \varepsilon_{\beta\beta}(r^*_{\beta\beta})^6]^{-1}.[2r^*_{\alpha\alpha}r^*_{\beta\beta}/(r^*_{\alpha\alpha} + r^*_{\beta\beta})]^6 \qquad \ldots (5.97)$$

Combining equations (5.96) and (5.97) with appropriate equations from equations (5.8) and (5.9), one obtains

$$T^c_{\alpha\beta} = 2T^c_\alpha T^c_\beta/(T^c_\alpha + T^c_\beta) \qquad \ldots (5.98)$$

$$T^c_{\alpha\beta} = 2T^c_\alpha T^c_\beta\left\{\frac{[2(V^c_\alpha V^c_\beta)^{1/3}/\{(V^c_\alpha)^{1/3} + (V^c_\beta)^{1/3}\}]^6}{T^c_\alpha(V^c_\alpha)^2 + T^c_\beta(V^c_\beta)^2}\right\} \qquad \ldots (5.99)$$

The combination of equations (5.99) and (5.46) gives

$$T^c_{\alpha\beta} = 2T^c_\alpha T^c_\beta.[T^c_\alpha(V^c_\alpha)^2 + T^c_\beta(V^c_\beta)^2]^{-1}.(V^c_\alpha V^c_\beta/V^c_{\alpha\beta})^2 \quad \ldots (5.100)$$

The relation given by equation (5.98) is thus the Fender-Halsey version of the Kirkwood-Muller rules whereas that given by equation (5.100) is our version of those rules.

Hicks-Young(17):

$$T^c_{\alpha\beta} = 2(T^c_\alpha T^c_\beta)^{2/3}.[(T^c_\alpha)^{1/3} + (T^c_\beta)^{1/3}]^{-1} \quad \ldots (5.101)$$

5.7 CALCULATION OF EXCESS FUNCTIONS: PROCEDURE

In order to calculate excess functions via the p.c.s using equations that have been discussed in this chapter, the following procedure is adopted.

1. After collecting sufficient data, universal functions are developed using equations (5.14), (5.15) and (5.16).

2. Combining rules are selected in order to evaluate $V^c_{\alpha\beta}$, $T^c_{\alpha\beta}$, and $P^c_{\alpha\beta}$. $V^c_{\alpha\beta}$ is evaluated using equation (5.46) whilst $T^c_{\alpha\beta}$ is obtained from any of equations (5.45), (5.93), (5.94), (5.98), (5.100) and (5.101). $P^c_{\alpha\beta}$ is obtained from equation (5.17) when the Lorentz-Berthelot combining rules are used. Otherwise it is obtained from equation (5.90).

3. The critical parameters of the hypothetical fluids are then calculated. A fluid theory, as well as the approach to be used, is selected. For the "one-fluid" theory in which the RPP approach is used, equations (5.60), (5.61) and (5.62) are used to calculate V^c_ψ, T^c_ψ and P^c_ψ, respectively. In the "one-fluid"-RVC approach, equation (5.64), (5.65) and (5.66) are used to calculate V^c_ψ, T^c_ψ and P^c_ψ, respectively.

In the "two-fluid"-RPP approach, equations (5.78) to (5.83) are used to calculate, respectively, $V^c_{\psi\alpha}$, $V^c_{\psi\beta}$, $T^c_{\psi\alpha}$, $T^c_{\psi\beta}$, $P^c_{\psi\alpha}$ and $P^c_{\psi\beta}$. The corresponding quantities are obtained via the "two-fluid"-RVC approach from equations (5.84) to (5.89).

4. Universal functions, which are obtained by analytical fitting of data to equations (5.14) to (5.16), are applied in order to calculate residual functions. The relations for the residual functions are given by equations (5.34), (5.35) and (5.36).

5. The excess functions, according to the "one-fluid" theory, are then calculated using equations (5.54) to (5.56). Equations (5.73) to (5.75) give excess functions according to the "two-fluid" theory.

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CHAPTER 6

PREDICTION OF EXCESS FUNCTIONS:
USE OF EQUATIONS OF STATE

6.1 INTRODUCTION AND SCOPE

In Chapter 5, an experimental basis for formulating a theory for the prediction of excess functions was used. It is now the intention to use equations of state as models for viewing or accounting for the physical nature of liquids. Equations of state have been applied previously in the prediction of excess functions of binary mixtures(1)-(3). The present work is an extension of previous efforts. Two equations of state, namely the van der Waals and the Guggenheim equations of state, are applied to a number of binary systems of interest. The expressions for these equations of state are then generalised. Thus a number of other equations of state may be proposed. In the present work, two equations are proposed and subjected to analysis.

In the past, it was usually the case that excess functions were calculated from equations of state in combination with a few - usually one or two - combining rules. It is thought that the combination of given equations of state with various combining rules sheds more light on the predictive capacity of the equations of state. Evidently, this entails a lot of work. However, a systematic approach to the problem ought to lessen the burden of the workload. The approach which has been made in this study involves the development of a computer program which consists of algorithms for various equations of state and various combining rules. To date, the program consists of nine equations of state and eight combining rules. Although any of the equations of state may be used in conjunction with any of the combining rules, only four equations of state and six combining rules are used for detailed study. A summary for the basis of selecting the four equations of state is now presented.

Equations of state can be subdivided into two groups. This subdivision is based on the mathematical form of the relations. Of the equations of state in the computer program , the relations are expressed either as series forms or as non-series forms. The four equations of state which are studied in detail are given by relations which are expressed in non-series forms. They are;:

(a) the van der Waals equation of state,

(b) the Guggenheim equation of state, and

(c) two equations of state which we have proposed.

McGlashan(1) and Hewitt(4), for example, have used the van der Waals and the Guggenheim equations of state in non-series forms.

A number of authors have used equations of state expressed in series form(2),(3),(5). Such equations include those proposed by Frisch and co-workers(6) and by Thiele(7). They are represented by a general relation which is given by

$$pV_m/RT = \phi(y) - a/RTV_m \qquad \ldots (6.1)$$

where p is the pressure of the fluid, V_m is the molar volume, and $\phi(y)$ is a series function in y. If the fluid particles are assumed to be non-interacting hard spheres, then

$$y = b/4V_m \qquad \ldots (6.2)$$

In equations (6.1) and (6.2) the parameters a and b are constants which have values characteristic of a given substance. However, the values vary with different equations of state. The term $\phi(y)$, which is an infinite convergence series, may be expanded binomially to give approximations of the type

$$\phi(y) = \sum_{j=1}^{\ell} A_j y^{(j-1)} \qquad \ldots (6.3)$$

where A_j is the j^{th} coefficient and ℓ is the number of coefficients which, for a given equation of state, is considered suitable for furnishing results of the desired level of accuracy.

Now, the evaluation of excess molar functions of liquid binary mixtures via an equation of state depends on obtaining the relevant root for molar volume V_m at zero pressure. The predicted or calculated excess functions are dependent on, and quite sensitive to, these values of V_m. It may be seen therefore that, for equations of state expressed in series form, the values for V_m depend on the number of coefficients used in the expansion of the $\phi(y)$ terms. The possibility that the termination in the number of coefficients may be premature, with consequent loss of predictive potential, renders this approach unappealing. Although it is possible to check that a sufficient number of coefficients is used, this may be tedious. For example, in the van der Waals case, calculations have shown that convergence to the required value of V_m is relatively slow(this work). The use of series forms, however, does have some advantages. The main advantage is that a number of equations of state are represented by a general relation with a common structure. In this respect, computer programming is simplified. On the other hand, the use of equations of state in non-series forms ensures the securement of accurate values of V_m. Computer programming is marginally more cumbersome. However, such a disadvantage becomes virtually insignificant when one is assured of accuracy.

6.2 THE SELECTED EQUATIONS OF STATE

The van der Waals equation of state for a pure fluid is given by$^{(1)}$

$$p = RT/(V_m - b) - a/V_m^2 \quad \ldots (6.4)$$

The Guggenheim equation of state can be written as$^{(5)}$

$$p = RTV_m^3/(V_m - b)^4 - a/V_m^2 \quad \ldots (6.5)$$

Relations given by equations (6.4) and (6.5) are expressed in a general form thus

$$p = RTV_m^{(n-1)}/(V_m - b)^n - a/V_m^2 \quad \ldots (6.6)$$

where $n = 1$ for the van der Waals case and $n = 4$ for the Guggenheim case. From the generalisation as expressed by equation (6.6), we propose two equations of state. These are given by corresponding relations for $n = 2$ and $n = 3$. Thus we obtain:

Proposed equation of state (I)

$$p = RTV_m/(V_m - b)^2 - a/V_m^2 \quad \ldots (6.7)$$

Proposed equation of state(II)

$$p = RTV_m^2/(V_m - b)^3 - a/V_m^2 \quad \ldots (6.8)$$

6.3 THE EXTENSION TO FLUID MIXTURES

The equation of state for a fluid mixture, which is given by equation (6.9), is obtained by extending the relations for pure fluids. Hence

$$p = RT\{V_m(x)\}^{n-1}/\{V_m(x) - b(x)\}^n - a(x)/\{V_m(x)\}^2 \quad \ldots (6.9)$$

where p is the pressure of the fluid mixture and x is the mole fraction of second component. $V_m(x)$, a(x) and b(x) are the mixture quantities which are defined in corresponding fashion as the pure component quantities V_m, a and b. In order to facilitate nomenclature, a(x) and b(x) shall, with reference to the four equations of state under discussion, be termed as VDWTP, which is an abbreviation for van der Waals type parameters.

There are a number of methods for obtaining a solution for $V_m(x)$ at zero pressure. The Newton-Raphson method was adopted. Hence

$$V_{r+1} = V_r - \left\{\frac{\{RTV_r^{n-1}/(V_r - b)^n - a/V_r^2\}}{\{-(RTV_r^{n-2})[V_r + b(n-1)]/(V_r - b)^{n+1} + 2a/V_r^3\}}\right\} \quad \ldots (6.10)$$

where V_r is the trial value of $V_m(x)$ and V_{r+1} is the improved value of $V_m(x)$ on successive iterations of equation (6.10). In that equation, it is to be understood that a and b are in fact a(x) and b(x), respectively. Due care must be taken in order to obtain the relevant root of $V_m(x)$. The relevant root is obtained when the following requirements are met:

$$V_m(x) > b(x) \quad \ldots (6.11)$$

$$\partial p/\{\partial V_m(x)\} < 0 \quad \ldots (6.12)$$

In addition to the trial value of $V_m(x)$, the evaluation of the relation given by equation (6.10) requires the assumption of model(s) for the fluid mixture so that expressions for VDWTP in terms of the corresponding parameters of the pure fluids may be formulated. As in Chapter 5, the "one-fluid" and the "two-fluid" theories are adopted. Hence, for the "one-fluid" theory, one has(1),(2)

$$a(x) = (1-x)^2 a_{11} + 2x(1-x)a_{12} + x^2 a_{22} \quad \ldots (6.13)$$

$$b(x) = (1-x)^2 b_{11} + 2x(1-x)b_{12} + x^2 b_{22} \quad \ldots (6.14)$$

For the "two-fluid" theory, the relations are(2)

$$a_1(x) = (1-x)a_{11} + xa_{12} \quad \ldots (6.15)$$

$$a_2(x) = (1-x)a_{12} + xa_{22} \quad \ldots (6.16)$$

$$b_1(x) = (1-x)b_{11} + xb_{12} \quad \ldots (6.17)$$

$$b_2(x) = (1-x)b_{12} + xb_{22} \quad \ldots (6.18)$$

The quantities a_{ii} and b_{ii}, where i = 1 or 2, are proportional to $T_i^c V_i^c$ and V_i^c, respectively. T_i^c and V_i^c are the critical temperature and critical molar volume for component i. Correspondingly, the cross-term quantities, namely a_{12} and b_{12}, are proportional to $T_{12}^c V_{12}^c$ and V_{12}^c, respectively. For the evaluation of T_{12}^c and V_{12}^c, the same combining rules as used in Chapter 5 are applied. Thus the VDWTP are expressed in terms of the critical parameters of the pure substances.

6.3.1 The expressions for a_{ii} and b_{ii}

At the critical point,

$$(\partial p/\partial V_m)_T = (\partial^2 p/\partial V_m^2)_T = 0 \quad \ldots (6.19)$$

Using the generalised equation of state as given by equation (6.6), one has

$$(\partial p/\partial V_m)_T = - RTV_m^{n-2}[V_m + (n-1)b]/(V_m - b)^{n+1} + 2a/V_m^3 \quad \ldots (6.20)$$

$$(\partial^2 p/\partial V_m^2)_T = - [RTV_m^{n-3}/(V_m - b)^{n+2}][2V_m^2 + 4b(n-1)V_m + (n-1)(n-2)b^2] - 6a/V_m^4 \quad \ldots (6.21)$$

Critical conditions are adopted and equations (6.20) and (6.21) are solved simultaneously to give

$$a_{ii} = RT_i^c V_i^c / c_a \quad \ldots (6.22)$$

$$b_{ii} = V_i^c / c_b \quad \ldots (6.23)$$

where,

$$c_b = [(n + 2) + (5n^2 + 4n)^{0.5}]/2 \quad \ldots (6.24)$$

and $$c_a = 2(c_b - 1)^{n+1}/[c_b^n\{c_b + (n - 1)\}] \quad \ldots (6.25)$$

It may be seen that c_a and c_b are evaluated by merely substituting for n in equations (6.24) and (6.25). For the four equations of state under discussion, the values of c_a and c_b are displayed in Table 6.1.

TABLE 6.1 The values of c_a and c_b for the equations of state.

VALUE OF n	CONSTANTS FOR EVALUATING a_{ii} AND b_{ii}			
	c_a	$(c_a)^{-1}$	c_b	$(c_b)^{-1}$
1	0.8888889	1.1250	3.00	0.3333333
2	0.7953485	1.2573105	4.6457513	0.2152504
3	0.7573645	1.3203682	6.2749172	0.1593647
4	0.7366895	1.3574236	7.8989795	0.1265986

6.4 EVALUATION OF EXCESS FUNCTIONS

Equations (6.26) and (6.27) are relations for any excess molar function $X_m^E(T,P,x)$ according to the "one-fluid" theory and "two-fluid" theory, respectively.

$$X_m^E(T,P,x) = X_m^{res}\{T,P,x,a(x),b(x)\} - (1-x)X_m^{res}(T,P,0,a_{11},b_{11}) - xX_m^{res}(T,P,1,a_{22},b_{22}) \quad \ldots (6.26)$$

$$X_m^E(T,P,x) = (1-x)[X_m^{res}\{T,P,x,a_1(x),b_1(x)\} - X_m^{res}(T,P,0,a_{11},b_{11})] + x[X_m^{res}\{T,P,x,a_2(x),b_2(x)\} - X_m^{res}(T,P,1,a_{22},b_{22})] \quad \ldots (6.27)$$

where P is the external pressure, and X_m may be the molar Gibbs function, the molar enthalpy or the molar volume. The quantities $X_m^{res}\{\ldots\}$ or $X_m^{res}(\ldots)$ are the residual molar functions; the former corresponds to the hypothetical fluid of a given "n-fluid" theory whilst the latter corresponds to the pure fluids.

It is now instructive to give relations for the various residual functions derived from the application of the equations of state. It may be shown that the residual molar Gibbs function $G_m^{res}(T,P)$ of a pure fluid is given by

$$G_m^{res}(T,P) = RT\ln(RT/PV_m) + A_m^{res}(T,V) \quad \ldots (6.28)$$

where $A_m^{res}(T,V)$ is the residual molar Helmholtz function(see Appendix 6.1). But, by definition,

$$A_m^{res}(T,V) = -\int_{\infty}^{V_m}(p - RT/V_m)dV \quad \ldots (6.29)$$

where p is the pressure of the pure fluid and is defined according to equation (6.6). Thus the use of equations (6.28) and (6.29) in combination with equation (6.6) leads to

$$G_m^{res}(T,P) = RT\ln(RT/PV_m) - \int_{\infty}^{V_m}\{RTV_m^{n-1}/(V_m - b)^n - a/V_m^2 - RT/V_m\}dV \quad \ldots (6.30)$$

From equation (6.30), the relations for residual molar Gibbs functions associated with the selected equations of state - see Section 6.2 - are given by equations (6.31) to (6.34).

For n = 1(van der Waals):

$$G_m^{res}(T,P)/RT = -\ln\{(V_m - b)P/RT\} - a/RTV_m \quad \ldots (6.31)$$

For n = 2(proposal I):

$$G_m^{res}(T,P)/RT = -\ln\{(V_m - b)P/RT\} + b/(V_m - b) - a/RTV_m \quad \ldots (6.32)$$

For n = 3(proposal II):

$$G_m^{res}(T,P)/RT = -\ln\{(V_m - b)P/RT\} + b^2/\{2(V_m - b)^2\} + 2b/(V_m - b) - a/RTV_m \quad \ldots (6.33)$$

For n = 4(Guggenheim):

$$G_m^{res}(T,P)/RT = -\ln\{(V_m - b)P/RT\} + b^3/\{3(V_m - b)^3\} + 3b^2/\{2(V_m - b)^2\} + 3b/(V_m - b) - a/RTV_m \quad \ldots (6.34)$$

Now, the relations for the corresponding residual molar enthalpies are obtained by applying the Gibbs-Helmholtz relation to each of equations (6.31) to (6.34). The resulting relations are identical in format and are represented by equation (6.35).

$$H_m^{res}(T,P) = - a/V_m - RT + \text{constant} \qquad \ldots (6.35)$$

The relations for the residual molar volumes are also identical in format. They are represented by equation (6.36).

$$V_m^{res}(T,P) = V_m + \text{constant} \qquad \ldots (6.36)$$

6.5 CALCULATION OF EXCESS FUNCTIONS: PROCEDURE

In order to calculte excess functions of binary mixtures, critical temperatures and critical volumes of both components are required. The calculation is accomplished by adopting the following procedure.

1. The equation of state to be used is selected. This is done by substituting for n in equation (6.6), where n takes the integer values of 1 to 4.

2. The constants c_a and c_b are calculated via the use of equations (6.24) and (6.25). Hence the quantities a_{11}, a_{22}, b_{11} and b_{22} can then be calculated using equations (6.22) and (6.23).

3. Combining rules are used to calculate the critical quantities for unlike interactions, T_{12}^c and V_{12}^c. In all cases, V_{12}^c is calculated via equation (5.46). T_{12}^c is obtained from any of equations (5.45), (5.93), (5.94), (5.98), (5.100) and (5.101).

4. The cross-term Van der Waals type parameters, a_{12} and b_{12}, are then calculated in similar fashion as that used in step 2.

5. Adopting the "one-fluid" model, the quantities a(x) and b(x) are calculated using equations (6.13) and (6.14), respectively. For the "two-fluid" model, equations (6.15) to (6.18) are used to furnish $a_1(x)$, $a_2(x)$, $b_1(x)$ and $b_2(x)$.

6. Equation (6.10) is then used to give values of the molar volumes for:

(a) both pure fluids,

(b) mixture fluid according to the "one-fluid" model, and

(c) mixture fluids according to the "two-fluid" model.

7. The molar volumes are then used for obtaining the following:

(a) $X_m^{res}(T,P,0,a_{11},b_{11})$ - residual molar quantities of component 1,

(b) $X_m^{res}(T,P,1,a_{22},b_{22})$ - residual molar quantities of component 2,

(c) $X_m^{res}\{T,P,x,a(x),b(x)\}$ - residual molar quantities of hypothetical fluid according to the "one-fluid" model,

(d) $X_m^{res}\{T,P,x,a_i(x),b_i(x)\}$ - residual molar quantities of hypothetical fluid i according to the "two-fluid" model; i takes the value of 1 or 2. X may be G, H or V. The corresponding G values are calculated from any of equations (6.31) to (6.34), depending on the selected equation of state. H and V are obtained via the use of equations (6.35) and (6.36), respectively, irrespective of the equation of state.

8. The excess functions, $X_m^E(T,P,x)$, are then obtained from equations (6.26) and (6.27) in accordance with the "n-fluid" theory.

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CHAPTER 7 : PREDICTION OF EXCESS FUNCTIONS: RESULTS

7.1 INTRODUCTION

The results of the predictions based on stated theories are presented and compared to experimental results. The equations of state that have been used belong to two classes, namely,

(a) experimental equations of state, and

(b) analytical equations of state.

The former class of equations are based on the principle of corresponding states as described in Chapter 5 and these are subdivided further depending on the approach(see p.113 and p.115 for descriptions of RPP and RVC approaches). The following experimental equations of state, with abbreviated names as well, were studied:

(1) principle of corresponding states using the 12-6 potential, PCS(12,6);

(2) principle of corresponding states using the 6-4 potential, PCS(6,4);

(3) principle of corresponding states using the 3-2 potential, PCS(3,2); and

(4) principle of corresponding states using the RVC approach, PCS(RVC).

The analytical equations of state are those that are described in Chapter 6. They are:

(1) Van der Waals equation of state, VdW;

(2) Guggenheim equation of state, G;

(3) Proposed equation of state(I), P1; and

(4) Proposed equation of state(II), P2.

Each equation of state is studied in conjunction with six combining rules, namely:

(1) Lorentz-Berthelot, LB;

(2) Hudson-McCoubrey, HM;

(3) Wormald and co-workers, W;

(4) Fender-Halsey, FH;

(5) Hicks-Young, HY; and

(6) proposed combining rules, Pr.

In Chapters 5 and 6, it is stated that fluid mixtures may be visualised as consisting of n fluids, where n is an integral number. In particular, the one-fluid and two-fluid mixtures are considered. Thus for a given equation of state which is combined with one of the combining rules, the predicted excess thermodynamic functions are obtainable in terms of the adopted n-fluid model. Taking into account the foregoing details, 96 combinations are available for predicting a given excess function. For the purposes of discussion, each of these combinations is termed a theory. Also, the nomenclature has been facilitated by use of abbreviations. For example, the theory involving the use of the Van der Waals equation of state in conjunction with Lorentz-Berthelot combining rules in which the one-fluid model of a mixture is adopted is given the abbreviation VdW-LB(1F).

Faced with such quantities of information, selected results are presented. However, the analysis of results and formulation of general remarks about the predictive capacities of the various theories are based on presented and unpresented results.

7.2 SELECTION OF PURE SUBSTANCES AND MIXTURES

For substances to be considered to be suitable for theory testing, certain a priori assumptions were made about the nature of such substances. The main assumptions were:

(1) the substances are non-polar or slightly polar,

(2) they are spherical or pseudo-spherical, and

(3) they have a reasonably high degree of symmetry.

The properties of such substances were then subjected to tests to see if the substances belonged to a conformal set. In doing so, the assumptions of the principle of corresponding states were adopted. Equations (5.14) to (5.16) were used as bases for analyses and plots of

$\ln(P^{\sigma}/P^{c})$ against T^{c}/T,

B/V^{c} against T/T^{c}, and

$V^{l\sigma}/V^{c}$ against T/T^{c}

were made. As a result of such plots, it was decided that the following substances were conformal: benzene, tetramethylmethane, tetramethylsilane, cyclopentane and cyclohexane. The data on these substances were compiled and analysed. The following relations were obtained:

$$\ln(P^{\sigma}/P^{c}) = 6.66 - 6.66(T^{c}/T) \qquad \ldots (7.1)$$

$$B/V^{c} = -48.72 + 154.72T^{r} - 175.29(T^{r})^2 + 68.08(T^{r})^3 \qquad \ldots (7.2)$$

$$V^{l\sigma}/V^{c} = 0.526 - 0.876T^{r} + 1.026(T^{r})^2 \qquad \ldots (7.3)$$

where T^{r} is the reduced temperature. The data for the critical quantities were obtained from a compilation by Ambrose(1). Second virial coefficients were obtained from Dymond and Smith(2). Vapour pressures and molar volumes at saturation vapour pressure were obtained from a variety of sources(3)-(6).

From the above group of substances, binary mixtures were selected for testing the predictive capacities of the various theories. The selection of combinations of mixtures was dictated by the availability of experimental data on excess functions. The selected mixtures are:

(1) tetramethylmethane+tetramethylsilane,

(2) benzene+cyclohexane,

(3) cyclopentane+cyclohexane,

(4) tetramethylmethane+cyclohexane, and

(5) tetramethylsilane+cyclohexane.

For the first three mixtures, experimental information is available on excess Gibbs functions, excess enthalpies, and excess volumes. For the other two mixtures, excess Gibbs functions have not yet been obtained experimentally. The grid below indicates the sources of excess data on the mixtures.

	thermodynamic function		
System	G^E	H^E	V^E
tetramethylmethane+tetramethylsilane	Ref.7	Ref.6	Ref.6
benzene+cyclohexane	Ref.8	Ref.9	Ref.10
cyclopentane+cyclohexane	Ref.4	Ref.4	Ref.4
tetramethylmethane+cyclohexane		Ref.10	Ref.10
tetramethylsilane+cyclohexane		Ref.10	Ref.10

7.3 RESULTS: PRESENTATION AND ANALYSIS

Procedures for the calculation of excess functions are given in Sections 5.7 and 6.5. For each binary mixture, preliminary studies were made. This involved comparison between experimental and theoretical results across the whole composition range. This information was then summarised into tables of the form of Tables 7.1 to 7.8. This group of tables gives information on tetramethylmethane(TMC)+tetramethylsilane(TMS). Each of the tables shows the prediction of excess functions by a particular equation of state in conjunction with various combining rules as well as employing the one-fluid and two-fluid models. Excess functions are given at mole fractions of 0.3, 0.5 and 0.7. This was done so that comparison between experiment and theory could be made on actual values and also on skewness.

TABLE 7.1 Prediction of excess functions via the van der Waals equation of state.
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:		LB	HM	W	FH	HY	Pr
Value of ξ		1.000	0.99737	0.99868	0.99986	0.99998	0.97875
x	**Expt. values**	**Calculated values using various combining rules**					
Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-10.1	0.5	-4.8	-9.5	-10.0	74.6
0.50	7.0	-11.8	0.4	-5.7	-11.1	-11.7	85.8
0.70	5.9	-9.7	0.2	-4.8	-9.2	-9.6	69.8
Excess enthalpies/J mol^{-1}							
0.30	19.8	-9.1	7.0	-1.0	-8.2	-9.0	121.3
0.50	22.3	-10.6	7.9	-1.3	-9.6	-10.4	138.7
0.70	17.7	-8.6	6.3	-1.2	-7.9	-8.6	111.9
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1544	-0.0659	-0.1102	-0.1497	-0.1538	0.5731
0.50	0.0513	-0.1833	-0.0810	-0.1320	-0.1776	-0.1824	0.6582
0.70	0.0378	-0.1531	-0.0701	-0.1116	-0.1487	-0.1526	0.5289

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-5.3	5.1	-0.1	-4.7	-5.2	78.1
0.50	7.0	-6.2	6.0	-0.1	-5.5	-6.1	91.5
0.70	5.9	-5.1	4.9	-0.1	-4.5	-5.0	75.7
Excess enthalpies/J mol^{-1}							
0.30	19.8	-4.4	11.5	3.6	-3.5	-4.3	123.8
0.50	22.3	-5.1	13.4	4.2	-4.1	-4.9	144.5
0.70	17.7	-4.1	11.1	3.5	-3.3	-4.0	119.1
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1435	-0.0561	-0.0998	-0.1388	-0.1429	0.5765
0.50	0.0513	-0.1704	-0.0680	-0.1193	-0.1649	-0.1697	0.6735
0.70	0.0378	-0.1429	-0.0582	-0.1005	-0.1383	-0.1423	0.5557

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.2 Prediction of excess functions via the Guggenheim equation of state.
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:		LB	HM	W	FH	HY	Pr
Value of ξ		1.000	0.99737	0.99868	0.99999	0.99998	0.97875
x	**Expt. values**	**Calculated values using various combining rules**					
Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-12.2	4.0	-4.1	-11.3	-12.1	111.4
0.50	7.0	-14.3	4.5	-4.9	-13.3	-14.1	136.5
0.70	5.9	-11.8	3.5	-4.1	-10.9	-11.7	111.2
Excess enthalpies/J mol^{-1}							
0.30	19.8	-15.4	13.8	-0.8	-13.8	-15.2	220.2
0.50	22.3	-17.9	15.6	-1.1	-16.0	-17.6	252.3
0.70	17.7	-14.6	12.5	-1.1	-13.2	-14.4	204.1
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1093	-0.0059	-0.0576	-0.1036	-0.1085	0.7370
0.50	0.0513	-0.1294	-0.0098	-0.0696	-0.1230	-0.1286	0.8532
0.70	0.0378	-0.1082	-0.0103	-0.0593	-0.1030	-0.1074	0.6925

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-6.0	10.0	2.0	-5.1	-5.9	122.7
0.50	7.0	-7.0	11.8	2.4	-6.0	-6.9	143.9
0.70	5.9	-5.8	9.8	2.0	-4.9	-5.7	119.1
Excess enthalpies/J mol^{-1}							
0.30	19.8	-7.1	21.6	7.3	-5.5	-6.9	224.6
0.50	22.3	-8.2	25.3	8.6	-6.4	-8.0	262.5
0.70	17.7	-6.7	21.0	7.1	-5.2	-6.5	216.6
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.0984	0.0038	-0.0472	-0.0928	-0.0976	0.7404
0.50	0.0513	-0.1167	0.0032	-0.0567	-0.1102	-0.1158	0.8685
0.70	0.0378	-0.0977	0.0017	-0.0480	-0.0924	-0.0971	0.7194

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.3 Prediction of excess functions via the proposed equation of state(I).
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:	LB	HM	W	FH	HY	Pr
Value of ξ	1.000	0.99737	0.99868	0.99986	0.99998	0.97875

x	**Expt. values**	**Calculated values using various combining rules**					
Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-11.2	2.3	-4.4	-10.5	-11.1	97.8
0.50	7.0	-13.1	2.5	-5.3	-12.3	-13.0	112.7
0.70	5.9	-10.8	1.9	-4.4	-10.1	-10.7	91.7
Excess enthalpies/J mol^{-1}							
0.30	19.8	-12.4	10.4	-1.0	-11.1	-12.2	171.7
0.50	22.3	-14.4	11.8	-1.3	-13.0	-14.2	196.5
0.70	17.7	-11.8	9.4	-1.2	-10.1	-11.6	158.8
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1264	-0.0286	-0.0776	-0.1212	-0.1258	0.6768
0.50	0.0513	-0.1499	-0.0366	-0.0933	-0.1438	-0.1491	0.7817
0.70	0.0378	-0.1254	-0.0328	-0.0792	-0.1204	-0.1248	0.6325

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-5.7	7.7	1.0	-5.0	-5.6	101.8
0.50	7.0	-6.6	9.0	1.2	-5.8	-6.5	119.3
0.70	5.9	-5.5	7.5	1.0	-4.8	-5.4	98.7
Excess enthalpies/J mol^{-1}							
0.30	19.8	-5.8	16.6	5.4	-4.6	-5.6	175.2
0.50	22.3	-6.7	19.4	6.3	-5.3	-6.6	204.7
0.70	17.7	-5.5	16.1	5.3	-4.3	-5.4	168.8
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1156	-0.0188	-0.0673	-0.1104	-0.1150	0.6802
0.50	0.0513	-0.1373	-0.0237	-0.0806	-0.1312	-0.1365	0.7969
0.70	0.0378	-0.1151	-0.0209	-0.0681	-0.1100	-0.1145	0.6592

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.4 Prediction of excess functions via the proposed equation of state(II).
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:		LB	HM	W	FH	HY	Pr
Value of ξ		1.000	0.99737	0.99868	0.99986	0.99998	0.97875
x	**Expt. values**	**Calculated values using various combining rules**					
Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-11.8	3.4	-4.2	-11.0	-11.8	110.5
0.50	7.0	-13.4	3.7	-5.0	-12.9	-13.7	127.3
0.70	5.9	-11.4	2.9	-4.2	-10.6	-11.3	103.7
Excess enthalpies/J mol^{-1}							
0.30	19.8	-14.2	12.5	-0.9	-12.8	-14.0	201.0
0.50	22.3	-16.5	14.1	-1.2	-14.9	-16.3	230.3
0.70	17.7	-13.5	11.2	-1.1	-12.2	-13.4	186.3
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1153	-0.0139	-0.0646	-0.1099	-0.1147	0.7163
0.50	0.0513	-0.1366	-0.0192	-0.0779	-0.1304	-0.1358	0.8287
0.70	0.0378	-0.1142	-0.0182	-0.0663	-0.1091	-0.1136	0.6720

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}							
0.30	5.9	-5.9	9.1	1.6	-5.1	-5.8	114.7
0.50	7.0	-6.9	10.7	1.9	-5.9	-6.8	134.4
0.70	5.9	-5.7	8.9	1.6	-5.0	-5.6	111.2
Excess enthalpies/J mol^{-1}							
0.30	19.8	-6.6	19.6	6.5	-5.2	-6.4	205.2
0.50	22.3	-7.6	23.0	7.7	-6.0	-7.4	239.8
0.70	17.7	-6.2	19.0	6.4	-4.9	-6.1	197.8
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	-0.1044	-0.0040	-0.0542	-0.0990	-0.1037	0.7198
0.50	0.0513	-0.1239	-0.0061	-0.0651	-0.1176	-0.1231	0.8440
0.70	0.0378	-0.1038	-0.0062	-0.0550	-0.0986	-0.1032	0.6988

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.5 Prediction of excess functions via the principle of corresponding states.
The 12-6 Brown parameters are used and calculations are based on critical temperatures and critical pressures.
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:	LB	HM	W	FH	HY	Pr
Value of ξ	1.000	0.99788	0.99894	0.99986	0.99998	0.98259

x	**Expt. values**	**Calculated values using various combining rules**					
Excess Gibbs functions/J mol^{-1}							
0.30	5.9	245.0	265.6	255.5	246.3	244.9	415.7
0.50	7.0	270.9	295.6	283.2	272.3	270.8	474.2
0.70	5.9	212.9	233.6	223.2	214.3	212.9	382.9
Excess enthalpies/J mol^{-1}							
0.30	19.8	374.8	405.8	390.6	377.0	374.8	634.1
0.50	22.3	403.0	439.2	421.1	405.1	403.0	706.4
0.70	17.7	305.4	334.7	320.1	307.5	305.4	549.1
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	2.0522	2.1410	2.0983	2.0602	2.0560	2.7927
0.50	0.0513	2.2958	2.4069	2.3544	2.3041	2.2998	3.2272
0.70	0.0378	1.8074	1.9033	1.8564	1.8157	1.8116	2.5990

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}							
0.30	5.9	123.6	144.3	133.9	125.1	123.9	293.8
0.50	7.0	136.8	161.5	149.2	138.8	136.9	339.4
0.70	5.9	107.4	128.0	117.9	109.0	107.5	277.6
Excess enthalpies/J mol^{-1}							
0.30	19.8	183.8	213.8	198.7	185.9	184.3	433.5
0.50	22.3	197.2	232.6	215.0	200.0	197.5	491.7
0.70	17.7	149.5	178.4	164.3	151.7	149.7	392.6
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	0.9762	1.0647	1.0224	0.9838	0.9809	1.7010
0.50	0.0513	1.0887	1.1950	1.1437	1.0960	1.0925	1.9722
0.70	0.0378	0.8569	0.9457	0.9038	0.8623	0.8606	1.6068

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.6 Prediction of excess functions via the principle of corresponding states.
The 6-4 Brown parameters are used and calculations are based on critical temperatures and critical pressures.
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:	LB	HM	W	FH	HY	Pr
Value of ξ	1.000	0.99788	0.99894	0.99986	0.99998	0.98259

x Expt. values Calculated values using various combining rules

Excess Gibbs functions/J mol^{-1}

0.30	5.9	77.0	97.7	87.2	78.2	77.3	248.4
0.50	7.0	87.2	112.0	99.7	89.0	87.5	291.5
0.70	5.9	70.1	91.0	80.7	71.6	70.7	241.7

Excess enthalpies/J mol^{-1}

0.30	19.8	113.6	143.6	128.4	115.3	113.9	365.3
0.50	22.3	124.5	159.7	142.1	126.9	124.8	418.5
0.70	17.7	96.6	125.3	111.0	98.5	97.1	335.9

Excess volumes/cm^3 mol^{-1}

0.30	0.0484	0.7857	0.8699	0.8250	0.7900	0.7816	1.4875
0.50	0.0513	0.9048	1.0102	0.9533	0.9083	0.8984	1.7834
0.70	0.0378	0.7313	0.8225	0.7727	0.7332	0.7265	1.4893

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}

0.30	5.9	39.3	60.2	49.9	40.7	39.4	210.8
0.50	7.0	44.6	69.5	57.2	46.2	44.9	248.9
0.70	5.9	35.9	57.0	46.4	37.2	36.3	207.4

Excess enthalpies/J mol^{-1}

0.30	19.8	54.4	84.2	69.3	56.4	54.5	301.9
0.50	22.3	59.5	94.5	77.0	61.7	59.8	351.1
0.70	17.7	46.0	75.2	60.4	47.8	46.4	287.6

Excess volumes/cm^3 mol^{-1}

0.30	0.0484	0.3459	0.4310	0.3841	0.3504	0.3414	1.0514
0.50	0.0513	0.3975	0.5009	0.4447	0.4022	0.3922	1.2578
0.70	0.0378	0.3172	0.4050	0.3593	0.3226	0.3135	1.0526

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.7 Prediction of excess functions via the principle of corresponding states.
The 3-2 Brown parameters are used and calculations are based on critical temperatures and critical pressures.
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:		LB	HM	W	FH	HY	Pr
Value of ξ		1.000	0.99788	0.99894	0.99986	0.99998	0.98259
x	**Expt. values**	**Calculated values using various combining rules**					
Excess Gibbs functions/J mol^{-1}							
0.30	5.9	16.2	37.1	26.6	17.6	16.3	188.1
0.50	7.0	18.8	43.7	31.2	20.4	18.9	223.3
0.70	5.9	15.4	36.3	25.8	16.8	15.5	187.2
Excess enthalpies/J mol^{-1}							
0.30	19.8	18.3	48.2	33.2	20.2	18.5	267.8
0.50	22.3	20.1	54.9	37.4	22.3	20.3	310.7
0.70	17.7	15.4	44.0	29.6	17.3	15.7	252.8
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	0.2235	0.3066	0.2652	0.2291	0.2242	0.9156
0.50	0.0513	0.2603	0.3640	0.3124	0.2671	0.2613	1.1258
0.70	0.0378	0.2156	0.3054	0.2597	0.2215	0.2159	0.9666

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}							
0.30	5.9	8.5	29.5	19.0	9.9	8.7	180.4
0.50	7.0	9.9	34.8	22.4	11.6	10.1	214.5
0.70	5.9	8.1	29.1	18.6	9.6	8.3	179.9
Excess enthalpies/J mol^{-1}							
0.30	19.8	6.6	36.1	21.3	8.5	6.8	253.2
0.50	22.3	7.0	41.8	24.3	9.3	7.2	297.1
0.70	17.7	5.2	34.1	19.6	7.1	5.4	245.9
Excess volumes/cm^3 mol^{-1}							
0.30	0.0484	0.0708	0.1551	0.1129	0.0764	0.0718	0.7762
0.50	0.0513	0.0812	0.1841	0.1324	0.0875	0.0822	0.9394
0.70	0.0378	0.0668	0.1551	0.1103	0.0724	0.0671	0.8017

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.8 Prediction of excess functions via the principle of corresponding states.
The Van der Waals parameters are used and calculations are based on critical temperatures and critical pressures.
(1-x)-tetramethylmethane + x-tetramethylsilane at 283.15 K

'ONE-FLUID' THEORY

Combining rule:	LB	HM	W	FH	HY	Pr
Value of ξ	1.000	0.99788	0.99894	0.99986	0.99998	0.98259

x **Expt. values** **Calculated values using various combining rules**

Excess Gibbs functions/J mol^{-1}

x	Expt. values	LB	HM	W	FH	HY	Pr
0.30	5.9	-15.2	6.4	-4.4	-13.9	-15.0	161.8
0.50	7.0	-17.8	7.1	-5.3	-16.1	-17.6	186.8
0.70	5.9	-14.7	5.6	-4.5	-13.3	-14.5	152.3

Excess enthalpies/J mol^{-1}

x	Expt. values	LB	HM	W	FH	HY	Pr
0.30	19.8	-31.6	-0.8	-16.2	-29.7	-31.4	224.5
0.50	22.3	-36.5	-1.9	-19.2	-34.3	-36.2	251.9
0.70	17.7	-29.8	-2.3	-16.0	-27.9	-29.5	198.7

Excess volumes/cm^3 mol^{-1}

x	Expt. values	LB	HM	W	FH	HY	Pr
0.30	0.0484	-0.1127	-0.0244	-0.0686	-0.1068	-0.1120	0.6249
0.50	0.0513	-0.1335	-0.0319	-0.0827	-0.1267	-0.1327	0.7180
0.70	0.0378	-0.1117	-0.0292	-0.0705	-0.1063	-0.1111	0.5779

'TWO-FLUID' THEORY

Excess Gibbs functions/J mol^{-1}

x	Expt. values	LB	HM	W	FH	HY	Pr
0.30	5.9	-7.1	14.1	3.5	-5.7	-6.9	167.4
0.50	7.0	-8.3	16.6	4.1	-6.7	-8.1	196.4
0.70	5.9	-6.9	13.8	3.4	-5.5	-6.7	162.6

Excess enthalpies/J mol^{-1}

x	Expt. values	LB	HM	W	FH	HY	Pr
0.30	19.8	-18.4	11.6	-3.4	-16.4	-18.2	232.1
0.50	22.3	-21.4	13.4	-3.9	-19.1	-21.1	268.5
0.70	17.7	-17.5	10.9	-3.3	-15.6	-17.2	219.5

Excess volumes/cm^3 mol^{-1}

x	Expt. values	LB	HM	W	FH	HY	Pr
0.30	0.0484	-0.0985	-0.0114	-0.0549	-0.0926	-0.0977	0.6307
0.50	0.0513	-0.1169	-0.0150	-0.0659	-0.1101	-0.1160	0.7369
0.70	0.0378	-0.0981	-0.0139	-0.0560	-0.0925	-0.0975	0.6078

NOTE: The experimental values for the excess molar Gibbs functions were obtained at 279.95 K.

TABLE 7.9 Selection and ranking of theories which compare best with experiment. The binary system is TMC + TMS . The excess function values are for x = 0.5.

Method	Value	|Deviation|
G^E/J mol^{-1}(at 279.95 K)		
Exprimemental	7.0	0
PCS(RVC)-HM(1F)	7.1	0.1
VdW-HM(2F)	6.0	1.0
P1-HM(2F)	9.0	2.0
G-HM(1F)	4.5	2.5
PCS(RVC)-W(2F)	4.1	2.9
PCS(3,2)-LB(2F)	9.9	2.9
PCS(3,2)-HY(2F)	10.1	3.1
P2-HM(1F)	3.7	3.3
H^E/J mol^{-1}(at 283.15 K)		
Experimental	22.3	0
PCS(3,2)-FH(1F)	22.3	0
P2-HM(2F)	23.0	0.7
PCS(3,2)-HY(1F)	20.3	2.0
PCS(3,2)-W(2F)	24.3	2.0
PCS(3,2)-LB(1F)	20.1	2.2
P1-HM(2F)	19.4	2.9
G-HM(2F)	25.3	3.0
G-HM(1F)	15.6	6.7
P2-HM(1F)	14.1	8.2
V^E/cm^3 mol^{-1}(at 283.15K)		
Experimental	0.0513	0
PCS(3,2)-LB(2F)	0.0812	0.0299
PCS(3,2)-HY(2F)	0.0822	0.0309
PCS(3,2)-FH(2F)	0.0875	0.0362
G-HM(2F)	0.0032	0.0481
P2-HM(2F)	-0.0061	0.0574
G-HM(1F)	-0.0098	0.0611
PCS(RVC)-HM(2F)	-0.0150	0.0663
P2-HM(1F)	-0.0192	0.0705
P1-HM(2F)	-0.0237	0.0750

TABLE 7.10 Selection and ranking of theories which compare best with experiment. The binary system is benzene+cyclohexane. The excess function values are for x = 0.5.

Method	Value	|Deviation|
G^E/J mol^{-1}(at 313.15 K)		
Experimental	300.5	0
PCS(6,4)-Pr(2F)	295.6	4.9
PCS(3,2)-Pr(1F)	259.8	40.9
PCS(3,2)-Pr(2F)	245.1	55.4
PCS(6,4)-Pr(1F)	360.6	60.1
PCS(12,6)-HM(2F)	236.3	64.2
PCS(RVC)-Pr(1F)	235.7	64.8
PCS(RVC)-Pr(2F)	233.4	67.1
PCS(12,6)-W(2F)	218.5	82.0
H^E/J mol^{-1}(at 298.15 K)		
Experimental	799.3	0
PCS(12,6)-Pr(1F)	569.4	229.9
PCS(12,6)-HM(1F)	398.6	400.7
PCS(12,6)-Pr(2F)	383.3	416.0
PCS(12,6)-W(1F)	383.2	416.1
PCS(12,6)-FH(1F)	367.8	431.5
PCS(12,6)-LB(1F)	367.4	431.9
PCS(12,6)-HY(1F)	367.4	431.9
PCS(6,4)-Pr(1F)	323.3	476.0
V^E/cm^3 mol^{-1}(at 298.15 K)		
Experimental	0.6432	0
PCS(6,4)-Pr(1F)	0.6869	0.0437
PCS(12,6)-HM(2F)	0.5917	0.0515
PCS(12,6)-W(2F)	0.5690	0.0742
PCS(12,6)-FH(2F)	0.5479	0.0953
PCS(12,6)-LB(2F)	0.5476	0.0956
PCS(12,6)-HY(2F)	0.5458	0.0974
PCS(12,6)-Pr(2F)	0.8356	0.1924

TABLE 7.11 Selection and ranking of theories which compare best with experiment. The binary system is cyclopentane+cyclohexane. The excess function values are for x = 0.5.

Method	Value	|Deviation|
G^E/J mol^{-1}(at 298.15 K)		
Experimental	-4.0	0
VdW-HM(1F)	-3.6	0.4
G-HY(2F)	-4.7	0.7
P2-HY(2F)	-5.0	1.0
G-LB(2F)	-5.5	1.5
P1-HY(2F	-5.5	1.5
P2-LB(2F)	-5.8	1.8
VdW-HY(2F)	-6.0	2.0
VdW-FH(2F)	-1.9	2.1
P1-LB(2F)	-6.1	2.1
VdW-LB(2F)	-6.5	2.5
P1-HM(1F)	-1.2	2.8
PCS(RVC) - W(2F)	-0.4	3.6
H^E/J mol^{-1}(at 298.15 K)		
Experimental	27.8	0
PCS(3,2)-W(1F)	25.8	2.0
G-HM(2F)	22.6	5.2
PCS(3,2)-HM(2F)	35.6	7.8
P2-HM(2F)	19.8	8.0
PCS(3,2)-FH(1F)	18.0	9.8
PCS(3,2)-W(2F)	17.6	10.2
P1-HM(2F)	15.8	12.0
PCS(3,2)-HM(1F)	43.7	15.9
PCS(3,2)-FH(2F)	9.8	18.0
VdW-HM(2F)	9.6	18.2
PCS(3,2)-HY(1F)	9.0	18.8
PCS(3,2)-LB(1F)	7.8	20.0
V^E/cm^3 mol^{-1}(at 298.15 K)		
Experimental	0.0412	0
PCS(3,2)-HY(2F)	0.0347	0.0065
PCS(3,2)-LB(2F)	0.0328	0.0084
PCS(3,2)-FH(2F)	0.0503	0.0091
PCS(3,2)-W(2F)	0.0634	0.0222
PCS(3,2)-HM(2F)	0.0943	0.0531
G-HM(2F)	-0.0324	0.0736
P2-HM(2F)	-0.0405	0.0817
P1-HM(2F)	-0.0558	0.0970

TABLE 7.12 Selection and ranking of theories which compare best experiment. The binary system is tetramethylmethane+cyclohexane at 298.15 K. The excess function values are for x = 0.5.

Method	Value	|Deviation|
H^E/J mol^{-1}		
Experimental	97.7	0
VdW-Pr(2F)	89.4	8.3
P1-FH(1F)	111.4	13.7
G-HM(2F)	81.6	16.1
G-W(2F)	81.4	16.3
G-LB(2F)	81.2	16.5
P2-HY(2F)	77.1	20.6
VdW-Pr(1F)	74.0	23.7
VdW-FH(2F)	73.2	24.5
G-HM(1F)	69.9	27.8
G-W(1F)	69.8	27.9
G-LB(1F)	69.6	28.1
P1-FH(2F)	126.3	28.6
P2-HM(2F)	66.9	30.8
P2-W(2F)	66.7	31.0
P2-LB(2F)	66.5	31.2
V^E/cm^3 mol^{-1}		
Experimental	-1.3306	0
G-Pr(1F)	-1.3581	0.0275
P2-Pr(1F)	-1.3604	0.0298
P1-Pr(1F)	-1.3676	0.0370
VdW-Pr(1F)	-1.4003	0.0697
P1-FH(1F)	-1.4394	0.1016
G-FH(1F)	-1.4346	0.1040
P2-FH(1F)	-1.4353	0.1047
VdW-LB(2F)	-1.2189	0.1117
VdW-W(2F)	-1.2185	0.1121
VdW-HM(2F)	-1.2181	0.1125
G-LB(2F)	-1.2144	0.1162
G-W(2F)	-1.2140	0.1166
G-HM(2F)	-1.2135	0.1171
P2-LB(2F)	-1.2128	0.1178
P2-W(2F)	-1.2123	0.1183
P2-HM(2F)	-1.2119	0.1187
P1-LB(2F)	-1.2117	0.1189
P1-W-(2F)	-1.2112	0.1194
P1-HM(2F)	-1.2108	0.1198

TABLE 7.13 Selection and ranking of theories which compare best with experiment. The binary system is tetramethylsilane+cyclohexane at 298.15 K. The excess function values are for x = 0.5.

Method	Value	|Deviation|
H^E/J mol^{-1}		
Experimental	191.1	0
P2-HM(1F)	191.9	0.8
P1-FH(1F)	189.2	1.9
G-LB(1F)	187.9	3.2
G-HY(1F)	196.6	5.5
P2-FH(2F)	184.6	6.5
G-Pr(2F)	184.1	7.0
G-W(1F)	203.4	12.3
P2-W(1F)	177.9	13.2
G-FH(2F)	208.8	17.7
P2-HY(1F)	171.7	19.4
V^E/cm^3 mol^{-1}		
Experimental	-1.0944	0
P1-FH(2F)	-1.1666	0.0722
P2-FH(2F)	-1.1670	0.0726
G-FH(2F)	-1.1677	0.0733
VdW-FH(2F)	-1.1692	0.0748
VdW-Pr(2F)	-1.2251	0.1307
P1-Pr(2F)	-1.2301	0.1357
P2-Pr(2F)	-1.2333	0.1389
G-Pr(2F)	-1.2354	0.1410
VdW-HM(2F)	-1.2763	0.1819
P1-HM(2F)	-1.2883	0.1939
P2-HM(2F)	-1.2940	0.1996
G-HM(2F)	-1.2974	0.2030

Although excess Gibbs functions were obtained at 279.95 K, the calculations were carried out using 283.15 K as the temperature. The difference between G^E values at these temperatures is not significant and the general conclusions are not affected.

The function ξ must be mentioned at this point. This is defined in the manner

$$T_{12}^{c} = \xi(T_{11}^{c}T_{22}^{c})^{1/2} \qquad \ldots (7.4)$$

and its value is obtained from relations which define the various combining rules. ξ affects values of excess functions quite markedly and this explains the number of decimal places which appear in the tables.

The compilation of tables of the nature 7.1 to 7.8 facilitated the analysis of comparison between experimental and theoretical values. Having observed that the skewness of experimental and theoretical values was the same in most instances, it was decided to use values at mole fraction of 0.5 as the basis of comparison. The theories which gave the best match between experiment and theory were then extracted. A rank order for such theories was made. Tables 7.9 to 7.13 show the ranked results of the mixtures that were studied.

7.4 CONCLUSIONS

From this work it is inadvisable to make definite statements regarding theories which give the best predictions for mixtues. This is because it is considered that the number of systems is too few to warrant conlusions of that nature. It is considered more fruitful to discuss the binary systems separately.

(1-x)-tetramethylmethane + x-tetramethylsilane

From experimental data, this binary system deviates slightly from ideal behaviour. Thus it may be argued that the system offers a rigorous test to the various theories. From the outset, it is reported that theories based on PCS(12,6) and PCS(6,4) give values that are extremely large compared to experimental data. This applies to all the excess functions. The two-fluid based theories generally give better predictions than their one-fluid counterparts. This is even the case in those situations where the predicted values are wayward.

From Table 7.9, the excess functions are predicted well especially if one takes into account the relative slight deviation of the system from ideality. The HM combining rules feature prominently particularly in those theories which are based on analytical equations of state. Also, if the same set of theories is considered, it can be seen that values of excess functions increase as the value of n is raised in those equations of state represented by equation (6.6). This is for both the one-fluid and the two-fluid models. For example, VdW-HM(2F) predicts G^E to be 6.0 J mol^{-1} and P1-HM(2F) gives 9.0 J mol^{-1} as the predicted G^E value. This pattern is followed in all the other combining rules; the exception are the LB set of rules.

(1-x)-benzene + x-cyclohexane

It can be seen from Table 7.10 that the analytical equations of state do not feature amongst those which give better predictions. They produce values which are very much lower than experimental values. With regards to p.c.s based theories, the following points can be made. For all the excess functions, the values from the one-fluid model are greater than those from the two-fluid model. In the case of G^E, the values from the one-fluid model in which the PCS(12,6) equation of state is used are considerably greater than experiment. In the case of PCS(6,4), they are of moderate magnitude but lower than the experimental value.

A recurring feature of the work on prediction was the magnitude of excess functions obtained when the Pr combining rules were employed. Generally, relatively large values were obtained. Thus when other combining rules would give low G^E values with PCS(6,4) theories for the two-fluid model, the Pr based values are large enough. In part, this explains the relative position of PCS(6,4)-Pr(2F) in Table 7.10. A similar argument could be used to account for PCS(3,2)-PR(1F) and PCS(3,2)-Pr(2F). The relative positions of PCS(12,6)-HM(2F) and PCS(12,6)-W(2F) could be explained in terms of being hybrid situations of the following considerations:

(a) PCS(12,6) renders predicted values to be large,

(b) the two-fluid based theories give low values for this binary system, and

(c) all combining rules, other than Pr, give low values.

Excess enthalpies are predicted poorly. The values are low compared to experiment. This is the case even with PCS(12,6). The picture is somewhat different with respect to excess volumes. Values obtained from 1F theories of the PCS(12,6) variety are quite large, values of greater than 1.2 cm^3 mol^{-1} being common. The 2F theories based on PCS(12,6) furnish results which compare fairly well with experiment. Values predicted by PCS(6,4), PCS(3,2) and PCS(RVC) are low. The exception is PCS(6,4)-Pr(1F); this is line with the observation that theories in which Pr combining rules are used produce relatively large values.

(1-x)-cyclopentane+x-cyclohexane

This binary system, like the tetramethylmethane+tetramethysilane system, shows slight deviation from ideality. The general impression from Table 7.11 is of a good comparison between experiment and theoretical predictions. G^E seems to be predicted best by the analytical equations of state whereas H^E and V^E are predicted better by the p.c.s.

With respect to G^E prediction, the p.c.s results give poor comparison. The values obtained are extremely large. Only a few PCS(RVC) combinations give reasonable predictions. From the table, theories based on the two-fluid model give better predictions than their one-fluid counterparts. However, the latter give reasonable predictions as well. If theories based on VdW equation of state are considered, it is found that, with the exception of Pr theories, the worst deviation is 13.7 J mol^{-1}. When Pr combining rules are used, the predicted values are considerably larger than experimental values.

H^E is predicted reasonably by PCS(3,2) theories. Values obtained from PCS(12,6) and PCS(6,4) are rather large and those from PCS(RVC) are rather low. Values from the analytical equations of state are moderate in magnitude but tend to be lower than the experimental values. The prediction of V^E does not seem to be as impressive as for the other themodynamic functions. The prediction pattern follows the same trend as H^E prediction with respect to the various equations of state.

(1-x)-tetramethylmethane+x-cyclohexane

It can be seen from Table 7.12 that thoeries based on the p.c.s do not feature in the prediction of H^E and V^E. This is because values obtained from such theories are generally much lower than experimental values. The H^E values are excessively negative; the most positive has a value of -302 J mol^{-1}, and is obtained from PCS(12,6)-Pr(2F). V^E values from p.c.s theories are also negative, with those obtained from one-fluid theories being much more negative than those from two-fluid theories. It must be pointed out, however, that the prediction of V^E is moderately good. For example, quite a number of theories which do not appear in the table produce values which deviate by about 0.22 cm^3 mol^{-1}. An interesting feature of the predictions is that, for H^E and V^E, two-fluid theories produce values which are greater than those from one-fluid theories whereas the situation is reversed in the prediction of G^E. Unfortunately, lack of experimental G^E data precludes any meaningful discussion.

(1-x)-tetramethylsilane+x-cyclohexane

As in the previous system, theories based on p.c.s do not feature prominently in the prediction of H^E and V^E. Values obtained from these theories are very low. However, some PCS(12,6) combinations produce moderate values. This is particularly the case with V^E prediction. The theories depicted in Table 7.13 give very good predictions of H^E and fair predictions for V^E. There does not seem to be a pattern in H^E prediction. The V^E prediction is dominated by the two-fluid model in which the combining rules FH, Pr, and HM play an active role.

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APPENDICES: LISTINGS OF COMPUTER PROGRAMS

APPENDIX 1

The program is a general program for solution of linear equations by least squares. The routine for matrix inversion was adopted from a book by T.R. McCalla.[The reference is given in SUBROUTINE MATNVS of the program listed in Appendix 5. Also, all matrix inversions routines are based on that source.]

```
C      PROGRAM GENERAL
C       THIS IS A GENERAL FITTING ROUTINE

       REAL JCB,EPS
       DIMENSION Z(40),X(40),W(40),JCB(40,40),TRSJCB(40,40),P(40),
      1WTN(40,40),ZET(40,10),WTNZ(40,10),TRWTNZ(40,10),WTNJCB(40,40),
      2TRWTJC(40,40),COLVEC(40,10),REMAT(40,40),A(10),B(10),ZC(40)
      3,ZDEV(40)
       WRITE(4,*)
       WRITE(4,*)"TYPE IN VALUE OF J1."
       WRITE(4,*)"J1 IS A SWITCH W.R.T. STATISTICAL WEIGHTING OF DATA"
       WRITE(4,*)"FOR NON-WEIGHTED ANALYSIS, J1 = 1."
       WRITE(4,*)"FOR WEIGHTED ANALYSIS, J1 = 2."
       WRITE(4,*)
       READ(3,*)J1
       WRITE(4,*)
       WRITE(4,*)J1
       WRITE(4,*)
       WRITE(4,*)"TYPE IN NUMBER OF PTS. & COEFFS & CONST"
       WRITE(4,*)
       READ(3,*)N,M,EPS
       WRITE(4,*)
       WRITE(4,*)"TYPE IN Z & X VALUES & WTS"
       WRITE(4,*)
       READ(3,*)(Z(I),X(I),W(I),I=1,N)
       WRITE(4,*)
       CALL MAINP(Z,P,X,W,JCB,TRSJCB,WTN,ZET,WTNZ,TRWTNZ,WTNJCB,TRWTJC,
      1         REMAT,N,M,L,EPS,COLVEC,M1,A,B,ZC,STDEV,J1,ZDEV)
       STOP
       END

       SUBROUTINE MAINP(Z,P,X,W,JCB,TRSJCB,WTN,ZET,WTNZ,TRWTNZ,WTNJCB,
      1         TRWTJC,REMAT,N,M,L,EPS,COLVEC,M1,A,B,ZC,STDEV,J1,ZDEV)
       REAL JCB
       DIMENSION Z(N),X(N),W(N),JCB(N,M),TRSJCB(M,N),WTN(N,N),ZET(N,M),
      1         WTNZ(N,M),TRWTNZ(N,M),WTNJCB(N,M),TRWTJC(M,M),REMAT(M,M)
      2,COLVEC(M,M),P(N),A(M),B(M),ZC(N),ZDEV(N)


       IF (J1.EQ.1) GO TO 4
       MP1 = M + 1
       DO 40 M1 = 1,MP1

    4  CONTINUE


C      SET UP A JACOBIAN MATRIX,JCB
       DO 5 I = 1,N
       DO 5 J = 1,M
       A(J) = X(I)**(J-1)
       B(J) = A(J)
   5   JCB(I,J) = B(J)
   6   CONTINUE

C      GENERATE TRANSPOSE OF THE JACOBIAN MATRIX,TRSJCB
       DO 10 J = 1,M
       DO 10 I = 1,N
       TRSJCB(J,I) = JCB(I,J)
   10  CONTINUE
```

```
C     GENERATE THE WEIGHTING MATRIX WTN--A DIAGONAL MATRIX
      IF (J1.EQ.1) GO TO 11
      IF (M1.EQ.1) GO TO 11
      CALL EQUFIT(COLVEC,P,Z,X,A,B,N,M,ZC,STDEV,ZDEV)
   11 DO 15 I = 1,N
      DO 15 K = 1,N
      IF (J1.EQ.1) GO TO 12
      IF (M1.EQ.1) GO TO 12
      IF (J1.NE.1) GO TO 13
   12 WTN(I,K) = W(I)
      GO TO 14
   13 WTN(I,K) = W(I)/(STDEV**2)
   14 IF (K.NE.I) WTN(I,K) = 0.0
   15 CONTINUE


C     GENERATE THE EXPERIMENTAL DATA COLUMN VECTOR ZET
      DO 20 I =1,N
      P(I) = Z(I)
      ZET(I,1) = P(I)
   20 CONTINUE

C     DO THE PRODUCT OF THE MATRICES WTN(W) AND ZET(Z) TO OBTAIN WTNZ
      CALL MATMUL(WTN,ZET,WTNZ,N,N,1)
C     DO THE PROUCT OF THE MATRICES TRSJCB(JT) AND WTNZ(WZ) TO OBTAIN
C     TRWTNZ.
      CALL MATMUL(TRSJCB,WTNZ,TRWTNZ,M,N,1)
C     DO THE PRODUCT OF THE MATRICES WTN(W) AND JCB(J) TO OBTAIN WTNJCB
      CALL MATMUL(WTN,JCB,WTNJCB,N,N,M)
C     DO THE PRODUCT OF THE MATRICES TRSJCB(JT) WTNJCB(WJ) TO OBTAIN
C     TRWTJC.
      CALL MATMUL(TRSJCB,WTNJCB,TRWTJC,M,N,M)
C     INVERT THE RESULTING MATRIX TRWTJC(MXM)
      IFAIL = 0
      CALL MATNVS(TRWTJC,REMAT,M,EPS,IFAIL)
      IF (IFAIL.EQ.1) GO TO 29
C     THE COLUMN VECTOR,COLVEC,IS THEN OBTAINED BY PREMULTIPLYING
C     THE MATRIX TRWTNZ(JT.W.Z) BY THE INVERSE OF TRWTJC(JT.W.J),
C     WHICH WE CALL REMAT.
      CALL MATMUL(REMAT,TRWTNZ,COLVEC,M,M,1)
      WRITE(4,*)
   40 CONTINUE
      WRITE(4,*)
      DO 25 J = 1,M
      WRITE(4,*)"COEFFICIENT",J, "=", COLVEC(J,1)
   25 CONTINUE
      WRITE(4,*)
      CALL EQUFIT(COLVEC,Z,P,X,A,B,N,M,ZC,STDEV,ZDEV)
      WRITE(4,*)
      WRITE(4,270)
      DO 27 I = 1,N
      WRITE(4,280)X(I),Z(I),ZC(I),ZDEV(I)
   27 CONTINUE
      WRITE(4,290)
      WRITE(4,300)STDEV
  270 FORMAT(5X,66H  RTPLUSBPDIVP      EXPT DV VALUE      CALC DV VALUE
     1   DIFFERENCE ,//)
  280 FORMAT(6X,E13.6,4X,E13.6,4X,E13.6,5X,E13.6/)
  290 FORMAT(/10X,10H STD.DEV.=)
  300 FORMAT(22X,E13.6)
```

```
   29 CONTINUE
      RETURN
      END

      SUBROUTINE MATMUL(A,B,C,N,L,M)
C     THIS IS AN F.A.HEWITT VERSION
      DOUBLE PRECISION MAT
      DIMENSION A(N,L),B(L,M),C(N,M)
      DO 50 I = 1,N
      DO 50 K = 1,M
      MAT = 0.0
      DO 45 J = 1,L
      MAT = A(I,J)*B(J,K) + MAT
   45 CONTINUE
      C(I,K) = MAT
   50 CONTINUE
      RETURN
      END

      SUBROUTINE MATNVS(A,B,M,EPS,IFAIL)
      REAL EPS
      DIMENSION A(M,M),B(M,M)
      DOUBLE PRECISION DET
C     CONSTRUCT AN IDENTITY MATRIX B(I,J) = I
      DO 68 I = 1,M
      DO 66 J = 1,M
      IF (I-J) 64,62,64
   62 B(I,J) = 1.0
      GO TO 66
   64 B(I,J) = 0.0
   66 CONTINUE
   68 CONTINUE
C     LOCATE MAXIMUM MAGNITUDE A(I,K) ON OR BELOW MAIN DIAGGONAL
      DET = 1.0
      DO 100 K = 1,M
      IF (K-M) 70,86,86
   70 IMAX = K
      AMAX = ABS(A(K,K))
      KP1 = K + 1
      DO 76 I = KP1,M
      IF (AMAX-ABS(A(I,K))) 72,76,76
   72 IMAX = I
      AMAX = ABS(A(I,K))
   76 CONTINUE
C     INTERCHANGE ROWS IMAX AND K IF IMAX IS NOT EQUAL TO K
      IF (IMAX-K) 78,86,78
   78 DO 80 J = 1,M
      ATMP = A(IMAX,J)
      A(IMAX,J) = A(K,J)
      A(K,J) = ATMP
      BTMP = B(IMAX,J)
      B(IMAX,J) = B(K,J)
   80 B(K,J) = BTMP
      DET = -DET
   86 CONTINUE
C     TEST FOR SINGULAR MATRIX
      IF (ABS(A(K,K))-EPS) 104,104,88
   88 DET = A(K,K)*DET
```

```
C       DIVIDE PIVOT ROW BY ITS MAIN DIAGONAL ELEMENT
        DIV = A(K,K)
        DO 90 J = 1,M
        A(K,J) = A(K,J)/DIV
   90   B(K,J) = B(K,J)/DIV
C       REPLACE EACH ROW BY LINEAR COMBINATION WITH PIVOT ROW
        DO 98 I = 1,M
        AMULT = A(I,K)
        IF (I-K) 92,98,92
   92   DO 96 J = 1,M
        A(I,J) = A(I,J)-AMULT*A(K,J)
   96   B(I,J) = B(I,J)-AMULT*B(K,J)
   98   CONTINUE
  100   CONTINUE
        GO TO 112
  104   WRITE(4,110) K
        IFAIL = 1
        GO TO 112
  110   FORMAT(25H SINGULAR MATRIX FOR K =,I2)
  112   RETURN
        END

        SUBROUTINE EQUFIT(COLVEC,P,Z,X,A,B,N,M,ZC,STDEV,ZDEV)
        DIMENSION COLVEC(M,1),Z(N),X(N),A(M),B(M),P(N),ZC(N)
       1,ZDEV(N)
        SUMSQ = 0.0
        DO 35 I =1,N
        ZCALC = 0.0
        DO 32 J = 1,M
        A(J) = X(I)**(J-1)
        B(J) = A(J)
        SUM = COLVEC(J,1)*B(J)
   32   ZCALC = ZCALC + SUM
        ZC(I) = ZCALC
        ZDEV(I) = Z(I) - ZC(I)
   35   SUMSQ = SUMSQ + ZDEV(I)**2
        STDEV = SQRT(SUMSQ/(N-M))
        RETURN
        END
```

APPENDIX 2

This program was used for converting heights of mercury in the DPBP manometers into pressure and volume readings. Corrections for

(a) expansivity of cathetometer,

(b) mercury density, and

(c) acceleration due to local gravity are taken into account.

```
C     PROGRAM .PEEVEE

C     PROGRAM FOR CALCULATING PRESSURE-VOLUME ISOTHERMS USING
C     DATA FROM CATHETOMETER READINGS

      REAL LOCALG
      DIMENSION H1(40),H2(40),H3(40),H4(40),RMT(40),VHT(40),
     1PHT(40),DELTAV(40),VOLUME(40),PRESHA(40)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN NO. OF PTS; PI; AND REF. VOL"
      WRITE(4,*)"5.06670, the value for REFVOL, was calculated using"
      WRITE(4,*)"71.248 cm as the reference height. Thus volumes have"
      WRITE(4,*)"to be readjusted if different reference mark heights"
      WRITE(4,*)"are used."
      WRITE(4,*)
      READ(3,*)N,PI,REFVOL
      WRITE(4,*)
      WRITE(4,*)"TYPE IN VALUE FOR REFERENCE MARK HEIGHT, HR"
      WRITE(4,*)
      READ(3,*)HR
      WRITE(4,*)
      WRITE(4,*)"TYPE IN STD. ROOM TEMP. AND BATH TEMP"
      WRITE(4,*)
      READ(3,*)SRMT,TMT
      WRITE(4,*)
      WRITE(4,*)"TYPE IN ALPHA AND BETA"
      WRITE(4,*)
      READ(3,*)ALPHA,BETA
      WRITE(4,*)
      WRITE(4,*)"TYPE IN DENSITY OF HG AT 20 AND LOCAL G VALUE"
      WRITE(4,*)
      READ(3,*)ROHG20,LOCALG
      WRITE(4,*)
      WRITE(4,*)"TYPE IN ROOM TEMP,HT1,HT2,HT3,AND HT4"
      WRITE(4,*)"THE REAL THING--KNOW WHAT I MEAN"
      WRITE(4,*)
      READ(3,*)(RMT(I),H1(I),H2(I),H3(I),H4(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"     VOLUME/cu.cm          PRESSURE/Pa"
      WRITE(4,*)
      DELVOL = (71.248 - HR)*PI
      ADJVOL = REFVOL + DELVOL
      DO 20 I = 1,N
      VHT(I) = (HR-H1(I))*(1.0+ALPHA*(RMT(I)-SRMT))
      PHT(I) = (H2(I)-H1(I)+H4(I)-H3(I))*(1.0+ALPHA*(RMT(I)-SRMT))
      DELTAV(I) = PI*VHT(I)
      VOLUME(I) = ADJVOL + DELTAV(I)
      PRESHA(I) = ROHG20*LOCALG*PHT(I)/(100.0*(1.0+BETA*(TMT-SRMT)))
      WRITE(4,15)VOLUME(I),PRESHA(I)
 15   FORMAT(3X,E15.6,9X,E13.6/)
 20   CONTINUE
      STOP
      END
```

APPENDIX 3

This is the program for the dew point-bubble point method.

```
C     THIS PROGRAM DEALS WITH DATA ANALYSIS FROM THE PD-PB
C     EXPERIMENT.
C     PR(J),J=1 OR 2 - VAPOUR PRESSURE OF EITHER COMPT AT T
C     PB(I,1) = EXPERIMENTAL BUBBLE POINT PRESSURE
C     PD(I,1) = EXPERIMENTAL DEW POINT PRESSURE
C     P(I,1) = EST. OR CALC. BUBBLE POINT PRESSURE
C     P(I,2) = EST. OR CALC. DEW POINT PRESSURE
C     XL(I,1) = X(I)...LIQUID COMPOSITION AT P(I,1)
C     XL(I,2) = Z(I)...LIQUID COMPOSITION AT P(I,2)
C     XV(I,1) = Y(I)...VAPOUR COMPOSITION AT P(I,1)
C     XV(I,2) = X(I)...VAPOUR COMPOSITION AT P(I,2)
C     PC(R,1) = THIS QUANTITY REPRESENTS CALCULATED
C     BUBBLE OR DEW POINT PRESSURES; USING TRIAL VALUES OF
C     X,Y,Z, AND A(L).

C     XL(I,1);XL(I,2);XV(I,1);XV(I,2)...MOLE FRACTIONS OF
C     COMPONENT 2. THEY ARE TRIAL VALUES WHICH ARE USED IN
C     THE FIRST CYCLE OF THE CALCULATION. PROGRAM
C     .PHASDIAG(SEE ELSEWHERE) IS USED IN THE ESTIMATION
C     OF THE MOLE FRACTIONS AND THE PRESSURES.
C     LIQUID COMPOSITION AT THE BUBBLE POINT = VAPOUR
C     COMPOSITION AT THE DEW POINT.

C     A(L),L=1,M...REDLICH-KISTER COEFFICIENTS.
C     AIMP(L),L=1,M...IMPROVED REDLICH-KISTER COEFFICIENTS

      COMMON/PDDATA/P(40,2),XL(40,2),XV(40,2),CJB(40,40),PR(4)
      COMMON/PDEXT/A(10),V(4),B(4)
      COMMON/LOOPVL/N,M1,MMAX,NCYMAX
      COMMON/LOOPVR/B11,B22,B12,T,EPS,RC
      INTEGER R,Q
      REAL JCB,EPS
      DIMENSION PC(40,4),PB(40,4),PD(40,4),X(40,2),Y(40,2),
     1Z(40,2),W(40),JCB(40,40),TRSJCB(40,40),WTN(40,40),
     2ZET(40,4),WTNZ(40,40),TRWTNZ(40,40),WTNJCB(40,40),
     3TRWTJC(40,40),REMAT(40,40),COLVEC(40,4),AIMP(10),CAXSGX(40),
     4CAXSGZ(40),XMFRSM(10),ZMFRSM(10),XSMU1(10),XSMU2(10),
     5XSG(40),XPXSGX(40),XPXSGZ(40),DFXSGX(40),DFXSGZ(40)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN N,M1,EPS,NCYMAX, AND MMAX"
      WRITE(4,*)"M1 = 1, IF VIRIAL COEFFS ARE KNOWN"
      WRITE(4,*)
      READ(3,*)N,M1,EPS,NCYMAX,MMAX
      WRITE(4,*)
      WRITE(4,*)"TYPE IN P1 AND P2 AND DESIRED STD.DEV "
      WRITE(4,*)
      READ(3,*)P1,P2,STDDEV
      WRITE(4,*)
      WRITE(4,*)"TYPE IN EXPERIMENTAL PB AND PD VALUES"
      WRITE(4,*)
      DO 1 I = 1,N
      READ(3,*)PB(I,1),PD(I,1)
 1    CONTINUE
      WRITE(4,*)
      WRITE(4,*)"TYPE IN VAP. PRESS. OF PURE SUBS"
      WRITE(4,*)
      READ(3,*)(PR(K),K=1,2)
      WRITE(4,*)
```

```
      WRITE(4,*)"TYPE IN LIQUID MOLAR VOLUMES"
      WRITE(4,*)
      READ(3,*)(V(K),K=1,2)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN VIRIAL COEFFS OF PURE SUBS"
      WRITE(4,*)
      READ(3,*)(B(K),K=1,2)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE VIRIAL COEFFICIENTS"
      WRITE(4,*)
      READ(3,*)B11,B22,B12
      WRITE(4,*)
      WRITE(4,*)"TYPE IN TEMPERATURE AND GAS CONSTANT"
      WRITE(4,*)
      READ(3,*)T,RC
      WRITE(4,*)
      WRITE(4,*)"TYPE IN PB,PD,X,Y,Z,X"
      WRITE(4,*)
      DO 2 I = 1,N
      READ(3,*)P(I,1),P(I,2),XL(I,1),XV(I,1),XL(I,2),XV(I,2)
2     CONTINUE
      WRITE(4,*)
      WRITE(4,*)"TYPE IN MMAX VALUES OF A(L)"
      WRITE(4,*)
      READ(3,*)(A(L),L=1,MMAX)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE WEIGHTS"
      WRITE(4,*)
      READ(3,*)(W(I),I=1,4*N)
      WRITE(4,*)
      WRITE(4,*)
      CALL MAINP(PB,PD,X,Y,Z,I,K,J,L,STDDEV,COLVEC,R,Q,JCB,TRSJCB,
     1WTN,PC,ZET,W,WTNZ,TRWTNZ,WTNJCB,TRWTJC,REMAT,
     2NT4,NT3PM,AIMP,CAXSGX,CAXSGZ,XMFRSM,ZMFRSM,XSMU1,XSMU2,XSG,
     3XPXSGX,XPXSGZ,DFXSGX,DFXSGZ)
      STOP
      END

      SUBROUTINE MAINP(PB,PD,X,Y,Z,I,K,J,L,STDDEV,COLVEC,R,Q,JCB,
     1TRSJCB,WTN,PC,ZET,W,WTNZ,TRWTNZ,WTNJCB,TRWTJC,REMAT,
     2NT4,NT3PM,AIMP,CAXSGX,CAXSGZ,XMFRSM,ZMFRSM,XSMU1,XSMU2,XSG,
     3XPXSGX,XPXSGZ,DFXSGX,DFXSGZ)
      REAL JCB
      INTEGER R,Q
      COMMON/PDDATA/P(40,2),XL(40,2),XV(40,2),CJB(40,40),PR(4)
      COMMON/PDEXT/A(10),V(4),B(4)
      COMMON/LOOPVL/N,M1,MMAX,NCYMAX
      COMMON/LOOPVR/B11,B22,B12,T,EPS,RC
      DIMENSION PC(40,4),PB(40,4),PD(40,4),X(40,2),
     1Y(40,2),Z(40,2),W(40),JCB(40,40),TRSJCB(40,
     240),WTN(40,40),ZET(40,4),WTNZ(40,4),TRWTNZ
     3(40,40),WTNJCB(40,40),TRWTJC(40,40),
     4REMAT(40,40),COLVEC(40,4),AIMP(10),CAXSGX(40),
     5CAXSGZ(40),XMFRSM(10),ZMFRSM(10),XSMU1(10),XSMU2(10),XSG(40),
     6XPXSGX(40),XPXSGZ(40),DFXSGX(40),DFXSGZ(40)

      DO 42 M = 1,MMAX
      DO 40 NCY = 1,NCYMAX
      IF (NCY.EQ.1) GO TO 3
      DO 38 I = 1,N
```

```
      XL(I,1) = X(I,1)
      XV(I,1) = Y(I,1)
      XL(I,2) = Z(I,1)
      XV(I,2) = X(I,1)
   38 CONTINUE
      DO 39 L = 1,M
      A(L) = AIMP(L)
   39 CONTINUE

    3 M2 = M1 - 1
      NT3PM = 3*N + M2 + M
      NT4 = 4*N


C     SET UP THE JACOBIAN MATRIX
    6 CALL PARDEV(M,N,M1,B11,B22,B12,T,R,Q,JCB)
    5 CONTINUE

C     GENERATE TRANSPOSE OF THE JACOBIAN MATRIX,TRSJCB
      DO 10 Q = 1,NT3PM
      DO 10 R = 1,NT4
      TRSJCB(Q,R) = JCB(R,Q)
   10 CONTINUE

C     GENERATE THE WEIGHTING MATRIX WTN--A DIAGONAL MATRIX
      DO 15 I1 = 1,NT4
      DO 15 K1 = 1,NT4
      WTN(I1,K1) = W(I1)
      IF (K1.NE.I1) WTN(I1,K1) = 0.0
   15 CONTINUE

C     GENERATE THE EXPERIMENTAL DATA COLUMN VECTOR ZET

      CALL PCALC(M,PC,ZET)

C     DO THE PRODUCT OF THE MATRICES WTN(W) AND ZET(Z) TO OBTAIN WTNZ
      CALL MATMUL(WTN,ZET,WTNZ,NT4,NT4,1)
C     DO THE PROUCT OF THE MATRICES TRSJCB(JT) AND WTNZ(WZ) TO OBTAIN
C     TRWTNZ.
      CALL MATMUL(TRSJCB,WTNZ,TRWTNZ,NT3PM,NT4,1)
C     DO THE PRODUCT OF THE MATRICES WTN(W) AND JCB(J) TO OBTAIN WTNJCB
      CALL MATMUL(WTN,JCB,WTNJCB,NT4,NT4,NT3PM)
C     DO THE PRODUCT OF THE MATRICES TRSJCB(JT) WTNJCB(WJ) TO OBTAIN
C     TRWTJC.
      CALL MATMUL(TRSJCB,WTNJCB,TRWTJC,NT3PM,NT4,NT3PM)
C     INVERT THE RESULTING MATRIX TRWTJC(MXM)
      IFAIL = 0
      CALL MATNVS(TRWTJC,REMAT,NT3PM,EPS,IFAIL)
      IF (IFAIL.EQ.1) GO TO 29
C     THE COLUMN VECTOR,COLVEC,IS THEN OBTAINED BY PREMULTIPLYING
C     THE MATRIX TRWTNZ(JT.W.Z) BY THE INVERSE OF TRWTJC(JT.W.J),
C     WHICH WE CALL REMAT.
      CALL MATMUL(REMAT,TRWTNZ,COLVEC,NT3PM,NT3PM,1)
      SMXSGX = 0.0
      SMXSGZ = 0.0
      DO 18 I = 1,N
      Q = 3*(I-1)
      X(I,1) = XL(I,1) + COLVEC(Q+1,1)
      Y(I,1) = XV(I,1) + COLVEC(Q+2,1)
      Z(I,1) = XL(I,2) + COLVEC(Q+3,1)
```

```
      RKXSUM = 0.0
      RKZSUM = 0.0
      DO 7 L = 1,M
      Q = 3*N + L
      AIMP(L) = A(L) + COLVEC(Q,1)
      XMFRSM(L) = AIMP(L)*(1.0-2.0*X(I,1))**(L-1)
      ZMFRSM(L) = AIMP(L)*(1.0-2.0*Z(I,1))**(L-1)
      RKXSUM = XMFRSM(L) + RKXSUM
      RKZSUM = ZMFRSM(L) + RKZSUM
 7    CONTINUE
      CAXSGX(I) = RC*T*X(I,1)*(1.0-X(I,1))*RKXSUM
      CAXSGZ(I) = RC*T*Z(I,1)*(1.0-Z(I,1))*RKZSUM
      X(I,1) = X(I,1)
      X(I,2) = Z(I,1)
      Y(I,1) = Y(I,1)
      Y(I,2) = X(I,1)
      DO 27 J = 1,2
      XSMU1(J) = RC*T*ALOG(P(I,J)*(1.0-Y(I,J))/(PR(1)*(1.0-X(I,J))))
     1+ (B(1)-V(1))*(P(I,J)-PR(1)) + P(I,J)*Y(I,J)**2*
     2(2.0*B12 - B11 - B22)
      XSMU2(J) = RC*T*ALOG(P(I,J)*Y(I,J)/(PR(2)*X(I,J)))
     1+ (B(2)-V(2))*(P(I,J)-PR(2)) + P(I,J)*(1.0-Y(I,J))**2*
     2(2.0*B12 - B11 - B22)
      XSG(J) = (1.0-X(I,J))*XSMU1(J) + X(I,J)*XSMU2(J)
27    CONTINUE
      XPXSGX(I) = XSG(1)
      XPXSGZ(I) = XSG(2)
      DFXSGX(I) = (XPXSGX(I)-CAXSGX(I))**2
      DFXSGZ(I) = (XPXSGZ(I)-CAXSGZ(I))**2
      SMXSGX = DFXSGX(I) + SMXSGX
      SMXSGZ = DFXSGZ(I) + SMXSGZ
18    CONTINUE
      RMXSGX = SQRT(SMXSGX/FLOAT(N-1))
      RMXSGZ = SQRT(SMXSGZ/FLOAT(N-1))
      CALL SIGMAP(STDZP,M,PC,ZET)
      IF (STDZP.GE.STDDEV) GO TO 40
      NCYMAX = NCY
      MMAX = M
40    CONTINUE
42    CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"SOLUTION TO THE EQUATIONS"
      WRITE(4,*)
       WRITE(4,*)
      DO 23 L = 1,M
      WRITE(4,*)"REDLICH-KISTER COEFFICIENT",L,     AIMP(L)
23    CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,22)
22    FORMAT(6X,90H BUBBLE PT.   DEW POINT   XL(I,1)   XV(I,1)   XL(I,2)
     1   XPXSGX   CAXSGX   XPXSGZ   CAXSGZ /)
      DO 28 I = 1,N
      WRITE(4,*)
      WRITE(4,24)PB(I,1),PD(I,1),X(I,1),Y(I,1),Z(I,1),XPXSGX(I),
     1CAXSGX(I),XPXSGZ(I),CAXSGZ(I)
24    FORMAT(5X,F10.1,3X,F10.1,3X,F7.4,3X,F7.4,3X,F7.4,4X,F6.1,3X,F6.1,
     13X,F6.1,3X,F6.1/)
28    CONTINUE
```

```
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"ROOT-MEAN-SQUARE VALUE OF XSG(PB,X) =",      RMXSGX
      WRITE(4,*)
      WRITE(4,*)"ROOT-MEAN-SQUARE VALUE OF XSG(PD,Z) =",      RMXSGZ
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"STD.DEV. OF THE PRESSURES =",      STDZP
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,11)
   11 FORMAT(3X,63H EQUATION NUMBER    CALC.PRESSURE/Pa    PRESSURE DEVI
     1ATION/Pa  /)
      DO 14 R = 1,NT4
      WRITE(4,12)R,PC(R,1),ZET(R,1)
   12 FORMAT(11X,I3,12X,F7.1,15X,F6.2/)
   14 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
   29 CONTINUE
      RETURN
      END

      SUBROUTINE MATMUL(A,B,C,N,L,M)
C     THIS IS AN F.A.HEWITT VERSION
      DOUBLE PRECISION MAT
      DIMENSION A(40,L),B(40,M),C(40,M)
      DO 50 I = 1,N
      DO 50 K = 1,M
      MAT = 0.0
      DO 45 J = 1,L
      MAT = A(I,J)*B(J,K) + MAT
   45 CONTINUE
      C(I,K) = MAT
   50 CONTINUE
      RETURN
      END

      SUBROUTINE MATNVS(A,B,M,EPS,IFAIL)
      REAL EPS
      DIMENSION A(40,40),B(40,40)
      DOUBLE PRECISION DET
C     CONSTRUCT AN IDENTITY MATRIX B(I,J) = I
      DO 68 I = 1,M
      DO 66 J = 1,M
      IF (I-J) 64,62,64
   62 B(I,J) = 1.0
      GO TO 66
   64 B(I,J) = 0.0
   66 CONTINUE
   68 CONTINUE
C     LOCATE MAXIMUM MAGNITUDE A(I,K) ON OR BELOW MAIN DIAGGONAL
      DET = 1.0
      DO 100 K = 1,M
      IF (K-M) 70,86,86
   70 IMAX = K
      AMAX = ABS(A(K,K))
      KP1 = K + 1
      DO 76 I = KP1,M
      IF (AMAX-ABS(A(I,K))) 72,76,76
```

```
   72 IMAX = I
      AMAX = ABS(A(I,K))
   76 CONTINUE
C     INTERCHANGE ROWS IMAX AND K IF IMAX IS NOT EQUAL TO K
      IF (IMAX-K) 78,86,78
   78 DO 80 J = 1,M
      ATMP = A(IMAX,J)
      A(IMAX,J) = A(K,J)
      A(K,J) = ATMP
      BTMP = B(IMAX,J)
      B(IMAX,J) = B(K,J)
   80 B(K,J) = BTMP
      DET = -DET
   86 CONTINUE
C     TEST FOR SINGULAR MATRIX
      IF (ABS(A(K,K))-EPS) 104,104,88
   88 DET = A(K,K)*DET
C     DIVIDE PIVOT ROW BY ITS MAIN DIAGONAL ELEMENT
      DIV = A(K,K)
      DO 90 J = 1,M
      A(K,J) = A(K,J)/DIV
   90 B(K,J) = B(K,J)/DIV
C     REPLACE EACH ROW BY LINEAR COMBINATION WITH PIVOT ROW
      DO 98 I = 1,M
      AMULT = A(I,K)
      IF (I-K) 92,98,92
   92 DO 96 J = 1,M
      A(I,J) = A(I,J)-AMULT*A(K,J)
   96 B(I,J) = B(I,J)-AMULT*B(K,J)
   98 CONTINUE
  100 CONTINUE
      GO TO 112
  104 WRITE(4,110) K
      IFAIL = 1
      GO TO 112
  110 FORMAT(25H SINGULAR MATRIX FOR K =,I2)
  112 RETURN
      END

      SUBROUTINE PCALC(M,PC,ZET)
      INTEGER R
      COMMON/PDDATA/P(40,2),XL(40,2),XV(40,2),CJB(40,40),PR(4)
      COMMON/PDEXT/A(10),V(4),B(4)
      COMMON/LOOPVL/N,M1,MMAX,NCYMAX
      COMMON/LOOPVR/B11,B22,B12,T,EPS,RC
      DIMENSION ZET(40,4),PC(40,4),PB(40,4),PD(40,4)
      DO 20 I = 1,N
      DO 20 J = 1,2
      DO 20 K = 1,2
      R = 4*(I-1) + 2*(J-1) + K
      K2 = 2 - K
      RK = 0.0
      DO 16 L = 1,M
      XLI = FLOAT(2*L*K2+2*K) - 3.0 - FLOAT(2*L)*XL(I,J)
      SUM = A(L)*(FLOAT(K-1)-XL(I,J))**2*(1.0-2.0*XL(I,J))**(L-2)*
     1XLI
      RK = SUM + RK
   16 CONTINUE
      VBP = (V(K)-B(K))*(PR(K)-P(I,J))
      PDEL = P(I,J)*(2.0*B12-B11-B22)*(FLOAT(K-1)-XV(I,J))**2
```

```
      VBPRT = (VBP + PDEL)/(RC*T)
      XPFUN = EXP(RK - VBPRT)
      PC1 = PR(K)*(FLOAT(K2)-XL(I,J))*XPFUN/(FLOAT(K2)-XV(I,J))
      PC(R,1) = PC1
      ZET1 = P(I,J) - PC(R,1)
      ZET(R,1) = ZET1
   20 CONTINUE
      RETURN
      END

      SUBROUTINE SIGMAP(STDZP,M,PC,ZET)
      REAL STDZP
      INTEGER R
      COMMON/PDDATA/P(40,2),XL(40,2),XV(40,2),CJB(40,40),PR(4)
      COMMON/PDEXT/A( 10),V(4),B(4)
      COMMON/LOOPVL/N,M1,MMAX,NCYMAX
      COMMON/LOOPVR/B11,B22,B12,T,EPS,RC
      DIMENSION ZET(40,4),PC(40,4)
      M2 = M1 - 1
      NT4 = 4*N
      NT3PM = 3*N + M2 + M
      CALL PCALC(M,PC,ZET)
      SUMZSQ = 0.0
      DO 10 R =1,NT4
      SUMZSQ = SUMZSQ + ZET(R,1)**2
   10 CONTINUE
      STDZP = SQRT(SUMZSQ/FLOAT(NT4-NT3PM))
      RETURN
      END

      SUBROUTINE PARDEV(M,N,M1,B11,B22,B12,T,R,Q,JCB)

C      THIS ROUTINE EVALUATES APPROXIMATE PARTIAL DERIVATIVES OF
C     BUBBLE AND DEW PRESSURES W.R.T. R-K COEFFS, VAPOUR AND
C     LIQUID COMPOSITIONS,AND VIRIAL COEFFICIENTS(IF UNKNOWN)
C      FUNCTIONS ARE MADE USE OF

      REAL JCB
      INTEGER R,Q
      DIMENSION JCB(40,40)
      COMMON/PDDATA/P(40,2),XL(40,2),XV(40,2),CJB(40,40),PR(4)
      COMMON/PDEXT/A( 10),V(4),B(4)
      DO 210 Q = 1,40
      DO 210 R = 1,40
      CJB(R,Q) = 0.0
  210  CONTINUE
      DO 280 I = 1,N
      DO 280 J = 1,2
      DO 280 K = 1,2
      R = 4*(I-1) + 2*(J-1) + K
      DO 220 L = 1,M
      Q = L + 3*N
      CJB(R,Q) = PRKF(P(I,J),XL(I,J),L,K,B11,B22,B12,T,XV(I,J))
  220  CONTINUE
      M2 = M1 - 1
      IF(M2.EQ.0) GO TO 260
      Q = M2 + M + 3*N
```

```
      CJB(R,Q) = PVIRT(P(I,J),XV(I,J),K,B11,B22,B12,T)
 230   CONTINUE
      Q = (3*N-1) + M2
      IF (K.EQ.2) GO TO 240
      CJB(R,Q) = PVIRO(P(I,J),PR(1),XV(I,J),K,B11,B22,B12,T,V(1),B(1))
      CJB(R,Q+1) = PVIRX(P(I,J),XV(I,J),K,B11,B22,B12,T,V(1),B(1))
      GO TO 250
 240   CJB(R,Q) = PVIRX(P(I,J),XV(I,J),2,B11,B22,B12,T,V(2),B(2))
      CJB(R,Q+1)=PVIRO(P(I,J),PR(2),XV(I,J),2,B11,B22,B12,T,V(2),B(2))
 250   CONTINUE
 260    Q = 3*(I-1)
      IF (J.EQ.2) GO TO 270
      CJB(R,Q+1) = PLIQ(P(I,1),XL(I,1),K,M,B11,B22,B12,T,XV(I,1))
      CJB(R,Q+2) = PVAP(P(I,1),XV(I,1),K,B11,B22,B12,T)
      GO TO 280
 270    CJB(R,Q+3) = PLIQ(P(I,2),XL(I,2),K,M,B11,B22,B12,T,XV(I,2))
      CJB(R,Q+1) = PVAP(P(I,2),XV(I,2),K,B11,B22,B12,T)
 280    CONTINUE
      NT3PM = N*3 + M2 + M
      NT4 = N*4
      DO 300 R = 1,NT4
      DO 300 Q = 1,NT3PM
      JCB(R,Q) = CJB(R,Q)
300   CONTINUE
      RETURN
      END

      REAL FUNCTION PLIQ(P,X,K,M,B11,B22,B12,T,Y)
      REAL P,X,B11,B22,B12,T,Y
      INTEGER K,M
      COMMON/PDEXT/A(10),V(4),B(4)
      SUM = 1.0/(X+FLOAT(K-2))
      DO 330 L = 1,M
      SUM = SUM-2.0*A(L)*(FLOAT(K-1)-X)*(1.0-2.0*X)**(L-3)*
     1((FLOAT(2*L-1))-FLOAT(2*L*(L+1))*X*(1.0-X))
 330    CONTINUE
      DEL = 2.0*B12 - B11 - B22
      PDENT = 8.31441*T + P*(B(K)-V(K)) + P*DEL*(FLOAT(K-1)-Y)**2
      PLIQ = 8.31441*T*P*SUM/PDENT
      RETURN
      END

      REAL FUNCTION PVAP(P,Y,K,B11,B22,B12,T)
      REAL P,Y,B11,B22,B12,T
      INTEGER K
      COMMON/PDEXT/A(10),V(4),B(4)
      DEL = 2.0*B12 - B11 - B22
      PNUMT = P/(FLOAT(2-K)-Y) + 2.0*(FLOAT(K-1)-Y)*DEL*P**2/(8.31441*T)
      PDENT = 8.31441*T + P*(B(K)-V(K)) + P*DEL*(FLOAT(K-1)-Y)**2
      PVAP = 8.31441*T*PNUMT/PDENT
      RETURN
      END

      REAL FUNCTION PRKF(P,X,L,K,B11,B22,B12,T,Y)
      REAL P,X,B11,B22,B12,T,Y
      INTEGER L,K
      COMMON/PDEXT/A(10),V(4),B(4)
      DEL = 2.0*B12 - B11 - B22
      PDENT = 8.31441*T + P*(B(K)-V(K)) + P*DEL*(FLOAT(K-1)-Y)**2
      PRKF = P*(FLOAT(K-1)-X)**2*(1.0-2.0*X)**(L-2)*(FLOAT(2*L*(2-
```

```
1K)+2*K-3)-FLOAT(2*L)*X)*8.31441*T/PDENT
 RETURN
 END

 REAL FUNCTION PVIRO(P,PR,Y,K,B11,B22,B12,T,V,B)
 REAL P,PR,Y,B11,B22,B12,T,V,B
 INTEGER K
 PNUMT = P*(PR + P*(FLOAT(K-1)-Y)**2 - P)
 DEL = 2.0*B12 - B11 - B22
 PDENT = 8.31441*T + P*(B-V) + P*DEL*(FLOAT(K-1)-Y)**2
 PVIRO = PNUMT/PDENT
 RETURN
 END

 REAL FUNCTION PVIRX(P,Y,K,B11,B22,B12,T,V,B)
 REAL P,Y,B11,B22,B12,T,V,B
 INTEGER K
 DEL = 2.0*B12 - B11 - B22
 PDENT = 8.31441*T + P*(B-V) + P*DEL*(FLOAT(K-1)-Y)**2
 PVIRX = P**2*(FLOAT(K-1)-Y)**2/PDENT
 RETURN
 END

 REAL FUNCTION PVIRT(P,Y,K,B11,B22,B12,T)
 REAL P,Y,B11,B22,B12,T
 INTEGER K
 COMMON/PDEXT/A(10),V(4),B(4)
 DEL = 2.0*B12 - B11 - B22
 PDENT = 8.31441*T + P*(B(K)-V(K)) + P*DEL*(FLOAT(K-1)-Y)**2
 PVIRT = -2.0*P**2*(FLOAT(K-1)-Y)**2/PDENT
 RETURN
 END
```

APPENDIX 4

This program was used for comparing excess functions obtained from this work with published work. It assumes the use of the Redlich-Kister equation as the analytical form.

```
C     PROGRAM .COMPXSF

C     THIS PROGRAM IS USED FOR COMPARING RESULTS OF VARIOUS
C     WORKERS IN THE FIELD.THE PRINCIPAL AIM IS TO COMPARE
C     RESULTS USING THE REDLICH-KISTER EQUATION AS A BASIS.
C     ALSO, THERE IS AN OPTION FOR OBTAINING VALUES FOR
C     EXCESS FUNCTIONS AT ANY REQUIRED MOLE FRACTION VALUES.

C     A(L) = REDLICH-KISTER COEFFS FROM THE LITERATURE
C     AV(LV) = R-K COEFFS FROM MY RESULTS,OR FROM PUBLISHED
C     WORK,GENERATED FROM PROGRAM .MAINPROG
C     X(I) = MOLE FRACTIONS,HOPEFULLY OF COMPONENT 2
C     PXSF = XS FUNCTIONS OBTAINED USING A(L)
C     VXSF = XS FUNCTIONS OBTAINED USING AV(LV)

C     RC AND T,GAS CONST. AND TEMP,RESP., ARE TAKEN AS UNITY
C     WHEN CALCULATING XS VOLS. AND WHEN XS ENTHALPIES AND
C     XS GIBBS FUNCTIONS HAVE BEEN DIVIDED BY RC*T PRIOR TO
C     THE ANALYSIS FOR DATA FITTING.

      DIMENSION A(10),AV(10),X(40),VXSF(40),PXSF(40),DIFF(40)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN N,M, AND MV"
      WRITE(4,*)"N IS THE NUMBER OF X(I) POINTS:"
      WRITE(4,*)"M IS THE NUMBER OF A(L) COEFFICIENTS. THAT IS THE"
      WRITE(4,*)"COEFFICIENTS FROM THE LITERATURE."
      WRITE(4,*)"MV IS THE NUMBER OF AV(LV) COEFFICIENTS - THAT IS THE"
      WRITE(4,*)"SET FROM THE ANALYSIS USING .MAINPROG"
      WRITE(4,*)
      READ(3,*)N,M,MV
      WRITE(4,*)
      WRITE(4,*)"TYPE IN R-K COEFFS FROM THE LITERATURE-A(M)"
      WRITE(4,*)
      READ(3,*)(A(L),L=1,M)
      WRITE(4,*)
      WRITE(4,*)(A(L),L=1,M)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN R-K COEFFS FROM .MAINPROG-AV(MV)"
      WRITE(4,*)
      READ(3,*)(AV(LV),LV=1,MV)
      WRITE(4,*)
      WRITE(4,*)(AV(LV),LV=1,MV)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN N MOLE FRACTIONS"
      WRITE(4,*)
      READ(3,*)(X(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN GAS CONST. AND TEMP AND TEMPV"
      WRITE(4,*)"TEMP,T, IS FROM LITERATURE"
      WRITE(4,*)"TEMPV,TV, IS FROM CURRENT WORK"
      WRITE(4,*)"RC, T AND TV ARE UNITY WHEN CALCULATING XS VOLS"
      WRITE(4,*)"AND WHEN XS ENTHALPIES AND XS GIBBS FUNCTIONS"
      WRITE(4,*)"ARE NOT TAKEN AS HE/RT AND GE/RT IN DATA ANALYSIS"
      WRITE(4,*)"FOR THE REDLICH-KISTER COEFFICIENTS."
      WRITE(4,*)
      READ(3,*)RC,T,TV
      WRITE(4,*)
      WRITE(4,*)"TYPE IN ISWXSF. ISWXSF IS AN INDICATOR OF THE"
      WRITE(4,*)"EXCESS FUNCTION UNDER CONSIDERATION. HERE IS A"
      WRITE(4,*)"LIST SHOWING ISWXSF VALUES WITH CORRESPONDING"
```

```
      WRITE(4,*)"EXCESS FUNCTIONS:"
      WRITE(4,*)"ISWXSF = 1; FOR EXCESS MOLAR GIBBS FUNCTIONS."
      WRITE(4,*)"ISWXSF = 2; FOR EXCESS MOLAR ENTHALPIES."
      WRITE(4,*)"ISWXSF = 3; FOR EXCESS MOLAR VOLUMES."
      WRITE(4,*)
      WRITE(4,*)"NOW TYPE IN THE REQUIRED VALUE OF ISWXSF."
      WRITE(4,*)
      READ(3,*)ISWXSF
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE VALUE ISW"
      WRITE(4,*)"ISW is the switch for either making a comparison"
      WRITE(4,*)"between experimental and literature data or its"
      WRITE(4,*)"use is in direct calculations of excess functions"
      WRITE(4,*)"from any source without the need for comparison."
      WRITE(4,*)"ISW = 1; for comparison"
      WRITE(4,*)"ISW = 2; for direct calculation"
      WRITE(4,*)"NOTE: THIS IS LAST PIECE OF DATUM. After this,"
      WRITE(4,*)"wait for the computer to do the calculation."
      WRITE(4,*)"NOW TYPE IN THE THE VALUE OF ISW."
      WRITE(4,*)
      READ(3,*)ISW
      WRITE(4,*)
      WRITE(4,*)
  1   WRITE(4,*)"(1-X)-BENZENE + X-HEXANE AT 298.15 K:"
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWXSF.EQ.1) GO TO 2
      IF (ISWXSF.EQ.2) GO TO 3
      IF (ISWXSF.EQ.3) GO TO 4
  2   WRITE(4,*)"EXCESS MOLAR GIBBS FUNCTIONS:"
      GO TO 5
  3   WRITE(4,*)"EXCESS MOLAR ENTHALPIES:"
      GO TO 5
  4   WRITE(4,*)"EXCESS MOLAR VOLUMES:"
  5   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      DO 15 I = 1,N
      PXSF(I) = 0.0
      VXSF(I) = 0.0
      DO 6 L = 1,M
      PSUM = RC*T*X(I)*(1.0-X(I))*(A(L)*(1.0-2.0*X(I))**(L-1))
  6   PXSF(I) = PXSF(I) + PSUM
      DO 10 LV = 1,MV
      VSUM = RC*TV*X(I)*(1.0-X(I))*(AV(LV)*(1.0-2.0*X(I))**(LV-1))
 10   VXSF(I) = VXSF(I) + VSUM
      DIFF(I) = VXSF(I) - PXSF(I)
 15   CONTINUE
      IF (ISW.EQ.2) GO TO 28
      WRITE(4,20)
 20   FORMAT(5X,57H MOLE FRACTION  EXPT.XS.FUNC. LITE.XS.FUNC.   DIFFERE
     1NCE //)
      DO 26 I = 1,N
      WRITE(4,25)X(I),VXSF(I),PXSF(I),DIFF(I)
 25   FORMAT(9X,F6.4,2X,E13.5,2X,E13.5,2X,E14.5/)
 26   CONTINUE
      IF (ISW.EQ.1) GO TO 40
 28   WRITE(4,30)
 30   FORMAT(5X,30H MOLE FRACTION  LITE.XS.FUNC. //)
      DO 36 I = 1,N
```

```
      WRITE(4,35)X(I),PXSF(I)
35    FORMAT(9X,F6.4,2X,E13.5/)
36    CONTINUE
40    CONTINUE
      STOP
      END
```

APPENDIX 5

This program was used for obtabining excess volumes from the mass readings obtained by weighing of the components.

```
C     PROGRAM .MAINPROG

C     THIS PROGRAM CARRIES OUT ANALYSIS FOR EXCESS VOLUMES OF MIXING.
C     EXCESS MOLAR VOLUME VALUES ARE CALCULATED FROM HEIGHT AND MASS
C     MEASUREMENTS. THE RESULTS ARE THEN ANALYSED BY LINEAR LEAST
C     SQUARES METHODS TO OBTAIN VALUES FOR COEFFICIENTS OF THE FITTING
C     EQUATIONS(REDLICH-KISTER EQUATIONS).
C     THE PROGRAM MAY ALSO BE USED FOR ANALYSING FOR REDLICH-KISTER
C     COEFFICIENTS FROM GIVEN VALUES OF THE EXCESS MOLAR FUNCTIONS -
C     VOLUMES, ENTHALPIES, AND GIBBS FUNCTIONS - PROVIDED SUCH VALUES
C     ARE INPUT AS DATA.

      REAL JCB,EPS
      DIMENSION Z(40),X(40),W(40),JCB(40,40),TRSJCB(40,40),XSF(40),
     1WTN(40,40),ZET(40,10),WTNZ(40,10),TRWTNZ(40,10),WTNJCB(40,40),
     2TRWTJC(40,40),COLVEC(40,10),REMAT(40,40),W1(40),W2(40),HTA(40),
     3HTB(40),TA(40),TB(40),AMT1(40),AMT2(40),TAMT(40),CORHTA(40),
     4CORHTB(40),DELTAH(40),XSVOL(40)
      COMMON/COMDAT/RMM1,RMM2,ALPHA,PI,RAD,DB1,DB2,DA,DS
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE FOLLOWING DATA:"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)" N, M, AND EPS"
      WRITE(4,*)
      WRITE(4,*)"N IS THE NUMBER OF EXPERIMENTAL POINTS"
      WRITE(4,*)"M IS THE NUMBER OF REDLICH-KISTER COEFFICIENTS"
      WRITE(4,*)"EPS IS A CONSTANT WHICH FINDS USAGE IN THE "
      WRITE(4,*)"MATRIX INVERSION ROUTINE. THE RECOMMENDED"
      WRITE(4,*)"VALUE IS 1.00E-20 - IT'S A FIGURE I CONJURED UP!"
      WRITE(4,*)
      WRITE(4,*)
      READ(3,*)N,M,EPS
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"THE TYPE OF DATA TO BE INPUT DEPENDS ON WHETHER"
      WRITE(4,*)"USER HAS RAW OR REFINED DATA. HERE, RAW DATA IS"
      WRITE(4,*)"DEFINED AS HAVING THE AMOUNTS OF THE COMPONENTS"
      WRITE(4,*)"IN THE FORM OF MASSES/GRAM AS WELL AS HEIGHT"
      WRITE(4,*)"READINGS FROM THE CATHETOMETER WITH THE"
      WRITE(4,*)"TEMPERATURE READINGS THAT GO WITH THEM. REFINED"
      WRITE(4,*)"DATA ARE IN THE FORM OF EXCESS VOLUMES/CU.CM"
      WRITE(4,*)"AND CORRESPONDING MOLE FRACTIONS."
      WRITE(4,*)"   DEPENDING ON THE FORM OF THE USER'S DATA, AN"
      WRITE(4,*)"OPTION IS AVAILABLE VIA THE USE OF THE PARAMETER"
      WRITE(4,*)"ISW. ISW = 1 FOR REFINED DATA; OTHERWISE ISW = 2"
      WRITE(4,*)"(THE PROGRAM MAY ALSO BE USED FOR ANALYSING OTHER"
      WRITE(4,*)"EXCESS FUNCTIONS. HOWEVER, AT PRESENT, THE"
      WRITE(4,*)"ANALYSIS OF OTHER FUNCTIONS MAY ONLY BE DONE BY"
      WRITE(4,*)"USING ISW=1 OPTION.)"
      WRITE(4,*)
      WRITE(4,*)"NOW TYPE THE DESIRED(!!) VALUE OF ISW"
      WRITE(4,*)
      READ(3,*)ISW
      WRITE(4,*)
      IF (ISW.EQ.2) GO TO 1
      WRITE(4,*)
      WRITE(4,*)"TYPE IN EXCESS VOLUMES, MOLE FRACTIONS, AND WEIGHTS"
      WRITE(4,*)"MOLE FRACTIONS ARE THOSE OF THE SECOND COMPONENT;"
```

```
      WRITE(4,*)"WEIGHTS, IN THIS CONTEXT, REFERS TO STATISTICAL"
      WRITE(4,*)"WEIGHTING OF THE DATA. FOR NON-WEIGHTED DATA, USE"
      WRITE(4,*)"VALUES OF 1.0 FOR EACH CASE."
      WRITE(4,*)"   THE LAYOUT OF THE DATA MUST BE OF THE FORM"
      WRITE(4,*)"EXCESS VOLUMES,MOLE FRACTIONS,WEIGHTS"
      WRITE(4,*)"AND ONE MUST HAVE N(THE EXPERIMENTAL NO. OF POINTS)"
      WRITE(4,*)"LINES. FOR EXAMPLE, FOR TWO EXPERIMENTAL POINTS, "
      WRITE(4,*)"ONE HAS:"
      WRITE(4,*)"-0.7526,0.5739,1.0"
      WRITE(4,*)"-0.7018,0.6917,1.0"
      WRITE(4,*)"COMPRENEZ?"
      WRITE(4,*)
      READ(3,*)(XSF(I),X(I),W(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)
      IF (ISW.EQ.1) GO TO 2
1     CONTINUE
      WRITE(4,*)
      WRITE(4,*)"THE RELATIVE MOLAR MASSES FOR COMPONENTS 1 AND 2"
      WRITE(4,*)" - IN THAT ORDER"
      WRITE(4,*)
      READ(3,*)RMM1,RMM2
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE DENSITIES FOR COMPONENTS 1 AND 2 - DB1"
      WRITE(4,*)"AND DB2 - RESPECTIVELY. ALSO TYPE IN DA AND DS, THE"
      WRITE(4,*)"DENSITY VALUES FOR AIR AND STEEL, RESPECTIVELY. These"
      WRITE(4,*)"density values are required so as to enable for"
      WRITE(4,*)"buoyancy corrections. Although variation of density"
      WRITE(4,*)"with temperature will be taken into account for liquid"
      WRITE(4,*)"components - as much as possible - such effects will"
      WRITE(4,*)"be considered as negligible so far as calculated"
      WRITE(4,*)"values are concerned, unless measurements are carried"
      WRITE(4,*)"out at temperatures far lower or higher than usual"
      WRITE(4,*)"room temperature conditions."
      WRITE(4,*)"Use DA = 0.0012; DS = 8.0"
      WRITE(4,*)"NOW TYPE IN DB1,DB2,DA,DS."
      WRITE(4,*)
      READ(3,*)DB1,DB2,DA,DS
      WRITE(4,*)
      WRITE(4,*)"TYPE IN N VALUES OF MASS FOR COMPONENT 1"
      WRITE(4,*)
      READ(3,*)(W1(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN N VALUES OF MASS FOR COMPONENT 2 - THE"
      WRITE(4,*)"ORDER MUST BE SUCH THAT THEY CORRESPOND WITH THE"
      WRITE(4,*)"SEQUENCE IN MASSES FOR COMPONENT 1 SO AS TO OBTAIN"
      WRITE(4,*)"THE APPROPRIATE MOLE FRACTIONS."
      WRITE(4,*)
      READ(3,*)(W2(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"THE HEIGHT READINGS REQUIRED IN THIS SECTION ARE"
      WRITE(4,*)"THE DIFFERENCES IN HEIGHT BETWEEN THE LEVEL OF THE"
      WRITE(4,*)"MERCURY MENISCUS AND THE REFERENCE MARK ON THE"
      WRITE(4,*)"DILATOMETER - FOR EACH MEASUREMENT. NORMALLY, ROOM"
      WRITE(4,*)"TEMPERATURE MEASUREMENTS ARE TAKEN AS THESE HEIGHT"
      WRITE(4,*)"DIFFERENCES ARE MEASURED."
      WRITE(4,*)
      WRITE(4,*)"TYPE IN N VALUES OF HEIGHT DIFFERENCES WHICH ARE TAKEN"
      WRITE(4,*)"BEFORE MIXING. - STICK IN AS MANY VALUES ON ONE LINE "
      WRITE(4,*)" AS POSSIBLE - THEY SHOULD BE SEPARATED BY COMMAS."
```

```
      WRITE(4,*)
      READ(3,*)(HTB(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"SIMILARLY, TYPE IN N VALUES OF HEIGHT DIFFERENCES "
      WRITE(4,*)"WHICH ARE TAKEN AFTER MIXING."
      WRITE(4,*)
      READ(3,*)(HTA(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN ROOM TEMPERATURE READINGS WHICH ARE OBTAINED "
      WRITE(4,*)"AS HEIGHT DIFFERENCES ARE MEASURED BEFORE MIXING - USE"
      WRITE(4,*)"THE UNIT OF KELVIN. "
      WRITE(4,*)
      READ(3,*)(TB(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"SIMILARLY, ENTER THE TEMPERATURES READINGS OBTAINED"
      WRITE(4,*)"AFTER MIXING."
      WRITE(4,*)
      READ(3,*)(TA(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE WEIGHTS(STATISTICAL) - FOR NON-WEIGHTED"
      WRITE(4,*)"ANALYSIS USE VALUES OF 1.0 FOR EACH CASE. N SUCH"
      WRITE(4,*)"VALUES ARE REQUIRED."
      WRITE(4,*)
      READ(3,*)(W(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE RADIUS OF THE CAPILLARY BORE, THE VALUE"
      WRITE(4,*)"PI(=3.1415927), & THE COEFFICIENT OF THERMAL EXPANSION"
      WRITE(4,*)"FOR THE CATHETOMETER - USE  1.84E-05 FOR THIS"
      WRITE(4,*)"COEFFICIENT."
      WRITE(4,*)"After typing in values for the radius and pi and the"
      WRITE(4,*)"other coefficient, just relax. WAIT FOR THE OUTPUT!"
      WRITE(4,*)
      READ(3,*)RAD,PI,ALPHA
      WRITE(4,*)
    2 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"(1-X)-NEOPENTANE + X-TETRAMETHYLSILANE AT 283.15 K:"
      WRITE(4,*)
      WRITE(4,*)
      CALL MAINP(XSF,X,W,JCB,TRSJCB,WTN,ZET,WTNZ,TRWTNZ,WTNJCB,TRWTJC,
     1         REMAT,N,M,L,EPS,COLVEC,M1,ISW,W1,W2,AMT1,AMT2,TAMT,HTA,
     2         HTB,TA,TB,CORHTA,CORHTB,DELTAH,XSVOL)
      STOP
      END

      SUBROUTINE MAINP(XSF,X,W,JCB,TRSJCB,WTN,ZET,WTNZ,TRWTNZ,WTNJCB,
     1        TRWTJC,REMAT,N,M,L,EPS,COLVEC,M1,ISW,W1,W2,AMT1,AMT2,TAMT,
     2        HTA,HTB,TA,TB,CORHTA,CORHTB,DELTAH,XSVOL)
      REAL JCB
      DIMENSION X(N),W(N),JCB(N,M),TRSJCB(M,N),WTN(N,N),ZET(N,M),
     1        WTNZ(N,M),TRWTNZ(N,M),WTNJCB(N,M),TRWTJC(M,M),REMAT(M,M)
     2,COLVEC(M,M),XSF(N),W1(N),W2(N),AMT1(N),AMT2(N),TAMT(N),HTA(N),
     3HTB(N),TA(N),TB(N),CORHTA(N),CORHTB(N),DELTAH(N),XSVOL(N)
      COMMON/COMDAT/RMM1,RMM2,ALPHA,PI,RAD,DB1,DB2,DA,DS

      IF (ISW.EQ.1) GO TO 4
      BC1 = (DS*DB1 + DA*(DS-DB1))/(DS*DB1)
```

```
      BC2 = (DS*DB2 + DA*(DS-DB2))/(DS*DB2)
      DO 3 I = 1,N
      AMT1(I) = BC1*W1(I)/RMM1
      AMT2(I) = BC2*W2(I)/RMM2
      TAMT(I) = AMT1(I) + AMT2(I)
      X(I) = AMT2(I)/TAMT(I)
      CORHTA(I) = HTA(I)*(1.0 + ALPHA*(TA(I) - 293.15))
      CORHTB(I) = HTB(I)*(1.0 + ALPHA*(TB(I) - 293.15))
      DELTAH(I) = CORHTA(I) - CORHTB(I)
      XSVOL(I) = PI*(RAD**2)*DELTAH(I)/TAMT(I)
      XSF(I) = XSVOL(I)
    3 CONTINUE
    4 CONTINUE

C     SET UP THE JACOBIAN MATRIX, JCB
      DO 5 I = 1,N
      DO 5 J = 1,M
      JCB(I,J) = (1.0-2.0*X(I))**(J-1)
   5  CONTINUE

C     GENERATE TRANSPOSE OF THE JACOBIAN MATRIX,TRSJCB
      DO 10 J = 1,M
      DO 10 I = 1,N
      TRSJCB(J,I) = JCB(I,J)
   10 CONTINUE

C     GENERATE THE WEIGHTING MATRIX WTN--A DIAGONAL MATRIX
      DO 15 I = 1,N
      DO 15 K = 1,N
      WTN(I,K) = W(I)
      IF (K.NE.I) WTN(I,K) = 0.0
   15 CONTINUE

C     GENERATE THE EXPERIMENTAL DATA COLUMN VECTOR ZET
      DO 20 I =1,N
      ZET(I,1) = XSF(I)/(X(I)*(1.0-X(I)))
   20 CONTINUE

C     DO THE PRODUCT OF THE MATRICES WTN(W) AND ZET(Z) TO OBTAIN WTNZ
      CALL MATMUL(WTN,ZET,WTNZ,N,N,1)
C     DO THE PROUCT OF THE MATRICES TRSJCB(JT) AND WTNZ(WZ) TO OBTAIN
C     TRWTNZ.
      CALL MATMUL(TRSJCB,WTNZ,TRWTNZ,M,N,1)
C     DO THE PRODUCT OF THE MATRICES WTN(W) AND JCB(J) TO OBTAIN WTNJCB
      CALL MATMUL(WTN,JCB,WTNJCB,N,N,M)
C     DO THE PRODUCT OF THE MATRICES TRSJCB(JT) WTNJCB(WJ) TO OBTAIN
C     TRWTJC.
      CALL MATMUL(TRSJCB,WTNJCB,TRWTJC,M,N,M)
C     INVERT THE RESULTING MATRIX TRWTJC(MXM)
      IFAIL = 0
      CALL MATNVS(TRWTJC,REMAT,M,EPS,IFAIL)
      IF (IFAIL.EQ.1) GO TO 29
C     THE COLUMN VECTOR,COLVEC,IS THEN OBTAINED BY PREMULTIPLYING
C     THE MATRIX TRWTNZ(JT.W.Z) BY THE INVERSE OF TRWTJC(JT.W.J),
C     WHICH WE CALL REMAT.
      CALL MATMUL(REMAT,TRWTNZ,COLVEC,M,M,1)
      WRITE(4,*)
```

```
      CALL EQUFIT(COLVEC,XSF,X,N,M)
      WRITE(4,*)
      DO 25 J = 1,M
      WRITE(4,*)"REDLICH-KISTER COEFFICIENT ",J,"=",COLVEC(J,1)
   25 CONTINUE
      WRITE(4,*)
   29 CONTINUE
      RETURN
      END

      SUBROUTINE MATMUL(A,B,C,N,L,M)
C     THIS IS AN F.A.HEWITT VERSION
      DOUBLE PRECISION MAT
      DIMENSION A(N,L),B(L,M),C(N,M)
      DO 50 I = 1,N
      DO 50 K = 1,M
      MAT = 0.0
      DO 45 J = 1,L
      MAT = A(I,J)*B(J,K) + MAT
   45 CONTINUE
      C(I,K) = MAT
   50 CONTINUE
      RETURN
      END

      SUBROUTINE MATNVS(A,B,M,EPS,IFAIL)
C     THIS SUBROUTINE WAS ADOPTED FROM A BOOK BY
C     McCALLA,T.R. "Introduction to Numerical Methods and FORTRAN
C     Programming",J.Wiley & Sons, Inc., 1967.
      REAL EPS
      DIMENSION A(M,M),B(M,M)
      DOUBLE PRECISION DET
C     CONSTRUCT AN IDENTITY MATRIX B(I,J) = I
      DO 68 I = 1,M
      DO 66 J = 1,M
      IF (I-J) 64,62,64
   62 B(I,J) = 1.0
      GO TO 66
   64 B(I,J) = 0.0
   66 CONTINUE
   68 CONTINUE
C     LOCATE MAXIMUM MAGNITUDE A(I,K) ON OR BELOW MAIN DIAGGONAL
      DET = 1.0
      DO 100 K = 1,M
      IF (K-M) 70,86,86
   70 IMAX = K
      AMAX = ABS(A(K,K))
      KP1 = K + 1
      DO 76 I = KP1,M
      IF (AMAX-ABS(A(I,K))) 72,76,76
   72 IMAX = I
      AMAX = ABS(A(I,K))
   76 CONTINUE
C     INTERCHANGE ROWS IMAX AND K IF IMAX IS NOT EQUAL TO K
      IF (IMAX-K) 78,86,78
   78 DO 80 J = 1,M
      ATMP = A(IMAX,J)
      A(IMAX,J) = A(K,J)
      A(K,J) = ATMP
      BTMP = B(IMAX,J)
```

```
      B(IMAX,J) = B(K,J)
   80 B(K,J) = BTMP
      DET = -DET
   86 CONTINUE
C     TEST FOR SINGULAR MATRIX
      IF (ABS(A(K,K))-EPS) 104,104,88
   88 DET = A(K,K)*DET
C     DIVIDE PIVOT ROW BY ITS MAIN DIAGONAL ELEMENT
      DIV = A(K,K)
      DO 90 J = 1,M
      A(K,J) = A(K,J)/DIV
   90 B(K,J) = B(K,J)/DIV
C     REPLACE EACH ROW BY LINEAR COMBINATION WITH PIVOT ROW
      DO 98 I = 1,M
      AMULT = A(I,K)
      IF (I-K) 92,98,92
   92 DO 96 J = 1,M
      A(I,J) = A(I,J)-AMULT*A(K,J)
   96 B(I,J) = B(I,J)-AMULT*B(K,J)
   98 CONTINUE
  100 CONTINUE
      GO TO 112
  104 WRITE(4,110) K
      IFAIL = 1
      GO TO 112
  110 FORMAT(25H SINGULAR MATRIX FOR K =,I2)
  112 RETURN
      END

      SUBROUTINE EQUFIT(COLVEC,XSF,X,N,M)
      DIMENSION COLVEC(M,1),XSF(N),X(N)
      WRITE(4,270)
      SUMSQ = 0.0
      DO 35 I =1,N
      ZCALC = 0.0
      DO 32 J = 1,M
      SUM = COLVEC(J,1)*(1.0-2.0*X(I))**(J-1)
   32 ZCALC = ZCALC + SUM
      XSFC = ZCALC*X(I)*(1.0-X(I))
      XSFDEV = XSF(I) - XSFC
      WRITE(4,280)X(I),XSF(I),XSFC,XSFDEV
   35 SUMSQ = SUMSQ + XSFDEV**2
      STDEV = SQRT(SUMSQ/(N-M))
      WRITE(4,290)
   40 WRITE(4,300)STDEV
  270 FORMAT(5X,57H MOLE FRACTION  EXPT.XS.FUNC. CALC.XS.FUNC.   DIFFERE
     1NCE ,//)
  280 FORMAT(9X,F6.4,6X,F9.4,6X,F9.4,6X,F10.4/)
  290 FORMAT(/10X,10H STD.DEV.=)
  300 FORMAT(22X,F6.4)
      RETURN
      END
```

APPENDIX 6

This program calculates excess functions by application of the principle of corresponding states.

```
C       THE PRINCIPLE OF CORRESPONDING STATES IS USED AS A BASIS FOR
C      THE PREDICTION OF EXCESS THERMODYNAMIC FUNCTIONS. A NUMBER OF
C      COMBINING RULES ARE USED AND THUS COMPARISONS ARE MADE
C      BETWEEN THE RESULTS FROM THE USE OF THESE VARIOUS RULES.

      REAL N,M
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/LOOPNM/N,M
      COMMON/RTPDAT/R,T,P
      COMMON/PTNSWI/NPTS,ISWCR,ISWHCP,ISWST
      COMMON/XSDATA/X2(40),XPGE(40),XPHE(40),XPVE(40)
      COMMON/CFDATA/AP(10),AB(10),AV(10),APD(10),ABD(10),AVD(10)
      COMMON/NUMCFS/JPM,JBM,JVM,JPMD,JBMD,JVMD
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      DIMENSION X1(40),CAGE1(40),CAGE2(40),CAHE1(40),CAHE2(40),
     1CAVE1(40),CAVE2(40),DEVGE1(40),DEVGE2(40),DEVHE1(40),DEVHE2(40),
     2DEVVE1(40),DEVVE2(40)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE FOLLOWING DATA :"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"CRITICAL TEMP,CRIT.VOL., AND CRIT.PRESS. FOR COMPT.1"
      WRITE(4,*)
      READ(3,*)CT1,CV1,CP1
      WRITE(4,*)
      WRITE(4,*)CT1,CV1,CP1
      WRITE(4,*)
      WRITE(4,*)"CRITICAL TEMP,CRIT.VOL., AND CRIT.PRESS. FOR COMPT.2"
      WRITE(4,*)
      READ(3,*)CT2,CV2,CP2
      WRITE(4,*)
      WRITE(4,*)CT2,CV2,CP2
      WRITE(4,*)
      WRITE(4,*)"THE IONISATION POTENTIALS FOR COMPONENTS 1 AND 2"
      WRITE(4,*)
      READ(3,*)PI1,PI2
      WRITE(4,*)
      WRITE(4,*)PI1,PI2
      WRITE(4,*)
      WRITE(4,*)"ISWVC - THIS IS A SWITCH USED FOR THE SELECTION OF"
      WRITE(4,*)"THE PAIRS OF CRITICAL PARAMETERS TO BE USED IN THE"
      WRITE(4,*)"CALCULATIONS."
      WRITE(4,*)"ISWVC = 1; WHEN USING CRIT. TEMPS AND CRIT. VOLUMES:"
      WRITE(4,*)"ISWVC = 2; WHEN USING CRIT. TEMPS AND CRIT. PRESS.:"
      WRITE(4,*)
      READ(3,*)ISWVC
      WRITE(4,*)
      WRITE(4,*)ISWVC
      WRITE(4,*)
      WRITE(4,*)"THE POLARISABILITIES FOR COMPONENTS 1 AND 2"
      WRITE(4,*)
      READ(3,*)POL1,POL2
      WRITE(4,*)
      WRITE(4,*)POL1,POL2
      WRITE(4,*)
      WRITE(4,*)"THE DIAMAGNETIC SUSCEPTIBILITIES FOR COMPTS. 1 AND 2"
      WRITE(4,*)
      READ(3,*)DMS1,DMS2
```

```
WRITE(4,*)
WRITE(4,*)DMS1,DMS2
WRITE(4,*)
WRITE(4,*)"THE INTERMOLECULAR SEPARATION PARAMETERS FOR 1 AND 2"
WRITE(4,*)
READ(3,*)RINTM1,RINTM2
WRITE(4,*)
WRITE(4,*)RINTM1,RINTM2
WRITE(4,*)
WRITE(4,*)"ISWVOL--THIS IS A SWITCH! ITS USE DEPENDS ON THE"
WRITE(4,*)"AVAILABILITY, OR THEIR LACK, OF DATA ON INTERMOLECULAR"
WRITE(4,*)"SEPARATION PARAMETERS. USE ISWVOL=1 IF DATA ARE AVAIL-"
WRITE(4,*)"ABLE; OTHERWISE USE A VALUE OF 2."
WRITE(4,*)
READ(3,*)ISWVOL
WRITE(4,*)
WRITE(4,*)ISWVOL
WRITE(4,*)
WRITE(4,*)"THE GAS CONSTANT, TEMPERATURE, AND PRESSURE"
WRITE(4,*)
READ(3,*)R,T,P
WRITE(4,*)
WRITE(4,*)R,T,P
WRITE(4,*)
WRITE(4,*)"THE CRITICAL COMPRESSIBILITY FACTOR, AZ"
WRITE(4,*)
READ(3,*)AZ
WRITE(4,*)
WRITE(4,*)AZ
WRITE(4,*)
WRITE(4,*)"NUMBER OF POINTS; AND THE HIGHER AND LOWER INDICES"
WRITE(4,*)"OF THE LENNARD-JONES POTENTIAL"
WRITE(4,*)
READ(3,*)NPTS,N,M
WRITE(4,*)
WRITE(4,*)NPTS,N,M
WRITE(4,*)
WRITE(4,*)"NPTS MOLE FRACTIONS OF THE SECOND COMPONENT"
WRITE(4,*)
READ(3,*)(X2(I),I=1,NPTS)
WRITE(4,*)
WRITE(4,*)(X2(I),I=1,NPTS)
WRITE(4,*)
WRITE(4,*)"THE NUMBER OF COEFFICIENTS FOR THE UNIVERSAL FUNCTIONS"
WRITE(4,*)"JPM:  NUMBER OF COEFFICIENTS FOR Ln(P/PC) = PHI1(T/TC)"
WRITE(4,*)"JBM: THE NUMBER OF COEFFICIENTS FOR B/VC = PHI2(T/TC)"
WRITE(4,*)"JVM: THE NUMBER OF COEFFICEINTS FOR V/VC = PHI3(T/TC)"
WRITE(4,*)
READ(3,*)JPM,JBM,JVM
WRITE(4,*)
WRITE(4,*)JPM,JBM,JVM
WRITE(4,*)
WRITE(4,*)"THE NUMBER OF COEFFICIENTS FOR THE DERIVATIVE FORMS OF"
WRITE(4,*)"THE UNIVERSAL FUNCTIONS"
WRITE(4,*)"JPMD: NO. OF COEFFS FOR dLn(P/PC)/d(T/TC)"
WRITE(4,*)"JBMD: NO. OF COEFFS FOR d(B/VC)/d(T/TC)"
WRITE(4,*)"JVMD: NO. OF COEFFS FOR d(V/VC)/d(T/TC)"
WRITE(4,*)
READ(3,*)JPMD,JBMD,JVMD
WRITE(4,*)
```

```
WRITE(4,*)JPMD,JBMD,JVMD
WRITE(4,*)
WRITE(4,*)"THE COEFFICIENTS, AP(JP), FOR PHI1(T/TC)"
WRITE(4,*)
READ(3,*)(AP(JP),JP=1,JPM)
WRITE(4,*)
WRITE(4,*)(AP(JP),JP=1,JPM)
WRITE(4,*)
WRITE(4,*)"THE COEFFICIENTS, AB(JB), FOR PHI2(T/TC)"
WRITE(4,*)
READ(3,*)(AB(JB),JB=1,JBM)
WRITE(4,*)
WRITE(4,*)(AB(JB),JB=1,JBM)
WRITE(4,*)
WRITE(4,*)"THE COEFFICIENTS, AV(JV), FOR PHI3(T/TC)"
WRITE(4,*)
READ(3,*)(AV(JV),JV=1,JVM)
WRITE(4,*)
WRITE(4,*)(AV(JV),JV=1,JVM)
WRITE(4,*)
WRITE(4,*)"THE COEFFICIENTS FOR THE DERIVATIVES-APD,ABD,AVD"
WRITE(4,*)
READ(3,*)(APD(JPD),JPD=1,JPMD)
WRITE(4,*)
WRITE(4,*)(APD(JPD),JPD=1,JPMD)
WRITE(4,*)
READ(3,*)(ABD(JBD),JBD=1,JBMD)
WRITE(4,*)
WRITE(4,*)(ABD(JBD),JBD=1,JBMD)
WRITE(4,*)
READ(3,*)(AVD(JVD),JVD=1,JVMD)
WRITE(4,*)
WRITE(4,*)(AVD(JVD),JVD=1,JVMD)
WRITE(4,*)
WRITE(4,*)"CHOICE OF  OF N-FLUID MODEL"
WRITE(4,*)"THIS IS DONE BY USING THE IDENTIFIER ISWHCP."
WRITE(4,*)"ISWHCP = 1; FOR THE ONE-FLUID MODEL ONLY."
WRITE(4,*)"ISWHCP = 2; FOR THE TWO-FLUID MODEL ONLY."
WRITE(4,*)"ISWHCP = 3; FOR BOTH MODELS."
WRITE(4,*)
READ(3,*)ISWHCP
WRITE(4,*)
WRITE(4,*)ISWHCP
WRITE(4,*)
WRITE(4,*)"ISWST - THE VALUE FOR SELECTING THE PROCEDURE FOR"
WRITE(4,*)"CALCULATING CRITICAL PARAMETERS OF THE HYPOTHETICAL"
WRITE(4,*)"FLUIDS."
WRITE(4,*)"Two procedures are available:"
WRITE(4,*)"(i) Randomisation of the Van der Waals parameters,"
WRITE(4,*)"(ii) Randomisation of the pair-interacton energies."
WRITE(4,*)"ISWST = 1; FOR (i)"
WRITE(4,*)"ISWST = 2; FOR (ii)"
WRITE(4,*)"NOW TYPE IN ISWST"
WRITE(4,*)
READ(3,*)ISWST
WRITE(4,*)
WRITE(4,*)ISWST
WRITE(4,*)
WRITE(4,*)"CHOICE OF COMBINING RULES."
WRITE(4,*)"THE IDENTIFIER ISWCR IS USED FOR THIS PURPOSE."
```

```
      WRITE(4,*)"HERE IS A LIST OF ISWCR VALUES WITH CORRESPONDING"
      WRITE(4,*)"SETS OF COMBINING RULES:"
      WRITE(4,*)"ISWCR = 1; LORENTZ-BERTHELOT"
      WRITE(4,*)"ISWCR = 2; HUDSON-McCOUBREY"
      WRITE(4,*)"ISWCR = 3; WORMALD, et al(Mk I)"
      WRITE(4,*)"ISWCR = 4; WORMALD, et al(Mk II)"
      WRITE(4,*)"ISWCR = 5; MUNN"
      WRITE(4,*)"ISWCR = 6; FENDER-HALSEY"
      WRITE(4,*)"ISWCR = 7; this work"
      WRITE(4,*)"ISWCR = 8; HICKS-YOUNG"
      WRITE(4,*)"NOW TYPE IN THE REQUIRED VALUE OF ISWCR"
      WRITE(4,*)
      READ(3,*)ISWCR
      WRITE(4,*)
      WRITE(4,*)ISWCR
      WRITE(4,*)
      WRITE(4,*)"EXCESS FUNCTIONS-FROM PUBLISHED ANALYTICAL EQTNS"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"NPTS VALUES OF EXCESS GIBBS FUNCTIONS"
      WRITE(4,*)
      READ(3,*)(XPGE(I),I=1,NPTS)
      WRITE(4,*)
      WRITE(4,*)(XPGE(I),I=1,NPTS)
      WRITE(4,*)
      WRITE(4,*)"NPTS VALUES OF EXCESS ENTHALPIES"
      WRITE(4,*)
      READ(3,*)(XPHE(I),I=1,NPTS)
      WRITE(4,*)
      WRITE(4,*)(XPHE(I),I=1,NPTS)
      WRITE(4,*)
      WRITE(4,*)"NPTS VALUES OF EXCESS VOLUMES"
      WRITE(4,*)"This is the last set of data to be input. After"
      WRITE(4,*)"inserting the excess volume values, sit and relax"
      WRITE(4,*)"and let the computer work for a while!"
      WRITE(4,*)
      READ(3,*)(XPVE(I),I=1,NPTS)
      WRITE(4,*)
      WRITE(4,*)(XPVE(I),I=1,NPTS)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"DETERMINATION OF EXCESS FUNCTIONS VIA THE P.C.S"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
    1 WRITE(4,*)"(1-X)-NEOPENTANE + X-TETRAMETHYLSILANE AT 283.15 K"
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWCR.EQ.1) GO TO 10
      IF (ISWCR.EQ.2) GO TO 12
      IF (ISWCR.EQ.3) GO TO 14
      IF (ISWCR.EQ.4) GO TO 16
      IF (ISWCR.EQ.5) GO TO 18
      IF (ISWCR.EQ.6) GO TO 20
      IF (ISWCR.EQ.7) GO TO 22
      IF (ISWCR.EQ.8) GO TO 24
   10 WRITE(4,*)"COMBINING RULES USED:  LORENTZ-BERTHELOT"
      GO TO 80
   12 WRITE(4,*)"COMBINING RULES USED:  HUDSON-McCOUBREY"
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```
      GO TO 80
   14 WRITE(4,*)"COMBINING RULES USED:  WORMALD, et al (Mk I)"
      GO TO 80
   16 WRITE(4,*)"COMBINING RULES USED:  WORMALD, et al (Mk II)"
      GO TO 80
   18 WRITE(4,*)"COMBINING RULES USED:  MUNN"
      GO TO 80
   20 WRITE(4,*)"COMBINING RULES USED:  FENDER-HALSEY"
      GO TO 80
   22 WRITE(4,*)"COMBINING RULES USED:  this work"
      GO TO 80
   24 WRITE(4,*)"COMBINING RULES USED: HICKS-YOUNG"
   80 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWST.EQ.1) GO TO 84
      IF (ISWST.EQ.2) GO TO 88
   84 WRITE(4,*)"RANDOMISATION OF VAN DER WAALS PARAMETERS:"
      GO TO 90
   88 WRITE(4,*)"TYPE OF N-M POTENTIAL USED:",IFIX(N),IFIX(M)
   90 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWVC.EQ.1) GO TO 92
      IF (ISWVC.EQ.2) GO TO 96
   92 WRITE(4,*)"USE OF CRITICAL TEMPERATURES AND VOLUMES:"
      GO TO 100
   96 WRITE(4,*)"USE OF CRITICAL TEMPERATURES AND PRESSURES:"
  100 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      CALL MAIN(CAGE1,CAHE1,CAVE1,CAGE2,CAHE2,CAVE2)
      STOP
      END

      SUBROUTINE MAIN(CAGE1,CAHE1,CAVE1,CAGE2,CAHE2,CAVE2)
C     EXCESS FUNCTIONS ARE CALCULATED IN THIS SECTION.
C     THERE IS AN OPTION FOR OBTAINING CALCULATED QUANTITIES
C     FROM EITHER ONE OR BOTH OF THE "N-FLUID" MODELS. IN EITHER
C     CASE, THOUGH, ONE OBTAINS INFORMATION ON EXCESS GIBBS
C     FUNCTIONS, EXCESS ENTHALPIES, AND EXCESS VOLUMES.
      REAL N,M
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/LOOPNM/N,M
      COMMON/RTPDAT/R,T,P
      COMMON/PTNSWI/NPTS,ISWCR,ISWHCP,ISWST
      COMMON/XSDATA/X2(40),XPGE(40),XPHE(40),XPVE(40)
      COMMON/CFDATA/AP(10),AB(10),AV(10),APD(10),ABD(10),AVD(10)
      COMMON/NUMCFS/JPM,JBM,JVM,JPMD,JBMD,JVMD
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      DIMENSION X1(40),CAGE1(40),CAGE2(40),CAHE1(40),CAHE2(40),
     1CAVE1(40),CAVE2(40),DEVGE1(40),DEVGE2(40),DEVHE1(40),DEVHE2(40),
     2DEVVE1(40),DEVVE2(40)
      IF (ISWCR.EQ.1) GO TO 110
      GO TO 120
  110 CALL CRLB(CT12,CV12,CP12,VXI)
      GO TO 170
  120 CALL NOTHER(CT12,CV12,CP12,VXI)
```

```
170   CONTINUE
      DO 210 I = 1,NPTS
      X1(I) = 1.0 - X2(I)
      IF (ISWHCP.EQ.2) GO TO 180
      CALL PCQ1(CT1F,CV1F,CP1F,CT12,CV12,CP12,X2(I))
      IF (ISWHCP.EQ.3) GO TO 180
      GO TO 190
180   CALL PCQ2(CT2F1,CT2F2,CV2F1,CV2F2,CP2F1,CP2F2,CT12,CV12,
     1CP12,X2(I))
190   CONTINUE
      ISWNF = ISWHCP
      IF (ISWNF.EQ.2) GO TO 200
      CALL XRES(CT1,CV1,CP1,GRESA,HRESA,VRESA)
      CALL XRES(CT2,CV2,CP2,GRESB,HRESB,VRESB)
      CALL XRES(CT1F,CV1F,CP1F,GRESY,HRESY,VRESY)
      CAGE1(I) = R*T*(GRESY - X1(I)*GRESA -X2(I)*GRESB)
      CAHE1(I) = R*T*(HRESY - X1(I)*HRESA - X2(I)*HRESB)
      CAVE1(I) = (1.0E06)*(VRESY-X1(I)*VRESA-X2(I)*VRESB)
      DEVGE1(I) = XPGE(I) - CAGE1(I)
      DEVHE1(I) = XPHE(I) - CAHE1(I)
      DEVVE1(I) = XPVE(I) - CAVE1(I)
      IF (ISWNF.EQ.3) GO TO 200
      GO TO 210
200   CALL XRES(CT2F1,CV2F1,CP2F1,GRESYA,HRESYA,VRESYA)
      CALL XRES(CT1,CV1,CP1,GRESA,HRESA,VRESA)
      CALL XRES(CT2F2,CV2F2,CP2F2,GRESYB,HRESYB,VRESYB)
      CALL XRES(CT2,CV2,CP2,GRESB,HRESB,VRESB)
      CAGE2(I) = R*T*(X1(I)*(GRESYA-GRESA) + X2(I)*(GRESYB-GRESB))
      CAHE2(I) = R*T*(X1(I)*(HRESYA-HRESA) + X2(I)*(HRESYB-HRESB))
      CAVE2(I) = (1.0E6)*(X1(I)*(VRESYA-VRESA)+X2(I)*(VRESYB-VRESB))
      DEVGE2(I) = XPGE(I) - CAGE2(I)
      DEVHE2(I) = XPHE(I) - CAHE2(I)
      DEVVE2(I) = XPVE(I) - CAVE2(I)
210   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"THE VALUE OF XI FOR THE GIVEN COMBINING RULES"
      WRITE(4,*)
      WRITE(4,*)"VALUE OF XI =", VXI
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWNF.EQ.1) GO TO 212
      IF (ISWNF.EQ.2) GO TO 260
      IF (ISWNF.EQ.3) GO TO 705
212   WRITE(4,*)"THE 'ONE-FLUID' MODEL"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS GIBBS FUNCTIONS"
      WRITE(4,*)
      WRITE(4,215)
215   FORMAT(5X,57H MOLE FRACTION     CALC.XSG     EXPT.XSG       DIFFERE
     1NCE ,/)
      DO 225 I = 1,NPTS
      WRITE(4,220)X2(I),CAGE1(I),XPGE(I),DEVGE1(I)
220   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
225   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS ENTHALPIES"
```

```
      WRITE(4,*)
      WRITE(4,230)
230   FORMAT(5X,57H MOLE FRACTION     CALC.XSH     EXPT.XSH      DIFFERE
     1NCE ,/)
      DO 240 I = 1,NPTS
      WRITE(4,235)X2(I),CAHE1(I),XPHE(I),DEVHE1(I)
235   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
240   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS VOLUMES"
      WRITE(4,*)
      WRITE(4,245)
245   FORMAT(5X,57H MOLE FRACTION     CALC.XSV     EXPT.XSV      DIFFERE
     1NCE ,/)
      DO 255 I = 1,NPTS
      WRITE(4,250)X2(I),CAVE1(I),XPVE(I),DEVVE1(I)
250   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
255   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      GO TO 740
260   WRITE(4,*)"THE TWO-FLUID MODEL"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS GIBBS FUNCTIONS"
      WRITE(4,*)
      WRITE(4,265)
265   FORMAT(5X,57H MOLE FRACTION     CALC.XSG     EXPT.XSG      DIFFERE
     1NCE ,/)
      DO 275 I = 1,NPTS
      WRITE(4,270)X2(I),CAGE2(I),XPGE(I),DEVGE2(I)
270   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
275   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS ENTHALPIES"
      WRITE(4,*)
      WRITE(4,280)
280   FORMAT(5X,57H MOLE FRACTION     CALC.XSH     EXPT.XSH      DIFFERE
     1NCE ,/)
      DO 290 I = 1,NPTS
      WRITE(4,285)X2(I),CAHE2(I),XPHE(I),DEVHE2(I)
285   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
290   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS VOLUMES"
      WRITE(4,*)
      WRITE(4,295)
295   FORMAT(5X,57H MOLE FRACTION     CALC.XSV     EXPT.XSV      DIFFERE
     1NCE ,/)
      DO 305 I = 1,NPTS
      WRITE(4,300)X2(I),CAVE2(I),XPVE(I),DEVVE2(I)
300   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
305   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      GO TO 740
705   WRITE(4,*)"1. SYSTEM:"
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      WRITE(4,*)"2. METHOD OF CALCULATION:"
      WRITE(4,*)"   Supplementary notes:"
      WRITE(4,*)"3. SET OF COMBINING RULES:"
      WRITE(4,*)"   Value of ξ:",  VXI
      WRITE(4,*)
      WRITE(4,*)"   A             B             C             D
     1 E             F"
      WRITE(4,*)
      WRITE(4,*)"EXCESS GIBBS FUNCTIONS"
      WRITE(4,*)
      DO 715 I = 1,NPTS
      WRITE(4,710)X2(I),XPGE(I),CAGE1(I),CAGE2(I),DEVGE1(I),DEVGE2(I)
 710  FORMAT(2X,F4.2,7X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2)
 715  CONTINUE
      WRITE(4,*)
      WRITE(4,*)"REDLICH-KISTER COEFFICIENTS:"
      WRITE(4,*)"(a) EXPERIMENTAL   :"
      WRITE(4,*)"(b) ONE-FLUID MODEL:"
      WRITE(4,*)"(c) TWO-FLUID MODEL:"
      WRITE(4,*)
      WRITE(4,*)"EXCESS ENTHALPIES"
      WRITE(4,*)
      DO 725 I = 1,NPTS
      WRITE(4,720)X2(I),XPHE(I),CAHE1(I),CAHE2(I),DEVHE1(I),DEVHE2(I)
 720  FORMAT(2X,F4.2,7X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2)
 725  CONTINUE
      WRITE(4,*)
      WRITE(4,*)"REDLICH-KISTER COEFFICIENTS:"
      WRITE(4,*)"(a) EXPERIMENTAL   :"
      WRITE(4,*)"(b) ONE-FLUID MODEL:"
      WRITE(4,*)"(c) TWO-FLUID MODEL:"
      WRITE(4,*)
      WRITE(4,*)"EXCESS VOLUMES"
      WRITE(4,*)
      DO 735 I = 1,NPTS
      WRITE(4,730)X2(I),XPVE(I),CAVE1(I),CAVE2(I),DEVVE1(I),DEVVE2(I)
 730  FORMAT(2X,F4.2,8X,F7.4,6X,F7.4,6X,F7.4,6X,F7.4,6X,F7.4)
 735  CONTINUE
      WRITE(4,*)
      WRITE(4,*)"REDLICH-KISTER COEFFICIENTS:"
      WRITE(4,*)"(a) EXPERIMENTAL   :"
      WRITE(4,*)"(b) ONE-FLUID MODEL:"
      WRITE(4,*)"(c) TWO-FLUID MODEL:"
 740  CONTINUE
      RETURN
      END

      SUBROUTINE CRLB(CT12,CV12,CP12,VXI)
C     THIS SUBROUTINE IS FOR OBTAINING CRITICAL PARAMETERS DUE TO
C     UNLIKE INTERACTIONS BY USE OF THE LORENTZ-BERTHELOT COMBINING
C     RULES.
      COMMON/RTPDAT/R,T,P
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      IF (ISWVC.EQ.1) GO TO 307
      CV1 = AZ*R*CT1/CP1
      CV2 = AZ*R*CT2/CP2
 307  CONTINUE
```

```
      CT12 = (CT1*CT2)**(1.0/2.0)
      CVNUM = CV1**(1.0/3.0) + CV2**(1.0/3.0)
      CV12 = CVNUM**3/8.0
      CPNUM = CT1**(1.0/3.0)*(CP1**(-1.0/3.0)) + CT2**(1.0/3.0)*
     1(CP2**(-1.0/3.0))
      CP12 = 8.0*((CT1*CT2)**(1.0/2.0))*(CPNUM**(-3))
      VXI = ISWVC/ISWVC
      RETURN
      END

      SUBROUTINE NOTHER(CT12,CV12,CP12,VXI)
C     THIS SUBROUTINE IS FOR OBTAINING CRITICAL PARAMETERS DUE TO
C     UNLIKE INTERACTIONS USING COMBINING RULES OTHER THAN THE
C     LORENTZ-BERTHELOT RULES. THE IDENTIFIER ISWCR(for ISWCR
C     greater than 1) IS USED FOR SELECTING THE REQUIRED RULES.
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/RTPDAT/R,T,P
      COMMON/CFDATA/AP(10),AB(10),AV(10),APD(10),ABD(10),AVD(10)
      COMMON/NUMCFS/JPM,JBM,JVM,JPMD,JBMD,JVMD
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      COMMON/PTNSWI/NPTS,ISWCR,ISWHCP,ISWST
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      IF (ISWVC.EQ.1) GO TO 309
      CV1 = AZ*R*CT1/CP1
      CV2 = AZ*R*CT2/CP2
 309  CONTINUE
      PRODIP = 2.0*(PI1*PI2)**(0.5)/(PI1+PI2)
      PRODR = (RINTM1**3)*(RINTM2**3)/(RINTM1+RINTM2)**6
      VC12 = (CV1**(1.0/3.0) + CV2**(1.0/3.0))**3/8.0
      QUOTV = (CV1**(1.0/3.0) + CV2**(1.0/3.0))**6
      IF (ISWCR.EQ.2) GO TO 310
      IF (ISWCR.EQ.3) GO TO 325
      IF (ISWCR.EQ.4) GO TO 330
      IF (ISWCR.EQ.5) GO TO 335
      IF (ISWCR.EQ.6) GO TO 340
      IF (ISWCR.EQ.7) GO TO 345
      IF (ISWCR.EQ.8) GO TO 350
 310  IF (ISWVOL.EQ.2) GO TO 315
      CT12 = (2.0**6)*PRODR*PRODIP*(CT1*CT2)**(0.5)
      IF (ISWVOL.EQ.1) GO TO 320
 315  CT12 = (2.0**6)*CV1*CV2*PRODIP*(CT1*CT2)**(0.5)/QUOTV
 320  CONTINUE
      GO TO 375
 325  CT12 = (CT1*CT2)**(1.0/2.0)*(CV1*CV2)**(1.0/2.0)/VC12
      GO TO 375
 330  CT12 = PRODIP*(CT1*CT2)**(1.0/2.0)*(CV1*CV2)**(1.0/2.0)/VC12
      GO TO 375
 335  CT12 = 2.0*CT1*CT2*(CV1*CV2)**2*VC12**(-2)*POL1*POL2/(CT1*(CV1*
     1       POL2)**2 + CT2*(CV2*POL1)**2)
      GO TO 375
 340  CT12 = 2.0*CT1*CT2/(CT1 + CT2)
      GO TO 375
 345  CT12 = 2.0*CT1*CT2*2.0**6*(CV1*CV2)**2/(QUOTV*(CT1*CV1**2 + CT2*
     1       CV2**2))
      GO TO 375
 350  CT12 = 2.0*(CT1*CT2)**(2.0/3.0)/(CT1**(1.0/3.0) + CT2**(1.0/3.0))
 375  CONTINUE
```

```
      CV12 = VC12
      CP12 = AZ*R*CT12/CV12
      VXI = CT12/((CT1*CT2)**(1.0/2.0))
      RETURN
      END

      SUBROUTINE PCQ1(CT1F,CV1F,CP1F,CT12,CV12,CP12,X2)
C     THIS SUBROUTINE FURNISHES THE CRITICAL PARAMETERS OF THE
C     HYPOTHETICAL FLUID,NAMELY,TEMPERATURE(CT1F),VOLUME(CV1F),
C     AND PRESSURE(CP1F).THE MIXTURE IS TAKEN TO BE "ONE-FLUID".
      REAL N,M
      COMMON/RTPDAT/R,T,P
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/LOOPNM/N,M
      COMMON/PTNSWI/NPTS,ISWCR,ISWHCP,ISWST
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      IF (ISWVC.EQ.1) GO TO 400
      CV1 = AZ*R*CT1/CP1
      CV2 = AZ*R*CT2/CP2
 400  CONTINUE
      IF (ISWCR.EQ.1) GO TO 410
      GO TO 420
 410  CALL CRLB(CT12,CV12,CP12,VXI)
      GO TO 430
 420  CALL NOTHER(CT12,CV12,CP12,VXI)
 430  CONTINUE
      X1 = 1.0 - X2
      IF (ISWST.EQ.1) GO TO 440
      GO TO 450
 440  CV1F = X1**2*CV1 + 2.0*X1*X2*CV12 + X2**2*CV2
      CT1F = (X1**2*CT1*CV1+2.0*X1*X2*CT12*CV12+X2**2*CT2*CV2)/CV1F
      CP1F = AZ*R*CT1F/CV1F
      GO TO 460
 450  CONTINUE
      CTVNUM = X1**2*CT1*(CV1**(N/3.0))+2.0*X1*X2*CT12*(CV12**(N/3.0))
     1        + X2**2*CT2*(CV2**(N/3.0))
      CTVDEN = X1**2*CT1*(CV1**(M/3.0))+2.0*X1*X2*CT12*(CV12**(M/3.0))
     1        + X2**2*CT2*(CV2**(M/3.0))
      CTPNUM = X1**2*(CT1**((3.0+N)/3.0))*(CP1**(-N/3.0)) +
     12.0*X1*X2*(CT12**((3.0+N)/3.0))*(CP12**(-N/3.0)) +
     2X2**2*(CT2**((3.0+N)/3.0))*(CP2**(-N/3.0))
      CTPDEN = X1**2*(CT1**((3.0+M)/3.0))*(CP1**(-M/3.0)) +
     12.0*X1*X2*(CT12**((3.0+M)/3.0))*(CP12**(-M/3.0)) +
     2X2**2*(CT2**((3.0+M)/3.0))*(CP2**(-M/3.0))
      CT1F = CTVNUM**(M/(M-N))*(CTVDEN**(N/(N-M)))
      CV1F = CTVNUM**(3.0/(N-M))*(CTVDEN**(3.0/(M-N)))
      CP1F = CTPNUM**((3.0+M)/(M-N))*(CTPDEN**((3.0+N)/(N-M)))
 460  CONTINUE
      RETURN
      END

      SUBROUTINE PCQ2(CT2F1,CT2F2,CV2F1,CV2F2,CP2F1,CP2F2,CT12,CV12
     1,CP12,X2)
C     THE FUNCTION OF THIS SUBROUTINE IS SIMILAR TO THAT OF PCQ1.
C     THE DIFFERENCE IS THAT, IN THIS CASE, THE MIXTURE IS TAKEN AS
C     "TWO-FLUID".
      REAL N,M
```

```
      COMMON/RTPDAT/R,T,P
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/LOOPNM/N,M
      COMMON/PTNSWI/NPTS,ISWCR,ISWHCP,ISWST
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      IF (ISWVC.EQ.1) GO TO 500
      CV1 = AZ*R*CT1/CP1
      CV2 = AZ*R*CT2/CP2
  500 CONTINUE
      IF (ISWCR.EQ.1) GO TO 510
      GO TO 520
  510 CALL CRLB(CT12,CV12,CP12,VXI)
      GO TO 530
  520 CALL NOTHER(CT12,CV12,CP12,VXI)
  530 CONTINUE
      X1 = 1.0 - X2
      IF (ISWST.EQ.1) GO TO 540
      GO TO 550
  540 CV2F1 = X1*CV1 + X2*CV12
      CV2F2 = X2*CV2 + X1*CV12
      CT2F1 = (X1*CT1*CV1 + X2*CT12*CV12)/CV2F1
      CT2F2 = (X2*CT2*CV2 + X1*CT12*CV12)/CV2F2
      CP2F1 = AZ*R*CT2F1/CV2F1
      CP2F2 = AZ*R*CT2F2/CV2F2
      GO TO 560
  550 CONTINUE
      CTVN1 = X1*CT1*(CV1**(N/3.0)) + X2*CT12*(CV12**(N/3.0))
      CTVN2 = X2*CT2*(CV2**(N/3.0)) + X1*CT12*(CV12**(N/3.0))
      CTVM1 = X1*CT1*(CV1**(M/3.0)) + X2*CT12*(CV12**(M/3.0))
      CTVM2 = X2*CT2*(CV2**(M/3.0)) + X1*CT12*(CV12**(M/3.0))
      CTPN1 = X1*(CT1**((3.0+N)/3.0))*(CP1**(-N/3.0)) +
     1        X2*(CT12**((3.0+N)/3.0))*(CP12**(-N/3.0))
      CTPN2 = X2*(CT2**((3.0+N)/3.0))*(CP2**(-N/3.0)) +
     1        X1*(CT12**((3.0+N)/3.0))*(CP12**(-N/3.0))
      CTPM1 = X1*(CT1**((3.0+M)/3.0))*(CP1**(-M/3.0)) +
     1        X2*(CT12**((3.0+M)/3.0))*(CP12**(-M/3.0))
      CTPM2 = X2*(CT2**((3.0+M)/3.0))*(CP2**(-M/3.0)) +
     1        X1*(CT12**((3.0+M)/3.0))*(CP12**(-M/3.0))
      CT2F1 = CTVN1**(M/(M-N))*(CTVM1**(N/(N-M)))
      CT2F2 = CTVN2**(M/(M-N))*(CTVM2**(N/(N-M)))
      CV2F1 = CTVN1**(3.0/(N-M))*(CTVM1**(3.0/(M-N)))
      CV2F2 = CTVN2**(3.0/(N-M))*(CTVM2**(3.0/(M-N)))
      CP2F1 = CTPN1**((3.0+M)/(M-N))*(CTPM1**((3.0+N)/(N-M)))
      CP2F2 = CTPN2**((3.0+M)/(M-N))*(CTPM2**((3.0+N)/(N-M)))
  560 CONTINUE
      RETURN
      END

      SUBROUTINE XRES(TC,VC,PC,GRES1,HRES1,VRES1)
C     THIS SUBROUTINE PROVIDES THE RESIDUAL  FUNCTIONS IN AN
C     ANALYTICAL FORM THAT IS A UNIVERSAL FUNCTION OF A GROUP OF
C     SUBSTANCES. A POWER SERIES IN THE REDUCED TEMPERATURE IS ADOPTED
C     AS A BASIS FOR THE CALCULATIONS.
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CP1,CP2,AZ
      COMMON/RTPDAT/R,T,P
      COMMON/CFDATA/AP(10),AB(10),AV(10),APD(10),ABD(10),AVD(10)
      COMMON/NUMCFS/JPM,JBM,JVM,JPMD,JBMD,JVMD
```

```
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL,ISWVC
      REAL LNREDP
      IF (ISWVC.EQ.1) GO TO 630
      VC = AZ*R*TC/PC
630   CONTINUE
      LNREDP = 0.0
      DO 640 JP = 1,JPM
      SUMLNP = AP(JP)*(TC/T)**(JP-1)
640   LNREDP = SUMLNP + LNREDP
      REDP = EXP(LNREDP)
      REDBV = 0.0
      DO 650 JB = 1,JBM
      SUMRBV = AB(JB)*(TC/T)**(JB-1)
650   REDBV = SUMRBV + REDBV
      REDV = 0.0
      DO 660 JV = 1,JVM
      SUMRV = AV(JV)*(T/TC)**(JV-1)
660   REDV = SUMRV + REDV
      DLNPDT = 0.0
      DO 670 JPD = 1,JPMD
      SMDLNP = APD(JPD)*(TC/T)**(JPD+1)
670   DLNPDT = SMDLNP + DLNPDT
      DREDV = 0.0
      DO 680 JVD = 1,JVMD
      SMDRVD = AVD(JVD)*(T/TC)**(JVD-1)
680   DREDV = SMDRVD + DREDV
      DIFFBV = REDBV - REDV
      DDBVDT = 0.0
      DO 690 JBD = 1,JBMD
      SMDBVD = ABD(JBD)*(TC/T)**(JBD+1)
690   DDBVDT = SMDBVD + DDBVDT
      DDFBDT = DDBVDT - DREDV
      GRES1 = LNREDP + AZ*(TC/T)*(REDP*DIFFBV+REDV*(P*VC/(AZ*R*TC)))
     1 + ALOG(AZ*R*TC/VC)
      HRES1 = -(T/TC)*DLNPDT - AZ*DIFFBV*REDP*(DLNPDT-(TC/T))
     1 - AZ*REDP*DDFBDT + (P*VC/(R*TC))*((TC/T)*REDV - DREDV)
      VRES1 = VC*REDV
      RETURN
      END
```

APPENDIX 7

This program calculates excess functions by use of equations of state, such as the Van der Waals equation of state.

```
C     PROGRAM .STEQTN
C     PROGRAM 'EQUATIONS OF STATE'.

C     THIS PROGRAM IS USED FOR FURNISHING DATA ON EXCESS FUNCTIONS FOR
C     SUITABLE OR SELECTED BINARY LIQUID MIXTURES BY EMPLOYING A NUMBER
C     OF EQUATIONS OF STATE.
C     THE EVALUATION OF THE EXCESS FUNCTIONS DEPENDS ON SOLVING FOR
C     THE MOLAR VOLUME AT ZERO PRESSURE. THE PROGRAM IS VERSATILE IN
C     ITS APPROACH TO THE SOLUTION FOR MOLAR VOLUME. THE ALTERNATIVES
C     MAY BE GROUPED THUS:
C     (i) The van der Waals and Guggenheim equations of state are
C         in their original forms. However, a general equation for
C         these two equations is used, the choice of equation being
C         determined by the appropriate selection for NEQST which is
C         index of the (V - B) term.
C         Also,the use of NEQST has facilitated the proposal of
C         other equations of state(see text).
C     (ii) A general equation, in series form,is available. This
C         represents all the equations of state to be discussed,
C         including the two mentioned above. The equations can be
C         distinguished by varying the values of the coefficients.
C     IN ALL APPROACHES, THE NEWTON-RAPHSON ITERATIVE METHOD IS USED.

      COMMON/COMPSN/X(40),XPGE(40),XPHE(40),XPVE(40)
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/CFDATA/A(20),M,N
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      DIMENSION CAGE1(40),CAGE2(40),CAHE1(40),CAHE2(40),
     1CAVE1(40),CAVE2(40),DEVGE1(40),DEVGE2(40),DEVHE1(40),DEVHE2(40),
     2DEVVE1(40),DEVVE2(40),AX(40),BX(40),A1X(40),A2X(40),
     3B1X(40),B2X(40),A1(40),A2(40),B1(40),B2(40)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"TYPE IN GAS CONSTANT AND TEMPERATURE"
      WRITE(4,*)
      READ(3,*)R,T
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE CRITICAL TEMPS AND VOLS FOR BOTH COMPTS."
      WRITE(4,*)
      READ(3,*)CT1,CT2,CV1,CV2
      WRITE(4,*)
      WRITE(4,*)CT1,CT2,CV1,CV2
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE CONSTANTS CA AND CB - THESE ARE FOR"
      WRITE(4,*)"CALCULATION OF A11 AND B11, etc."
      WRITE(4,*)
      READ(3,*)CA,CB
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE IONISATION POTENTIALS FOR COMPONENTS"
      WRITE(4,*)"1 AND 2"
      WRITE(4,*)
      READ(3,*)PI1,PI2
      WRITE(4,*)
      WRITE(4,*)"TYPE IN THE INTERMOLECULAR SEPARATION PARAMETERS"
      WRITE(4,*)"FOR COMPTS. 1 AND 2"
      WRITE(4,*)
      READ(3,*)RINTM1,RINTM2
```

```
WRITE(4,*)
WRITE(4,*)"TYPE IN THE POLARISABILITIES FOR COMPTS. 1 AND 2"
WRITE(4,*)
READ(3,*)POL1,POL2
WRITE(4,*)
WRITE(4,*)"TYPE IN THE DIAMAGNETIC SUSCEPTIBILITIES FOR COMPTS."
WRITE(4,*)"1 AND 2"
WRITE(4,*)
READ(3,*)DMS1,DMS2
WRITE(4,*)
WRITE(4,*)"TYPE IN ISWVOL. This is a switch! IT DEPENDS ON THE"
WRITE(4,*)"AVAILABILITY, OR LACK, OF DATA ON INTERMOLECULAR"
WRITE(4,*)"SEPARATION PARAMETERS. USE ISWVOL = 1 IF DATA ARE"
WRITE(4,*)"AVAILABLE; OTHERWISE USE A VALUE OF 2."
WRITE(4,*)
READ(3,*)ISWVOL
WRITE(4,*)
WRITE(4,*)"TYPE IN N - THE NUMBER OF POINTS"
WRITE(4,*)
READ(3,*)N
WRITE(4,*)
WRITE(4,*)"TYPE IN N MOLE FRACTION VALUES"
WRITE(4,*)
READ(3,*)(X(I),I=1,N)
WRITE(4,*)
WRITE(4,*)"TYPE IN N EXPERIMENTAL EXCESS GIBBS FUNCTION VALUES"
WRITE(4,*)
READ(3,*)(XPGE(I),I=1,N)
WRITE(4,*)
WRITE(4,*)(XPGE(I),I=1,N)
WRITE(4,*)
WRITE(4,*)"TYPE IN N EXPERIMENTAL EXCESS ENTHALPY VALUES"
WRITE(4,*)
READ(3,*)(XPHE(I),I=1,N)
WRITE(4,*)
WRITE(4,*)(XPHE(I),I=1,N)
WRITE(4,*)
WRITE(4,*)"TYPE IN N EXCESS VOLUME VALUES"
WRITE(4,*)
READ(3,*)(XPVE(I),I=1,N)
WRITE(4,*)
WRITE(4,*)(XPVE(I),I=1,N)
WRITE(4,*)
WRITE(4,*)"TYPE IN MOLSW. This is the value for selecting"
WRITE(4,*)"whether equations of state will be used in exact"
WRITE(4,*)"forms or in series forms."
WRITE(4,*)"MOLSW = 1; EXACT FORM OF THE GENERALISED EQUATION"
WRITE(4,*)"IN WHICH NEQST IS VARIABLE."
WRITE(4,*)"MOLSW = 2; SERIES FORM OF ANY EQUATION OF STATE."
WRITE(4,*)"NOW TYPE IN THE REQUIRED VALUE FOR MOLSW"
WRITE(4,*)
READ(3,*)MOLSW
WRITE(4,*)
WRITE(4,*)"If exact forms are to be used, which of the"
WRITE(4,*)"equations is required? The selection is via"
WRITE(4,*)"the use of NEQST."
WRITE(4,*)"NEQST = 1; FOR VAN DER WAALS EQUATION."
WRITE(4,*)"NEQST = 2; FOR PROPOSED STATE EQUATION(I)."
WRITE(4,*)"NEQST = 3; FOR PROPOSED STATE EQUATION(II)."
WRITE(4,*)"NEQST = 4; FOR GUGGENHEIM EQUATION."
```

```
WRITE(4,*)"NOW TYPE IN THE REQUIRED VALUE OF NEQST."
WRITE(4,*)
READ(3,*)NEQST
WRITE(4,*)
WRITE(4,*)"TYPE IN VFACT - THIS IS A FACTOR USED FOR OBTAINING"
WRITE(4,*)"THE TRIAL VALUE OF MOLAR VOLUME."
WRITE(4,*)"WHEN DEALING WITH EQUATIONS IN WHICH NEQST IS A"
WRITE(4,*)"VARIABLE, THE RECOMMENDED VALUES FOR VFACT ARE AS"
WRITE(4,*)"FOLLOWS:(NOTE - This is not law!)"
WRITE(4,*)"FOR NEQST = 1, VFACT = 1.10"
WRITE(4,*)"FOR NEQST = 2, VFACT = 1.80"
WRITE(4,*)"FOR NEQST = 3, VFACT = 2.30"
WRITE(4,*)"FOR NEQST = 4, VFACT = 2.50"
WRITE(4,*)"FOR OTHER EQUATIONS OF STATE, USE INTELLIGENT GUESSES"
WRITE(4,*)
READ(3,*)VFACT
WRITE(4,*)
WRITE(4,*)VFACT
WRITE(4,*)
WRITE(4,*)"TYPE IN THE VALUE FOR XI(SQUIGGLY' E VALUE)"
WRITE(4,*)"USE A VALUE OF 1 IN ALL CASES, EXCEPT WHERE THE"
WRITE(4,*)"VALUE OF XI HAS BEEN DETERMINED EXPERIMENTALLY;"
WRITE(4,*)"AND IF THAT IS THE CASE, THEN ONLY THE LORENTZ-"
WRITE(4,*)"BERTHELOT COMBINING RULES ARE TO BE USED."
WRITE(4,*)
READ(3,*)E
WRITE(4,*)
WRITE(4,*)"TYPE IN THE VALUE FOR CONST"
WRITE(4,*)"(This is the second term in R.H.S. of the equation"
WRITE(4,*)"which defines the residual volume.)"
WRITE(4,*)
READ(3,*)CONST
WRITE(4,*)
WRITE(4,*)"TYPE IN M - THE NUMBER OF COEFFICIENTS FOR THE SERIES"
WRITE(4,*)"FORM OF A GIVEN EQUATION OF STATE"
WRITE(4,*)
READ(3,*)M
WRITE(4,*)
WRITE(4,*)"TYPE IN THE COEFFICIENTS - M OF THEM"
WRITE(4,*)
READ(3,*)(A(L),L=1,M)
WRITE(4,*)
WRITE(4,*)"INDICATE WHICH 'N-FLUID' THEORY IS TO BE USED, OR, IF"
WRITE(4,*)"BOTH ARE TO BE USED, BY TYPING IN THE VALUE FOR NFLUID"
WRITE(4,*)"NFLUID = 1; FOR 'ONE-FLUID' THEORY."
WRITE(4,*)"NFLUID = 2; FOR 'TWO-FLUID' THEORY."
WRITE(4,*)"NFLUID = 3; IF BOTH MODELS ARE TO BE USED."
WRITE(4,*)"NOW TYPE IN THE VALUE FOR NFLUID"
WRITE(4,*)
READ(3,*)NFLUID
WRITE(4,*)
WRITE(4,*)"THE FOLLOWING SECTION IS FOR SELECTING THE EQUATION"
WRITE(4,*)"OF STATE TO BE USED. THIS IS DONE BY USING A SWITCH"
WRITE(4,*)" WHICH SHALL BE CALLED ISWEQS. THE FOLLOWING IS A"
WRITE(4,*)"LIST OF ISWEQS VALUES WITH THE CORRESPONDING"
WRITE(4,*)"EQUATIONS OF STATE:"
WRITE(4,*)"1 - THE VIRIAL EQUATION OF STATE"
WRITE(4,*)"2 - THE VAN DER WAALS EQUATION OF STATE"
WRITE(4,*)"3 - THE GUGGENHEIM EQUATION OF STATE"
WRITE(4,*)"4 - THE FRISCH et al EQUATION OF STATE"
```

```
      WRITE(4,*)"5 - THE THIELE EQUATON OF STATE"
      WRITE(4,*)"6 - THE SCOTT(1) EQUATION OF STATE"
      WRITE(4,*)"7 - THE SCOTT(2) EQUATION OF STATE"
      WRITE(4,*)"8 - THE PROPOSED EQUATION OF STATE(I)"
      WRITE(4,*)"9 - THE PROPOSED EQUATION OF STATE(II)"
      WRITE(4,*)"TYPE IN THE VALUE OF ISWEQS WHICH GOES WITH THE"
      WRITE(4,*)"DESIRED EQUATION OF STATE."
      WRITE(4,*)
      READ(3,*)ISWEQS
      WRITE(4,*)
      WRITE(4,*)"NOW WE NEED A SWITCH VALUE FOR THE SET OF COMBINING"
      WRITE(4,*)"RULES TO BE USED IN THIS CALCULATION - ISWCR."
      WRITE(4,*)"(By the way, this is the last bit of datum required"
      WRITE(4,*)"for this calculation. After typing in the value for"
      WRITE(4,*)"ISWCR just relax and let the computer do its thing!)"
      WRITE(4,*)"HERE IS A LIST OF ISWCR VALUES WITH CORRESPONDING"
      WRITE(4,*)"SETS OF COMBINING RULES:"
      WRITE(4,*)"1 - FOR THE LORENTZ-BERTHELOT COMBINING RULES"
      WRITE(4,*)"2 - FOR THE HUDSON-McCOUBREY COMBINING RULES"
      WRITE(4,*)"3 - WORMALD, et al(Mk I) COMBINING RULES"
      WRITE(4,*)"4 - WORMALD, et al(Mk II) COMBINING RULES"
      WRITE(4,*)"5 - MUNN COMBINING RULES"
      WRITE(4,*)"6 - FENDER-HALSEY COMBINING RULES"
      WRITE(4,*)"7 - this work"
      WRITE(4,*)"8 - HICKS-YOUNG COMBINING RULES"
      WRITE(4,*)
      WRITE(4,*)"NOW TYPE IN THE VALUE FOR ISWCR."
      WRITE(4,*)
      READ(3,*)ISWCR
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
    1 WRITE(4,*)"(1-X)-NEOPENTANE + X-TETRAMETHYLSILANE AT 283.15 K:"
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWEQS.EQ.1) GO TO 2
      IF (ISWEQS.EQ.2) GO TO 4
      IF (ISWEQS.EQ.3) GO TO 6
      IF (ISWEQS.EQ.4) GO TO 8
      IF (ISWEQS.EQ.5) GO TO 10
      IF (ISWEQS.EQ.6) GO TO 12
      IF (ISWEQS.EQ.7) GO TO 14
      IF (ISWEQS.EQ.8) GO TO 16
      IF (ISWEQS.EQ.9) GO TO 18
    2 WRITE(4,*)"THE VIRIAL EQUATION OF STATE:"
      GO TO 20
    4 WRITE(4,*)"THE VAN DER WAALS EQUATION OF STATE:"
      GO TO 20
    6 WRITE(4,*)"THE GUGGENHEIM EQUATION OF STATE:"
      GO TO 20
    8 WRITE(4,*)"THE FRISCH et al EQUATION OF STATE:"
      GO TO 20
   10 WRITE(4,*)"THE THIELE EQUATION OF STATE:"
      GO TO 20
   12 WRITE(4,*)"THE SCOTT(1) EQUATION OF STATE:"
      GO TO 20
   14 WRITE(4,*)"THE SCOTT(2) EQUATION OF STATE:"
      GO TO 20
   16 WRITE(4,*)"THE PROPOSED EQUATION OF STATE(I)"
      GO TO 20
```

```
   18 WRITE(4,*)"THE PROPOSED EQUATION OF STATE(II)"
   20 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      IF (ISWCR.EQ.1) GO TO 22
      IF (ISWCR.EQ.2) GO TO 24
      IF (ISWCR.EQ.3) GO TO 26
      IF (ISWCR.EQ.4) GO TO 28
      IF (ISWCR.EQ.5) GO TO 30
      IF (ISWCR.EQ.6) GO TO 32
      IF (ISWCR.EQ.7) GO TO 34
      IF (ISWCR.EQ.8) GO TO 36
   22 WRITE(4,*)"THE LORENTZ-BERTHELOT COMBINING RULES:"
      GO TO 40
   24 WRITE(4,*)"THE HUDSON-McCOUBREY COMBINING RULES:"
      GO TO 40
   26 WRITE(4,*)"THE WORMALD, et al(Mk I) COMBINING RULES:"
      GO TO 40
   28 WRITE(4,*)"THE WORMALD, et al(Mk II) COMBINING RULES:"
      GO TO 40
   30 WRITE(4,*)"THE MUNN COMBINING RULES:"
      GO TO 40
   32 WRITE(4,*)"THE FENDER-HALSEY COMBINING RULES:"
      GO TO 40
   34 WRITE(4,*)"COMBINING RULES USED: this work."
      GO TO 40
   36 WRITE(4,*)"THE HICKS-YOUNG COMBINING RULES:"
   40 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      CALL MAIN(CAGE1,CAHE1, CAVE1,CAGE2,CAHE2,CAVE2)
      WRITE(4,*)
      WRITE(4,*)
      STOP
      END

      SUBROUTINE MAIN(CAGE1,CAHE1,CAVE1,CAGE2,CAHE2,CAVE2)
C     EXCESS FUNCTIONS ARE CALCULATED IN THIS SECTION.
C     THERE IS AN OPTION FOR OBTAINING CALCULATED QUANTITIES
C     FROM EITHER ONE OR BOTH OF THE "N-FLUID" MODELS.

      COMMON/COMPSN/X(40),XPGE(40),XPHE(40),XPVE(40)
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/CFDATA/A(20),M,N
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      DIMENSION CAGE1(40),CAGE2(40),CAHE1(40),CAHE2(40),
     1CAVE1(40),CAVE2(40),DEVGE1(40),DEVGE2(40),DEVHE1(40),DEVHE2(40),
     2DEVVE1(40),DEVVE2(40),AX(40),BX(40),A1X(40),A2X(40),
     3B1X(40),B2X(40),A1(40),A2(40),B1(40),B2(40)
      IF (ISWCR.EQ.1) GO TO 110
      GO TO 120
  110 CALL CRLB(A12,B12,VXI)
      GO TO 150
  120 CALL NOTHER(A12,B21,VXI)
  150 CONTINUE
      DO 210 I = 1,N
```

```
      CALL PCQ1(X(I),A11,A22,B11,B22,AX(I),BX(I))
  160 CALL PCQ2((1.0-X(I)),X(I),A1X(I),B1X(I),CT1,CV1)
      CALL PCQ2(X(I),(1.0-X(I)),A2X(I),B2X(I),CT2,CV2)
  170 CONTINUE
      IF (MOLSW.EQ.1) GO TO 175
      IF (MOLSW.EQ.2) GO TO 190
  175 CALL RESVDW(A11,B11,VMNP1,GRES1,HRES1,VRES1)
      CALL RESVDW(A22,B22,VMNP2,GRES2,HRES2,VRES2)
      CALL RESVDW(AX(I),BX(I),VMNPY,GRESY,HRESY,VRESY)
      IF (NFLUID.EQ.2) GO TO 176
      CAGE1(I) = GRESY - (1.0-X(I))*GRES1 - X(I)*GRES2
      CAHE1(I) = HRESY - (1.0-X(I))*HRES1 - X(I)*HRES2
      CAVE1(I) = 1.0E06*(VRESY - (1.0-X(I))*VRES1 - X(I)*VRES2)
      DEVGE1(I) = XPGE(I) - CAGE1(I)
      DEVHE1(I) = XPHE(I) - CAHE1(I)
      DEVVE1(I) = XPVE(I) - CAVE1(I)
      IF (NFLUID.EQ.3) GO TO 176
      GO TO 210
  176 CALL RESVDW(A1X(I),B1X(I),VMNPY1,GRESY1,HRESY1,VRESY1)
      CALL RESVDW(A2X(I),B2X(I),VMNPY2,GRESY2,HRESY2,VRESY2)
      CAGE2(I) = (1.0-X(I))*(GRESY1-GRES1) + X(I)*(GRESY2-GRES2)
      CAHE2(I) = (1.0-X(I))*(HRESY1-HRES1) + X(I)*(HRESY2-HRES2)
      CAVE2(I) = 1.0E06*((1.0-X(I))*(VRESY1-VRES1)+X(I)*(VRESY2-VRES2))
      DEVGE2(I) = XPGE(I) - CAGE2(I)
      DEVHE2(I) = XPHE(I) - CAHE2(I)
      DEVVE2(I) = XPVE(I) - CAVE2(I)
      GO TO 210
  190 CALL MOLVOL(A11,B11,VMNP1)
      CALL MOLVOL(A22,B22,VMNP2)
      CALL MOLVOL(AX(I),BX(I),VMNPY)
      CALL XRES(A11,B11,VMNP1,GRES1,HRES1,VRES1)
      CALL XRES(A22,B22,VMNP2,GRES2,HRES2,VRES2)
      IF (NFLUID.EQ.2) GO TO 200
      CALL XRES(AX(I),BX(I),VMNPY,GRESY,HRESY,VRESY)
      CAGE1(I) = GRESY - (1.0-X(I))*GRES1 - X(I)*GRES2
      CAHE1(I) = HRESY - (1.0-X(I))*HRES1 - X(I)*HRES2
      CAVE1(I) = 1.0E06*(VRESY - (1.0-X(I))*VRES1 - X(I)*VRES2)
      DEVGE1(I) = XPGE(I) - CAGE1(I)
      DEVHE1(I) = XPHE(I) - CAHE1(I)
      DEVVE1(I) = XPVE(I) - CAVE1(I)
      IF (NFLUID.EQ.3) GO TO 200
      GO TO 210
  200 CALL MOLVOL(A1X(I),B1X(I),VMNPY1)
      CALL MOLVOL(A2X(I),B2X(I),VMNPY2)
      CALL XRES(A1X(I),B1X(I),VMNPY1,GRESY1,HRESY1,VRESY1)
      CALL XRES(A2X(I),B2X(I),VMNPY2,GRESY2,HRESY2,VRESY2)
      CAGE2(I) = (1.0-X(I))*(GRESY1-GRES1) + X(I)*(GRESY2-GRES2)
      CAHE2(I) = (1.0-X(I))*(HRESY1-HRES1) + X(I)*(HRESY2-HRES2)
      CAVE2(I) = 1.0E06*((1.0-X(I))*(VRESY1-VRES1)+X(I)*(VRESY2-VRES2))
      DEVGE2(I) = XPGE(I) - CAGE2(I)
      DEVHE2(I) = XPHE(I) - CAHE2(I)
      DEVVE2(I) = XPVE(I) - CAVE2(I)
  210 CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"THE VALUE OF XI FOR THE GIVEN COMBINING RULES"
      WRITE(4,*)
      WRITE(4,*)"VALUE OF XI =", VXI
      WRITE(4,*)
      WRITE(4,*)
```

```
     WRITE(4,*)
     IF (NFLUID.EQ.1) GO TO 212
     IF (NFLUID.EQ.2) GO TO 260
     IF (NFLUID.EQ.3) GO TO 805
212  WRITE(4,*)"THE 'ONE-FLUID' MODEL"
     WRITE(4,*)
     WRITE(4,*)
     WRITE(4,*)"MOLAR EXCESS GIBBS FUNCTIONS"
     WRITE(4,*)
     WRITE(4,215)
215  FORMAT(5X,57H MOLE FRACTION     CALC.XSG     EXPT.XSG      DIFFERE
    1NCE ,/)
     DO 225 I = 1,N
     WRITE(4,220)X(I),CAGE1(I),XPGE(I),DEVGE1(I)
220  FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
225  CONTINUE
     WRITE(4,*)
     WRITE(4,*)
     WRITE(4,*)"MOLAR EXCESS ENTHALPIES"
     WRITE(4,*)
     WRITE(4,230)
230  FORMAT(5X,57H MOLE FRACTION     CALC.XSH     EXPT.XSH      DIFFERE
    1NCE ,/)
     DO 240 I = 1,N
     WRITE(4,235)X(I),CAHE1(I),XPHE(I),DEVHE1(I)
235  FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
240  CONTINUE
     WRITE(4,*)
     WRITE(4,*)
     WRITE(4,*)"MOLAR EXCESS VOLUMES"
     WRITE(4,*)
     WRITE(4,245)
245  FORMAT(5X,57H MOLE FRACTION     CALC.XSV     EXPT.XSV      DIFFERE
    1NCE ,/)
     DO 255 I = 1,N
     WRITE(4,250)X(I),CAVE1(I),XPVE(I),DEVVE1(I)
250  FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
255  CONTINUE
     WRITE(4,*)
     WRITE(4,*)
     GO TO 840
260  WRITE(4,*)"THE 'TWO-FLUID' MODEL"
     WRITE(4,*)
     WRITE(4,*)
     WRITE(4,*)"MOLAR EXCESS GIBBS FUNCTIONS"
     WRITE(4,*)
     WRITE(4,265)
265  FORMAT(5X,57H MOLE FRACTION     CALC.XSG     EXPT.XSG      DIFFERE
    1NCE ,/)
     DO 275 I = 1,N
     WRITE(4,270)X(I),CAGE2(I),XPGE(I),DEVGE2(I)
270  FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
275  CONTINUE
     WRITE(4,*)
     WRITE(4,*)
     WRITE(4,*)"MOLAR EXCESS ENTHALPIES"
     WRITE(4,*)
     WRITE(4,280)
280  FORMAT(5X,57H MOLE FRACTION     CALC.XSH     EXPT.XSH      DIFFERE
    1NCE ,/)
```

```
      DO 290 I = 1,N
      WRITE(4,285)X(I),CAHE2(I),XPHE(I),DEVHE2(I)
285   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
290   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"MOLAR EXCESS VOLUMES"
      WRITE(4,*)
      WRITE(4,295)
295   FORMAT(5X,57H MOLE FRACTION     CALC.XSV      EXPT.XSV       DIFFERE
     1NCE ,/)
      DO 305 I = 1,N
      WRITE(4,300)X(I),CAVE2(I),XPVE(I),DEVVE2(I)
300   FORMAT(9X,F6.4,3X,E12.5,3X,E12.5,3X,E13.6/)
305   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      GO TO 840
805   WRITE(4,*)"1. SYSTEM:"
      WRITE(4,*)"2. METHOD OF CALCULATION:"
      WRITE(4,*)"   Supplementary notes:"
      WRITE(4,*)"3. SET OF COMBINING RULES:"
      WRITE(4,*)"   Value of ξ =",  VXI, "VFACT =",VFACT
      WRITE(4,*)
      WRITE(4,*)"   A               B               C               D
     1 E               F"
      WRITE(4,*)
      WRITE(4,*)"EXCESS GIBBS FUNCTIONS"
      WRITE(4,*)
      DO 815 I = 1,N
      WRITE(4,810)X(I),XPGE(I),CAGE1(I),CAGE2(I),DEVGE1(I),DEVGE2(I)
810   FORMAT(2X,F4.2,7X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2)
815   CONTINUE
      WRITE(4,*)
      WRITE(4,*)"REDLICH-KISTER COEFFICIENTS:"
      WRITE(4,*)"(a) EXPERIMENTAL   :"
      WRITE(4,*)"(b) ONE-FLUID MODEL:"
      WRITE(4,*)"(c) TWO-FLUID MODEL:"
      WRITE(4,*)
      WRITE(4,*)"EXCESS ENTHALPIES"
      WRITE(4,*)
      DO 825 I = 1,N
      WRITE(4,820)X(I),XPHE(I),CAHE1(I),CAHE2(I),DEVHE1(I),DEVHE2(I)
820   FORMAT(2X,F4.2,7X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2,5X,F8.2)
825   CONTINUE
      WRITE(4,*)
      WRITE(4,*)"REDLICH-KISTER COEFFICIENTS:"
      WRITE(4,*)"(a) EXPERIMENTAL   :"
      WRITE(4,*)"(b) ONE-FLUID MODEL:"
      WRITE(4,*)"(c) TWO-FLUID MODEL:"
      WRITE(4,*)
      WRITE(4,*)"EXCESS VOLUMES"
      WRITE(4,*)
      DO 835 I = 1,N
      WRITE(4,830)X(I),XPVE(I),CAVE1(I),CAVE2(I),DEVVE1(I),DEVVE2(I)
830   FORMAT(2X,F4.2,8X,F7.4,6X,F7.4,6X,F7.4,6X,F7.4,6X,F7.4)
835   CONTINUE
      WRITE(4,*)
      WRITE(4,*)"REDLICH-KISTER COEFFICIENTS:"
      WRITE(4,*)"(a) EXPERIMENTAL   :"
```

```
      WRITE(4,*)"(b) ONE-FLUID MODEL:"
      WRITE(4,*)"(c) TWO-FLUID MODEL:"
  840 CONTINUE
      RETURN
      END

      SUBROUTINE MOLVOL(AX,BX,VMNP1)
C     IN THIS SUBROUTINE, THE RELEVANT ROOT FOR THE MOLAR VOLUME OF A
C     MIXTURE, AS DESCRIBED BY A GIVEN EQUATION OF STATE, IS
C     ESTIMATED USING THE NEWTON-RAPHSON METHOD OF NUMERICAL ANALYSIS.
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/CFDATA/A(20),M,N
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,NEQST,VFACT
      VMN = VFACT*BX
      GO TO 360
  340 VMN = VMNP1
  360 SUMNUM = 0.0
      SUMDEN = 0.0
      DO 370 J = 1,M
      ABVNUM = A(J)*(BX/4.0)**(J-1)*(VMN)**(1-J)
      ABVDEN = (1-J)*A(J)*(BX/4.0)**(J-1)*(VMN)**(-J)
      SUMNUM = ABVNUM + SUMNUM
      SUMDEN = ABVDEN + SUMDEN
  370 CONTINUE
      VNUM = SUMNUM - (AX/(R*T*VMN))
      VDEN = SUMDEN + (AX/(R*T))*(VMN)**(-2)
      VMNP1 = VMN - (VNUM/VDEN)
      DVMN = VMNP1 - VMN
      IF (ABS(DVMN).LE.5.0E-11) GO TO 400
      GO TO 340
  400 CONTINUE
      RETURN
      END

      SUBROUTINE RESVDW(AX,BX,VMNP1,GRES,HRES,VRES)
C     THIS SUBROUTINE IS FOR EVALUATION OF RESIDUAL FUNCTIONS USING
C     THE EXACT FORMS OF THE EQUATIONS OF STATE.
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/CFDATA/A(20),M,N
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      VMN = VFACT*BX
      GO TO 420
  410 VMN = VMNP1
  420 CONTINUE
      VNUM = R*T*VMN**(NEQST-1)/(VMN-BX)**NEQST - AX/VMN**2
      VDEN = -R*T*VMN**(NEQST-2)*(VMN+(NEQST-1)*BX)/(VMN-BX)**(NEQST+1)
     1     + 2.0*AX/VMN**3
      VMNP1 = VMN - (VNUM/VDEN)
      DVMN = VMNP1 - VMN
      IF (ABS(DVMN).LE.5.00E-11) GO TO 430
      GO TO 410
  430 CONTINUE
      IF (NEQST.EQ.1) GO TO 450
      IF (NEQST.EQ.2) GO TO 455
      IF (NEQST.EQ.3) GO TO 460
      IF (NEQST.EQ.4) GO TO 470
  450 GRES = -R*T*ALOG(VMNP1 - BX) - (AX/VMNP1)
      GO TO 480
```

```
  455 GRES = -R*T*ALOG(VMNP1 - BX) - AX/VMNP1 + R*T*BX/(VMNP1-BX)
      GO TO 480
  460 GRES = -R*T*ALOG(VMNP1 - BX) - AX/VMNP1 + 2.0*R*T*BX/(VMNP1-BX)
     1       + R*T*BX**2/(2.0*(VMNP1 - BX)**2)
      GO TO 480
  470 CONST1 = 3.0*BX/(VMNP1-BX)
      CONST2 = 3.0*BX**2/(2.0*(VMNP1-BX)**2)
      CONST3 = BX**3/(3.0*(VMNP1-BX)**3)
      GRES = -R*T*ALOG(VMNP1-BX) + R*T*(CONST1+CONST2+CONST3) - AX/VMNP1
  480 CONTINUE
      HRES = - (AX/VMNP1)
      VRES = VMNP1 + CONST
      RETURN
      END

      SUBROUTINE XRES(AX,BX,VMNP1,GRES,HRES,VRES)
C     THE RESIDUAL FUNCTIONS(GIBBS FUNCTIONS, ENTHALPIES, AND VOLUMES)
C     ARE CALCULATED IN THIS SUBROUTINE.
C     THE VALUES FOR THE MOLAR VOLUMES HAVE BEEN OBTAINED VIA THE
C     SERIES FORMS OF THE EQUATIONS OF STATE.
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/CFDATA/A(20),M,N
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      SUMGR = 0.0
      DO 500 J = 2,M
      GRABV = A(J)*(BX/(4.0*VMNP1))**(J-1)/(J-1)
  500 SUMGR = GRABV + SUMGR
      GRES = R*T*SUMGR - (AX/VMNP1)
      HRES = -(AX/VMNP1)
      VRES = VMNP1 + CONST
      RETURN
      END

      SUBROUTINE PCQ1(X,A11,A22,B11,B22,AX,BX)
C     THIS SUBROUTINE IS FOR ANLYSIS BY THE 'ONE-FLUID' MODEL
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      IF (ISWCR.EQ.1) GO TO 510
      GO TO 520
  510 CALL CRLB(A12,B12,VXI)
      GO TO 550
  520 CALL NOTHER(A12,B12,VXI)
  550 A11 = CA*R*CT1*CV1
      A22 = CA*R*CT2*CV2
      B11 = CB*CV1
      B22 = CB*CV2
      AX = (1.0-X)**2*A11 + 2.0*X*(1.0-X)*A12 + X**2*A22
      BX = (1.0-X)**2*B11 + 2.0*X*(1.0-X)*B12 + X**2*B22
      RETURN
      END

      SUBROUTINE PCQ2(X1,X2,AX,BX,CT,CV)
C     THIS SUBROUTINE IS FOR ANALYSIS BY THE 'TWO-FLUID' MODEL
```

```
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      IF (ISWCR.EQ.1) GO TO 610
      GO TO 620
  610 CALL CRLB(A12,B12,VXI)
      GO TO 650
  620 CALL NOTHER(A12,B12,VXI)
  650 CONTINUE
      AX = X1*CT*CV*CA*R + X2*A12
      BX = X1*CV*CB + X2*B12
      RETURN
      END

      SUBROUTINE CRLB(A12,B12,VXI)
C     THE LORENTZ-BERTHELOT COMBINING RULES
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      CV12 = (CV1**(1.0/3.0) + CV2**(1.0/3.0))**3/8.0
      B12 = CB*CV12
      FIXNUM = (CT1*CT2*CV1*CV2)**(1.0/2.0)
      FIXDEN = (CV12**2/(CV1*CV2))**(1.0/2.0)
      A12 = E*FIXNUM*FIXDEN*CA*R
      VXI = E
      RETURN
      END

      SUBROUTINE NOTHER(A12,B12,VXI)
C     THIS SUBROUTINE IS FOR OBTAINING THE CRITICAL TEMPERATURE DUE TO
C     UNLIKE INTERACTIONS USING COMBINING RULES OTHER THAN THE
C     LORENTZ-BERTHELOT RULES. THE IDENTIFIER ISWCR(for ISWCR
C     greater than 1) IS UESD FOR SELECTING THE REQUIRED RULES.
      COMMON/CRITIC/CT1,CT2,CV1,CV2,CA,CB
      COMMON/RTPDAT/R,T,CONST,E
      COMMON/SWITCH/ISWEQS,ISWCR,NFLUID,MOLSW,NEQST,VFACT
      COMMON/MOLSEP/RINTM1,RINTM2,PI1,PI2,ISWVOL
      COMMON/POLDMS/POL1,POL2,DMS1,DMS2
      CV12 = (CV1**(1.0/3.0) + CV2**(1.0/3.0))**3/8.0
      B12 = CB*CV12
      PRODIP = 2.0*(PI1*PI2)**(1.0/2.0)/(PI1+PI2)
      PRODR = (RINTM1**3)*(RINTM2**3)/(RINTM1 + RINTM2)**6
      QUOTV = (CV1**(1.0/3.0) + CV2**(1.0/3.0))**6
      IF (ISWCR.EQ.2) GO TO 710
      IF (ISWCR.EQ.3) GO TO 725
      IF (ISWCR.EQ.4) GO TO 730
      IF (ISWCR.EQ.5) GO TO 735
      IF (ISWCR.EQ.6) GO TO 740
      IF (ISWCR.EQ.7) GO TO 745
      IF (ISWCR.EQ.8) GO TO 750
  710 IF (ISWVOL.EQ.2) GO TO 715
      CT12 = 2.0**6*PRODR*PRODIP*(CT1*CT2)**(1.0/2.0)
      A12 = CV12*CT12*R*CA
      IF (ISWVOL.EQ.1) GO TO 720
  715 CT12 = 2.0**6*CV1*CV2*PRODIP*(CT1*CT2)**(1.0/2.0)/QUOTV
      A12 = CV12*CT12*CA*R
  720 CONTINUE
      GO TO 775
  725 CT12 = (CT1*CT2*CV1*CV2)**(1.0/2.0)/CV12
```

```
      A12 = CV12*CT12*R*CA
      GO TO 775
730   CT12 = PRODIP*(CT1*CT2*CV1*CV2)**(1.0/2.0)/CV12
      A12 = CV12*CT12*R*CA
      GO TO 775
735   CT12 = 2.0*CT1*CT2*(CV1*CV2)**2*CV12**(-2)*POL1*POL2/(CT1*(CV1*
     1        POL2)**2 + CT2*(CV2*POL1)**2)
      A12 = CV12*CT12*R*CA
      GO TO 775
740   CT12 = 2.0*CT1*CT2/(CT1 + CT2)
      A12 = CV12*CT12*R*CA
      GO TO 775
745   CT12 = 2.0*CT1*CT2*2.0**6*(CV1*CV2)**2/(QUOTV*(CT1*CV1**2 + CT2*
     1        CV2**2))
      A12 = CV12*CT12*R*CA
      GO TO 775
750   CT12 = 2.0*(CT1*CT2)**(2.0/3.0)/(CT1**(1.0/3.0) + CT2**(1.0/3.0))
      A12 = CV12*CT12*R*CA
775   CONTINUE
      VXI = CT12/((CT1*CT2)**(1.0/2.0))
780   CONTINUE
      RETURN
      END
```

APPENDIX 8

The program was used for compiling calculated data so that it came in the form of tables shown in TABLES 7.1 to 7.8

```
C     This program tabulates the results of calculations of
C     excess functions using a given theoretical model and
C     various combining rules. Experimental data are also
C     included.

      INTEGER N
      DIMENSION X(10),XPGE(10),XPHE(10),XPVE(10),GELB1(10),
     1GELB2(10),HELB1(10),HELB2(10),VELB1(10),VELB2(10),GEHM1(10),
     2GEHM2(10),HEHM1(10),HEHM2(10),VEHM1(10),VEHM2(10),GEWO1(10),
     3GEWO2(10),HEWO1(10),HEWO2(10),VEWO1(10),VEWO2(10),GEFH1(10),
     4GEFH2(10),HEFH1(10),HEFH2(10),VEFH1(10),VEFH2(10),GEHY1(10),
     5GEHY2(10),HEHY1(10),HEHY2(10),VEHY1(10),VEHY2(10),GEPR1(10),
     6GEPR2(10),HEPR1(10),HEPR2(10),VEPR1(10),VEPR2(10)

      READ(3,*)VLB,VHM,VW1,VFH,VHY,VPR
      READ(3,*)N
      READ(3,*)(X(I),I=1,N)
      READ(3,*)(XPGE(I),XPHE(I),XPVE(I),I=1,N)
      READ(3,*)(GELB1(I),HELB1(I),VELB1(I),I=1,N)
      READ(3,*)(GELB2(I),HELB2(I),VELB2(I),I=1,N)
      READ(3,*)(GEHM1(I),HEHM1(I),VEHM1(I),I=1,N)
      READ(3,*)(GEHM2(I),HEHM2(I),VEHM2(I),I=1,N)
      READ(3,*)(GEWO1(I),HEWO1(I),VEWO1(I),I=1,N)
      READ(3,*)(GEWO2(I),HEWO2(I),VEWO2(I),I=1,N)
      READ(3,*)(GEFH1(I),HEFH1(I),VEFH1(I),I=1,N)
      READ(3,*)(GEFH2(I),HEFH2(I),VEFH2(I),I=1,N)
      READ(3,*)(GEHY1(I),HEHY1(I),VEHY1(I),I=1,N)
      READ(3,*)(GEHY2(I),HEHY2(I),VEHY2(I),I=1,N)
      READ(3,*)(GEPR1(I),HEPR1(I),VEPR1(I),I=1,N)
      READ(3,*)(GEPR2(I),HEPR2(I),VEPR2(I),I=1,N)
      WRITE(4,*)
      WRITE(4,*)"TABLE 7.1 Prediction of excess functions via the"
      WRITE(4,*)"          equation of state(I)."
      WRITE(4,*)"(1-x)-neopentane + x-tetramethylsilane at 283.15 K"
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"'ONE-FLUID' THEORY"
      WRITE(4,*)
      WRITE(4,*)"Combining rule:       LB         HM         W(I)       FH
     1  HY     present"
      WRITE(4,10)VLB,VHM,VW1,VFH,VHY,VPR
   10 FORMAT(1X,10HValue of u,10X,F5.3,3X,F7.5,2X,F7.5,2X,F7.5,2X,F7.5,
     12X,F7.5)
      WRITE(4,*)
      WRITE(4,*)"     x  Expt. values   Calculated values using various c
     1ombining rules"
      WRITE(4,*)
      WRITE(4,*)"Excess Gibbs functions/J mol^-1"
      WRITE(4,*)
      DO 30 I = 1,N
      WRITE(4,20)X(I),XPGE(I),GELB1(I),GEHM1(I),GEWO1(I),GEFH1(I),
     1GEHY1(I),GEPR1(I)
   20 FORMAT(4X,F4.2,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,
     1F7.1)
   30 CONTINUE
      WRITE(4,*)
      WRITE(4,*)"Excess enthalpies/J mol^-1"
      WRITE(4,*)
      DO 50 I = 1,N
      WRITE(4,40)X(I),XPHE(I),HELB1(I),HEHM1(I),HEWO1(I),HEFH1(I),
```

```
     1HEHY1(I),HEPR1(I)
 40   FORMAT(4X,F4.2,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,
     1F7.1)
 50   CONTINUE
      WRITE(4,*)
      WRITE(4,*)"Excess volumes/cm3 mol-1"
      WRITE(4,*)
      DO 70 I = 1,N
      WRITE(4,60)X(I),XPVE(I),VELB1(I),VEHM1(I),VEWO1(I),VEFH1(I),
     1VEHY1(I),VEPR1(I)
 60   FORMAT(4X,F4.2,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,
     1F7.4)
 70   CONTINUE
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)
      WRITE(4,*)"'TWO-FLUID' THEORY"
      WRITE(4,*)
      WRITE(4,*)"Excess Gibbs functions/J mol-1"
      WRITE(4,*)
      DO 90 I = 1,N
      WRITE(4,80)X(I),XPGE(I),GELB2(I),GEHM2(I),GEWO2(I),GEFH2(I),
     1GEHY2(I),GEPR2(I)
 80   FORMAT(4X,F4.2,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,
     1F7.1)
 90   CONTINUE
      WRITE(4,*)
      WRITE(4,*)"Excess enthalpies/J mol-1"
      WRITE(4,*)
      DO 110 I = 1,N
      WRITE(4,100)X(I),XPHE(I),HELB2(I),HEHM2(I),HEWO2(I),HEFH2(I),
     1HEHY2(I),HEPR2(I)
100   FORMAT(4X,F4.2,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,F7.1,2X,
     1F7.1)
110   CONTINUE
      WRITE(4,*)
      WRITE(4,*)"Excess volumes/cm3 mol-1"
      WRITE(4,*)
      DO 130 I = 1,N
      WRITE(4,120)X(I),XPVE(I),VELB2(I),VEHM2(I),VEWO2(I),VEFH2(I),
     1VEHY2(I),VEPR2(I)
120   FORMAT(4X,F4.2,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,F7.4,2X,
     1F7.4)
130   CONTINUE
      WRITE(4,*)
      STOP
      END
```