Treatment of Thermodynamic Data for Homogeneous Binary Systems

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This paper describes general methods for the treatment of binary data which are both precise and convenient. In particular a new and accurate graphical method of determining partial molal quantities is presented.

The basic equations applicable to homogeneous binary solutions are given in Table 1. In these equations G represents any molal (or unit mass) property of a homogeneous binary system. ΔG represents the property change resulting from mixing the pure components at constant temperature and pressure to form 1 mole (or a unit mass) of the solution. The notation $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$ to represent partial property changes resulting from mixing has not been widely used but seems convenient.

The derivation of Equation (5) is given in most advanced thermodynamics texts. Equations (7) and (8) follow directly from Equations (5) and (6) after differentiation at constant temperature and pressure. Equations (7) and (8) represent the form of the Gibbs-Duhem equation valid for systems at constant temperature and pressure. The generality of this equation in its applicability to many different properties has sometimes been overlooked.

Equations (4), (6), and (8) are valid for the excess properties of mixing as well as for the property changes themselves. An excess partial molal property of a component in solution is defined as the difference between the true partial property and the partial property the component would have in an ideal solution at the same temperature, pressure, and composition; that is,

$$\overline{G}_i^{\,E} = \overline{G}_i - \overline{G}_i^{\,ideal}$$

Similarly

$$\overline{\Delta G}_i^{\,E} = \overline{\Delta G}_i - \overline{\Delta G}_i^{\,ideal}$$

and

$$\Delta G^E = \Delta G - \Delta G^{ideal}$$

When the property is volume, internal energy, enthalpy, residual volume, compressibility factor, or heat capacity, $\overline{G}_i^{\,ideal} = G_i$ and $\overline{\Delta G}_i^{\,ideal} = 0$. Hence

$$\overline{\Delta G}_i^{\,E} = \overline{\Delta G}_i \quad \text{and} \quad \Delta G^E = \Delta G$$

Thus the excess properties do not represent new functions for these quantities.

The excess properties, however, are distinct quantities for the entropy and free energy. Thus

$$\Delta S^E = \Delta S + R\Sigma x_i \ln x_i$$

$$\Delta A^E = \Delta A - RT\Sigma x_i \ln x_i$$

$$\Delta F^E = \Delta F - RT\Sigma x_i \ln x_i$$

Yet another useful function can be obtained from the Gibbs free energy (*4*):

$$\frac{\Delta F^E}{RT} = x_A \ln \gamma_A + x_B \ln \gamma_B \quad (9)$$

Comparison of Equation (9) with Equation (4) shows $\ln\gamma_A$ and $\ln\gamma_B$ to be related to $\Delta F^E/RT$ exactly as $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$ are related to ΔG. Table 2 presents a summary of the functions which are of interest.

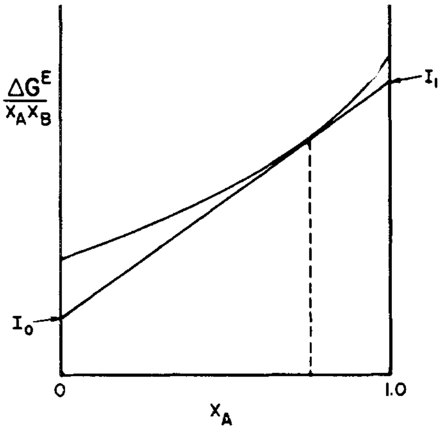

Fig. 1. Graphical procedure for determining partial properties.

The well-known method of tangent intercepts for the calculation of partial quantities is subject to considerable error because of the inherent uncertainty of the graphical techniques. A new method is presented here which greatly reduces this uncertainty. This method makes use of the plot of $\Delta G^E/x_A x_B$ vs. x_A, which has been used increasingly in recent years for the simple presentation of data; its new use is illustrated in Figure 1. The partial properties are shown to be related to the intercepts I_0 and I_1 as follows:

$$I_0 = \frac{\Delta G^E}{x_A x_B} - x_A \frac{d\left(\dfrac{\Delta G^E}{x_A x_B}\right)}{dx_A}$$

but

$$\frac{d\left(\dfrac{\Delta G^E}{x_A x_B}\right)}{dx_A} = \frac{\left(\dfrac{d\,\Delta G^E}{dx_A}\right)}{x_A x_B} + \left(\frac{\Delta G^E}{x_A x_B}\right)\left(\frac{x_A - x_B}{x_A x_B}\right)$$

Therefore

$$I_0 = \frac{\Delta G^E}{x_A x_B} - x_A\left[\frac{\left(\dfrac{d\,\Delta G^E}{dx_A}\right)}{x_A x_B} + \frac{\Delta G^E}{x_A x_B}\left(\frac{x_A - x_B}{x_A x_B}\right)\right]$$

With a little algebraic manipulation this reduces to

$$I_0 = 2\left(\frac{\Delta G^E}{x_A x_B}\right)$$

TABLE 1. BASIC EQUATIONS FOR BINARY SYSTEMS AT CONSTANT T AND p

$$x_A + x_B = 1 \quad (1)$$

$$\left.\begin{array}{ll} G = x_A G_A + x_B G_B + \Delta G & (2) \\ G = x_A \overline{G}_A + x_B \overline{G}_B & (3) \end{array}\right\} \rightarrow \left.\begin{array}{l} \Delta G = x_A(\overline{G}_A - G_A) + x_B(\overline{G}_B - G_B) \\ \Delta G = x_A\,\overline{\Delta G}_A + x_B\,\overline{\Delta G}_B \end{array}\right\} (4)$$

$$\left.\begin{array}{l} \overline{G}_A = G + (1 - x_A)\left(\dfrac{dG}{dx_A}\right) \\ \overline{G}_B = G - x_A\left(\dfrac{dG}{dx_A}\right) \end{array}\right\} (5) \qquad \left.\begin{array}{l} \overline{\Delta G}_A = \Delta G + (1 - x_A)\left(\dfrac{d\,\Delta G}{dx_A}\right) \\ \overline{\Delta G}_B = \Delta G - x_A\left(\dfrac{d\,\Delta G}{dx_A}\right) \end{array}\right\} (6)$$

$$\left(\frac{d\overline{G}_B}{dx_A}\right) = -\left(\frac{x_A}{1 - x_A}\right)\left(\frac{d\overline{G}_A}{dx_A}\right) \quad (7) \qquad \left(\frac{d\,\overline{\Delta G}_B}{dx_A}\right) = -\left(\frac{x_A}{1 - x_A}\right)\left(\frac{d\,\overline{\Delta G}_A}{dx_A}\right) \quad (8)$$

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$$- \frac{1}{x_B^2}\left[\Delta G^E + x_B\left(\frac{d\,\Delta G^E}{dx_A}\right)\right]$$

By Equation (6)

$$\Delta G^E + x_B\left(\frac{d\,\Delta G^E}{dx_A}\right) = \overline{\Delta G}_A{}^E$$

Thus

$$\overline{\Delta G}_A{}^E = x_B^2\left[2\left(\frac{\Delta G^E}{x_A x_B}\right) - I_0\right] \qquad (10)$$

Similarly

$$\overline{\Delta G}_B{}^E = x_A^2\left[2\left(\frac{\Delta G^E}{x_A x_B}\right) - I_1\right] \qquad (11)$$

In the limit as x_A approaches zero, x_B approaches unity, and $\Delta G^E/x_A x_B$ approaches I_0. Thus by Equation (10)

$$\lim_{x_A \to 0} \overline{\Delta G}_A{}^E = (1)(2I_0 - I_0) = I_0 \qquad (12)$$

In the limit as x_A approaches unity, $\Delta G^E/x_A x_B$ approaches I_1.

By Equation (11)

$$\lim_{x_B \to 0} \overline{\Delta G}_B{}^E = (1)(2I_1 - I_1) = I_1 \qquad (13)$$

The same derivation could be presented in terms of either G or ΔG as well as ΔG^E; however $G/x_A x_B$ and $\Delta G/x_A x_B$ (except for the cases where $\Delta G = \Delta G^E$) approach infinity at both $x_A = 0$ and $x_A = 1$, and the method breaks down. This is not true of $\Delta G^E/x_A x_B$, which remains finite. This does not impose a practical limitation on the method, because data can always be easily converted to excess values.

At first thought it might seem that the determination of $\overline{\Delta G}_A{}^E$ and $\overline{\Delta G}_B{}^E$ by the method just described would be subject to errors of the same order as the usual method of tangent intercepts, because it too requires the graphical determination of the intercepts of tangents drawn to a curve; however this is not the case. The difference lies in the fact that the opposite intercepts come into play in the two cases. On the usual plot of ΔG vs. x_A the intercept at $x_A = 1$ is used to determine $\overline{\Delta G}_A$; whereas on the plot of $\Delta G^E/x_A x_B$ the intercept at $x_A = 0$ is employed. This is particularly well exemplified in the determination of the limiting values of $\overline{\Delta G}_A{}^E$ at $x_A = 0$ and $\overline{\Delta G}_B{}^E$ at $x_B = 0$, that is, the partial properties at infinite dilution. These values are almost impossible to obtain accurately from the usual plot because of the long extrapolations required, but they are simply the intercepts of the curve of $\Delta G^E/x_A x_B$ vs. x_A at $x_A = 0$ and $x_A = 1$, as indicated by Equations (12) and (13).

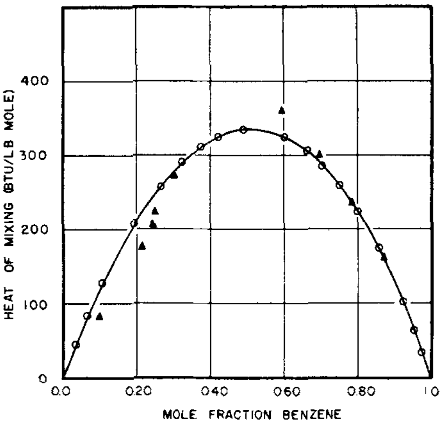

Fig. 2. Integral heat of mixing for the cyclohexane-benzene system: ○, (*5*) △, (*1*)

The intercepts of the tangents drawn to the $\Delta G^E/x_A x_B$ curve are of course subject to the normal errors involved in drawing tangents. However the uncertainty of an intercept increases as the distance of the point of tangency from the intercept increases, and it is clear from Equations (10) and (11) that the greater this distance, the smaller the number by which the intercept is multiplied. Since the multiplying factor x^2 decreases as the uncertainty in I increases, the uncertainty in the $\overline{\Delta G}^E$ values remains small.

Another advantage of drawing the $\Delta G^E/x_A x_B$ plot is that it is a very sensitive indication of the precision of the data. If the data are of poor quality, this is usually obvious from the graph; if the data are reasonably good, this plot provides an excellent means of smoothing them. In addition this plot shows at a glance whether sufficient data have been taken to allow the determination of partial properties with accuracy over the entire composition range.

These points are well illustrated by the data for the heats of mixing ($\Delta H = \Delta H^E$) of the cyclohexane-benzene system. The data of Schnaible (*5, 6*) at 25°C. will be compared with those of Brown, Mathieson, and Thynne (*1*) at 20°C.

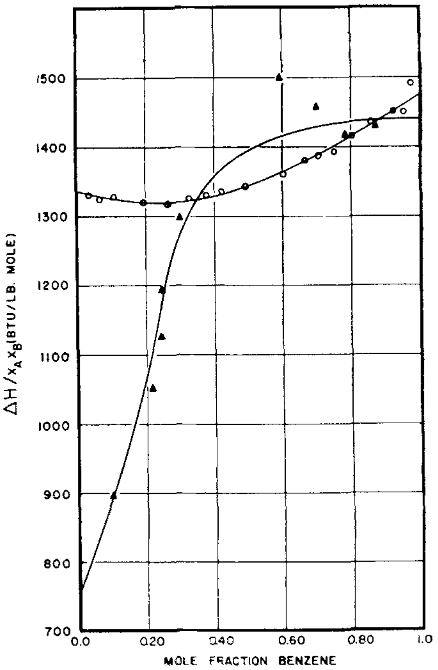

Fig. 3. The cyclohexane-benzene system: ○, (*5*) △, (*1*)

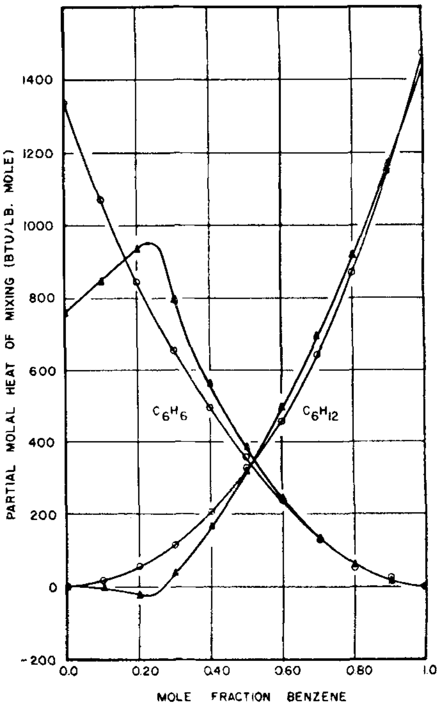

Fig. 4. Partial molal heats of mixing for the cyclohexane-benzene system: ○, (*5*) △, (*1*)

TABLE 2. SUMMARY OF PROPERTIES

Property	ΔG	$\overline{\Delta G}_i$
Volume (v)	$\Delta v = \Delta v^E$	$\overline{\Delta v}_i = \overline{\Delta v}_i{}^E$
Residual volume (α)	$\Delta\alpha = -\Delta v$	
Compressibility factor (z)	$\Delta z = p\Delta v/RT$	
Internal energy (E)	$\Delta E = \Delta E^E$	$\overline{\Delta E}_i = \overline{\Delta E}_i{}^E$
Enthalpy (H)	$\Delta H = \Delta H^E$	$\overline{\Delta H}_i = \overline{\Delta H}_i{}^E$
Heat capacity (C_p or C_v)	$\Delta C_p = \Delta C_p{}^E$	$\overline{\Delta C}_{pi} = \overline{\Delta C}_{pi}{}^E$
Entropy (S)	ΔS	$\overline{\Delta S}_i$
Helmholtz free energy (A)	ΔA	$\overline{\Delta A}_i$
Gibbs free energy (F)	ΔF	$\overline{\Delta F}_i$
Excess entropy (S^E)	ΔS^E	$\overline{\Delta S}_i{}^E$
Excess Helmholtz free energy (A^E)	ΔA^E	$\overline{\Delta A}_i{}^E$
Excess Gibbs free energy (F^E)	ΔF^E	$\overline{\Delta F}_i{}^E$
Function defined by Equation (9)	$\Delta F^E/RT$	$\ln \gamma_i$

This small temperature difference should have an insignificant effect on the data Both sets of data are shown on Figure 2, a plot of ΔH vs. $x_{C_6H_6}$, and on Figure 3, a plot of $\Delta H/x_{C_6H_6}x_{C_6H_{12}}$ vs. $x_{C_6H_6}$. The data of Schnaible for this uncomplicated system are of obvious superiority, and the sensitivity of Figure 3 in showing inadequacies in the data is evident. Values of $\overline{\Delta H}_i$ for both components have been determined from Figure 3 by the method described for both curves shown. The partial molal heats of mixing (also called differential heats of mixing and partial relative enthalpies) so determined are shown in Figure 4.

For highly nonideal systems, for example methanol-benzene, plots of $\Delta G^E/x_Ax_B$ vs. x_A may exhibit marked curvature. This curvature reduces the precision with which slopes can be drawn and makes the extrapolation of the curve to the edges of the diagram uncertain. It is advantageous in such cases to plot the reciprocal function, $x_Ax_B/\Delta G^E$ vs. x_A, as this often results in a much more nearly linear curve. The data for the methanol-benzene system plotted both ways are shown in Figure 5. The partial quantities are readily determined from the reciprocal plot by

$$\overline{\Delta G}_A{}^E = \frac{(x_B)^2 I_0}{\left(\dfrac{x_Ax_B}{\Delta G^E}\right)^2} \qquad (14)$$

$$\overline{\Delta G}_B{}^E = \frac{(x_A)^2 I_1}{\left(\dfrac{x_Ax_B}{\Delta G^E}\right)^2} \qquad (15)$$

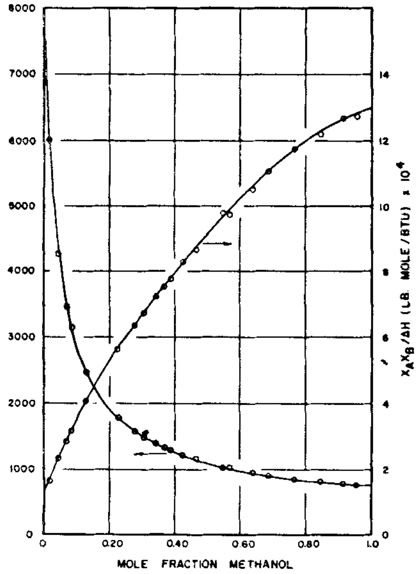

Fig. 5. The methanol-benzene system (*5*).

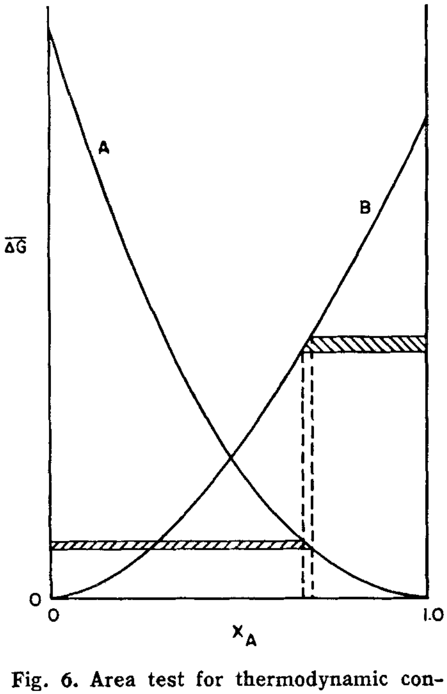

Fig. 6. Area test for thermodynamic consistency.

These equations are derived in a fashion analogous to the derivations of Equations (10) and (11), and all the advantages previously described are retained. Here of course I_0 and I_1 are the intercepts on a plot of $x_Ax_B/\Delta G^E$ vs. x_A.

Equations (7) and (8), the Gibbs-Duhem relationships for binary systems at constant temperature and pressure, are applicable to any of the properties listed in Table 2. This form of the Gibbs-Duhem equation is sometimes called the *slope test*, because it relates the slopes of curves of $\overline{G}_A$ and $\overline{G}_B$ or $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$ vs. x_A at each value of x_A. In addition to the slope test there is an *area test*, which is directly applicable to data for $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$. This test has been presented in the literature for the special case of $\ln\gamma_i$ data only. It is more convenient than the *slope test* but not so stringent and follows directly from Equation (8), which may be written

$$(1 - x_A)\left(\frac{d\,\overline{\Delta G}_B}{dx_A}\right) dx_A = x_A\left(-\frac{d\,\overline{\Delta G}_A}{dx_A}\right) dx_A$$

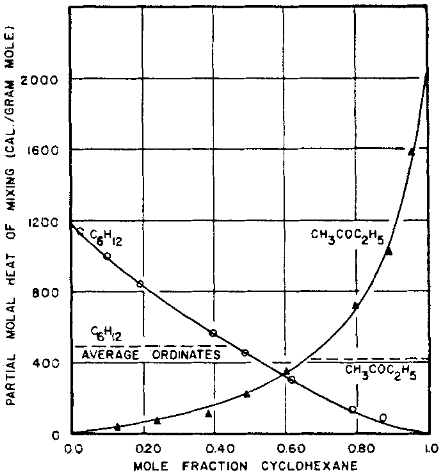

Fig. 7. Independently measured partial molal heats of mixing for the cyclohexane-methylethylketone system as reported by Donald and Ridgway (*2*).

The two terms of this equation (on the left and right sides) represent the shaded areas shown on Figure 6. Integration from $x_A = 0$ to $x_A = 1$ will give the total areas under the two curves, and these must be equal for the area test to be satisfied. This result depends on the fact that the $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$ curves start at zero at $x_A = 1$ and 0 respectively. The mathematical expression for the area test is

$$\int_0^1 \overline{\Delta G}_A\, dx_A = \int_0^1 \overline{\Delta G}_B\, dx_A \qquad (16)$$

which may also be written

$$\int_0^1 (\overline{\Delta G}_A - \overline{\Delta G}_B)\, dx_A = 0 \qquad (17)$$

The easiest way to compare the two areas of Equation (16) is to determine the average ordinate for each curve by the graphical equivalent of Simpson's rule. It is also possible to plot the differences of the ordinates of the two curves vs. x_A. According to Equation (17) the area under this curve should be zero. As applied to $\ln\gamma_i$ values, $(\overline{\Delta G}_A - \overline{\Delta G}_B)$ becomes $\ln \gamma_A/\gamma_B$. This particular plot was proposed independently by Herington (*3*) and by Redlich and Kister (*4*).

There would seem to be little point in drawing this latter plot in most cases, because the area test can just as easily be made on the former plot (Figure 6) and examined for at least qualitative agreement with the slope test. It should be noted that the area test will automatically be met when the slope test is satisfied at all values of x_A. However the reverse is not true. It is entirely possible to have data which satisfy the area test, but not the slope test, and so it is not generally sufficient merely to adjust the curve of $(\overline{\Delta G}_A - \overline{\Delta G}_B)$ vs. x_A to achieve zero area. There is no sure method of adjusting an inconsistent set of independently measured $\overline{\Delta G}_A$ and $\overline{\Delta G}_B$ values to get correct results.

If the original data are a set of ΔG values, the Gibbs-Duhem equation assures thermodynamic consistency for the partial quantities, provided that the calculations are accurate. No objective test for the accuracy of such data is known. The two sets of results presented in Figure 3 illustrate this point. The partial molal heats of mixing calculated from both curves are shown in Figure 4. Both sets of data lead to thermodynamically consistent sets of results, which show merely the excellence of the procedure proposed for the calculation of partial quantities.

The measurements made by Donald and Ridgway (*2*) of the differential (or partial molal) heats of mixing for the cyclohexane-methylethylketone system provide an excellent example of the testing of data by the Gibbs-Duhem equation. The independently measured values of $\overline{\Delta H}_i$ for these components are plotted vs. mole fraction of cyclohexane in Figure 7. The area test shows them to be inconsistent and hence of uncertain accuracy. This test should always be applied to data of this sort.

NOTATION

f_i = fugacity of pure i at the T and p of the solution
$\bar{f}_i$ = fugacity of component i in solution
G = an extensive property of a binary system on a mole basis
G_i = an extensive property of pure i on a mole basis
I_0 = an intercept at $x_A = 0$
I_1 = an intercept at $x_A = 1$
x_i = mole fraction of component i in solution
γ_i = activity coefficient of component i in solution = $\bar{f}_i/x_i f_i$
Δ = designates a property change as a result of mixing at constant T and p
E = an excess property (superscript)
— placed over the symbol for an extensive property designates the molal property in solution, that is, the partial molal property

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The Molecular Structure of Liquids

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This survey presents a rather qualitative description of the present knowledge of liquid structure. The physical picture of this structure, which has been drawn from the interpretation of experimental data will be employed to explain and justify the theoretical methods necessary in the development of a more quantitatively reliable description of the liquid.

Understanding of liquids is much less complete than of the other states of matter. In the case of liquids there would appear to be no obvious element of simplicity comparable to the scarcity of molecular encounters in gases or of the small amplitudes of the thermal motions and high degree of spatial ordering in solids. Despite these difficulties an understanding of the liquid state is gradually emerging, and although knowledge is still far from complete, a qualitative and in some cases almost quantitative explanation of liquid behavior is within reach.

Simple nonassociated liquids of spherical, structureless molecules will be discussed. The interaction of two molecules will in this case depend only upon the distance between their centers. These interactions, together with the thermal motions of the molecules, are responsible for the changes in the physical state of matter that occur when the density and temperature are varied. Indeed it is the object of this survey clearly to describe the roles played by these two factors in the establishment of the detailed molecular structure of liquids.

In principle a precise description of the intermolecular forces can be determined by direct quantum mechanical calculations; however in all but the simplest cases the success of this approach has been severely limited by mathematical difficulties. Therefore the interactions of most molecular species are actually obtained not from rigorous quantum mechanical arguments but from the semiempirical analysis of experimental data. An excellent account of these methods is included in the recent treatise of Hirschfelder, Curtiss, and Bird (*1*). Despite the many limitations, such methods give a fairly complete description of the intermolecular forces. Thus it is found that for small separations of the molecules these forces are of a strongly repulsive nature, suggesting the existence of a hard molecular core. When the intermolecular separation increases beyond the diameter of this rigid core, the forces between the two molecules become weakly attractive and tend rapidly to zero.

In liquids one is not usually concerned with the interaction of a single pair of molecules but rather with the potential energy of a molecule due to its simultaneous interactions with several of its neighbors. The total force upon such a molecule is assumed given by the vector sum of its individual and separate interactions with the others. Although the validity of this assumption is certainly suspect, very little information is presently available concerning the affects of nonadditive intermolecular forces upon the behavior of liquids. Moreover it is probably safe to say that the other approximations included in the existing theories of liquids are more serious in their consequencies.

A DESCRIPTION OF LIQUID STRUCTURE

A precise microscopic description for the state of a liquid would include a complete specification of the positions and motions for all the molecules. This description is not only complicated, but is wholly lacking in operational significance. One does not experimentally observe the behavior of separate molecules in the liquid but instead observes the heat capacity, thermal conductivity, viscosity, etc. Since these properties bear only a statistical relationship to the molecular-scale description of the liquid, real significance can be associated only with the average or most probable behavior of the molecules and not with a detailed specification of their individual motions. In principle this information can be determined directly from the methods of statistical mechanics; however in practice the success of the statistical approach will depend very largely upon the ability to ascribe a simple and at the same time realistic description to the average behavior of the molecules. Therefore attention is directed toward a qualitative description of liquid structure and the characterization of the molecular-scale processes responsible for the observed macroscopic properties of the liquid.

In the absence of a direct experimental procedure for obtaining this information one must construct a model of the liquid upon the basis of intuitive arguments, its success being judged by its ability to account for the physical properties of the liquid. The rules for constructing this model have changed very little since they were first announced in 1937 by Eyring and Hirschfelder (*2*).

In the search for a clue to the structure of liquids no single source of information has proved so valuable as the analysis of X-ray diffraction experiments. In these experiments one allows a monochromatic

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