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by

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Abstract

STUDIES ON SOLUTIONS OF NON-ELECTROLYTES

by

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The present work is concerned with a study of the thermodynamic behavior of binary non-electrolyte solutions. The methods of approach to this problem have been divided into three categories: theoretical, semi-empirical, and empirical.

The theoretical methods attempt to evaluate the properties of solutions from properties of the pure components. While such theoretical treatments offer the only promise of the eventual understanding of and prediction of the behavior of mixtures, various obstacles in the way of developing a universal theory at present are discussed. As a consequence, the need for semi-empirical approaches, which attempt to predict the behavior of solutions from a limited number of experimental data is emphasized.

The isothermal excess Gibbs free energies of six especially selected binary mixtures have been determined via vapor-liquid equilibrium studies over the whole concentration range. The corresponding Redlich-Kister expansion

coefficients have been calculated by the method of least squares, and the Gibbs-Duhem equation has been applied to test the thermodynamic consistency of the data.

The concept of the divisibility of the excess Gibbs free energy of a binary system into separate contributions due to size, shape, and polarity differences between the component molecules has been investigated. Results based on the study of three binary mixtures, each differing essentially in only one of the three factors indicate that excess thermodynamic behavior in these systems is an extremely complex phenomenon and is not reducible to such an approach.

The effect of the polarity of a molecule on the π electron cloud of the second component is investigated by comparison of the excess Gibbs free energies of benzene--tetrachloroethylene, thiophene--tetrachloroethylene, and pyridine--tetrachloroethylene with parallel mixtures where tetrachloroethylene is substituted by carbon tetrachloride. Here again the concept of separability of factors influencing non-ideal behavior does not seem to be successful, probably because of complex mixed interactions.

In another series of comparative studies, the relative density of the ring π electron system in benzene, substituted benzene compounds, thiophene, and pyridine is thought to be the reason for the unusual excess Gibbs free energy values of some binary mixtures. Charge-transfer complex formation is postulated to explain these results.

Guggenheim's "interchange energy" concept in the first approximation of strictly regular solution theory is used in a group contribution approach to predict the excess free energies of binary mixtures having tetrachloroethylene as one component from the excess free energies of systems having carbon tetrachloride as one component.

Finally, a semi-empirical theory is developed which deals with the calculation of the enthalpy of mixing of binary non-associated solutions from isothermal excess Gibbs free energies. The theory also permits the prediction of the excess Gibbs free energy from single temperature values of the enthalpy of mixing. The method is applied to a great number of systems taken from the literature, and good agreement is obtained between experimental and calculated results.

As a corollary, excess Gibbs free energy values have been predicted at different temperatures from single temperature data. The method has been applied to twenty-five systems, and excellent agreement has been found between observed and calculated results within a wide temperature interval.

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I. INTRODUCTION

The properties of solutions of non-electrolytes are of interest to chemical engineers, for whom they provide immediate design data, and to physicists and chemists, for whom they represent a potential source of information on the nature of the intermolecular forces and on the way in which these forces determine the structure and the macroscopic properties of matter. From either point of view the ultimate aim of the researcher is to develop methods of predicting properties of solutions either from a very limited number of measurements on solutions or from the properties of the pure components of the solution only.

While a tremendous effort has been made recently toward the solution of problems of mixtures of non-electrolytes, little has been achieved, especially in the theoretical treatment of solutions.

In dealing with problems of solutions, either in thermodynamics or in chemical kinetics, the practice has been, and still commonly is, to assume ideal behavior of the system. Such an assumption, by no means justified, is required because there are no adequate methods, theoretical or semi-empirical, which would enable one to predict with a reasonable degree of certainty the behavior

of solutions. It is the intention of this study to look into this problem and to recommend approaches which would facilitate and speed up the development of exact theories of solutions.

The methods by which the problem of solutions may be attacked belong into three broad groups: theoretical, semi-empirical, and empirical.

The theoretical methods, classical as well as statistical, attempt to evaluate the properties of solutions from properties of the pure components. These methods, when properly developed, would enable one to predict the properties of solutions from the behavior of the pure components only. Many papers have been published recently on this topic (1,2,3,4); unfortunately, none of them represents a general comprehensive theory of solutions. To develop such a theory, it is necessary, first, to find a proper intermolecular potential function which should possess two essential properties: a) it must be universally applicable; b) it must be mathematically manageable enough not to require crude approximations. This does not seem to be forthcom g in the near future.

The semi-empirical methods predict the behavior of solutions from a limited number of experimental data. These theories are further developed (4,5,6,7), and provide reasonable results. In our opinion, these theories will be mainly employed in the near future rather than purely theoretical methods. Further development of

these theories is therefore very desirable.

The empirical methods require a complete set of experimental data. When combined with semi-empirical theories, they may enable the evaluation of some properties of a solution from some other more easily obtainable data.

The present work is a study of the behavior of solutions of non-electrolytes and is concerned with a variety of problems. We have tried to investigate the influence of various factors on the non-ideal behavior of solutions--the excess free energy of binary solutions of non-electrolytes. We have developed semi-empirical relations which may have predictive ability. Specifically, we have concentrated our efforts on the following:

a. Experimental determination of vapor-liquid equilibrium in single component systems.

b. Experimental determination of vapor-liquid equilibrium in specially selected two-component systems.

c. Determination of the influence of the size, shape, and polarity of components on the excess free energy of liquid mixtures.

d. Determination of the effect of the interaction between the dipole moment of one component and the electrons in the π orbital(s) of the other component on the excess free energy of solutions.

e. Thermodynamic study of possible charge-transfer complexes.

f. Determination of structural group contribution to the excess free energy of a mixture.

g. Prediction of the enthalpy of a binary mixture from the excess free energy at a single temperature.

h. Prediction of the excess free energy of a binary mixture at a certain temperature from the value of its excess free energy at another temperature.

II. SOME BASIC THERMODYNAMIC EQUATIONS

In dealing with solutions of non-electrolytes, it is convenient to compare the behavior of a real solution with that of a "model" solution. Such a model solution, which is called an ideal one, must satisfy certain requirements.

An ideal solution is defined by the relation

$$\mu_i(P,T,x_i) = \mu_i^0(P,T) + RT \ln x_i \qquad (i=1, \ldots q)$$

$$= \mu_i^0(P_i^0,T) + \int_{P_i^0}^{P} V_i^0 dP + RT \ln x_i \qquad (1)$$

where $\mu_i^0(P,T)$ is the chemical potential of the pure component i at the temperature and pressure of the system, and $\mu_i^0(P_i^0,T)$ is the chemical potential of the pure component i at its saturated vapor pressure at the temperature of the system (1,8).

From the above definition of an ideal mixture, the following results may be derived for one mole of a solution

$$V = \Sigma x_i V_i^0 \qquad (2a)$$

Consequently,

$$\Delta V_{mix} = 0 \qquad (2b)$$

Further

$$H = \Sigma x_i H_i^0 \tag{3a}$$

Following from this

$$\Delta H_{mix} = 0 \tag{3b}$$

For the thermodynamic functions defined by the second law

$$S = \Sigma x_i S_i^0 - R\Sigma_i x_i \ln x_i \tag{4a}$$

and again

$$\Delta S_{mix} = -R\Sigma_i x_i \ln x_i \tag{4b}$$

Finally

$$G = \Sigma x_i G_i^0 + RT\Sigma_i x_i \ln x_i \tag{5a}$$

and

$$\Delta G_{mix} = RT\Sigma_i x_i \ln x_i \tag{5b}$$

In Eqs. (1 through 5b) V, H, S, and G denote the volume, the enthalpy, the entropy, and the Gibbs free energy of one mole of the mixture, while V_i^0, H_i^0, S_i^0, and μ_i^0 represent the same properties of the pure components; x_i is the mole fraction of component i in the solution.

As is obvious, in the case of an ideal solution, the partial molal properties defined by the first law are equal to the molar properties of the pure components. This is not the case for the thermodynamic properties defined by the second law.

On introducing from Eq. (1) into the condition of vapor-liquid equilibrium, $\mu_{i(g)} = \mu_{i(\ell)}$, we obtain

$$\mu^0_{i(\ell)}(P^0_i,T) + \int_{P^0_i}^{P} V^0_{i(\ell)}\,dP + RT\ \ln x_i$$

$$= \mu^0_{i(g)}(P^0_i,T) + \int_{P^0_i}^{P} V^0_{i(g)}\,dP + RT\ \ln y_i \qquad (6)$$

where the subscripts ℓ and g denote the liquid and the vapor phases, respectively, and y_i is the mole fraction of component i in the vapor phase.

Assuming that the liquid is incompressible, and that the volume of the vapor may be expressed by the virial equation of state (using the second virial coefficient only) we have (1,9)

$$\mu_{i(\ell)}(P^0_i) + RT\ \ln x_i + (P-P^0_i)\ V^0_i$$

$$= \mu_{i(g)}(P^0_i) + RT\ \ln(Py_i/P^0_i) + (P-P^0_i)B_{ii} + 2P\Delta y^2_j \qquad (7)$$

Rearranging Eq. (7) for a two component system results in

$$P = x_1 P^0_1 \exp\left[\frac{(P-P^0_1)(V^0_1-B_{11}) - 2P\Delta y^2_2}{RT}\right] +$$

$$x_2 P^0_2 \exp\left[\frac{(P-P^0_2)(V^0_2-B_{22}) - 2P\Delta y^2_1}{RT}\right] \qquad (8)$$

where Δ is given by

$$\Delta = B_{12} - (1/2)B_{11} - (1/2)B_{22}$$

B_{12} is known as the interaction or cross coefficient.

For mixtures under low pressures and with non-interacting components ($\Delta \simeq 0$) Dalton's law may be applied.

$$P = P_1 + P_2 \tag{10}$$

and the partial pressure of component i can be written as

$$P_i = x_i P_i^0 \exp\left[\frac{(P-P_i^0)(V_i^0-B_{ii}) - 2P\Delta y_j^2}{RT}\right] \tag{11}$$

If the value of the argument of the exponential is negligibly small (close to zero), Eq. (11) reduces to the form

$$P_i = x_i P_i^0 \tag{12}$$

which is Raoult's law.

As is obvious from the aforementioned, Raoult's law does not exactly define an ideal solution. It follows from the exact definition of an ideal solution only after making some simplifying assumptions such as $B_{ii} = 0$, $V_i^0 = 0$. Because the condition $V_i^0 = 0$ is never met, Raoult's law represents only an approximation to an ideal solution (8,10).

Solutions which obey the equations derived for an ideal solution exactly are not found in practice. Real solutions exhibit deviations from ideal behavior. In order to make Eq. (1) applicable to non-ideal solutions,

G. N. Lewis (11) recommended a new thermodynamic property, called activity. This property is related to the chemical potential in the same manner as is the mole fraction to the chemical potential in an ideal solution. Thus

$$\mu_i(P,T,x_i) = \mu_i^0(P,T) + RT \ln a_i \tag{13}$$

where the activity a_i is pressure[†] (slightly), temperature, and concentration dependent. The value of a_i, however, depends strongly on the standard state chosen. Using the pure component at the temperature and pressure of the system as standard state, we may write

$$a_i = \gamma_i x_i \tag{14}$$

where γ_i is the activity coefficient. If $\gamma_i<1$, the system is said to exhibit negative deviation from ideal behavior, and if $\gamma_i>1$, the system is said to show a positive deviation from ideal behavior. Both kinds of solutions can be found; nevertheless, solutions exhibiting positive deviations are more common.

Replacing the mole fraction in Eq. (5b) with activity results in the Gibbs free energy of mixing of a non-ideal solution

$$\Delta G_{mix} = RT\sum_i x_i \ln a_i \tag{15}$$

[†]In the liquid phase.

Since $a_i = \gamma_i x_i$, Eq. (15) may also be written as

$$\Delta G_{mix} = RT\sum_i x_i \ln x_i + RT\sum_i x_i \ln\gamma_i \qquad (16)$$

where the first term on the right-hand side of the equation is identical with the ideal Gibbs free energy of mixing. The second term on the right-hand side of the equation, which is responsible for the non-ideal behavior of the solution, is called the Excess Gibbs Free Energy of Mixing (12). Thus

$$G^E = RT\sum_i x_i \ln\gamma_i \qquad (17)$$

Replacing the mole fraction in Eq. (11) by the activity, we obtain

$$P_i = x_i\gamma_i P_i^0 \exp\left[\frac{(P-P_i^0)(V_i^0-B_{ii}) - 2P\Delta y_j^2}{RT}\right] \qquad (18)$$

For a two-component liquid mixture in equilibrium with its vapor phase it follows that

$$\ln\gamma_1 = \ln\frac{y_1 P}{x_1 P_1^0} - \frac{(P-P_1^0)(V_1^0-B_{11})}{RT} + \frac{2Py_2^2\Delta_{12}}{RT} \qquad (19)$$

$$\ln\gamma_2 = \ln\frac{y_2 P}{x_2 P_2^0} - \frac{(P-P_2^0)(V_2^0-B_{22})}{RT} + \frac{2Py_1^2\Delta_{12}}{RT} \qquad (20)$$

When the activity coefficient of only one of the components is known as a function of the concentration,

and the dependence of the activity coefficient of the second component on the concentration has to be evaluated, the Gibbs-Duhem equation is applied

$$SdT - VdP + \sum_i x_i d\mu_i = 0 \tag{21}$$

Since $\mu_i^E = RT \ln\gamma_i$, the Gibbs-Duhem equation may be written in a more useful form

$$\sum_i (x_i d\ln\gamma_i)_{T,P} = 0 \tag{22}$$

Thus, if the activity coefficients of both components are known in a wide range of concentration, the Gibbs-Duhem equation may serve as a test for the thermodynamic consistency of the experimental vapor-liquid equilibrium data, from which the activity coefficients have been calculated. The consistency test is derived as follows:

For a two component system at constant P and T, Eq. (22) may be written as

$$x_1 \left(\frac{\partial \mu_1^E}{\partial x_1}\right)_{T,P} dx_1 = x_2 \left(\frac{\partial \mu_2^E}{\partial x_2}\right)_{T,P} dx_2 \tag{23}$$

Upon integrating within the limits $x_1 = 0$, $x_1 = 1$, and $x_2 = 0$, $x_2 = 1$, we obtain

$$x_1 \mu_1^E \Big|_{x_1=0}^{x_1=1} - \int_{x_1=0}^{x_1=1} \mu_1^E dx_1 = x_2 \mu_2^E \Big|_{x_2=0}^{x_2=1} - \int_{x_2=0}^{x_2=1} \mu_2^E dx_2 \qquad (24)$$

Since μ_1^E is finite at $x_1 = 0$ and zero at $x_2 = 1$, Eq. (24) reduces to the form

$$\int_{x_1=0}^{x_1=1} (\mu_1^E - \mu_2^E) dx_1 = 0 \qquad (25)$$

Consequently,

$$\int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2) dx_1 = 0 \qquad (26)$$

which implies that, for thermodynamic consistency, the value of the integral in the given limit is equal to zero at constant T and P.

Eq. (26) provides an area test for the consistency of phase-equilibrium data. A plot of $\ln(\gamma_1/\gamma_2)$ versus x_1 is prepared and the areas above and below the x_1 axis are compared. The requirement of thermodynamic consistency is met if the two areas are equal. A small difference in the two areas, which may be caused by the fact that vapor-liquid equilibrium data are either taken at constant temperature or at constant pressure (both cannot be kept

constant as required by Eq. (26)) is not necessarily an indication of the non-consistency of the data.

III. THEORIES OF LIQUID MIXTURES

It is impossible in this introductory chapter to discuss in detail all the known theories of solutions. Our effort will be therefore concentrated on the most commonly applied ones and on those which are in some way connected with the results presented in this work.

A. Regular Solution Theory

Solutions which behave ideally with respect to only some of their thermodynamic properties cannot be treated as ideal solutions. Non-ideal solutions exhibiting ideal entropies of mixing are called Regular Solutions (13,14), while mixtures having zero values of enthalpy of mixing are called Athermal Solutions (13,15).

The theory of regular solutions was developed by Hildebrand (14,16) and Scatchard (17,18,19). From its basic definition

$$\Delta S = -R\sum_i x_i \ln x_i \qquad (27)$$

it follows that the mixing of a regular solution is random. Hildebrand, making use of the classical van der Waals equation (20), derived the following equation for the excess Gibbs free energy of a binary mixture[†]

[†] $G^E = H^E - TS^E = H^E$ since $S^E = 0$.

$$G^E = H^E = (x_1 V_1^0 + x_2 V_2^0)(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \qquad (28)$$

where ϕ_i is the volume fraction defined by

$$\phi_i = (x_i V_i^0)/(\sum_i x_i V_i^0) \qquad (29)$$

and δ_i, called the "solubility parameter", is given as

$$\delta_i = \left(\frac{\Delta E^{vap}}{V_i^0}\right)^{1/2} = \left(\frac{\Delta H^{vap}-RT}{V_i^0}\right)^{1/2} \qquad (30)$$

As is obvious from the last few equations, the behavior of regular solutions may be discussed on the basis of properties of the pure components only: the heats of vaporization and the molar volumes of the individual components. Since $(\delta_1-\delta_2)^2$ is always positive, this theory predicts only positive values for the thermodynamic excess properties.

Differentiation of Eq. (28) with respect to the number of moles results in

$$RT \ln\gamma_1 = V_1^0 \phi_2^2 (\delta_1-\delta_2)^2 \qquad (31)$$

and

$$RT \ln\gamma_2 = V_2^0 \phi_1^2 (\delta_1-\delta_2)^2 \qquad (32)$$

These two equations can be rearranged easily into the forms

$$\ln\gamma_1 = A\phi_2^2 \qquad (33)$$

and

$$\ln\gamma_2 = B\phi_1^2 \tag{34}$$

where

$$A = V_1^0(\delta_1-\delta_2)^2/RT \tag{35}$$

and

$$B = V_2^0(\delta_1-\delta_2)^2/RT \tag{36}$$

When the difference between the two molar volumes of the pure components is negligibly small, then A = B. It will be seen in Ch. IV that in such a case the regular solution theory yields exactly the same expressions for the activity coefficients as do the third order Margules and van Laar equations for symmetrical systems (Eqs. 88 and 89).

The regular solution theory predicts the activity coefficients of many solutions containing non-polar as well as polar components fairly well. Because of the various assumptions made in the derivation, quantitative agreement between the calculated and the experimentally found results is not expected. However, for approximate work, i.e. for reasonable estimates in the absence of any mixture data, the regular solution theory can provide useful information. Better results are obtained from the extended regular solution theory (21).

$$\ln\gamma_i = \left[(V_i^0\phi_j^2)/(RT)\right]\left[(\delta_i-\delta_j)^2 + 2\ell_{ij}\delta_i\delta_j\right] \tag{37}$$

where ℓ_{ij} is a binary interaction parameter, to be determined experimentally. As Eq. (37) indicates, the interaction term becomes especially significant for systems in which the solubility parameters of the constituents are approximately equal.

X-ray studies on liquids have proved that even in the liquid state there exists a certain degree of regularity in structure. This is especially true at temperatures near the melting point. Therefore, some researchers have applied the theories of solids to liquid systems. These are the so-called solid-like or lattice theories of liquids (22).

Guggenheim developed the lattice theory of regular solutions which he called "The Strictly Regular Solution Theory" (15). A brief discussion of only the zeroth approximation of this theory is presented here.

In the zeroth approximation of the "Strictly Regular Solution" theory, the following assumptions are made (23):

a. The particles are regularly arranged at the crystal lattice sites.

b. Each particle occupies one lattice site only.

c. The only motion possible is the oscillation of the particles around their equilibrium positions.

d. Interactions are possible between the nearest neighbors only.

e. Molecules of species A and B are sufficiently similar in size and shape so that they are interchangeable at the lattice sites.

f. The lattice is solid and therefore $V^E = 0$.

g. The partition function is factorable and only the lattice (configurational) partition function is concentration dependent.

Under such conditions, the following equation may be applied to the total interaction energy:

$$W_m = N_{AA}w_{AA} + N_{AB}w_{AB} + N_{BB}w_{BB} \tag{38}$$

where N_{AA}, N_{BB}, and N_{AB} denote the number of neighboring pairs of type A-A, B-B, and A-B respectively, while w_{AA}, w_{BB}, and w_{AB} are the corresponding interaction energies. W_m is the total potential energy of the mixture.

Next it will be shown that N_{AA}, N_{BB}, and N_{AB} are mutually related. Defining z as the number of nearest neighbors (the lattice coordination number: simple cubic lattice, z = 6, body-centered cubic lattice, z = 8, face-centered cubic lattice, z = 12), the products zN_A and zN_B denote the total number of nearest occupied positions around molecules A and B, respectively. Subtracting from these the number of pairs of type A-B, we obtain twice the number of pairs of type A-A and B-B:

$$2N_{AA} = zN_A - N_{AB} \tag{39}$$

$$2N_{BB} = zN_B - N_{AB} \tag{40}$$

Eq. (38) can thus assume the form

$$W_m = \frac{zN_A w_{AA}}{2} + \frac{zN_B w_{BB}}{2} + N_{AB}\left(w_{AB} - \frac{w_{AA}}{2} - \frac{w_{BB}}{2}\right)$$

$$= N^0_{AA} w_{AA} + N^0_{BB} w_{BB} + N_{AB}\left(w_{AB} - \frac{w_{AA}}{2} - \frac{w_{BB}}{2}\right)$$

$$= W^0_{AA} + W^0_{BB} + N_{AB} w \qquad (41)$$

where

$$N^0_{AA} = \frac{zN_A}{2};\quad N^0_{BB} = \frac{zN_B}{2};\quad W^0_{AA} = N^0_{AA} w_{AA};$$

$$W^0_{BB} = N^0_{BB} w_{BB};\quad w = \left(w_{AB} - \frac{w_{AA}}{2} - \frac{w_{BB}}{2}\right)$$

The partition functions of the pure components are given merely by the Boltzmann factors

$$Q_A = \exp(-W^0_{AA}/kT) \qquad (42)$$

$$Q_B = \exp(-W^0_{BB}/kT) \qquad (43)$$

In the partition function of the mixture, the degeneracy number of the levels, due to the different distributions of the molecules A and B over the lattice sites, must be considered.

With each potential energy of the mixture, $W_{m,i}$ (dependent on N_{AB}), a certain degeneracy factor, $g_i(N_A, N_B, N_{AB})$ is associated. The partition function of the mixture is thus given by

$$Q_m = \sum_i g_i(N_A, N_B, N_{AB}) \exp(-W_{m,i}/kT) \qquad (44)$$

In the case where w = 0 (ideal system), the interaction energy of the system remains the same for all possible arrangements of the molecules, and $W_{m,i}$ ($\equiv W^0_{AA} + W^0_{BB}$) may be factored out of the summation. The sum of the degeneracy numbers is then equal to the number of possible (distinguishable) arrangements of the N_A and N_B elements among the $N_A + N_B$ ($\equiv N$) positions:

$$\sum_i g_i(N_A, N_B, N_{AB}) = \frac{(N_A + N_B)!}{N_A! N_B!} \qquad (45)$$

For values of w slightly different from zero, it can be assumed that the distribution of the molecules (A and B) among the lattice positions is random; this is the basis of the crude treatment or the so-called zeroth approximation. Thus, the number of molecules of a certain type surrounding any given molecule in a system is given by the product of the nearest neighbors, z, and the mole fraction of that certain type of molecule in the mixture. The number of A-B pairs is then given by the relation

$$N_{AB} = N_A z \frac{N_B}{N} = N_B z \frac{N_A}{N} = N z x_A x_B \qquad (46)$$

The lattice partition function of the random mixture thus takes the form

$$Q_m = \frac{N!}{N_A!N_B!} \exp\left[-(W^0_{AA}/kT) - (W^0_{BB}/kT) - (Nzx_Ax_Bw/kT)\right] \tag{47}$$

and its Helmholtz free energy is

$$F_m = -kT \ lnQ_m = -kT \ ln\frac{N!}{N_A!N_B!} + W^0_{AA} + W^0_{BB} + Nzx_Ax_Bw \tag{48}$$

Using Stirling's folmula, we obtain

$$F_m = -kT(NlnN - N_AlnN_A - N_BlnN_B) + W^0_{AA} + W^0_{BB} + Nzx_Ax_Bw \tag{49}$$

For the Helmholtz free energy of mixing, we write

$$\Delta F_{mix} = F_m - F_A - F_B$$

$$= -kT \ (NlnN - N_AlnN_A - N_BlnN_B) +$$

$$W^0_{AA} + W^0_{BB} + Nzx_Ax_Bw - W^0_{AA} - W^0_{BB}$$

$$= -kT \ (NlnN - N_AlnN_A - N_BlnN_B) + Nzx_Ax_Bw$$

$$= -kTN(lnN - x_Alnx_AN \ - x_Blnx_BN \ ) + Nzx_Ax_Bw$$

$$= -RT \ (lnN - x_Alnx_AN \ - x_Blnx_BN \ ) + Nzx_Ax_Bw$$

$$= -RT \ (x_Alnx_A + x_Blnx_B) + Nzx_Ax_Bw \tag{50}$$

Since $V^E = 0$, and therefore $\Delta F_{mix} = \Delta G_{mix}$, it is seen upon comparison of Eq. (50) with Eq. (16) that

$$G^E = Nzx_Ax_Bw = N_AkT\ \ln\gamma_A + N_BkT\ \ln\gamma_B \qquad (51)$$

Taking the derivative of Eq. (51) with respect to N_i and making use of the Gibbs-Duhem equation results in

$$(\partial G^E/\partial N_i)_{N_j,T} = kT\ \ln\gamma_i = zwx_j^2 \qquad (52)$$

Consequently

$$\ln\gamma_A = \frac{zw}{kT}\,x_B^2 = Ax_B^2 \qquad (53)$$

and

$$\ln\gamma_B = \frac{zw}{kT}\,x_A^2 = Ax_A^2 \qquad (54)$$

Eqs. (53 and 54) are identical to Eqs. (33 and 34) when the molar volumes of the two components are almost equal. Thus the results of this statistical theory are similar to the results given by the Hildebrand-Scatchard theory of regular solutions (6).

One of the major assumptions in the derivation of both Hildebrand's regular solution theory and the zeroth approximation of the strictly regular solution theory is that the excess entropy of mixing is zero (random mixing). The study of preferential ordering in mixtures due to the differences in the interaction energies and the corresponding entropy contribution has received much attention

recently (24). It is known in the literature as the order-disorder effect (25,26).

A rigorous solution to the order-disorder problem has not yet been developed. Guggenheim (27), Rushbrooke (28), and Kirkwood (29) made exhaustive studies of the order-disorder problem using the quasi-lattice model of the liquid mixtures. Although numerous treatments have appeared in recent years (30,31,32,33), the most preferred procedure still remains the quasi-chemical approximation of Guggenheim (15,27), which is sometimes referred to as the first approximation, as distinct from the zeroth approximation. Assuming without proof what has become known as the "quasi-chemical" condition, Guggenheim expresses the equilibrium condition for the formation of A-B pairs from A-A and B-B pairs in a form analogous to the mass-action law for chemical reaction. Thus he writes

$$\frac{(N_{AB}/z)}{(N_A - N_{AB}/z)(N_B - N_{AB}/z)} = \exp\left(-\frac{2\omega}{zkT}\right) \qquad (55)$$

where $\omega/z = w$. Guggenheim then derives all the thermodynamic properties of the mixture from Eq. (55). The expression for the excess Gibbs free energy of mixing is

$$G^E = \frac{RTz}{2}\left[x_1 \ln \frac{\beta-1+2x_1}{x_1(\beta+1)} + x_2 \ln \frac{\beta-1+2x_2}{x_2(\beta+1)}\right] \qquad (56)$$

where β is defined by

$$\beta = \left[1 + 4x_1 x_2 \left(e^{-\frac{2\omega}{zkT}} - 1 \right) \right]^{\frac{1}{2}} \qquad (57)$$

In Eqs. (55 to 57), ω is called the "interchange energy."

B. Molecular Theories

It is a well known fact that while exact molecular theories of solids and gases have been developed during the last twenty years, no reasonable theory of liquids is available in the literature. The same statement can be made about liquid solutions. Many papers (3) and books (1,2,4,6,7,13,15) dealing with the subject of theories of solutions have been published. Unfortunately, none of the derived theories is able to supply reasonably good results. Sometimes a certain theory may describe well the behavior of a given system, but fails completely when applied to another system.

Again, an exhaustive presentation of all the theories cannot possibly be given in this short discussion. Therefore, a rather selective review of the work done in this field will be presented. The study of these fundamental theories indicates that most of the results supplied by these theories are very poor indeed, even in the case of highly simple systems, such as O_2-N_2, Ar-Kr, etc. Since in our opinion there is no hope, at least in the forseeable future, for the derivation of a rigorous molecular theory (considerable time working on this problem has been spent in our laboratory without success), our efforts were

concentrated on developing semi-empirical methods. It is our strong belief that semi-empirical theories will prevail for a long time to come in the field of solutions.

Before entering into the discussion of the semi-empirical theories, a short summary of the most commonly used molecular theories of solutions is presented.

Common to all these theories is the so-called canonical partition function which in the case of a pure liquid is defined as

$$Q = q_{kin} \cdot q_{int} \cdot Z \tag{58}$$

where q_{kin} is the partition function responsible for the translational motion of the molecules, and q_{int} is the partition function responsible for the internal motion of the molecules (vibration, rotation). Both may be evaluated from the properties of substances in the ideal gas state. Z is the configurational part of the partition function. It is defined by the integral

$$Z = \frac{1}{N!} \int \ldots \int \exp\left(-\frac{U}{kT}\right) dr_1 \ldots dr_N \tag{59}$$

where U is the potential energy arising from the interaction of particles being at positions $r_1, \ldots r_N$. Since no exact potential energy function is known, the evaluation of the configurational integral cannot be done exactly.

For a mixture of spherically symmetrical molecules

of species 1, 2, etc., the configurational integral is written as

$$Z = \frac{1}{\prod_i N_i!} \int \cdots \int \exp\left(-\frac{U}{kT}\right) dr_1 \cdots dr_N \qquad (60)$$

where i is 1, 2, etc., and $\Sigma N_i = N$.

It must be understood that the potential energy, U, depends not only on the positions of the N molecules, but also on their assignment by species to these positions. A value of U = 0 defines an ideal solution. If U is averaged over all assignments of molecules to the positions of each configuration, the mixture is considered to be random. In real solutions, where assignments of molecules to different positions is irregular (some positions are preferred), the problem of evaluating U becomes more complex (34).

A random mixture of an arbitrary composition may be treated as having the same configurational thermodynamic properties as a hypothetical pure substance called the "equivalent substance." Thus, the configurational properties of the equivalent substance (which may be evaluated) are equal to the configurational properties of the random mixture. Such an approach is denoted as the <u>random mixture approach</u> by Brown (30), <u>the crude approximation</u> by Prigogine (2), and the <u>one-fluid model</u> by Scott (35).

The random mixture approximation provides reasonable results for systems containing molecules of equal size (1).

However, it fails completely for mixtures containing molecules of different sizes.

The corresponding states theory, originally proposed by Pitzer (36), seems to be the most promising approach towards the evaluation of Z. This theory is based on the universal potential function given as

$$\varepsilon_{ij} = \varepsilon^*_{ij}\phi(r_{ij}/r^*_{ij}) \tag{61}$$

where r_{ij} is the distance between centers of molecules i and j, ε^*_{ij} and r^*_{ij} are characteristic parameters of the pair, and $\phi(r/r^*)$ is a universal function of its argument. Usually, the pair potential ε_{ij} is expressed by the Lennard-Jones function (37)

$$\varepsilon_{ij} = \varepsilon^*_{ij}\left[(r^*_{ij}/r_{ij})^{12} - 2(r^*_{ij}/r_{ij})^{6}\right] \tag{62}$$

In Eq. (62) ε^*_{ij} and r^*_{ij} are the minimum value of the potential well and the corresponding intermolecular distance, respectively. They can be evaluated from the Lorentz-Berthelot combination rule (38), i.e.,

$$r^*_{ij} = (\tfrac{1}{2})(r^*_{ii} + r^*_{jj}) \tag{63}$$

$$\varepsilon^*_{ij} = (\varepsilon^*_{ii} \cdot \varepsilon^*_{jj})^{\frac{1}{2}} \tag{64}$$

Further application of the corresponding states principle was made by Longuet-Higgins in his development of the conformal solution theory (39). A generalized

theory derived from the corresponding states principle has been recommended by Prigogine and his coworkers (2,40), and by Scott (35). They combined the concept of the average potential from the cell model (22) with the theorem of corresponding states. This combined model of theories of solutions is called the Average Potential Model (2), or the Corresponding States Theory of Mixtures (35). Some modifications and extensions of this theory have been proposed by many researchers (30,41,42,43,44).

Scott (35) has recommended three different ways for the averaging of the intermolecular energy parameters for mixtures, the "one-fluid" model (already mentioned), the "two-fluid" and the "three-fluid" models. The first two models are equivalent to Prigogine's "crude approximation" and the "refined version," respectively.

Balescu (45) extended the Prigogine theory to solutions of molecules of different sizes and different central interactions. He discussed binary solutions with pure dipolar interactions and inductive forces for the case of one polar constituent and found good agreement for the system CCl_4-$CHCl_3$. Rowlinson (1) pointed out that Balescu's treatment suffers from a faulty averaging of the direct dipole-dipole term. The major difficulty with the theory was to find a mixture of spherical or near-spherical molecules in which the excess functions are determined mainly by dipole-dipole interactions. Anantaraman et al. (46,47) found that a departure from the combination rule

used in Balescu's theory gave good agreement with experiment (48-52). Of particular interest is the thorough discussion of the average potential model given by Bellemans, Mathot, and Simon (53). They also emphasize the unsatisfactory results of the geometric and arithmetic combining rules for the intermolecular energy parameters. Additionally, instead of using a Taylor series expansion to represent the properties of the mixture in terms of those of a single reference substance, they construct empirical relations between the reduced thermodynamic quantities and the reduced values of T and P. Thus they give a detailed analysis of the Average Potential Model ("two-liquid") for the excess properties of the following five mixtures: $CO-CH_4$, $Ar-CH_4$, N_2-O_2, N_2-Ar, and O_2-Ar. They conclude that this is a valuable method for predicting the sign of the main excess functions of mixtures of roughly spherical molecules. They find the situation less favorable, however, from a quantitative point of view. These remarks are also substantiated by Bellemans and Vilcu (54), Fuks and Bellemans (55), Wheeler and Smith (56), and Streett and Stavely (57) among others.

A very significant contribution in the field of molecular theories of solutions was made by Leland, Rowlinson, and Sather (58). They deal essentially with statistical thermodynamics of mixtures of molecules of different sizes based on the Percus-Yevick equation (59). Since a central aspect of the theory is based on an

approximation for mixtures of a type originally suggested by van der Waals (20), the method is called the "one-fluid van der Waals" approach. In his theory of mixtures van der Waals assumed that the parameters of his equation of state, a and b, were quadratic sums of a_{ij} and b_{ij}, or

$$a = \sum_{ij}\sum x_i x_j a_{ij} \tag{65}$$

$$b = \sum_{ij}\sum x_i x_j b_{ij} \tag{66}$$

This quadratic form is used by Leland et al., although the developed equations are not tied to the van der Waals equation of state. They observe that the work of previous years on pure fluids has shown that even at low temperatures the structure is determined primarily by the repulsive forces, and that the attractive forces merely provide the so-called "internal pressure" which maintains the high fluid density. This observation provides the basis for considering the Percus-Yevick result for mixtures of hard spheres to be equally relevant to mixtures of real molecules. Their calculations show that the van der Waals approximation avoids the false large positive contribution to G^E and H^E of earlier theories, and improves the agreement with experimental results.

In a second paper, Leland et al. (60) extended the van der Waals' approximation to a two-fluid model which takes into account the departures from a random distribution

induced by differences of intermolecular energy. Their treatment was also extended to mixtures of molecules of different shapes. The two-fluid van der Waals model has the advantages of (a) leading to results similar to those of the one-fluid van der Waals model for molecules that differ only in size (which avoids the basic fault of the random mixing approximation); (b) leading to the same degree of order in mixtures that differ only in energy as the two-fluid modification of the random mixing approximation (i.e., the Average Potential Model); and (c) having the reference substance which is used as the source of the free energy not necessarily the same for each component. Leland et al., present results based on the two-fluid van der Waals approximation assuming geometric mean rule. They take also "shape" factors into account by adjusting values of the cross-term in the energies. The results of using the van der Waals approximation seem to be significantly better than the random mixing approximation.

An approach not based on the theorem of corresponding states has been recommended by Flory and his coworkers (61,62). In their original work they dealt specifically with chain molecules and with their mixtures. Later they adapted the theory to mixtures of pseudospherical molecules of comparable volume and to mixtures differing in size and shape (63,64,65). In his theory Flory differs from most of the other authors by using a potential energy function recommended by Frank (66) instead of the tradi-

tionally used Lennard-Jones potential. Flory claims good results. Nevertheless, poor agreement with experimental data was observed when the theory was applied to systems investigated in this work.

In papers published very recently, Anderson and Chandler (67,68) have developed a generalization of the original Mayer cluster theory (69,70) using powerful mathematical techniques of topological reduction and functional differentiation. Their generalization arises when the intermolecular potential is separated into two parts, a "reference" part and a perturbation. Their work, still in progress, is a promising step towards the development of practical techniques for employing equilibrium statistical mechanics for the study of realistic models of dense molecular fluids.

The objective of this brief and selective review of the most commonly used statistical theories of liquid mixtures has been to present some of the basic premises of the theoretical approaches in the field. The list of workers who have used one or more of the molecular theories of solution to explain and predict the thermodynamic properties of liquid mixtures is quite extensive (3).

According to Rowlinson (71), McGlashan (72), and others, most of the theories of liquid solutions should be tested on simple systems composed of spherical, non-polar molecules. The strict assumptions inherent in the derivations of the statistical theories of solutions

prohibit the application of these theories to more complex systems. While much progress has been made in relaxing the rigorous conditions of non-polarity and spherical symmetry (1), we are still far from an adequate theory of liquid mixtures (4).

It is therefore clear that at this state of development in the theories of mixtures, one cannot have the expectation that the molecular or statistical theories will make it possible to predict reliably the thermodynamic properties of mixtures. Even though the qualitative agreement between theory and experiment for simple mixtures seems to be fairly good (53), quantitative agreement leaves much to be desired (3). The main interest in the present theories of solutions does not lie in the numerical agreement with experimental data, but in the possibility of arriving at a deeper understanding of the complex relations between intermolecular forces and thermodynamic excess functions.

At this point we would like to mention the work done by us in the field of statistical theories of solutions. We tried to separate the non-ideal behavior of solutions into different contributions: size-size, shape-shape, and dipole-dipole. Our experimental results, however, show not only disagreement between the measured and predicted values, but also prove that the separability theory as treated by us is not feasible and needs further improvement. The disagreement may be explained by the fact that

this approach ignores completely the contributions due to the mixed interactions, such as size-shape, size-dipole, etc. It is also worthwhile to mention that the theory developed by us cannot account for the contributions due to the polarizability of the molecules. Since at this moment we are not in a position to introduce further improvement into the theory, we have not made it the major concern of the dissertation.

IV. SEMI-EMPIRICAL METHODS

Since, at present, no satisfactory theory exists that provides a sound basis for either prediction or correlation of thermodynamic data for binary liquid mixtures in general, the practice of depending primarily upon direct experimental measurement of equilibria is widespread. Concurrently, the incentive to develop empirical and semi-empirical methods that can correlate thermodynamic properties of mixtures as a function of temperature, pressure, and composition, still remains strong.

A. Brief Survey

Many semi-empirical methods dealing with the properties of solutions are available in the literature (4,5,6). A common feature of all these methods is that they must obey the Gibbs-Duhem equation. The majority of them may be derived from the procedure proposed by Wohl (73,74).

Wohl (73) expressed the dependence of G^E on the composition of the liquid phase by the expansion

$$\frac{G^E}{2.303RT\sum_i q_i x_i} = \sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \sum_{ijkl} z_i z_j z_k z_l a_{ijkl} + \cdots \tag{67}$$

where q_i, q_j, q_k, q_l, . . . are constants which Wohl called the effective molar volumes of the constituents i, j, k, l, . . . and z_i, z_j, z_k, z_l, . . . are the effective volume fractions of these constituents, defined by the equation

$$z_i = \frac{q_i x_i}{\sum_j q_j x_j} \tag{68}$$

Volumetric fractions, like mole fractions, are related by the condition

$$\sum_i z_i = \sum_i \frac{q_i x_i}{\sum_j q_j x_j} = 1 \tag{69}$$

The empirical constants a_{ij}, a_{ijk}, a_{ijkl}, . . . measure the interactions in various groups of molecules, ij, ijk, ijkl, . . .

The first summation ($\sum_{ij}$) in Eq. (67) gives the sum of the products of the volumetric fractions ($z_i z_j$) of all pairs of dissimilar constituents that can be chosen from the given n-component system, where each product is multiplied by a constant, a_{ij}, which is related to the force interactions between the corresponding pair of molecules.

Similarly, the second summation, ($\sum_{ijk}$), gives the sum of the products of the volumetric fractions ($z_i z_j z_k$) of all triplets of at least partially dissimilar constituents that can be chosen from the given n-component system, where each product is multiplied by a constant, a_{ijk}, which

is related to the force interactions among this triplet of molecules etc.

For example for a binary system

$$\sum_{ij} z_i z_j a_{ij} = z_1 z_2 a_{12} + z_2 z_1 a_{21} = 2 z_1 z_2 a_{12} \tag{70}$$

since $a_{12} = a_{21}$. Similarly, for a ternary system

$$\begin{aligned} \sum_{ij} z_i z_j a_{ij} &= z_1 z_2 a_{12} + z_1 z_3 a_{13} \\ &+ z_2 z_3 a_{23} + z_3 z_1 a_{31} + z_3 z_2 a_{32} \\ &+ z_2 z_1 a_{21} = 2 z_1 z_2 a_{12} + 2 z_1 z_3 a_{13} + 2 z_2 z_3 a_{23} \end{aligned} \tag{71}$$

Eq. (67) as written is an equation of the fourth order. If the last summation is left out, it becomes an equation of the third order, which although simpler is less precise. It is obvious that the more summation terms there are in an equation, the better it will represent the behavior of the given system, but the more constants will need to be determined from experimental data. In practice equations of third and fourth order are mainly used.

Let us consider the derivation of the Wohl equation of the third order for a binary system.

According to Eq. (67)

$$\begin{aligned} \frac{G^E}{2.303RT} \cdot \frac{1}{(q_1 x_1 + q_2 x_2)} &= 2 z_1^2 z_2 a_{112} \\ &+ 3 z_1^2 z_2 a_{112} + 3 z_1 z_2^2 a_{122} \end{aligned} \tag{72}$$

Since the sum of the effective volumetric fractions of the constituents in the system is equal to unity, any term of Eq. (72) can be multiplied by $(z_1 + z_2)$ and this equation can be rearranged to the form

$$\frac{G^E}{2.303RT} = (x_1 + \frac{q_2}{q_1} x_2) z_1 z_2 \left[z_1 q_2 (2a_{12} + 3a_{112}) + z_2 q_1 (2a_{12} + 3a_{122}) \right] \quad (73)$$

After introducing the new constants

$$A = q_1 (2a_{12} + 3a_{122}) \; ; \; B = q_2 (2a_{12} + 3a_{112}) \quad (74)$$

one can write

$$\frac{G^E}{2.303RT} = \left[x_1 + (q_2/q_1) x_2 \right] z_1 z_2 \left[z_1 B (q_1/q_2) + z_2 A \right] \quad (75)$$

The relations giving the dependence of the activity coefficients of constituents 1 and 2 on the composition of the solution are obtained by partial differentiation of the excess free energy with respect to n_1 and n_2. Thus

$$\log \gamma_1 = \frac{\partial}{\partial n_1} \left[(n_1 + n_2) \frac{G^E}{2.303RT} \right] \quad (76)$$

After substituting the expressions

$$z_1 = \frac{n_1}{n_1 + n_2 (q_2/q_1)} \; ; \; z_2 = \frac{n_2 (q_2/q_1)}{n_1 + n_2 (q_2/q_1)} \quad (77)$$

for z_1 and z_2, we obtain

$$\log\gamma_1 = \frac{n_2^2 (q_2/q_1)^2 \left[-n_1 A + 2n_1 B(q_1/q_2) + n_2 A(q_2/q_1)\right]}{\left[n_1 + n_2(q_2/q_1)\right]^3} \tag{78}$$

If the effective volumetric fractions are introduced as variables in this relation, we find the final form of the Wohl equation of the third order for a binary system

$$\log\gamma_1 = z_2^2 \left[A + 2z_1 \left(B \frac{q_1}{q_2} - A\right)\right] \tag{79}$$

In an entirely analogous manner we find for the other constituent

$$\log\gamma_2 = z_1^2 \left[B + 2z_2 \left(A \frac{q_2}{q_1} - B\right)\right] \tag{80}$$

Eqs. (79 and 80) contain three constants, A, B, and q_2/q_1, which must be determined from the experimental measurements.

By introducing various simplifying assumptions, these equations are converted to relations derived earlier by various authors. Thus if the effective molar volumes q_1 and q_2 are replaced by the molar volumes of the pure constituents V_1^0 and V_2^0, we obtain the equation which was derived by Scatchard and Hamer (75).

$$\log\gamma_1 = z_2^2\left[A + 2z_1\left(B \cdot \frac{V_1^0}{V_2^0} - A\right)\right] \tag{81}$$

$$\log\gamma_2 = z_1^2\left[B + 2z_2\left(A \cdot \frac{V_2^0}{V_1^0} - B\right)\right] \tag{82}$$

and in this case

$$z_1 = \frac{x_1}{x_1 + x_2(V_2^0/V_1^0)} \text{ ; and } z_2 = \frac{x_2(V_2^0/V_1^0)}{x_1 + x_2(V_2^0/V_1^0)} \tag{83}$$

If it is assumed that $q_2/q_1 = B/A$, Eqs. (79 and 80) become the van Laar equations of the third order (76) in the Carlson and Colburn modification (77)

$$\log\gamma_1 = Az_2^2 = \frac{Ax_2^2}{\left[x_1(A/B) + x_2\right]^2} = \frac{A}{\left[1 + \frac{x_1}{x_2} \cdot \frac{A}{B}\right]^2} \tag{84}$$

$$\log\gamma_2 = Bz_1^2 = \frac{Bx_1^2}{\left[x_2(B/A) + x_1\right]^2} = \frac{B}{\left[1 + \frac{x_2}{x_1} \cdot \frac{B}{A}\right]^2} \tag{85}$$

Finally, on the assumption that $q_2/q_1 = 1$, Eqs. (79 and 80) take the form of the Margules equations of the third order (78)

$$\begin{aligned} \log\gamma_1 &= x_2^2\left[A + 2x_1(B - A)\right] \\ &= x_2^2(2B - A) + 2x_2^3(A - B) \end{aligned} \tag{86}$$

$$\log\gamma_2 = x_1^2\left[B + 2x_2(A - B)\right]$$
$$= x_1^2(2A - B) + 2x_1^3(B - A) \qquad (87)$$

With symmetrical systems for which A = B, both the Margules and van Laar equations further simplify to the common form

$$\log\gamma_1 = Ax_2^2 \qquad (88)$$

$$\log\gamma_2 = Ax_1^2 \qquad (89)$$

The constants A and B in all these equations are the limiting values of the logarithm of the activity coefficients. Thus

$$A = \lim_{x_1 \to 0} \log\gamma_1 \quad ; \quad B = \lim_{x_2 \to 0} \log\gamma_2 \qquad (90)$$

All the constants which occur in Eqs. (79 to 89) must be determined from experimental data. They can be determined

(a) from known equilibrium compositions of the vapor and liquid phases,

(b) from the known isothermal dependence of the saturated vapors on the composition (i.e. from the curve of P-x),

(c) from the known isobaric dependence of the azeotropic mixture,

(d) from the known isobaric dependence of the boiling points of the mixture on composition (i.e. from the curve T-x).

Wohl's work has had a profound influence on applied vapor-liquid equilibrium thermodynamics. However, it excludes some potentially very useful models for the excess Gibbs free energy. For example, it is not possible to derive from Wohl's expansion the equation of Flory (79,80) and Huggins (81,82). Furthermore, Wohl's expansion does not take into account the concept of local mole fractions, which appears to be particularly useful for applied work (83).

A solution model was proposed by Wilson (84) which is based on the concept of local mole fractions. The point of departure for the development of this model was the Flory-Huggins theory of athermal solutions ($H^E = 0$) whose components are chemically quite similar and differ only in size. The classic expression resulting from the Flory-Huggins treatment is

$$-G^E/RT = \sum_{i=1}^{k} x_i \ln(\phi_i/x_i) \tag{91}$$

where

$$\phi_i = \frac{x_i V_i^0}{\sum_{j=1}^{k} x_j V_j^0} \tag{92}$$

is the volume fraction of component i. The concept of local mole fractions is developed as follows: the proba-

bility of finding a molecule of type j relative to finding a molecule i in a mixture where molecule i is considered as the central molecule is expressed in terms of the overall mole fractions and two Bolzmann factors. Thus Wilson writes

$$\frac{x_{ji}}{x_{ii}} = \frac{x_j \exp(-\lambda_{ji}/RT)}{x_i \exp(-\lambda_{ii}/RT)} \tag{93}$$

which for a binary mixture becomes

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp(-\lambda_{21}/RT)}{x_1 \exp(-\lambda_{11}/RT)} \tag{94}$$

The parameters λ_{11} and λ_{21} are, respectively, related to the potential energies of a 1-1 and 1-2 pair of molecules. An analogous equation can be written for the local mole fraction of component 1.

Wilson now defines local volume fractions using Eq. (93), which for component 1, in a binary mixture, is written as

$$\xi_1 = \frac{V_1^0 x_{11}}{V_1^0 x_{11} + V_2 x_{21}} \tag{95}$$

Substitution for x_{11} and x_{21} gives

$$\xi_1 = \frac{V_1^0 x_1 \exp(-\lambda_{11}/RT)}{V_1^0 x_1 \exp(-\lambda_{11}/RT) + V_2^0 x_2 \exp(-\lambda_{12}/RT)} \tag{96}$$

Similarly, the local volume fraction of component 2 is

$$\xi_2 = \frac{V_2^0 x_2 \exp(-\lambda_{22}/RT)}{V_2^0 x_2 \exp(-\lambda_{22}/RT) + V_1^0 x_1 \exp(-\lambda_{12}/RT)} \qquad (97)$$

It can be seen clearly from Eqs. (96 and 97) that Wilson has considered two factors: (a) molecular size; (b) intermolecular forces.

Now, if local volume fractions are substituted for the overall volume fractions in the Flory-Huggins development for a binary mixture, the Wilson equation for the molar excess Gibbs energy results

$$G^E/RT = x_1 \ln(\xi_1/x_1) + x_2 \ln(\xi_2/x_2) \qquad (98)$$

To simplify notation, two new parameters, Λ_{12} and Λ_{21} are defined in terms of the molar volumes V_1^0 and V_2^0 and the energies λ_{11}, λ_{22}, and λ_{12}. These definitions are

$$\Lambda_{12} = \frac{V_2^0}{V_1^0} \cdot \exp - \frac{(\lambda_{12} - \lambda_{11})}{RT} \qquad (99)$$

$$\Lambda_{21} = \frac{V_1^0}{V_2^0} \cdot \exp - \frac{(\lambda_{12} - \lambda_{22})}{RT} \qquad (100)$$

Wilson's modification of the Flory-Huggins equation thus becomes

$$G^E/RT = -x_1 \ln(x_1 + \Lambda_{12} x_2) - x_2 \ln(x_2 + \Lambda_{21} x_1) \qquad (101)$$

It is important to note that even though $\lambda_{12} = \lambda_{21}$,

$\Lambda_{12} \neq \Lambda_{21}$.

The Wilson equation appears to provide a good representation of excess Gibbs energies for a variety of miscible mixtures (85,86). A study of Wilson's equation by Orye (87) shows that for approximately one hundred miscible binary mixtures of various chemical types, activity coefficients are satisfactorily represented by the Wilson equation. Holmes and van Winkle (89) calculated the parameters of third order Margules, van Laar, and Wilson equations for eighty-nine binary systems. Each equation requires the determination of two parameters. They also tested the capability of these equations to predict multicomponent vapor-liquid equilibrium data. For almost all ternary cases the Wilson equation proved to be a superior model. The disadvantage of Wilson's equation lies in its inability to predict limited miscibility. This limitation was later overcome by Renon (89), who combined the local mole fraction concept with Scott's two-liquid theory of mixtures (35). Renon's formulation, however, uses three parameters instead of Wilson's two.

None of the previous theories, fundamental or semi-empirical, enables the evaluation of the enthalpy of mixing from single temperature values of excess Gibbs free energy, and vice versa. Since there is a strong need for such theories, we concentrated our efforts to their development.

B. Estimation of H^E from G^E and Vice Versa

As it has been mentioned before, Wilson's treatment

seems to be superior to the other semi-empirical approaches. For this reason Wilson's theory is used as a starting point in our derivation.

The well known relation between the excess Gibbs free energy, G^E, and the enthalpy of mixing, H^E

$$\left[\frac{\partial (G^E/RT)}{\partial T}\right]_{P,x} = - \frac{H^E}{T^2} \tag{102}$$

permits the calculation of the enthalpy of mixing from the temperature dependence of the excess Gibbs free energy and vice versa. The strict application of Eq. (102), however, is not always feasible, since for most systems the excess Gibbs free energy as well as the enthalpy of mixing are available at single temperatures only.

Some attempts have been made recently to solve this problem on a semi-empirical basis (1,90,91). Our method is a further step in this direction.

We represent the deviation from ideal behavior expressed by the excess Gibbs free energy as the sum of two separate terms:

$$G^E/RT = - \frac{x_1 x_2 \ln(\alpha\beta)}{(x_1+x_2\alpha)(x_2+x_1\beta)} - \left[x_1 \ln(x_1+x_2\frac{V_2^0}{V_1^0}) + x_2 \ln(x_2+x_1\frac{V_1^0}{V_2^0})\right] \tag{103}$$

where V_1^0 and V_2^0 are the molar volumes of pure components

1 and 2 respectively, and α and β are parameters characteristic of the system. For the sake of simplicity, Eq. (103) is rewritten in the form

$$G^E = G^* - RT\ f(V) \tag{104}$$

G^* is the term derived by Bruin (87) as the "Enthalpic Wilson Equation." In our formulation G^* is responsible for the deviation from ideal behavior due to the intermolecular forces and is equal to the first term in Eq. (103).

$RT\ f(V)$ is the Flory-Huggins term, which takes care of the contribution of the different sizes of the molecules to the excess Gibbs free energy. It is defined by

$$RT\ f(V) = RT\left[x_1 \ln\left(x_1 + x_2 \frac{V_2^0}{V_1^0}\right) + x_2 \ln\left(x_2 + x_1 \frac{V_1^0}{V_2^0}\right)\right] \tag{105}$$

Combination of Eqs. (102 and 104) yields

$$H^E = -T^2 (\partial/\partial T)\left[(G^*/T) - Rf(V)\right]_{P,x} \tag{106}$$

If the thermal expansion coefficients of the solution components are not greatly different, the temperature dependence of the Flory-Huggins term, $\partial f(V)/\partial T$, can be neglected. Eq. (106) then takes the form

$$H^E = -T^2\left[\frac{\partial (G^*/T)}{\partial T}\right]_{P,x} \tag{107}$$

To facilitate the differentiation, Eq. (107) is

transformed into

$$H^E = TG^*\left[(1/T) - (\partial \ln G^*/\partial T)\right] \tag{108}$$

Now, differentiating the logarithm of G* with respect to T, we obtain

$$\frac{\partial \ln G^*}{\partial T} = (1/T) + \frac{\partial(\ln\alpha+\ln\beta)/\partial T}{\ln\alpha\beta} - \frac{x_2(\partial\alpha/\partial T)}{x_1+x_2\alpha} - \frac{x_1(\partial\beta/\partial T)}{x_2+x_1\beta} \tag{109}$$

Since

$$\partial(\ln\alpha+\ln\beta)/\partial T = \frac{1}{\alpha}\cdot\frac{\partial\alpha}{\partial T} + \frac{1}{\beta}\cdot\frac{\partial\beta}{\partial T}$$

Eq. (109) can also be written in the form

$$\frac{\partial \ln G^*}{\partial T} = \frac{1}{T} + \frac{\partial\alpha}{\partial T}\left[\frac{1}{\alpha\ln(\alpha\beta)} - \frac{x_2}{x_1+x_2\alpha}\right] + \frac{\partial\beta}{\partial T}\left[\frac{1}{\beta\ln(\alpha\beta)} - \frac{x_1}{x_2+x_1\beta}\right] \tag{110}$$

On combining Eqs. (108 and 110), we have

$$\frac{H^E}{G^*} = T\frac{\partial\alpha}{\partial T}\left[\frac{x_2}{x_1+x_2\alpha} - \frac{1}{\alpha\ln(\alpha\beta)}\right] + T\frac{\partial\beta}{\partial T}\left[\frac{x_1}{x_2+x_1\beta} - \frac{1}{\beta+\ln(\alpha\beta)}\right] \tag{111}$$

The next objective is to find expressions for the temperature derivatives of α and β. In order to do this without the introduction of new variables, the following assumption is made:

$$\lim_{x_1 \to 0} \frac{H^E}{G^*} = \lim_{x_2 \to 0} \frac{H^E}{G^*} = 2 \tag{112}$$

This limiting value (for which justification will be given in the Discussion section) introduced into Eq. (111) gives in the cases of $x_1 = 0$ and $x_2 = 0$:

$$x_1 = 0 \quad : \quad T \frac{\partial \alpha}{\partial T} \left[\frac{1}{\alpha} - \frac{1}{\alpha \ln(\alpha\beta)} \right] + T \frac{\partial \beta}{\partial T} \left[- \frac{1}{\beta \ln(\alpha\beta)} \right] = 2 \tag{113}$$

$$x_2 = 0 \quad : \quad T \frac{\partial \alpha}{\partial T} \left[- \frac{1}{\alpha \ln(\alpha\beta)} \right] + T \frac{\partial \beta}{\partial T} \left[\frac{1}{\beta} - \frac{1}{\beta \ln(\alpha\beta)} \right] = 2 \tag{114}$$

The solutions of the last two equations are

$$\frac{\partial \alpha}{\partial T} = \frac{2 \ln(\alpha\beta)}{\ln(\alpha\beta) - 2} \cdot \frac{\alpha}{T} \tag{115}$$

$$\frac{\partial \beta}{\partial T} = \frac{2 \ln(\alpha\beta)}{\ln(\alpha\beta) - 2} \cdot \frac{\beta}{T} \tag{116}$$

As seen, the temperature dependence of the two parameters may be obtained from the values of the parameters themselves at a given temperature.

Substitution of Eqs. (115 and 116) and the expression for G* into Eq. (111) leads to the final relation

$$H^E = \frac{2RTx_1x_2(\ln(\alpha\beta))^2}{(x_1+x_2\alpha)(x_2+x_1\beta)(2-\ln(\alpha\beta))} \cdot \left[\frac{x_2\alpha}{x_1+x_2\alpha} + \frac{x_1\beta}{x_2+(x_1\beta)} - \frac{2}{\ln(\alpha\beta)}\right] \quad (117)$$

The parameters α and β are obtained either from the experimental excess Gibbs free energy or from the enthalpy of mixing at any given temperature.

Eq. (117) enables the calculation of the enthalpy of mixing from excess Gibbs free energies and vice versa.

Eq. (117) was applied to a number of binary systems taken from the literature. As it will be seen later, the results are satisfactory in most cases.

C. Temperature Dependence of G^E

As a corollary to the previous section, we also tried to evaluate the temperature dependence of the excess Gibbs free energy of binary non-electrolyte systems. In order to achieve this objective, an equation relating the parameters α and β in Eq. (103) to temperature must be found. Such a relation can be obtained from Eqs. (115 and 116).

Rearrangement of Eqs. (115 and 116) and subtracting

the latter from the former gives

$$\frac{\partial \ln\alpha}{\partial T} - \frac{\partial \ln\beta}{\partial T} = \frac{\partial \ln(\alpha/\beta)}{\partial T} = 0 \qquad (118)$$

It follows from Eq. (118) that

$$\alpha_1/\beta_1 = \alpha_2/\beta_2 = C \qquad (119)$$

where subscripts 1 and 2 refer to two different temperatures and C is a constant independent of temperature.

Another relation between the parameters is obtained by rearrangement and addition of Eqs. (115 and 116)

$$\frac{\partial \ln\alpha}{\partial T} + \frac{\partial \ln\beta}{\partial T} = \frac{\partial \ln(\alpha\beta)}{\partial T} = \frac{4\ln(\alpha\beta)}{\ln(\alpha\beta)-2} \cdot \frac{1}{T} \qquad (120)$$

This is a differential equation of the form

$$\frac{dy}{dx} = \frac{4y}{x(y-2)} \qquad (121)$$

where $y = \ln(\alpha\beta)$ and $x = T$. Integration of Eq. (120) between the two limits yields

$$(1/4)\ln\frac{\alpha_2\beta_2}{\alpha_1\beta_1} - (1/2)\ln\frac{\ln(\alpha_2\beta_2)}{\ln(\alpha_1\beta_1)} = \ln(T_2/T_1) \qquad (122)$$

or

$$\frac{(\alpha_2\beta_2/\alpha_1\beta_1)}{\left[\frac{\ln(\alpha_2\beta_2)}{\ln(\alpha_1\beta_1)}\right]^2} = \left[\frac{T_2}{T_1}\right]^4 \qquad (123)$$

Now, from Eq. (119)

$$\alpha_2/\alpha_1 = \beta_2/\beta_1 = k \tag{124}$$

Thus

$$\alpha_2 = \alpha_1 k \tag{125}$$

$$\beta_2 = \beta_1 k \tag{126}$$

In contrast to C, k is temperature dependent. The problem is now reduced to the evaluation of k. If Eqs. (125 and 126) are introduced into Eq. (123) we obtain

$$\frac{k^2}{\left[\frac{\ln k^2 + \ln(\alpha_1\beta_1)}{\ln(\alpha_1\beta_1)}\right]^2} = \left[\frac{T_2}{T_1}\right]^4 \tag{127}$$

After some algebraic manipulations Eq. (127) reduces to the form

$$2\ln k - k(T_1/T_2)^2 \ln(\alpha_1\beta_1) + \ln(\alpha_1\beta_1) = 0 \tag{128}$$

Eqs. (125,126,and128) permit the calculation of the values of the parameters α and β at any temperature T_2 from their known values at another temperature T_1. The excess Gibbs free energy at T_2 is subsequently calculated using Eq. (103).

Since entropy is defined as the temperature derivative

of the excess Gibbs free energy, the proposed method also permits the calculation of the entropy of mixing (92,93).

V. METHODS BASED ON COMPLETE EXPERIMENTAL DATA

In dealing with solutions of non-electrolytes, experimental data are indispensible for the following purposes:

a. To test existing theories as well as to guide the formulation of new theories.

b. To evaluate the parameters characterizing a certain solution, in the semi-empirical theories.

c. To estimate data which would otherwise be difficult to measure from some other easily obtainable properties.

d. To estimate the behavior of a particular solution from the behavior of a similar system.

A common feature of all the experimental thermodynamic data of solutions is that they must obey the Gibbs-Duhem equation. Consequently, the Gibbs-Duhem equation may serve as a test for the consistency of the data. When only partial information is available for a solution, the Gibbs-Duhem equation may be applied to evaluate the complete data (e.g., when only one component of a solution is characterized, the behavior of the other component may be calculated).

It is evident from Eq. (102) that, thermodynamically, the excess enthalpy may be obtained from complete sets of experimental excess free energy data at different temper-

atures, and vice versa. It must be understood, however, that the enthalpy of mixing as calculated from Eq. (102) is less accurate (practically by one order of magnitude) than the excess Gibbs free energy.

In general, density measurements can be made with a high degree of accuracy. Consequently, it would be highly desirable if methods could be developed which would permit the calculation of other thermodynamic properties of solutions from density measurements.

With respect to this problem, we suggest further investigation of the possibility of using the following procedure to express V^E and G^E in a series expansion form

$$V^E = x_1 x_2 A' + B'(x_1 - x_2) + C'(x_1 - x_2)^2 + \ldots \quad (129)$$

$$G^E = x_1 x_2 A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \ldots \quad (130)$$

Expansions of this kind for thermodynamic properties of solutions were recommended by Redlich and Kister (94). What one really needs is a relation between the parameters of the volume series and the excess Gibbs free energy series expansion. Since volume and Gibbs free energy are related by

$$(\partial G^E/\partial P)_{T,x} = V^E \quad (131)$$

it is evident that the constants in the two series are related by

$$A' = \frac{\partial A}{\partial P} \quad ; \quad B' = \frac{\partial B}{\partial P} \quad ; \quad C' = \frac{\partial C}{\partial P} \tag{132}$$

The proposed method would probably provide reasonably good results for gaseous mixtures. The low compressibility of liquids may result in larger errors when this procedure is applied to liquid mixtures. Since high pressure equipment has not been available in this laboratory, the accuracy of this method could not be tested. Nevertheless, we recommend further studies in this direction.

VI. EXPERIMENTAL

Some of the experimental data required to prove the usefulness and reliability of the newly proposed semi-empirical methods were obtained in our laboratory.

The following measurements were performed in our laboratory:

1. Determination of the vapor pressures of pure substances
2. Determination of the isothermal vapor-liquid equilibrium data
3. Determination of the densities of pure liquids and liquid mixtures

The first two types required accurate temperature and pressure measurements. In addition, type 2 also required a precise analytical method for the determination of the compositions of the two coexisting equilibrium phases. Density measurements were performed for this purpose.

A. Chemicals

All the chemicals used in the course of this investigation were of spectroscopic grade. They were distilled at least once with a very efficient distillation column (approximately 40 theoretical plates) using a high reflux ratio.

To prove the purity of the chemicals, boiling points and condensation temperatures were measured with a Beckman thermometer in a modified Swietoslawski differential ebulliometer and no more than a difference of 0.004°C was tolerated. Densities and vapor pressures were also used as criteria of purity.

Fisher spectroanalyzed benzene was used in this investigation. Even though gas chromatographic analysis failed to show any significant impurities, the sample was distilled and only the middle fraction was used. The densities at 25°C and the vapor pressures at 70°C were in good agreement with literature values (95,96,97).

Toluene, chlorobenzene and carbon tetrachloride were Fisher spectrograde chemicals. They were twice distilled and subjected to chromatographic analysis. No impurities were detected. The difference between boiling point and condensation temperature, which is considered to be one of the best criteria of purity, was 0.002°C, 0.004°C, and 0.003°C for toluene, chlorobenzene, and carbon tetrachloride, respectively. Good agreement was observed between measured and literature values for densities and vapor pressures (91,98-103).

Spectrograde tetrachloroethylene stabilized with thymol was obtained from Eastmen-Kodak and was twice distilled before use. Densities and the vapor pressures agreed well with literature values (104,105,106). Trace amounts of thymol were added in order to prevent poly-

merization and decomposition.

Purissimo grade 2,3-dimethyl-2-butene was purchased from Aldrich Chemical Company and used without further purification. The reported purity of the sample was better than 99% and gas chromatographic analysis did not indicate any noticeable amount of impurity. Furthermore, the very small difference (0.004°C) between the boiling point and condensation temperature at atmospheric pressure also indicated that the sample did not contain sufficient impurities to affect significantly the vapor pressure measurements. The measured density was also in good agreement with the literature value (98,107).

In Table 1 the measured physical constants of all the components are listed along with literature values for comparison.

B. Vapor-Pressure Measurements

The vapor pressure of 2,3-dimethyl-2-butene was measured up to its boiling point by a dynamic method using two Swietoslawski-type ebulliometers (5) connected in parallel to the pressure controlling system. One of the ebulliometers contained deionized and twice distilled water, and the other was filled with the hydrocarbon. The temperature dependence of the vapor pressure of water is given by (108)

$$\ln P = -17.2583 + 0.0057113T + 8.3\ln(373.16/T) - 7235.44/T \qquad (133)$$

TABLE 1

DENSITIES AND THE VAPOR PRESSURES OF THE PURE COMPONENTS

Component	d^{25}			V.P. at 70.00°C		
	Measured	Literature	(Ref.)	Measured	Literature	(Ref.)
Benzene	0.87360 0.87351	0.87368 0.8734	(95) (96)	550.85 550.95	550.83	(97)
Thiophene	1.05846 1.05849 1.05804	1.0583	(98)	482.98 482.98 483.73	480	(97)
Toluene	0.86227	0.86220	(95, 98)	203.90	203.75	(99, 100)
Chlorobenzene	1.10106	1.1008	(98)	100.25	99.3	(98)
Carbon tetrachloride	1.58450	1.58448 1.58452 1.58461	(101) (98) (102)	617.53	617.43	(103)
Tetrachloroethylene	1.61456 1.61447 1.61440	1.61446	(104)	142.47 141.74 141.38	142.44 141.38	(105) (106)
2,3-Dimethyl-2-butene	0.70368	0.70336	(98)	689.28	685.89	(107)

as adopted by the International Steam Table Conference in 1935 (109). In Eq. (133) T is the absolute temperature and P is the pressure in atmospheres. Thus from the boiling point of water, the corresponding pressure in the system was determined.

In order to avoid overheating in the ebulliometers, the inside walls of the boiling flasks of the ebulliometers were effectively activated by ground glass of particle size 0.25 to 0.30 mm (0.50 mesh).

The temperature in the ebulliometers was measured with a 25-ohm platinum resistance thermometer (Leads and Northrop) calibrated by the National Bureau of Standards in a Mueller bridge circuit (Leads and Northrop) with an accuracy better than 0.01°C. Thus, the accuracy of the vapor pressure measurement was better than ±0.1 mm Hg.

C. Vapor-Liquid Equilibrium Measurements

Vapor-liquid equilibrium data were determined by a dynamic circulation method using a modified Gillespie still (110). A diagram of the still is shown in Fig. 1. The still was initially charged with approximately 200 ml of the liquid. The boiling flask of the equipment was wound with a heating tape. An internal platinum coil heater was used in order to obtain smooth boiling and homogeneity of the liquid. Bubbles of vapor that formed on the hot surface of the platinum coil, thoroughly mixed the contents of the boiling flask, and ensured quiet and steady boiling.

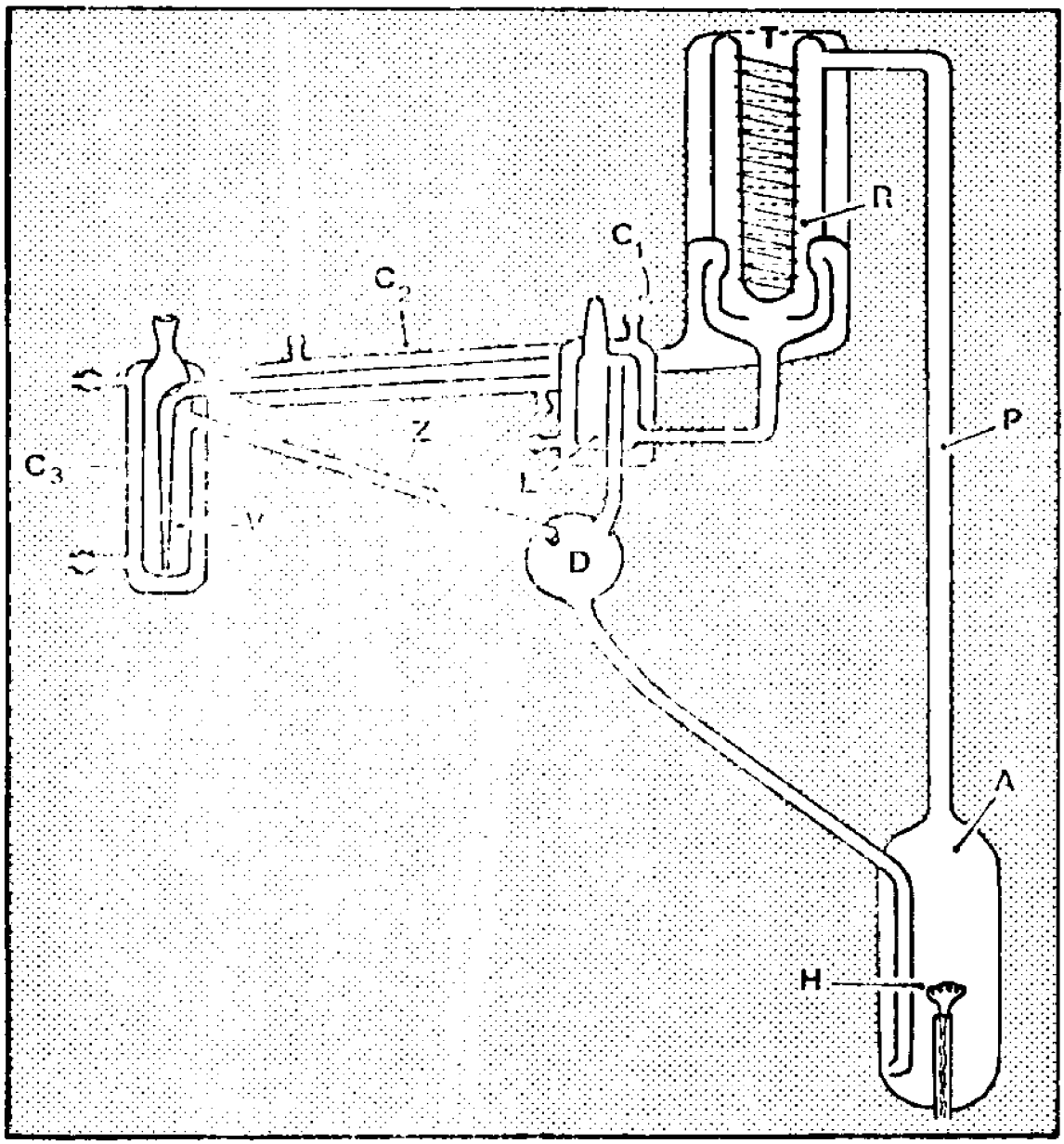


Fig. 1.--Vapor-liquid equilibrium still. A, boiling flask; P, Cottrell pump; T, thermometer well; R, separator; V, receiver; L, liquid chamber; C_1,C_2, C_3, coolers; Z, return line for condensate; D, drop counter; H, internal heater.

The evolved vapors carry a flow of liquid with them into the Cottrell pump from which this mixture spurts into the equilibrium chamber. The heterogeneous mixture then flows to the separator where the vapor is separated allowing the equilibrium liquid to return through the liquid collector to the boiling flask. The vapor leaving the equilibrium chamber is collected in the receiver after total condensation. The excess of condensate from the receiver returns through the drop counter to the boiling flask. The intensity of boiling should be such that the vapor-liquid mixture continuously rises through the Cottrell pump and that the level of liquid in the enlarged tube under the drop counter pulsates gently. In order to avoid condensation the Cottrell pump and the equilibrium chamber were insulated with an asbestos tape. Too high a velocity of distillation can lead to imperfect separation of the phases, while irregular or weak boiling allows vapor to rise without carrying a current of liquid with it.

The apparatus is made of glass. The main advantage of this kind of apparatus is that it enables exact measurement of the boiling points. The possibility of partial condensation in this still is very slight since the vapor and liquid are maintained in close contact as far as the equilibrium chamber. According to Hala and others (5,111, 112,113), two to three hours are required to reach steady state. The theoretical calculations of Erdos and Pouchly (114) also lead to the same results. They concluded that

the time required to achieve equilibrium depends on the ratio of the condensate receiver volume to the boiling flask volume, and that the contents of the condensate receiver should be exchanged six or seven times until equilibrium is established. It was found that in our equipment, the contents of the condensate receiver (25 ml) would be exchanged once every five minutes under steady boiling so that approximately 35 minutes would be required to reach an equilibrium state. To be sure that equilibrium was reached, the boiling was continued for about two hours.

At the beginning of each measurement the pressure inside the system was adjusted to a value corresponding to a boiling point of 70.00^{0}C. Small fluctuations in the pressure during the operation were buffered by a pressure controlling device. A cylindrical metal tank with a capacity of 120 liters was used as a pressure buffer. The equilibrium still and the ebulliometer were connected to the tank. A three-way stopcock inserted at the proper location enabled maintenance of the pressure at the required value either by letting air into the system or removing air by means of a vacuum pump. The vapors from the liquid phase would contribute to an increase in the pressure of the system if allowed to diffuse into the tank during the operation. A trap immersed into a mixture of acetone and dry ice condensed the small amount of vapors and gases before they entered the tank, thus preventing also any contamination of the oil in the pump.

At the termination of the experiment, the heating of both the mixture and the water in the ebulliometer was stopped and the system was abruptly connected to the atmosphere. This stopped the boiling immediately. Samples were withdrawn from the liquid chamber and the condensate receiver as quickly as possible for composition determinations.

The temperatures were measured in exactly the same way as in the vapor pressure measurements except for the boiling point of the liquid mixture in the equilibrium still where an NBS calibrated mercury in glass thermometer was used with an accuracy of $\pm 0.01^{\circ}C$.

D. Density Measurement

The compositions of the equilibrium vapor and liquid phases were determined by measurements of density. The pycnometric method seemed to be the most suitable for the purpose (115).

Single stem pycnometers were used in the present investigation. The bulb of each pycnometer had approximately 10 ml capacity. The inner diameter of the stem was less than 2 mm, and a thin reference line was etched on the outside with hydrofluoric acid.

The pycnometers were filled using a hypodermic syringe equipped with a long needle, and were then placed in a constant temperature bath of $25.00 \pm 0.01^{\circ}C$ for about 30 minutes. The density of the sample was determined from the equation

$$d = \frac{W_s}{W_w} (d_w - d_{air}) - d_{air} \qquad (134)$$

In Eq. (134) W_s stands for the weight of the sample; W_w is the weight of the same volume of distilled water, d_w is the density of distilled water at 25°C, and d_{air} is the density of air at the laboratory conditions. Values of d_w and d_{air} are obtained from the Handbook of Physics and Chemistry (116).

The average coefficient of expansion of organic solvents is such that thermostat temperatures should be controlled to ± 0.01°C to determine the density to ± 0.00001 $g.cm^{-3}$. Precautions should also be taken to minimize evaporation. In our arrangement, it was possible to determine densities with a reproducibility of ± 0.00005 $g.cm^{-3}$. Densities were measured in order to determine the compositions of the mixtures. The accuracy in the determination of the composition depends on the difference in the densities of the two components. The greater the difference in the densities, the more accurate is the determination of the composition. A density difference of 0.5 $g.cm^{-3}$ corresponds to an accuracy of 0.01 mole percent in the composition. As seen from Tables I and II, the density differences in the systems studied were much larger, and therefore, the errors in the compositions were much smaller.

About ten mixtures of known composition were prepared

and their densities at $25.00^0 \pm 0.01^0$C determined. These measurements, together with the pure component densities, were fitted by a least squares method to a polynomial of the form

$$d = \sum_{i=0}^{n} a_i x^i \qquad (135)$$

where d is the density of the mixture and x is the mole fraction of the more volatile component. Such a polynomial enabled the unknown composition of the equilibrium phases to be determined from their densities. "n" varied from one system to another and no greater value than four was needed to reproduce the experimental data within the limit of the experimental error.

VII. RESULTS

A. Density-Composition Data

The density-composition data necessary for the analysis of the vapor-liquid equilibrium data of the systems benzene--tetrachloroethylene, thiophene--tetrachloroethylene, thiophene--carbon tetrachloride, benzene--thiophene, toluene--chlorobenzene, and 2,3-dimethyl-2-butene--tetrachloroethylene were determined at 25°C and are summarized in Table 2. The data were fitted by a least squares method into a power series using a computer program[†], and the coefficients are given in Table 3. The number of constants necessary to obtain the best fit was chosen such that the deviation of the calculated values from the experimentally determined densities was within the limits of the experimental error (± 0.00005 $g.cm^{-3}$). The standard errors of estimate are also included in Table 3.

Excess volumes of the above mixtures were calculated and in turn fitted into a Redlich-Kister type equation. The coefficients for the six systems are given in Table 4.

B. Vapor Pressures

The vapor pressures of 2,3-dimethyl-2-butene and

[†]Here, and in subsequent applications of the least squares method, it has been assumed that the error is only in the determination of the dependent variable.

TABLE 2

DENSITIES OF MIXTURES AT 25°C.

x_1 is the mole fraction of the more volatile component (mentioned first)

x_1	d_4^{25} (Exp.)	d_4^{25} (Calc.)	x_1	d_4^{25} (Exp.)	d_4^{25} (Calc.)
Benzene--Thiophene			2,3-Dimethyl-2-butene--Tetrachlorethylene		
0.0676	1.0445	1.0445	0.1009	1.5115	1.5115
0.1434	1.0290	1.0291	0.1883	1.4243	1.4244
0.2201	1.0138	1.0138	0.2569	1.3574	1.3574
0.2921	0.9997	0.9997	0.3968	1.2243	1.2244
0.3653	0.9856	0.9856	0.4804	1.1471	1.1471
0.4475	0.9703	0.9702	0.6020	1.0378	1.0378
0.5240	0.9560	0.9560	0.7534	0.9065	0.9065
0.5944	0.9432	0.9433	0.8434	0.8308	0.8309
0.6434	0.9345	0.9345			
0.7403	0.9174	0.9175			
0.8301	0.9020	0.9020			
0.8976	0.8906	0.8906			
Benzene--Tetrachloroethylene			Thiophene--Tetrachloroethylene		
0.0725	1.5657	1.5658	0.1086	1.5641	1.5641
0.1511	1.5124	1.5124	0.1891	1.5257	1.5256
0.2302	1.4577	1.4577	0.2944	1.4736	1.4736
0.3226	1.3929	1.3929	0.3128	1.4643	1.4643
0.4018	1.3362	1.3363	0.4270	1.4051	1.4051
0.4941	1.2689	1.2690	0.5078	1.3614	1.3615
0.5733	1.2102	1.2102	0.5671	1.3286	1.3285
0.6524	1.1502	1.1503	0.6692	1.2697	1.2697
0.7052	1.1098	1.1098	0.7799	1.2026	1.2026
0.7843	1.0481	1.0481	0.8645	1.1489	1.1489
0.8635	0.9851	0.9851	0.9087	1.1199	1.1199
0.9295	0.9316	0.9316	0.9560	1.0882	1.0882

TABLE 2--Continued

x_1	d_4^{25} (Exp.)	d_4^{25} (Calc.)	x_1	d_4^{25} (Exp.)	d_4^{25} (Calc.)
Thiophene--Carbon tetrachloride			Toluene--Chlorobenzene		
0.0339	1.0800	1.0800	0.9044	0.8845	0.8845
0.0961	1.1189	1.1188	0.8662	0.8933	0.8934
0.1474	1.1500	1.1500	0.7489	0.9210	0.9209
0.1837	1.1717	1.1717	0.6702	0.9394	0.9395
0.2984	1.2381	1.2381	0.5604	0.9655	0.9655
0.4015	1.2952	1.2952	0.5124	0.9770	0.9770
0.4654	1.3293	1.3294	0.3711	1.0108	1.0108
0.5569	1.3769	1.3768	0.3024	1.0274	1.0274
0.6496	1.4232	1.4232	0.2363	1.0434	1.0434
0.6546	1.4256	1.4257	0.1911	1.0542	1.0543
0.7686	1.4803	1.4803	0.1318	1.0688	1.0688
0.8975	1.5394	1.5394	0.0810	1.0812	1.0812

TABLE 3

COEFFICIENTS OF THE DENSITY EQUATION

$$d_4^{25} = a + bx_1 + cx_1^2 + dx_1^3$$

WITH THE STANDARD ERRORS OF ESTIMATE Sy

System	a	b	c	d	Sy†
Benzene-- Thiophene	1.05846	-0.20897	-0.02750	-0.00339	6×10^{-5}
2,3-Dimethyl-2-butene-- Tetrachloroethylene	1.61447	-1.03368	0.13019	-0.00730	6×10^{-5}
Benzene-- Tetrachloroethylene	1.61440	-0.66613	-0.05875	-0.01601	6×10^{-5}
Thiophene-- Tetrachloroethylene	1.61456	-0.45730	-0.06172	-0.03750	5×10^{-5}
Carbon tetrachloride-- Thiophene	1.05849	0.64042	-0.13498	0.02056	6×10^{-5}
Toluene-- Chlorobenzene	1.10106	-0.24583	0.00704		6×10^{-5}

†$Sy = \sqrt{\Sigma \Delta_i^2 / N}$, where Δ_i is the deviation of point i and N is the total number of points.

TABLE 4

THE COEFFICIENTS OF THE EQUATION
REPRESENTING THE EXCESS VOLUME OF MIXING
$V^E = x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2)^2 \ . \ . \ .]$
FOR THE SIX BINARY MIXTURES

System	A	B	C
Benzene-- Thiophene	0.065	-0.039	
2,3-Dimethyl-2-butene-- Tetrachloroethylene	-1.88	-0.25	-0.07
Benzene-- Tetrachloroethylene	-1.50	-0.28	-0.17
Thiophene-- Tetrachloroethylene	1.58	0.06	0.19
Carbon tetrachloride-- Thiophene	0.043	-0.016	0.068
Toluene-- Chlorobenzene	-0.359	-0.028	

3,3-dimethyl-1-butene[†] are reported in Table 5. The experimental data were fitted by least squares method to an Antoine equation ($\log P = A + \frac{B}{t+C}$). The constants of the Antoine equation have the following values for the two species: A = 6.93075, B = -1205.663, and C = 224.460 for 2,3-dimethyl-2-butene; A = 6.75953, B = -1053.517, and C = 230.336 for 3,3-dimethyl-1-butene.

As evident from Table 5, the data calculated from these equations are in excellent agreement with the experimentally found values. Very good agreement is also observed between our results and the data (in the temperature interval available) of Camin and Rossini (117).

C. Vapor-Liquid Equilibria

Constant temperature vapor-liquid equilibrium data for six binary systems are reproduced in Table 6. Activity coefficients were calculated from Eqs. (19 and 20). All the auxiliary data necessary to calculate the activity coefficients can be found in Table 7. The virial coefficients were calculated following the method of Pitzer and Curl (118). The values of Δ were obtained from Eq. (9) with the cross virial coefficients, B_{12}, estimated by the following equation (8,10):

$$B_{12} = \left[\left(B_{11}^{1/3} + B_{22}^{1/3} \right) \right]^3 / 8 \qquad (136)$$

Values of the excess Gibbs free energy of mixing were

[†]This compound was not used further in this work.

TABLE 5

VAPOR PRESSURES OF 2,3-DIMETHYL-2-BUTENE
AND 3,3-DIMETHYL-1-BUTENE AT DIFFERENT TEMPERATURES

2,3-Dimethyl-2-butene			3,3-Dimethyl-1-butene		
Temp. ^0C	P^0 (Exp.) mm Hg	P^0 (Calc.) mm Hg	Temp. ^0C	P^0 (Exp.) mm Hg	P^0 (Calc.) mm Hg
73.85	774.68	774.67	41.51	766.17	765.71
71.66	723.23	723.14	41.46	764.81	764.60
69.16	667.80	667.57	38.45	692.04	691.87
66.51	612.75	612.52	35.12	617.99	617.77
63.89	561.74	561.70	32.66	567.25	567.21
61.07	510.80	510.68	29.77	511.97	511.89
56.91	458.22	458.02	26.88	461.08	460.96
54.64	408.46	408.29	24.18	416.94	417.13
51.57	365.52	365.48	21.19	372.50	372.45
47.46	313.90	313.90	17.64	324.29	324.43
43.33	268.22	268.19	13.62	276.16	276.10
38.57	222.31	222.36	9.71	234.81	234.79
34.19	185.88	185.96	4.39	186.63	186.74
28.50	146.03	146.05	0.48	156.65	156.74
26.13	131.56	131.65	-4.14	126.43	126.49
21.87	108.65	108.70	-9.46	97.72	97.69
16.33	83.88	83.87			

TABLE 6

VAPOR-LIQUID EQUILIBRIA AND THE MOLAR EXCESS FREE ENERGIES OF MIXTURES AT 70°C

Subscript 1 denotes the more volatile first component

x_1	y_1	P(mmHg)	G^E(J.mole^{-1})	x_1	y_1	P(mmHg)	G^E(J.mole^{-1})
Benzene--Thiophene				2,3-Dimethyl-2-butene--Tetrachloroethylene			
0.0860	0.0991	490.25	5.85	0.2948	0.6718	310.29	53.36
0.1762	0.1987	497.30	11.21	0.3603	0.7298	345.79	65.26
0.2585	0.2869	503.51	14.95	0.4236	0.7762	379.44	68.06
0.3385	0.3703	509.36	17.67	0.5161	0.8314	428.43	67.68
0.4652	0.4984	518.24	19.92	0.5887	0.8668	466.47	63.61
0.6475	0.6753	530.16	18.55				
0.6914	0.7168	532.89	17.45				
0.7869	0.8061	538.61	13.73				

TABLE 6--Continued

x_1	y_1	P(mmHg)	G^E(J.mole^{-1})	x_1	y_1	P(mmHg)	G^E(J.mole^{-1})
Benzene--Tetrachloroethylene				Thiophene--Tetrachloroethylene			
0.3041	0.6466	285.73	111.92	0.0256	0.1044	154.93	16.73
0.3649	0.7010	311.32	127.01	0.1352	0.3942	204.44	87.24
0.3907	0.7217	321.90	129.90	0.1945	0.4949	229.48	119.41
0.4316	0.7501	337.85	136.24	0.2625	0.5822	256.19	150.14
0.4458	0.7602	343.96	138.85	0.3368	0.6568	283.93	177.80
0.5351	0.8138	379.48	147.20	0.3991	0.7061	305.31	195.67
0.6135	0.8526	408.95	145.66	0.5054	0.7757	339.92	210.03
0.6901	0.8869	437.78	135.35	0.5705	0.8117	360.53	213.17
0.7276	0.9023	451.32	125.40	0.6091	0.8319	372.80	211.55
0.8568	0.9506	498.45	82.56	0.6369	0.8447	379.44	198.38
				0.7213	0.8835	405.08	182.60
				0.8487	0.9377	440.87	117.42
				0.9009	0.9593	455.20	79.40

TABLE 6--Continued

x_1	y_1	P(mmHg)	G^E(J.mole^{-1})	x_1	y_1	P(mmHg)	G^E(J.mole^{-1})
Carbon tetrachloride--Thiophene				Toluene--Chlorobenzene			
0.0758	0.1111	503.43	43.82	0.0552	0.1046	105.84	-1.24
0.1080	0.1544	511.58	60.76	0.1124	0.2015	111.53	-4.43
0.1567	0.2146	522.41	81.11	0.1969	0.3295	120.16	-6.66
0.2329	0.3017	538.51	110.44	0.2522	0.4035	125.84	-6.91
0.2910	0.3629	549.40	127.16	0.3121	0.4765	131.87	-9.84
0.3389	0.4100	557.53	137.82	0.4335	0.6071	144.48	-10.97
0.4059	0.4744	567.25	143.52	0.4698	0.6412	148.15	-11.85
0.5319	0.5877	584.49	149.56	0.5200	0.6871	153.37	-13.56
0.5995	0.6460	591.95	143.46	0.5797	0.7374	159.56	-15.03
0.6790	0.7137	599.04	127.23	0.7034	0.8294	172.49	-14.49
0.7983	0.8166	608.45	93.95	0.8345	0.9120	186.30	-9.56
0.9366	0.9400	615.86	35.65				

TABLE 7

LIQUID MOLAR VOLUMES AND THE SECOND VIRIAL COEFFICIENTS OF PURE COMPONENTS AT 70 °C

Component	V^0 ($cm^3.mole^{-1}$)	$-B_{ii}$ ($cm^3.mole^{-1}$)
Benzene	94.629[a]	1035
Thiophene	84.267[a]	990
Pyridine	84.944[b]	1330
Toluene	112.39[c]	1582
Chlorobenzene	106.93[c]	1863
Carbon tetrachloride	102.812[a]	1059
Tetrachloroethylene	107.610[a]	1592
2,3-Dimethyl-2-butene	127.228[d]	1277

a) Extrapolated from values given in Ref. 98

b) Taken from Ref. 98

c) Interpolated from values given in Ref. 98

d) Extrapolated from density equation in Ref. 107

obtained by means of Eq. (17). The Redlich-Kister type of equation was used to express the dependence of the excess Gibbs free energy on the composition. The coefficients of these relations were determined by the method of least squares. The mole fractions were considered to be known accurately, and equal weights were assigned to the experimental points in the whole concentration range. The effect of using different numbers of coefficients was examined, and the minimum number needed for an adequate representation of the data was selected. The resulting values of the coefficients for the Gibbs excess free energies at 70°C are summarized in Table 8, where the root-mean squares of the deviations about the fitted curves are also listed. Fig. 2 shows the experimental G^E values for the six mixtures. The smooth curves are given by the Redlich-Kister equation of each mixture, while the points represent the experimental values.

As will be shown later, the Gibbs-Duhem equation has proved the experimental data to be thermodynamically consistent within the limits of experimental error.

TABLE 8

COEFFICIENTS OF THE REDLICH-KISTER REPRESENTATION OF THE MOLAR EXCESS FREE ENERGIES AT 70°C, WITH STANDARD ERRORS OF ESTIMATE, Sy

System	A	B	C	D	Sy
Benzene-- Thiophene	80.02	4.11			0.79
2,3-Dimethyl-2-butene-- Tetrachloroethylene	274.55	4.87	-41.64		3.14
Benzene-- Tetrachloroethylene	578.17	136.64			4.55
Thiophene-- Tetrachloroethylene	844.16	156.01	-28.49	-102.12	9.98
Carbon tetrachloride-- Thiophene	599.61	-27.28	8.63		5.43
Toluene-- Chlorobenzene	-49.35	-20.85			6.12

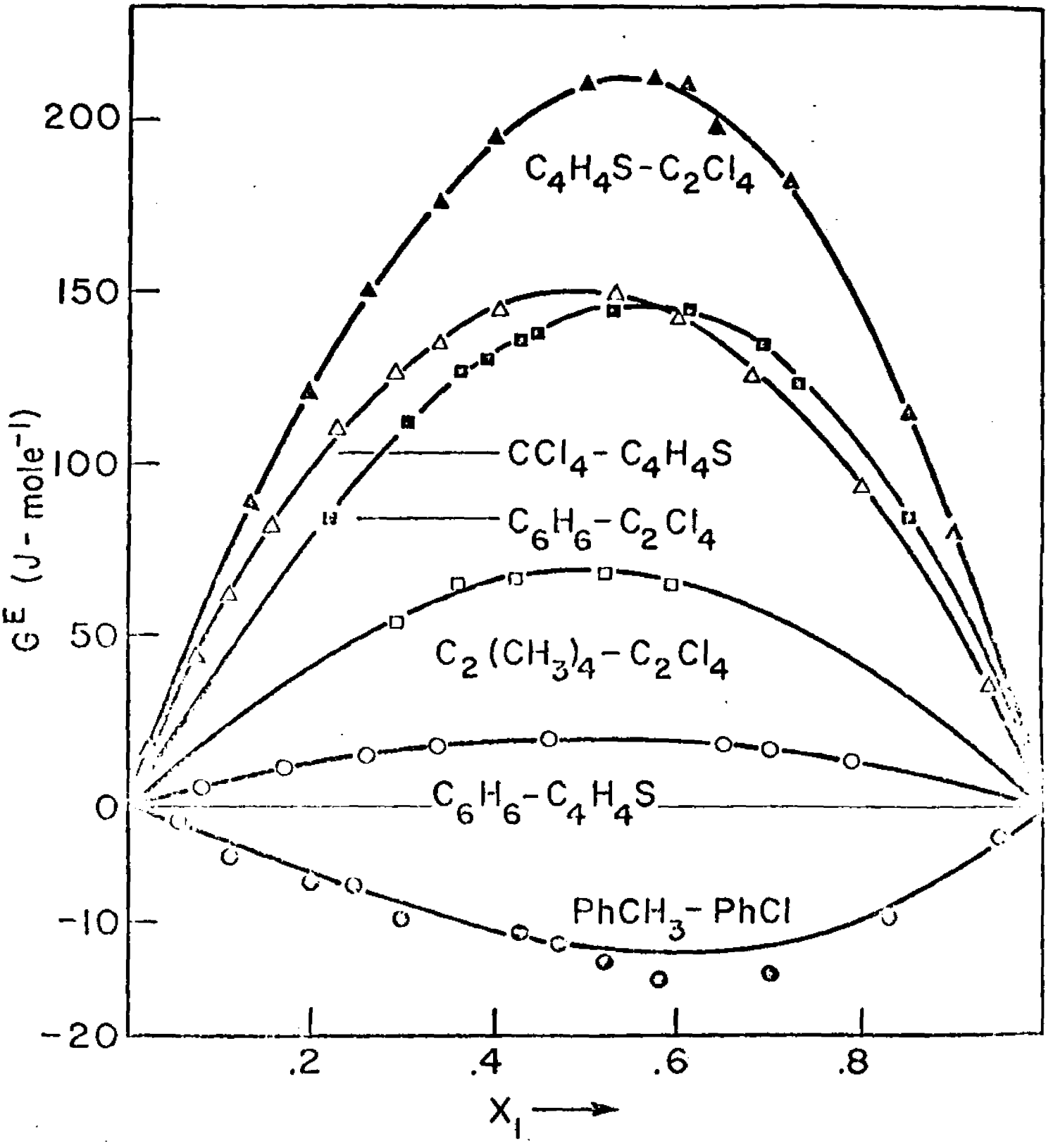


Fig. 2.--Molar excess Gibbs free energies of six binary systems at 70.00°C. x_1 is the mole fraction of the more volatile component (mentioned first). Curves obtained from least-squares representations in Table VIII.

VIII. DISCUSSION

A. Reliability of the Data

Vapor-liquid equilibrium data should be examined for reliability by what is generally termed a thermodynamic consistency test. In this work this was done by a variation of the Redlich-Kister area test. We shall first discuss the properties of the Redlich-Kister expansion of the excess free energy, Eq. (130), and then test our results for consistency.

Any expression for the molar excess Gibbs free energy must obey the two boundary conditions $G^E = 0$ when $x_1 = 0$, and $G^E = 0$ when $x_2 = 0$. The Redlich-Kister expansion obeys these boundary conditions and can conveniently be used to give an adequate representation regardless of the complexity of the mixture. The number of constants (A,B,C, . . .) which should be used to represent the experimental data depends on the molecular complexity of the solution, and on the number of data points available. Typical vapor-liquid equilibrium data reported in the literature have two or three constants. Very accurate and extensive data are needed to warrant the use of four or more empirical parameters.

The expression for the activity coefficients is

$$RT\ \ln\gamma_i = \mu_i^E = \left(\frac{\partial nG^E}{\partial n_i}\right)_{T,P,j} \tag{137}$$

where μ_i^E is the partial molal excess free energy of component i, and n is the total number of moles in the mixture.

For a binary mixture the Redlich-Kister expansion gives

$$RT\ \ln\gamma_1 = a^{(1)}x_2^2 + b^{(1)}x_2^3 + c^{(1)}x_2^4 + d^{(1)}x_2^5 + \ldots \tag{138}$$

$$RT\ \ln\gamma_2 = a^{(2)}x_1^2 + b^{(2)}x_1^3 + c^{(2)}x_1^4 + d^{(2)}x_1^5 + \ldots \tag{139}$$

where

$$a^{(1)} = A + 3B + 5C + 7D\ ;\ a^{(2)} = A - 3B + 5C - 7D$$

$$b^{(1)} = -4(B + 4C + 9D)\ ;\ b^{(2)} = 4(B - 4C + 9D)$$

$$c^{(1)} = 12\ (C + 5D)\ ;\ c^{(2)} = 12(C - 5D)$$

$$d^{(1)} = -32D \qquad ; \qquad d^{(2)} = 32D$$

After some rearrangement we can get

$$RT\ \ln(\gamma_1/\gamma_2) = A(x_2-x_1) + B(6x_1x_2-1) +$$

$$C(x_1-x_2)(8x_1x_2-1) + D(x_1-x_2)^2(10x_1x_2-1) + \ldots \tag{140}$$

Theoretically, there is an infinite number of combinations of experimental γ_1 and γ_2 that would give the same G^E. The data, however, would be consistent only

if the activity coefficients calculated from the Redlich-Kister expansion of the excess free energy coincide with experimentally determined activity coefficients. Thus, although a given curve of an excess property of mixing, Z^E, vs. concentration can be obtained from an infinite number of experimentally determined partial molal excess quantities Z_1^E and Z_2^E, only one consistent set of Z_1^E and Z_2^E values can result from a given curve of Z^E vs. concentration.

It is a well known fact that determinations of activity coefficients by vapor-liquid equilibrium studies are especially prone to experimental errors at the far ends of the liquid composition range. Redlich-Kister area tests have been used very often to proclaim data thermodynamically consistent, and in many instances it has been observed that this could be so only if the points at the far ends are neglected. The problem can become particularly acute in systems with components that differ widely in their volatilities.

The Redlich-Kister area test requires that the areas above and below the zero line of the curve $RT \ln(\gamma_1/\gamma_2)$ vs. x_1 should be equal. It is not uncommon to find that such curves in the literature drawn through experimentally determined γ_1 and γ_2 have been sometimes arbitrarily shifted in order to bring the ratio of the areas closer to unity. These are the reasons why an alternate procedure was adopted to test the thermodynamic consistency of

vapor-liquid equilibrium data obtained in this study.

The procedure is the following:

a. Obtain the coefficients of the Redlich-Kister expansion (Eq. 130) from experimentally determined excess free energies.

b. Use these coefficients to calculate the consistent set of γ_1, γ_2, and $\ln(\gamma_1/\gamma_2)$ given by Eqs. (138, 139, and 140) consecutively. The curve $\ln(\gamma_1/\gamma_2)$ vs. x_1 will necessarily give a ratio of unity for the areas below and above the zero line.

c. Plot the corresponding values determined experimentally on the curves obtained in (b). The data are consistent if these points coincide with the curves in (b).

It should be noted, however, that the above procedure places very strict demands on the accuracy of the experimental data. Consequently, in nearly ideal systems (activity coefficients very close to unity) more tolerance should be exercised in making decisions about the consistency of the data. When the agreement between the experimentally found activity coefficients and those calculated from the Redlich-Kister expansion is reasonably good, the data are considered to be thermodynamically consistent.

Fig. 3 shows the application of the thermodynamic consistency test as discussed above to five binary systems. The system toluene--chlorobenzene is not included because the excess free energy in this case was so small (-12 $J.mole^{-1}$

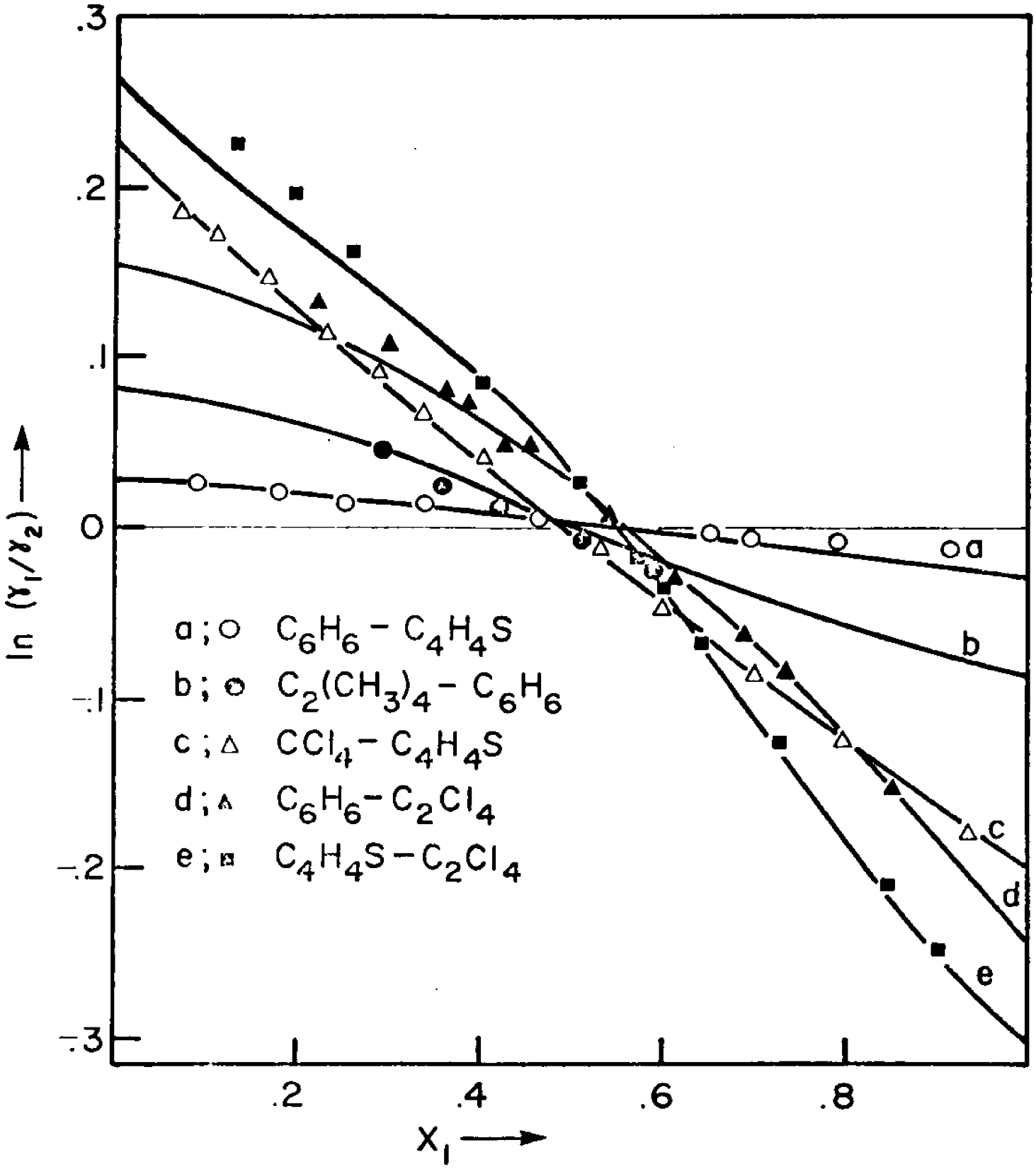


Fig. 3.--Thermodynamic consistency test. x_1 is the mole fraction of the more volatile component (mentioned first). Curves from Eq. (140).

at x = 0.5) that a larger scale was needed. The relative error in this case being large, however, a good coincidence between calculated and experimentally determined $\ln(\gamma_1/\gamma_2)$ could not be obtained even though the data did not show the wild scattering quite common for systems so close to ideal behavior. We believe, therefore, that our data are good and acceptable.

The only system studied previously in the literature with respect to excess free energy is the mixture benzene--thiophene. Coulson and Herington (119) studied this system under isobaric conditions. For this reason no quantitative comparison can be made with our isothermal data. Nevertheless, the value of G^E = 16.8 J.mole^{-1} at the benzene mole fraction of 0.47 is in close agreement with our results. Magnesco and Aguirre (120) determined the boiling points and the vapor phase compositions of the benzene--thiophene mixture at 760 torr. They also found nearly ideal behavior with benzene activity coefficients showing a small positive deviation with respect to Raoult's law, while in the case of thiophene the values of the activity coefficients were about unity for the entire composition range.

B. Size, Shape, and Polarity

Our discussion and survey in the preceding pages leads us to believe that three factors are responsible for the excess Gibbs free energy of a binary system, i.e., size, shape, and polarity differences between the component molecules. Thus, it is probably not too unrealistic to

expect that when molecules of two substances are non-polar and have the same symmetry, size, and shape, they will form an ideal solution (101). Moreover, if it were possible to make a judicious selection of binary systems such as to approximately eliminate two of the factors, one could hopefully then study the contribution to the excess free energy of size, shape, and polarity effects independently.

The assumption of equal molecular size, shape, and fields of force in the derivation of the ideal solution laws was realized very early. Huckel (121) published a comprehensive paper in 1936 discussing the effect of differences in molecular sizes of components on the equilibrium properties of solutions. He stressed forcefully that the ideal solution laws are inherently restricted to mixtures of interchangeable components.

Mixtures of molecules differing in size by a factor of the order of two were discussed from a thermodynamic standpoint by Guggenheim (122). Fowler and Rushbrooke (123) investigated the configurations of mixtures of spherical monomers and dumbbell shaped dimers. More recently, computer studies (124,125) on mixtures of hard spheres of different sizes at a constant pressure lead to small negative excess free energies. The theoretical studies of Singer (126) show that at equimolar concentration $G^E = -50 \pm 25$ J.mole^{-1} for a mixture in which the volume ratio of components is 2. Marsh (127) found

that the equimolar mixture of carbon tetrachloride and octamethylcyclotetrasiloxane (volume ratio, 3.2), G^E was about -160 J.mole^{-1} at 45^{0}C.

Rowlinson (128) discussed the relative importance of the factors of size and shape in determining the free energy. He suggests that the shape of molecules is often of less importance than their size in determining the free energy, and hence that theories of solutions of n-alkanes or of linear polymers do not differ greatly from those of mixtures of spherical molecules of different sizes in their results. With real mixtures it is difficult to determine experimentally that part of the observed G^E which arises specifically from differences in molecular size, since there are no means of choosing binary mixtures with $\epsilon^*_{11} = \epsilon^*_{12} = \epsilon^*_{22}$, while $r^*_{11} \neq r^*_{22}$. If the imtermolecular energies are such that ϵ^*_{11} and ϵ^*_{22} do not follow Berthelot's rule, Eq. (64), the system may exhibit a positive G^E in spite of differences in molecular sizes, which should give a negative contribution. This is because a departure from the Berthelot rule produces a relatively larger positive contribution to G^E. However, if the size ratio is appreciably greater than 2, then the negative contribution to the free energy cannot be ignored.

The effect of differences in size on the excess free energy of solutions is small and subtle, and has received little attention. The reason for this neglect was the greater attention paid to effects of differences

in the energies, ϵ_{11}, ϵ_{12}, and ϵ_{22}, for in simple mixtures these usually account for the greater part of G^E, H^E, V^E, and even S_v^E (128)

In part of the present work, we have assumed the separability of size, shape and polarity effects on the excess free energy of binary mixtures. This rough assumption can be written as

$$G^E = G^E_{\text{size-size}} + G^E_{\text{shape-shape}} + G^E_{\text{polarity-polarity}} \qquad (141)$$

For this purpose we have chosen to study three systems: (a) 2,3-dimethyl-2-butene--tetrachloroethylene (difference in size only). (b) carbon tetrachloride--tetrachloroethylene (difference in shape only). (c) toluene--chlorobenzene (difference in polarity only).

Our experimental data indicate that the system 2,3-dimethyl-2-butene--tetrachloroethylene has a value of $G^E = 68.6$ J.mole^{-1} at $x = 0.5$. This is contradictory to the argument made earlier that size difference contribution is always negative. An explanation for this behavior may be found, however, in the differences in intermolecular energies and in the departure of ϵ^*_{12} from the Berthelot rule.

The system carbon tetrachloride--tetrachloroethylene, having component molecules of different shape only, should exhibit very low G^E according to Rowlinson (128). The near ideal behavior of this system found experimentally by Fried

et al. (106), and the relatively low values of the heat of mixing reported by Poon and Lu (130), support Rowlinson's argument.

According to our measurements, the system toluene--chlorobenzene, differing in the polarity of the molecules, exhibits very small negative excess Gibbs free energy ($-12\ J.mole^{-1}$). No general statement can be made about the sign of G^E due to a difference in the dipole moments. Literature data, however indicate that in most cases the contribution due to differences in polarity is positive. In our case, the very small negative contribution may be attributed to the weak charge-transfer complex formation between the π electron donor toluene and the electron acceptor chlorobenzene, as will be discussed later.

C. Polar-Double Bond Interaction

The concept of separability of contributions to the excess free energy of mixtures can be investigated from another angle.

It has been suggested (106), on the basis of the nearly ideal behavior of the system carbon tetrachloride--tetrachloroethylene, that tetrachloroethylene behaves like a spherical molecule, although in the strict sense it has only the symmetry of the point group D_{2h}. Considering also the fact that the molar volumes of the two halide molecules are almost equal (within 5%) it would be possible to assume a similarity of size and shape between these two molecules. Furthermore, both molecules are non-polar, with one signi-

ficant difference, however. The carbon atom in carbon tetrachloride is sp^3 hybridized, whereas the two carbon atoms in tetrachloroethylene are sp^2 hybridized, thus giving a π bond between them.

The above arguments enable comparison between the behavior of mixtures having carbon tetrachloride as a component and mixtures having tetrachloroethylene as a component. Assuming then that the factors affecting the non-ideal behavior of these systems are separable into non-specific (volume, size, shape) and specific (polar-double bond) contributions, the excess free energy can be written as

$$G^E = G^E_{ns} + G^E_s \qquad (142)$$

where the subscripts ns and s stand for non-specific and specific interactions, respectively.

In order to investigate the applicability of this idea, we have chosen as second components molecules with similar shape and approximately similar size, but with increasing polarity. Thus, we have compared the excess free energy of the following mixtures:

Benzene-- Carbon tetrachloride (130)	:	Benzene-- Tetrachloroethylene (this work)
Thiophene-- Carbon tetrachloride (this work)	:	Thiophene-- Tetrachloroethylene (this work)

Pyridine-- Carbon tetrachloride (131)	:	Pyridine-- Carbon tetrachloride (132)

The dipole moments of thiophene and pyridine are listed in Table 9 together with the values for other molecules considered in this work. As is seen from Fig. 4, the excess free energy of both kinds of systems increases with the increasing dipole moment of the aromatic hydrocarbon. If the free energies are considered to be made up of additive parts, the interaction of the olefinic bond with the second component should become relatively larger with the increasing polarity of the latter. The difference in G^E, however, which presumably should be attributed to the dipole-double bond interaction goes through a minimum. This minimum is again an indication that the assumption of additivity is not valid.

It can be argued, on the other hand, that the minimum in Fig. 4 may result from the inaccuracy of the experimental data. Results found by Boublik et al. (140) and Polak et al. (105), however, for the excess free energies of the binary systems cyclopentane--carbon tetrachloride and cyclopentane--tetrachloroethylene, corrobrate our conclusion regarding the non-additivity of contributions.

Apparently, the factors affecting the non-ideal behavior of solutions interfere mutually, and thus, cannot be separated from each other. A term taking care of this mixed interaction must be introduced. Presently, there are

TABLE 9

PERMANENT DIPOLE MOMENTS OF SOME MOLECULES

Molecule	μ (Debyes)	Reference
Toluene	0.41	133
Ethylbenzene	0.58 (gas)	134
o-xylene	0.62 (gas)	135
Aniline	1.48	136
Fluorobenzene	1.50	137
Chlorobenzene	1.60	138
Thiophene	0.54	139
Pyridine	2.25	133

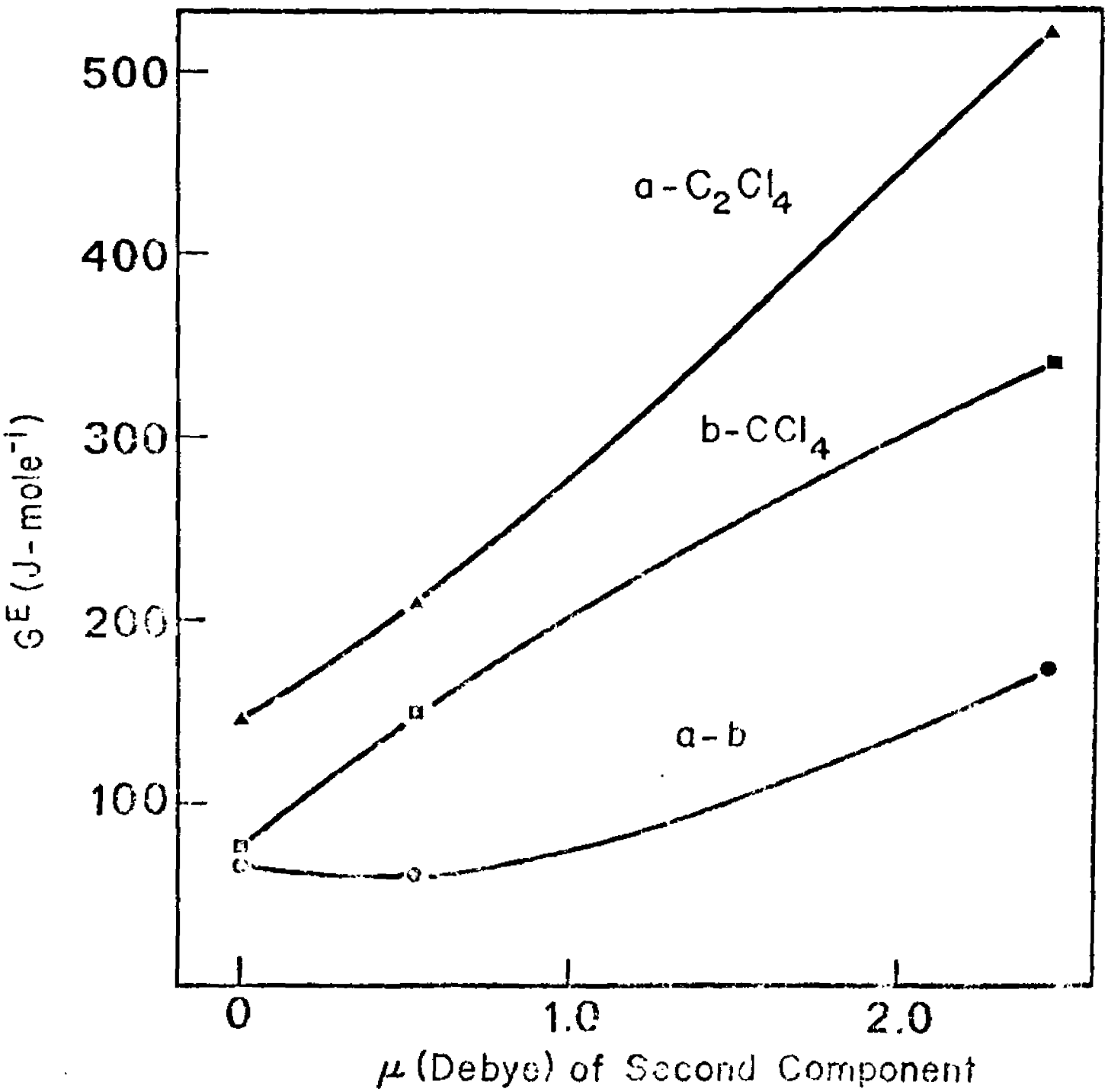


Fig. 4.— Molar excess Gibbs free energies at 70.00°C and x = 0.5 of C_2Cl_4 and CCl_4 mixtures plotted against the dipole moment of the second component (benzene, μ = 0; toluene, μ = 0.37; m-xylene, μ = 0.42). Curve a-b represents the difference between curves a and b.

no theories which would enable the prediction of this term from the behavior of the pure components. It must be concluded, therefore, that at present it is necessary to have at least one set of experimental data in order to evaluate the interaction term.

D. Charge-Transfer Complexes

Our discussion so far has shown that a deviation from Berthelot's rule as well as the shape and symmetry of molecules have an important influence on the structure of liquid mixtures and, consequently, on their thermodynamic properties. It is almost impossible to predict which of these effects will be predominant in a particular system. This can be strikingly illustrated when comparison is made between the thermodynamic behaviors of benzene and its cyclic analog, cyclohexane, in mixtures. The excess free energy of an equimolar mixture of benzene--cyclohexane at 70°C is 251 $J.mole^{-1}$ (141). Furthermore, if one compares the thermodynamic behavior of two mixtures, i.e., toluene--fluorobenzene and methylcyclohexane--fluorobenzene (142), one observes the following results: the heat of mixing of an equimolar mixture of toluene--fluorobenzene is -55 $J.mole^{-1}$ and that of methylcyclohexane--fluorobenzene is 738 $J.mole^{-1}$ at 25°C. The excess free energies for the same mixtures are, respectively, 8 $J.mole^{-1}$ and 350 $J.mole^{-1}$ at 70°C. Obviously, a comparison of systems involving cyclic compounds with those involving aromatic compounds is not warranted.

In general, therefore, extreme caution should be exercised in any comparative study of the thermodynamic behavior of liquid mixtures. Thus, attention was focused on mixtures of carbon tetrachloride with benzene and substituted benzene compounds. The purpose was to examine the variation of the excess free energy of these systems with a change in the electron density in the aromatic ring of the second component.

Measurements have indicated that carbon tetrachloride and benzene may probably form a weak complex. Evidence in support of this conclusion includes heat of mixing studies (143,144) which show that the endothermic heat of mixing rises with temperature over the range of 25^0 to 70^0C; freezing point diagrams (145) which show formation of addition compounds; and the dependence on the temperature (146) of the shape of the excess volume vs. concentration curves.

Spectroscopic and freezing point evidence for complex formation between aromatic hydrocarbons and halogen compounds has been reported (145). In these complexes, the aromatic component acts as an electron donor to the electron deficient halogen atom and it is probable that the same explanation holds for the benzene--carbon tetrachloride complex. Goates (143) has suggested π bonding between the benzene ring and the empty 3d level of the chlorine atom. Assuming such bonding it follows that substituents on the benzene ring which increase the electron density of the ring should enhance the stability of the complex formation.

Prausnitz and Anderson (146) compared the stability of the mesitylene (trimethyl benzene) complex with that of the benzene complex spectroscopically. Their data in the ultraviolet range at 25°C indicate that carbon tetrachloride forms a weak charge-transfer complex with benzene and with mesitylene. For 1:1 complexes the equilibrium constants are, respectively, 0.009 ± 0.004 and 0.113 ± 0.044 liter. $g.mole^{-1}$.

With this background in mind we have compiled a list of systems shown in Table 10. The excess free energies of these mixtures at x = 0.5 and the temperatures of measurement are included in the table. In the first part of Table 10 mixtures with carbon tetrachloride as one component and benzene and substituted benzene compounds as the second component are listed. In the second part of Table 10 the toluene--fluorobenzene mixture is compared with the toluene--chlorobenzene mixture. Finally, in the third part, mixtures of carbon tetrachloride with benzene, thiophene, and pyridine are compared.

We start our discussion with the first part of Table 10.

The system carbon tetrachloride--aniline has a positive value for the excess entropy of mixing (147) consistent with there being more randomness after mixing, and no strong interaction between the two components. The aniline-aniline interaction may be much stronger than the aniline-carbon tetrachloride interaction, and hence

TABLE 10

MOLAR EXCESS GIBBS FREE ENERGIES AT x = 0.5
OF SOME BINARY MIXTURES WITH DONOR-ACCEPTOR COMPONENTS

Mixture	Temp. ^{0}C	G^{E} ($J.mole^{-1}$)	Ref.
Aniline-- Carbon tetrachloride	45	945	147
Chlorobenzene-- Carbon tetrachloride	40	122	148
Benzene-- Carbon tetrachloride	40	80	130
Toluene-- Carbon tetrachloride	40	5	148
Ethylbenzene-- Carbon tetrachloride	40	-11	148
m-Xylene-- Carbon tetrachloride	0	-153	149
o-Xylene-- Carbon tetrachloride	0	-181	149
Toluene-- Fluorobenzene	70	8	142
Toluene-- Chlorobenzene	70	-12	
Benzene-- Carbon tetrachloride	70	77	130
Thiophene-- Carbon tetrachloride	70	150	
Pyridine-- Carbon tetrachloride	70	346	131

there is more ordering in pure aniline, because the π-bonds in the aromatic ring are highly polarizable and the molecule is anisotropic. Though the basicity of the nitrogen atom in aniline is much less than that in pyridine or any aliphatic amine, it is sufficient to form H-N-H hydrogen bonds and many spectroscopic and n.m.r. studies (150,151) support self-association in pure aniline. Kehiaian (152) has also supported the self-association of aniline from thermodynamic measurements on the system aniline--toluene. Thus, the inclusion of the carbon tetrachloride--aniline system in this comparative study is not justified. The reason why this system is included in Table 10 is to illustrate once more the influence of specific factors on the thermodynamic behavior of liquid mixtures.

The chlorine atom in chlorobenzene reduces the electron density in the ring. The methyl and ethyl group substituents increase the electron density in the ring on account of their electron donating ability. Infrared studies of the distortions of the π-electron system in mono-substituted benzenes indicate that the ethyl substituent induces a larger disturbance than the methyl group (153). This evidence coupled with the larger dipole moment of ethylbenzene proves a higher concentration of electron cloud in the ethylbenzene ring than that of methylbenzene.

Meta and ortho-xylenes have two methyl substituents. The ortho combination is probably more favorable for an overall inductive effect than the meta combination.

Ignoring the carbon tetrachloride--aniline system for reasons discussed earlier, it is seen from Table 10 that as we go down the list from chlorobenzene to ortho-xylene, the electron donor ability of the benzene ring increases, and the excess free energies of the corresponding mixtures with carbon tetrachloride decrease. This appears to be a strong thermodynamic evidence for donor-acceptor complexes.

A similar phenomenon has been observed in the thermodynamic study of mixtures of hexafluorobenzene with benzene and substituted benzenes (154,155,156). A charge-transfer complexing seems to occur between the electron poor hexafluorobenzene as the acceptor and the electron rich benzene and substituted benzenes as donors. The excess free energy becomes more negative as the benzene ring is substituted with methyl groups. Thus, in the equimolar mixture at 40^{0}C, the values of G^{E} are -44 J.mole^{-1} for hexafluorobenzene--benzene, -184 J.mole^{-1} for hexafluoro-benzene--toluene, and -395 J.mole^{-1} for hexafluorobenzene--p-xylene. Some doubt remains in this case, however, since the non-thermodynamic evidence (spectroscopic, n.m.r., dielectric constant, etc.) seems to be surprisingly weak (1).

The same arguments apply in the comparison of the excess free energies of the systems toluene--fluorobenzene and toluene--chlorobenzene. Toluene is the electron rich donor and fluorobenzene and chlorobenzene are the electron poor acceptors. Chlorobenzene has a slightly larger dipole

moment than fluorobenzene. This can be explained from the fact that although fluorine has a higher electronegativity than chlorine, its electron withdrawing power from the benzene ring is smaller on account of the available 3d orbital of the latter. Therefore, the benzene ring in chlorobenzene is poorer in electrons than that of fluorobenzene. Thus a stronger donor-acceptor complex is encountered in the case of toluene--chlorobenzene system as seen from its excess free energy which is slightly negative in contrast to the slightly positive excess free energy of toluene--fluorobenzene.

The line of reasoning in explaining the larger positive excess free energies of carbon tetrachloride--thiophene and carbon tetrachloride--pyridine compared to carbon tetrachloride--benzene is not different. The dipole moments of both thiophene and pyridine are directed towards the heteroatom. Since the sulfur atom in thiophene and the nitrogen atom in pyridine are themselves part of the corresponding ring systems, their electron withdrawing ability is considerably enhanced compared to the role of the chlorine in chlorobenzene.

E. Group Contributions in Mixtures

The basic aim of this approach is the calculation of activity coefficients of simple organic compounds by interpolation from one system to another. Such procedures have been found useful not only in making estimates when no direct data are available, but also in assessing data for

systems in terms of data obtained from related systems.

Probably the most significant early description of simple mixtures in terms of groups was given by Langmuir (157), whose basic premise was that the force field around a group radical is characteristic of that group or radical and is largely independent of the nature of the rest of the molecule.

Langmuir's approach was taken up by others. Butler et al. (158,159) considered the infinitely dilute solution of a series of solutes in a given solvent. He observed a simple relation between the number of carbon atoms in the molecular chain of the solute and its activity coefficient. He noted that partial molal excess free energies of solutions increased by roughly constant increments through the homologous series. Pierotti and coworkers (160,161) pursued this approach further with a more extensive and systematic study of homologous series. Redlich, Derr, and Pierotti (162) developed a group interaction model which calculates the heat of solution as the sum of contributions from interacting groups. Wilson (163) proposed a "solution of groups" approach which estimates the partial molal excess free energy as the sum of group contributions and provides a concentration dependence for these group contributions.

We have applied the strictly regular solution theory to calculate the interchange energy ω, Eq. (57), for binary mixtures from experimental excess free energy values. Using the group contribution approach to ω, an attempt was made

at predicting the excess free energy of systems having tetrachloroethylene as one component from the excess free energy of systems having carbon tetrachloride as one component. Specifically, three pairs of related systems were considered:

Carbon tetrachloride--Benzene	:	Tetrachloroethylene--Benzene
Carbon tetrachloride--Thiophene	:	Tetrachloroethylene--Thiophene
Carbon tetrachloride--Pyridine	:	Tetrachloroethylene--Pyridine

Two interesting observations were made from the determination of the interchange energies, ω, for various binary systems:

a) ω for all systems is independent of the lattice coordination number z, when z is varied from 6 to 12.

b) The value of ω is dependent on the concentration of the mixture.

ω has a constant value throughout the concentration range only when G^E/x_1x_2 for a system is constant. Table 11 shows the values of ω for various systems at three different concentrations. It should be noted that although the second observation was not unexpected due to the symmetrical nature of the expression for G^E in the first approximation of the strictly regular solution theory, Eq. (56), the first observation was somewhat surprising.

Going back to the three pairs of related systems

TABLE 11

VALUES OF THE INTERCHANGE ENERGY FOR SIX BINARY SYSTEMS AT 70°C. AND THREE DIFFERENT CONCENTRATIONS

System	x_1	ω (J.mole^{-1})
Benzene--		
Thiophene	0.2	77.62
	0.5	80.23
	0.8	82.47
2,3-Dimethyl-2-butene--		
Tetrachloroethylene	0.2	257.01
	0.5	274.74
	0.8	263.07
Benzene--		
Tetrachloroethylene	0.2	497.05
	0.5	581.17
	0.8	662.19
Thiophene--		
Tetrachloroethylene	0.2	766.92
	0.5	848.24
	0.8	909.05
Carbon tetrachloride--		
Thiophene	0.2	619.22
	0.5	602.73
	0.8	588.13
Toluene--		
Chlorobenzene	0.2	-36.81
	0.5	-49.37
	0.8	-61.81

under discussion, we compare carbon tetrachloride with tetrachloroethylene. A carbon tetrachloride molecule has four contact sites compared to six for a tetrachloroethylene molecule. We base further development of our discussion on two very rough assumptions: (1) all the contact sites in tetrachloroethylene are equivalent; (2) contact sites in tetrachloroethylene are equivalent to contact sites in carbon tetrachloride. These two assumptions lead to the following approximation: if carbon tetrachloride is considered as one group, then tetrachloroethylene is equivalent to one and one half carbon tetrachloride groups.

Let us derive the expressions for group concentrations pertinent to the binary systems under consideration.

The group fraction for group k in a mixture is defined as the ratio of the total number of groups, k, from all sources to the total number of groups of all kinds in the mixture. For a group k (164)

$$Z_k = \frac{\sum_i x_i n_{ki}}{\sum_i x_i \sum_k n_{ki}} \qquad (143)$$

where Z_k is the fraction of a given group k, x_i is the mole fraction of component i, and n_{ki} is the number of groups k in component i. The sums are to be taken over all components and groups.

For the three binary mixtures of carbon tetrachloride with benzene, thiophene, and pyridine, Eq. (143) gives the

following relationships between group fractions and mole fractions:

$$Z_A = x_A \tag{144}$$

$$Z_C = x_C \tag{145}$$

where x_A, x_C, Z_A, and Z_C are the mole fraction of the aromatic molecule, mole fraction of carbon tetrachloride, group fraction of the aromatic molecule, and the group fraction of carbon tetrachloride, respectively.

Similarly, for the three binary mixtures of tetrachloroethylene with benzene, thiophene, and pyridine, we obtain the following relationships if we assume a tetrachloroethylene molecule to be equivalent to one and one half carbon tetrachloride groups:

$$Z_A = \frac{x_A}{0.5x_T + 1} \tag{146}$$

$$Z_C = \frac{1.5x_T}{0.5x_T + 1} \tag{147}$$

where x_T is the mole fraction of tetrachloroethylene.

The assumption of the equivalence of a tetrachloroethylene molecule to one and one half carbon tetrachloride molecules implies also that the interchange energy between tetrachloroethylene and an aromatic molecule is one and one half times as large as the interchange energy between the

same aromatic molecule and carbon tetrachloride.

The procedure to predict the excess Gibbs free energy of tetrachloroethylene mixtures from the excess free energy of the corresponding carbon tetrachloride mixture is the following:

1. Find the interchange energy of a carbon tetrachloride mixture over the whole concentration area.

2. Find the constants of the equation

$$\omega = a + bx + cx^2 + dx^3 \ . \ . \ .$$

where x is the concentration of carbon tetrachloride.

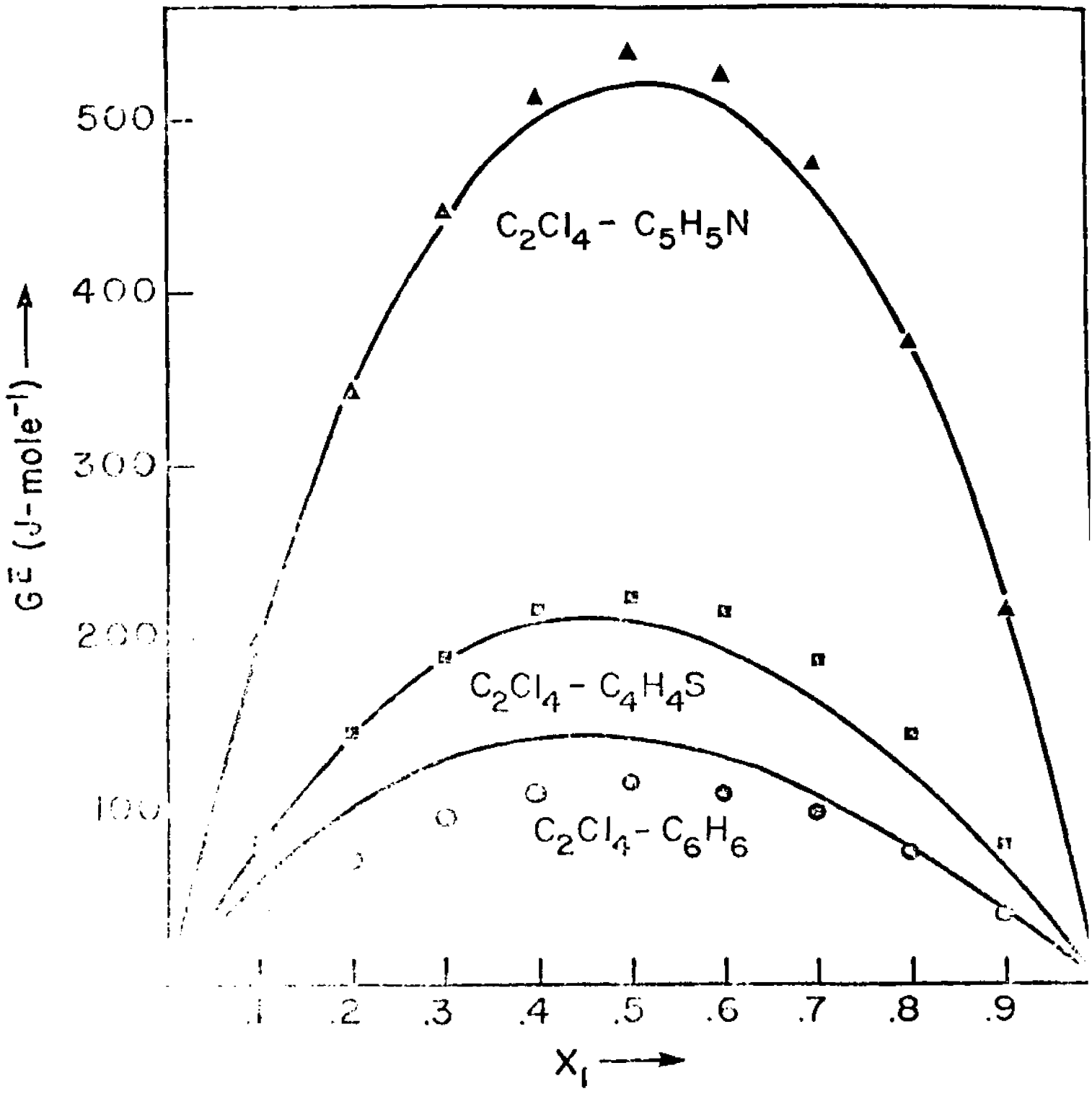
3. At infinite dilution $\omega = a$, thus $\omega' = 3a/2$, the corresponding interchange energy for the tetrachloroethylene mixture.

4. Keeping the same constants b, c, and d in the expression for ω, substitute group fractions for mole fractions, thus obtaining

$$\omega' = 3a/2 + bZ_c + cZ_c^2 + dZ_c^3 + \ . \ . \ .$$

5. Calculate the excess free energy from ω'.

Although the procedure outlined above is far from being rigorous just as the various assumptions which lead to it are certainly very rough, interesting results have been obtained. Fig. 5 shows the experimental G^E curves of tetrachloroethylene mixtures and the corresponding predicted values from the behavior of carbon tetrachloride



... Experimental and estimated molar excess ... of mixtures of tetrachloroethylene ... thiophene, and pyridine, at 70.00°C. Curves ... experimental values. Points represent values ... following the procedure outlined in part E of ...

mixtures.

F. Estimation of H^E from G^E and Vice Versa

Knowledge of the excess thermodynamic properties is of great importance, especially in the development of new classical and statistical theories of solutions. Rarely are all the data available in the literature. It is, therefore, very important to derive equations which interrelate the different excess thermodynamic functions; knowledge of some of these properties permits the evaluation of others. The possibility of even a reasonably approximate prediction saves a tremendous amount of experimental effort.

It is with this intention that the semi-empirical relations which enable us to predict the excess enthalpies of certain binary systems from single temperature measurements of excess free energies were developed.

Excess free energy and excess enthalpy data for twenty-eight binary systems were taken from the literature. The systems and the corresponding literature references are given in Table 12.

The parameters α and β for a particular system are determined in the following manner:

Experimental values of G^E and H^E (where available) are obtained at $x = 0.25$, $x = 0.50$, and $x = 0.75$ from the corresponding Redlich-Kister expansions, and inserted in Eq. (103) or Eq. (117) to calculate the constants α and β. These are taken as starting points in an iterative procedure to determine values of α and β which give the

TABLE 12

REFERENCES FOR LITERATURE DATA

System	Reference
Pentane-- Benzene	G^E: Funk and Prausnitz, 1970 (21) H^E: Not measured
Neopentane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
Cyclopentane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Watson et al., 1965 (167)
Hexane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Mathieson and Thynne, 1956 (168)
2-Methylpentane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
2,2-Dimethylbutane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
2,3-Dimethylbutane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
Cyclohexane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Lundberg, 1964 (169)
Methylcyclopentane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured

TABLE 12--Continued

System	Reference
Heptane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Lundberg, 1964
3-Methylhexane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
2,4-Dimethylpentane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
2,2,3-Trimethylbutane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
Methylcyclohexane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
Octane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
2,2,4-Trimethylpentane-- Benzene	G^E: Funk and Prausnitz, 1970 H^E: Lundberg, 1964
Hexane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Mathieson and Thynne, 1956
3-Methylpentane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
Cyclohexane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Watson et al., 1965

TABLE 12--Continued

System	Reference
Methylcyclopentane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
Heptane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Lundberg, 1964
Methylcyclohexane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
2,2,4-Trimethylpentane-- Toluene	G^E: Funk and Prausnitz, 1970 H^E: Not measured
1,2-Dibromoethane-- Benzene	G^E: Liebermann and Kohler, 1968 (170) H^E: Baud, 1915 (171)
1,2-Dibromoethane-- Cyclohexane	G^E: Liebermann and Kohler, 1968 H^E: Baud, 1915
1,2-Dichloroethane-- Cyclohexane	G^E: Miksch et al., 1969 (172) H^E: Korvezee, 1969, (173)
Carbon tetrachloride-- Benzene	G^E: Scatchard et al., 1940 (130) H^E: Scatchard et al., 1952 (174)
Pyridine-- Tetrachloroethylene	G^E: Fried et al., 1968 (106) H^E: Not measured

best possible representation of the excess thermodynamic property of the mixture over the whole concentration range.

The values of α and β determined by both equations are given in Table 13. In addition to that, the ratio of the molar volumes is also listed. For some systems certain discrepancies exist between the two sets of constants. This is, however, expected, since the assumption introduced by Eq. (112) is only partially justified, as is obvious from the following derivation.

For the estimation of the ratio of H^E/G^* as given by Eq. (112), we assume the case in which G^* is represented by the Scatchard-Hildebrand equation

$$G^* = \frac{x_1 x_2 V_1^0 V_2^0 (\delta_1 - \delta_2)^2}{x_1 V_1^0 + x_2 V_2^0} \tag{148}$$

Taking the logarithm of this equation and differentiating it with respect to T, at constant composition, we obtain

$$\frac{\partial \ln G^*}{\partial T} = \frac{1}{V_1^0} \cdot \frac{\partial V_1^0}{\partial T} + \frac{1}{V_2^0} \cdot \frac{\partial V_2^0}{\partial T} + \frac{2}{(\delta_1 - \delta_2)} \cdot \frac{\partial (\delta_1 - \delta_2)}{\partial T} - \frac{x_1 (\partial V_1^0)/\partial T + x_2 (\partial V_2^0)/\partial T}{x_1 V_1^0 + x_2 V_2^0} \tag{149}$$

Hildebrand's approximation (6) $\partial \delta_i / \partial T = -1.25 \alpha_i \delta_i$ combined with the requirement that the thermal expansion coefficients are equal ($\alpha_1 = \alpha_2 = \alpha$) leads to the result

TABLE 13

BEST FIT PARAMETERS OF EQUATION 103, WILSON EQUATION, EQUATION 117, AND THE RATIO OF MOLAR VOLUMES V_1^0/V_2^0 OF THE PURE LIQUID COMPONENTS

System	t, °C	Equation 103		Wilson Equation		t, °C	Equation 117		V_1^0/V_2^0
		α	β	λ_{12}	λ_{21}		α	β	
Pentane-- Benzene	25	0.725	0.795	0.615	0.765				1.30
Neopentane-- Benzene	25	0.718	0.687	0.630	0.545				1.38
Cyclopentane-- Benzene	25	0.891	0.759	0.926	0.643	25	0.766	0.854	1.06
Hexane-- Benzene	25	0.624	0.930	0.422	1.063	20	0.608	0.935	1.47
2-Methylpentane-- Benzene	25	0.613	0.864	0.428	0.908				1.49
2,2-Dimethylbutane-- Benzene	25	0.603	0.861	0.372	0.957				1.50
2,3-Dimethylbutane-- Benzene	25	0.656	0.835	0.498	0.873				1.50

TABLE 13--Continued

System	t, °C	Equation 103		Wilson Equation		t, °C	Equation 117		V_1^0/V_2^0
		α	β	λ_{12}	λ_{21}		α	β	
Cyclohexane-- Benzene	25	0.705	0.904	0.548	0.979	25	0.732	0.814	1.22
Methylcyclopentane-- Benzene	25	0.803	0.791	0.759	0.741				1.27
Heptane-- Benzene	25	0.578	0.999	0.340	1.244	25	0.602	0.918	1.65
3-Methylhexane-- Benzene	25	0.616	0.917	0.437	1.050				1.65
2,4-Dimethylpentane-- Benzene	25	0.584	0.856	0.369	0.950				1.68
2,2,3-Trimethylbutane-- Benzene	25	0.598	0.944	0.378	1.134				1.64
Methylcyclohexane-- Benzene	25	0.769	0.817	0.730	0.791				1.47
Octane-- Benzene	25	0.645	0.862	0.533	0.946				1.87
2,2,4-Trimethylpentane-- Benzene	25	0.571	0.923	0.356	1.112	25	0.586	0.911	1.86

TABLE 13--Continued

System	t, °C	Equation 103		Wilson Equation		t, °C	Equation 117		V_1^0/V_2^0
		α	β	λ_{12}	λ_{21}		α	β	
Hexane-- Toluene	25	0.758	0.840	0.662	0.841	20	0.902	0.800	1.23
3-Methylpentane-- Toluene	25	0.861	0.734	0.885	0.613				1.22
Cyclohexane-- Toluene	25	0.868	0.770	0.873	0.674	25	0.859	0.764	1.02
Methylcylopentane-- Toluene	25	0.875	0.795	0.885	0.711				1.06
Heptane-- Toluene	25	0.616	1.169	0.384	1.459	25	0.710	0.962	1.38
Methylcyclohexane-- Toluene	25	0.965	0.776	1.087	0.624				1.20
2,2,4-Trimethylpentane-- Toluene	25	0.702	0.844	0.609	0.868				1.55
1,2-Dibromoethane-- Benzene	10	1.014	0.788	1.090	0.690	20	0.902	0.895	0.97
1,2-Dibromoethane-- Cyclohexane	10	0.587	0.657	0.333	0.474	20	0.660	0.662	0.80

TABLE 13--Continued

System	t, °C	Equation 103		Wilson Equation		t, °C	Equation 117		V_1^0/V_2^0
		α	β	λ_{12}	λ_{21}		α	β	
1,2-Dichloroethane--Cyclohexane	20	0.643	0.641	0.504	0.412	25	0.640	0.625	0.73
Pyridine--Tetrachloroethylene	60	0.717	0.762	0.592	0.709				0.79

$$\frac{\partial \ln G^*}{\partial T} \simeq -1.5\alpha \qquad (150)$$

Substitution of Eq. (150) into Eq. (108) yeilds

$$H^E = G^*(1 + 1.5\alpha T)^{\dagger} \qquad (151)$$

As for most organic liquids α varies between 1×10^{-3} and $3 \times 10^{-3} K^{-1}$, the value of the expression in the parentheses of Eq. (151) fluctuates between 1.45 and 2.35. In our calculations a value of 2 was used. Table 14 shows that the experimentally found limiting values of the ratio H^E/G^* are in most systems only slightly different from 2 and the average value is 1.96. Kuhn and Massini (165) found for non-polar systems $H^E/G^E \simeq 2$. On the basis of the cell theory, Kohler (166) came to the same conclusion for polar mixtures.

As is evident from Tables 14 and 15 where calculated and experimental results are compared at $x = 0.5$, the agreement is reasonable in spite of the discrepancies in the two sets of constants.

For comparison, the enthalpy of mixing predicted by the Wilson equation

$$H^E = x_1 x_2 \left[\frac{\Lambda_{12}(\lambda_{12} - \lambda_{11})}{x_1 + x_2 \Lambda_{12}} + \frac{\Lambda_{21}(\lambda_{12} - \lambda_{22})}{x_2 + x_1 \Lambda_{21}} \right] \qquad (152)$$

---

†This α, the thermal expansion coefficient, should not be confused with the constant α of Eq. (103,117), etc.

TABLE 14

MEASURED AND PREDICTED EXCESS GIBBS FREE ENERGIES AT $x_1 = 0.5$ AND LIMITING VALUES OF H^E/G^* (EQUATION 112)

System	G^E in cal.mole^{-1}		lim H^E/G^*	
	Measured	Equation 103	$x_1=0$	$x_2=0$
Cyclopentane-- Benzene	69	76	2.4	1.8
Hexane-- Benzene	92	95	2.1	2.1
Cyclohexane-- Benzene	79	95	2.1	2.4
Heptane-- Benzene	85	96	2.2	2.4
2,2,4-Trimethylpentane-- Benzene	98	95	2.0	2.0
Hexane-- Toluene	79	52	1.3	1.7
Cyclohexane-- Toluene	72	76	1.9	1.9
Heptane-- Toluene	48	59	2.1	3.0
1,2-Dibromoethane-- Benzene	35	33	2.5	1.9
1,2-Dibromoethane-- Cyclohexane	200	171	1.4	1.5
1,2-Dichloroethane-- Cyclohexane	184	196	1.8	1.8
Carbon tetrachloride-- Benzene	18	15	1.3	1.3
			Average:	1.96

TABLE 15

MEASURED AND PREDICTED ENTHALPIES OF MIXING AT x = 0.5

System	H^E in cal.mole^{-1}		
	Measured	Equation 117	Wilson Equation
Pentane--Benzene	177[a]	205	93
Neopentane--Benzene	172[a]	276	113
Cyclopentane--Benzene	150	137	61
Hexane--Benzene	205	200	92
2-Methylpentane--Benzene	232[a]	241	110
2,2-Dimethylbutane--Benzene	179[a]	250	112
2,3-Dimethylbutane--Benzene	247[a]	227	103
Cyclohexane--Benzene	191	161	74
Methylcyclopentane--Benzene	171[a]	163	73
Heptane--Benzene	222	200	90
3-Methylhexane--Benzene	205[a]	211	98
2,4-Dimethylpentane--Benzene	224[a]	266	120

[a]Derived from G^E at different temperatures

TABLE 15--Continued

System	H^E in cal.mole^{-1}		
	Measured	Equation 117	Wilson Equation
2,2,3-Trimethylbutane--Benzene	175[a]	211	97
Methylcyclohexane--Benzene	187[a]	167	72
Octane--Benzene	202[a]	220	98
2,2,4-Trimethylpentane--Benzene	237	242	111
Hexane--Toluene	110	162	76
3-Methylpentane--Toluene	130[a]	164	67
Cyclohexane--Toluene	149	142	65
Methylcyclopentane--Toluene	120[a]	126	58
Heptane--Toluene	132	110	42
Methylcyclohexane--Toluene	130[a]	102	33
2,2,4-Trimethylpentane--Toluene	177[a]	192	86
1,2-Dibromoethane--Benzene	69	70	31
1,2-Dibromoethane--Cyclohexane	329	376	140

[a]Derived from G^E at different temperatures

TABLE 15--Continued

System	H^E in cal.mole^{-1}		
	Measured	Equation 117	Wilson Equation
1,2-Dichloroethane--Cyclohexane	379	373	146
Carbon tetrachloride--Benzene	31	38	18
Pyridine--Tetrachloroethylene	222[a]	255	108

[a]Derived from G^E at different temperatures

is also given in Table 15. The constants Λ_{12} and Λ_{21} of this equation calculated from the excess Gibbs free energies are given in Table 13.

As seen, in most cases the values calculated from Eq. (117) are in good agreement with the experimental results. For some systems the agreement is less satisfactory, but still acceptable. Consideration must be given to the fact that calorimetric data reported by different authors disagree in some cases significantly and that the accuracy of the excess enthalpy obtained from the temperature derivative of the excess Gibbs free energy is one order of magnitude lower than the accuracy of G^E itself. As evident from Table 15, the results obtained from Eq. (117) are in all cases closer to the measured values than those obtained from the Wilson equation.

Since the regular theory approach was used for the determination of the temperature dependence of the parameters, it must be understood that the derived equations can be applied only to mixtures of molecules not greatly differing in shape and non-associated mixtures in which the only negative contribution to the excess Gibbs free energy is due to the size effect. The term G* in Eq. (104) should always be positive and only positive excess enthalpies can be predicted.

G. Temperature Dependence of G^E

Comparative study of the thermodynamic behavior of binary systems is often necessary in evaluating and

hopefully understanding the effect of various factors on the excess properties of solutions. This comparison, however, is frequently rendered difficult by the fact that such studies are not made at the same temperature. A modification of the theory which permits the calculation of the excess Gibbs free energy from isothermal enthalpies of mixing and vice versa makes possible the extrapolation of the excess free energy from a given temperature to any temperature of concern. The problem, of course, is to find the temperature dependence of the parameters α and β that characterize a mixture.

It is seen from Eqs. (124, 125, and 126) that within any given temperature interval, α and β are multiplied by the same factor in order to obtain the new set corresponding to the temperature of interest. This constant k is calculated from Eq. (128).

This method was applied to twenty-six systems taken from the literature (see Table 12). Results are reported in Table 16. The second column in Table 16 gives the temperature range of the extrapolation of the excess Gibbs free energy between temperatures T_1 and T_2. With a few exceptions the reference temperature is 25°C and the temperature of concern 75°C. As is seen from Table 16 the extrapolated values of G^E agree very well with the experimental data. For most of the systems the error is within the limits of the experimental uncertainties. This can be considered as an evidence that Eqs. (115 and 116), respect-

TABLE 16

MEASURED AND EXTRAPOLATED VALUES OF THE EXCESS GIBBS FREE ENERGY G^E AT x = 0.5

System	Extrapolation Range, ^0C	G^E in cal.mole^{-1} Measured	G^E in cal.mole^{-1} Extrapolated
Pentane-- Benzene	25 → 75	90	85
Neopentane-- Benzene	25 → 50	134	126
Cyclopentane-- Benzene	25 → 75	61	60
Hexane-- Benzene	25 → 75	75	76
2-Methylpentane-- Benzene	25 → 75	97	95
2,2-Dimethylbutane-- Benzene	25 → 75	108	99
2,3-Dimethylbutane-- Benzene	25 → 75	83	87

TABLE 16--Continued

System	Extrapolation Range, ^{0}C	G^{E} in cal.mole^{-1} Measured	G^{E} in cal.mole^{-1} Extrapolated
Cyclohexane-- Benzene	25 → 75	65	67
Methylcyclopentane-- Benzene	25 → 75	67	67
Heptane-- Benzene	25 → 75	63	68
3-Methylhexane-- Benzene	25 → 75	70	73
2,4-Dimethylpentane-- Benzene	25 → 75	105	98
2,2,3-Trimethylbutane-- Benzene	25 → 75	79	73
Methylcyclohexane-- Benzene	25 → 75	59	62
Octane-- Benzene	25 → 75	68	67

TABLE 16--Continued

System	Extrapolation Range, °C	G^E in cal.mole^{-1} Measured	G^E in cal.mole^{-1} Extrapolated
2,2,4-Trimethylpentane-- Benzene	25 → 75	73	76
Hexane-- Toluene	25 → 75	73	67
3-Methylpentane-- Toluene	25 → 75	75	69
Cyclohexane-- Toluene	25 → 75	60	62
Methylcyclopentane-- Toluene	25 → 75	56	55
Heptane-- Toluene	25 → 75	46	39
Methylcyclohexane-- Toluene	25 → 75	37	41
2,2,4-Trimethylpentane-- Toluene	25 → 75	70	68

TABLE 16--Continued

System	Extrapolation Range, °C	G^E in cal.mole^{-1} Measured	G^E in cal.mole^{-1} Extrapolated
1,2,Dichloroethane-- Cyclohexane	20 → 32	176	177
Pyridine-- Tetrachloroethylene	60 → 80	122	120

ively, describe the temperature behavior of the parameters correctly.

IX. CONCLUDING REMARKS

Since the early days of physical chemistry thousands of articles have been written in an effort to understand the behavior of mixed fluids. While much progress has been made, we are still far from an adequate theory of liquid mixtures.

The methods of classical thermodynamics do not allow any prediction. Its axioms entail relationships between different equilibrium properties but do not allow us to infer anything beyond these direct consequences, unless hypotheses are introduced that are outside the realm of thermodynamics.

The extra-thermodynamic considerations that must be introduced to make progress are hypotheses about the behavior of molecules. Consequently, in order to construct a theory of liquid mixtures essentially two kinds of information are required: we need to know something about the structure of liquids (i.e., the way in which molecules in a liquid are arranged in space), and we need to know something about intermolecular forces between like and unlike molecules. Unfortunately, information of either kind is inadequate and as a result all of the theories must make simplifying assumptions in order to overcome this disadvantage.

The dependence of the configurational properties on the intermolecular pair potential $\epsilon(r)$ implies that the properties of a binary mixture of substances 1 and 2 depend on $\epsilon_{11}(r)$, $\epsilon_{12}(r)$, and $\epsilon_{22}(r)$. There is no universally valid rule for obtaining $\epsilon_{12}(r)$ from a knowledge of $\epsilon_{11}(r)$ and $\epsilon_{22}(r)$, and hence, no universal rule for predicting the properties of a binary mixture from those of the pure components. The problem is further conplicated by the fact that almost all substances with which chemists and physicists deal are polyatomic and necessarily lack spherical symmetry. Consequently, the intermolecular pair energy for polyatomic substances must depend upon other variables in addition to r, i.e., upon relative orientation, charge distribution, etc. This area remains one of the most challenging problems of molecular physics.

The calculation of macroscopic equilibrium properties lies in the domain of statistical mechanics. Here it is the molecular arrangement or structure of a fluid which is important, and much progress seems to have been achieved in recent years due to improved models of fluid structure. However, until an adequate potential function is provided by quantum mechanics, statistical thermodynamicicists have to rely on (a) approximate potential functions, (b) empirical correlations of potential parameters, and (c) essentially empirical and adjustable mixing rules for extension to mixtures (34).

Since simplifying assumptions must be made, it

follows that a rigorous general theory cannot be constructed at this stage; simplifying assumptions which are reasonable for one type of mixture (e.g., mixtures of hydrocarbons) may be most unreasonable for another type (e.g., aqueous mixtures of organic acids). As a result, we do not have a general theory of liquid mixtures but instead several restricted theories each of which could be useful for a particular type of mixture. Considering the enormous difficulty of the challenge, it is perhaps not at all surprising that the most useful information regarding the relative merits of theories of liquids and liquid mixtures is still derived by means of a comparison with results of quasi-experimental computer simulation studies (175).

In the absence of a general theory, therefore, semi-empirical and empirical methods of investigation and correlation assume particular usefulness. It is within this framework that the various attempts of the present study in the extremely complex field of liquid mixtures should be viewed.

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