EQUILIBRIUM IN NON-ELECTROLYTE MIXTURES[1]

GEORGE SCATCHARD

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts

Received October 25, 1948

The following subjects are discussed or reviewed: (*1*) the analytical expression of an extensive property interesting in thermodynamics as quantity per mole of unmixed components plus the product of two mole fractions multiplied by a power series in the difference between these mole fractions; (*2*) the related expressions for the two partial molal quantities and their difference; (*3*) the illustration of these methods applied to volume changes on mixing and to excess free energies; (*4*) the approximation of properties of polycomponent systems to those of the two-component systems comprising them; (*5*) the computation of analytical expressions for the excess free energy from measurements of vapor pressure and composition as functions of liquid composition, corrected or uncorrected for deviations of the vapor from perfect gas laws; (*6*) a "Gibbs–Duhem" test of consistency of vapor equilibrium measurements without differentiation, by plotting short segments of lines through corresponding potentials at $x = 0$ and 1, which should be tangent to the curve of molal free energy; (*7*) the computation of excess free energies from vapor pressures and liquid compositions, from liquid and vapor compositions, from the vapor pressure of one component, from azeotropic pressure and composition, from the solubility of a solid component, or from the composition of two saturated liquid phases; (*8*) the relation of the mole fraction expansion to the corresponding expression for the enthalpy of mixing in terms of volume fractions or other units, and to the Flory–Huggins expression for the excess entropy of mixing; (*9*) the possibility of expressing these two relations in terms of surface fractions rather than volume fractions; (*10*) the differences between the free energy, enthalpy, and entropy of mixing at constant pressure and the work content, energy, and entropy of mixing at constant total volume, and their effects upon the comparison of calculated and measured quantities; (*11*) the possibility of the cohesive energy density important in solutions being somewhat larger than the energy difference between the perfect gas and liquid states because of the intramolecular cohesive energy of the gas; (*12*) the molal volumes, the product of molal volume and the square root of the cohesive energy density of an homologous series and of the isomeric octanes; (*13*) the calculation of cohesive energy densities as proportional to the five-thirds power of the refraction; (*14*) the sorting or non-random distribution of molecules in solution; (*15*) partial accounting for sorting by use of the law of mass action for association of one component with one reactive group per molecule giving only dimers, with two reactive groups per molecule giving all linear polymers, with three or more reactive groups per molecule giving three-dimensional polymers, and for one-to-one combination.

INTRODUCTION

Most of our treatment of equilibrium is based upon the finding of Willard Gibbs (5) that, under certain simplifying conditions, the temperature, pressure, and chemical potential of each component are each constant throughout a system in

---

[1] Presented at the Symposium on Thermodynamics and Molecular Structure of Solutions, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 114th Meeting of the American Chemical Society, Portland, Oregon, September 13 and 14, 1948.

equilibrium. In some cases some of the simplifying conditions have to be removed, but we know pretty well now how to handle these more complicated cases. As a consequence we usually take temperature and pressure as independent variables. However, we seldom take the potentials. Instead, we usually use the number of units of each component and most often we choose as unit the mole. We reduce these to intensive quantities by dividing the number of moles of each component by the total number of moles in the phase, to give the composition as mole fractions of the components. It is then convenient to reduce the other extensive quantities to intensive ones in the same way. For the study of polycomponent systems, or for the determination of one kind of equilibrium from measurements of another kind, it is essential to have analytical expressions for these functions. It is always useful to have at least an approximate analytical expression, so that the small deviations may be plotted on a large scale.

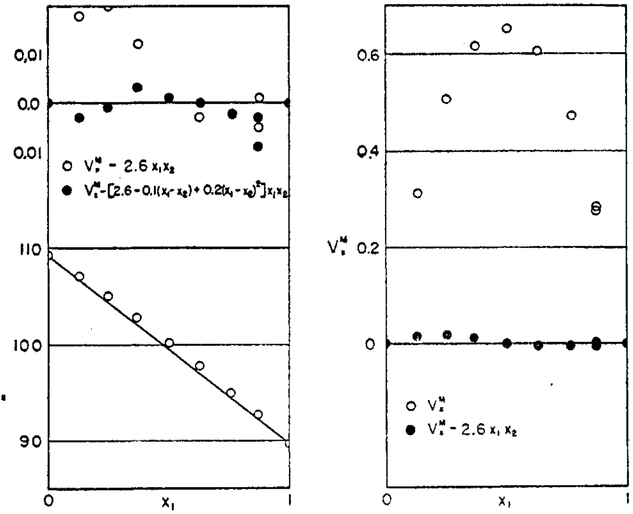

FIG. 1. Benzene–cyclohexane: volumes

VOLUME OF MIXING

We consider the volume first, because the relations are simple and the measurements are so direct that each step can be easily visualized. The phase consists of N_J moles of component J, N_K of component K, etc., and it has a volume V. Then the mole fraction x_K is defined by the relation $x_K = N_K/\Sigma_J N_J$, in which Σ_J means a sum over all the components. The volume per mole is defined by the relation, $V_x = V/\Sigma_J N_J$ and the partial molal volume of component K is defined by the relation

$$\bar{V}_K = (\partial V/\partial N_K)_{T,p,N} = (\partial V_x \Sigma_J N_J/\partial N_K)_{T,p,N}$$

In the pure component K, $\bar{V}_K = V/N_K = V_K$, which we call the molal volume of component K.

Figure 1 shows on the left V_x at 30°C. as a function of x_1 for mixtures of benzene (component 1) and cyclohexane (component 2) (21). Although in this case the change is only about 20 per cent, it is obvious that the accuracy of plotting can be increased by subtracting a straight line through the end points to give the volume of mixing per mole, V_x^M, defined by the relation

$$V_x^M = V_x - x_1V_1 - x_2V_2$$

This is represented in the upper scale on the right. The scale of ordinates is 50 times that of the plot of V^M, but a parabola will allow still more accurate plotting. The open circles in the upper left-hand section of figure 1 are

$$V_x^M - 2.6x_1x_2$$

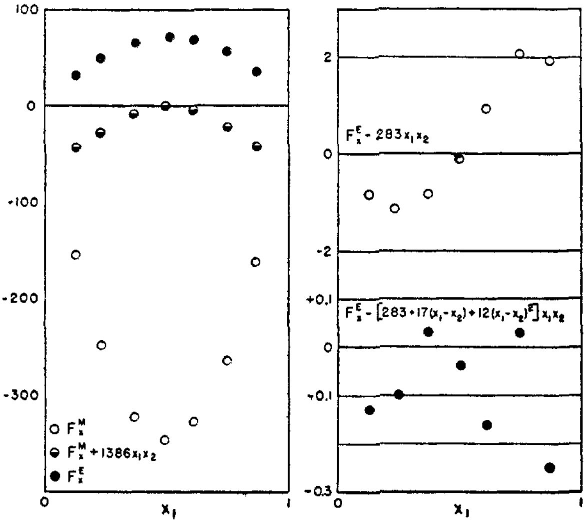

FIG. 2. Benzene–cyclohexane: free energies

The deviations are still apparently smooth, so that it should pay to consider higher terms. Since the parabola accounts for most of the volume of mixing, it is convenient to keep this term and to expand in the form

$$V_x^M = x_1x_2\,\Sigma_\nu V_{12}^\nu(x_1 - x_2)^\nu$$

with ν summed from 0 to n.[2] V_{12}^ν is the coefficient of the ν^{th} term (it is not V_{12} to the ν^{th} power). If we were trying to do the best job possible, we would use the method of least squares to determine the coefficients. Even then it is often

---

[2] This form was suggested by Guggenheim (6) for the excess free energy, and has since been used by many others. Redlich and Kister (15) have shown that with this form many polycomponent systems can be treated to a good approximation by adding the expressions for all the binary pairs composing them. A less elegant expression of this function was used by Scatchard and Hamer (18) to compare the development in mole fractions with that in volume fractions, and the latter expression was used for polycomponent mixtures by Scatchard, Wood, and Mochel (23).

For a binary system there is no fundamental difference between this and other methods of expressing concentrations, such as that used by Benedict, Johnson, Solomon, and Rubin convenient to work with deviation functions. Since we have already pinned down the function at the two ends and the middle, it is convenient to pin it down also at the one-quarter and three-quarters points and to determine two more constants by the relations:

$$V_{0.75} - V_{0.25} = 3V'_{12}/16$$

$$V_{0.25} + V_{0.75} = 3V^0_{12}/8 + 3V''_{12}/32$$

$V_{0.75}$ is the molal volume when $x_1 = 0.75$, and $V_{0.25}$ the volume when $x_1 = 0.25$,

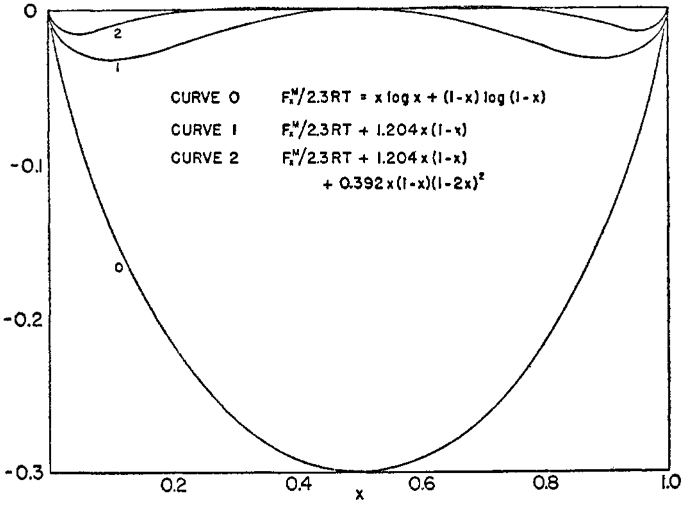

FIG 3. Ideal free energy of mixing

The filled circles in the upper left-hand section of figure 1 are

$$V_x^M - x_1x_2[2.6 - 0.1(x_1 - x_2) + 0.2(x_1 - x_2)^2]$$

The scale is 500 times that of V_x. Except for the last point the average deviation is less than 0.002 per cent.

THE EXCESS FREE ENERGY

The free energy of mixing per mole at 50°C., F_x^M, for the same system (21) is shown in the left side of figure 2 as open circles. The half-filled circles are $F_x^M + 1386x_1x_2$. The parabola does not give a satisfactory correction near the ends. If there had been accurate measurements in more dilute solutions, the discrepancy would have been even more obvious. The reason is that the slope of F_x^M is infinite at the ends, even for ideal solutions. Figure 3 shows the free energy of mixing for an ideal solution as curve 0. Curve 1 is corrected for the parabola and curve 2 for the fourth-degree term. All odd terms are zero, since the curve has axial symmetry.

---

(1) for the excess free energy of mixing. If one constant is used, their $2A_{12} = F^0_{12}$; for two constants $3A_{112} = F^0_{12} + F'_{12}$, $3A_{122} = F^0_{12} - \mathrm{F}_{12}$; and for three constants $4A_{1112} = F^0_{12} + F'_{12} + F''_{12}$, $3A_{1122} = F^0_{12} - F''_{12}$, $4A_{1222} = F^0_{12} - F'_{12} + F''_{12}$.

So we define the excess free energy of mixing per mole, F_x^E, as the free energy of mixing minus that of an ideal solution, or

$$F_x^E = F_x^M - RT\ \Sigma_i x_i \ln x_i$$

F_x^E for this system is plotted as filled circles on the left of figure 2.

The open circles on the right are

$$F_x^E - 283x_1x_2$$

on a 50 times larger scale, and the filled circles are

$$F_x^E - x_1x_2[283 + 17(x_1 - x_2) + 12(x_1 + x_2)^2]$$

on a scale 100 times larger again. The agreement could be improved still more by a more careful choice of constants.

POWER SERIES EXPANSION

These two applications show the usefulness of the method and its limitations. It can be applied to any function which is never infinite itself and has no infinite derivatives. It fails for F_x^M because of the infinite slope at zero concentration. It will fail also for F_x^E, V_x^M, or any similar functions of dilute electrolyte solutions. The Debye theory tells us that for such solutions F_x^E, V_x^M, H_x^M, etc. are proportional to the square root of the mole fraction of the ions when this mole fraction is very small. The theory also enables us to calculate an electrostatic term F_x^D, such that $(F_x^E - F_x^D)$ may be treated as F_x^E for a non-electrolyte mixture. One of the important achievements of the Debye theory is to confirm the assumption which had been made empirically for many years, that for very dilute solutions of non-electrolytes F_x^E is proportional to x. The method can be applied, of course, to the enthalpy and energy of mixing H_x^M and E_x^M, as to the volume, and to the excess entropy and work content, $S_x^E = S_x^M + R\Sigma_i x_i \ln x_i$ and $A_x^E = A_x^M - RT\Sigma_i x_i \ln x_i$, as to the excess free energy.

If a tangent is drawn to a curve of a molal quantity against the mole fraction, the intercepts at $x_1 = 1$ and at $x_2 = 1$ are the corresponding partial molal quantities of components 1 and 2, respectively. Thus when V_x is plotted against x, the intercepts of the tangent are $\bar{V}_1$ and $\bar{V}_2$; for V_x^M the intercepts are $\bar{V}_1^M = \bar{V}_1 - V_1$ and $\bar{V}_2^M = \bar{V}_2 - V_2$. For F_x^M the intercepts are $\mu_1^M = RT \ln a_1$ and $\mu_2^M = RT \ln a_2$, and for F_x^E they are $\mu_1^E = RT \ln \gamma_1$ and $\mu_2^E = RT \ln \gamma_2$, in which a_1 and a_2 are the activities of the components with the component liquids as the standard states, and $\gamma_1 = a_1/x_1$ and $\gamma_2 = a_2/x_2$ are the corresponding activity coefficients.

For the deviation curves it is necessary to add to the measured intercept the analytical expression corresponding to the equation used.

If

$$G_x = x_1x_2\ \Sigma_\nu G_{12}^\nu (x_1 - x_2)^\nu$$

$$\frac{\mathrm{d}G_x}{\partial x_2} = -\frac{\mathrm{d}G_x}{\partial x_1} = \bar{G}_2 - \bar{G}_1 = \Sigma_\nu G_{12}^\nu[(x_1 - x_2)^{\nu+1} - 2\nu x_1 x_2 (x_1 - x_2)^{\nu-1}]$$

$$\bar{G}_1 = x_2^2\ \Sigma_\nu G_{12}^\nu[(x_1 - x_2)^\nu + 2\nu x_1(x_1 - x_2)^{\nu-1}]$$

$$\bar{G}_2 = x_1^2\ \Sigma_\nu G_{12}^\nu[(x_1 - x_2)^\nu - 2\nu x_2(x_1 - x_2)^{\nu-1}]$$

in figure 4 are plotted the contributions of the first five terms to G_x, each expressed as G_x^ν/G_{12}^ν. Note that the maximum effect decreases as ν becomes larger, and that the maxima spread away from the center. It is obvious that $G_{21}^\nu = G_{12}^\nu(-1)^\nu$. Figure 5 shows the corresponding values of $\bar{G}_2 - \bar{G}_1$. It is worthy of note that the term with $\nu = 1$ is the only one which is not zero at the midpoint. Figure 6 gives the corresponding curves for $\bar{G}_2$. Those for $\bar{G}_1$ are obtained by interchanging subscripts and multiplying by $(-1)^\nu$. Each term beyond the first changes sign and each beyond the second changes sign twice, once at the midpoint and once at a lower concentration.

The excess free energy makes the best function for correlating vapor–liquid equilibrium data when both the equilibrium pressure and the vapor composition have been determined. Each point represents two potential measurements weighted as they would be for a least squares treatment, by multiplying by the corresponding mole fraction. It is sometimes convenient to use the corresponding function uncorrected for deviations from the perfect gas laws and divided by $2.3RT$:

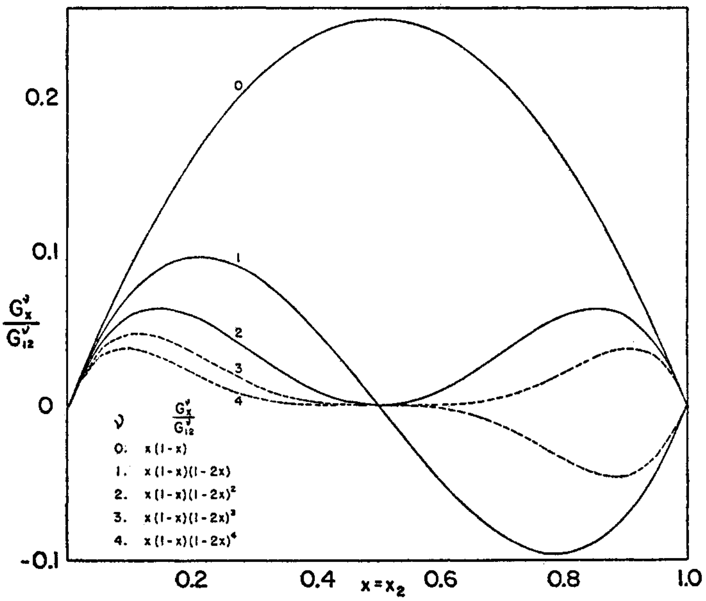

FIG. 4. Expansion of G_x

$$Q_x = x_1 \log Py_1/P_{10}x_1 + x_2 \log Py_2/P_{20}x_2$$

Figure 7 shows Q_x for chloroform–ethanol mixtures at 45°C. as open circles (20); x_2 is the mole fraction of ethanol. The filled circles are $Q_x - 0.470x_1x_2$ and the open circles near the zero line are

$$Q_x - x_1x_2[0.470 + 0.219(x_1 - x_2)] \text{ at } 45°\text{C.}$$

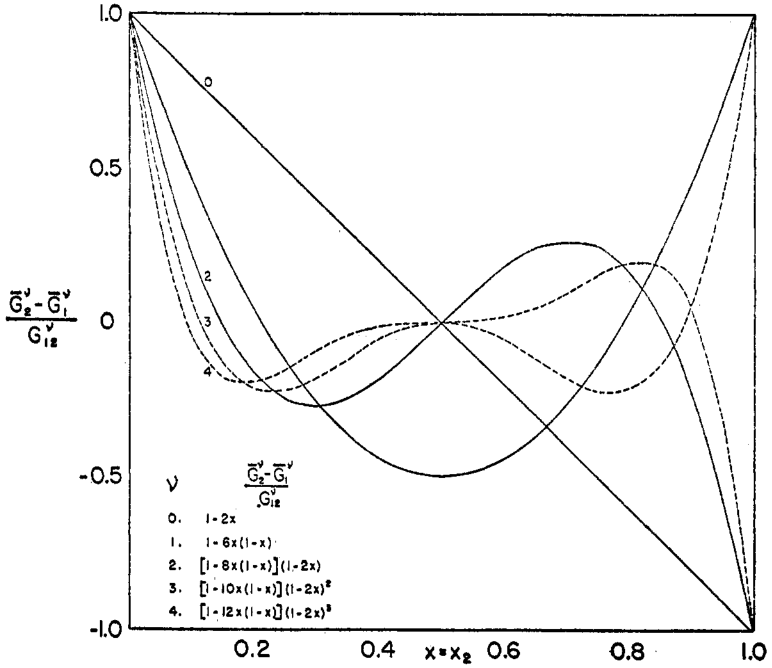

FIG. 5. Expansion of $\bar{G}_2 - \bar{G}_1$

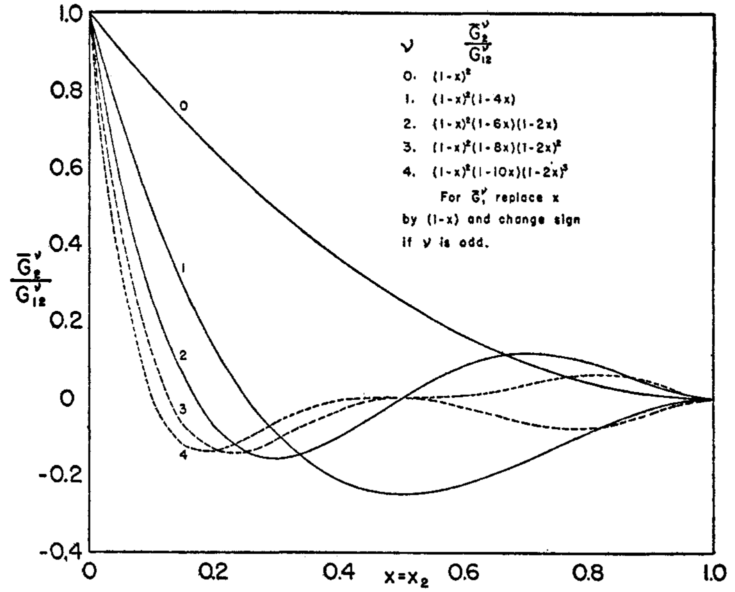

FIG. 6. Expansion of $\bar{G}_2$

These last are replotted on a larger scale in figure 8, together with the corresponding functions

$$Q_x - x_1 x_2[0.462 + 0.255(x_1 - x_2)] \text{ at } 35°\text{C}.$$

and

$$Q_x - x_1x_2[0.455 + 0.183(x_1 - x_2)] \text{ at } 55°\text{C.}$$

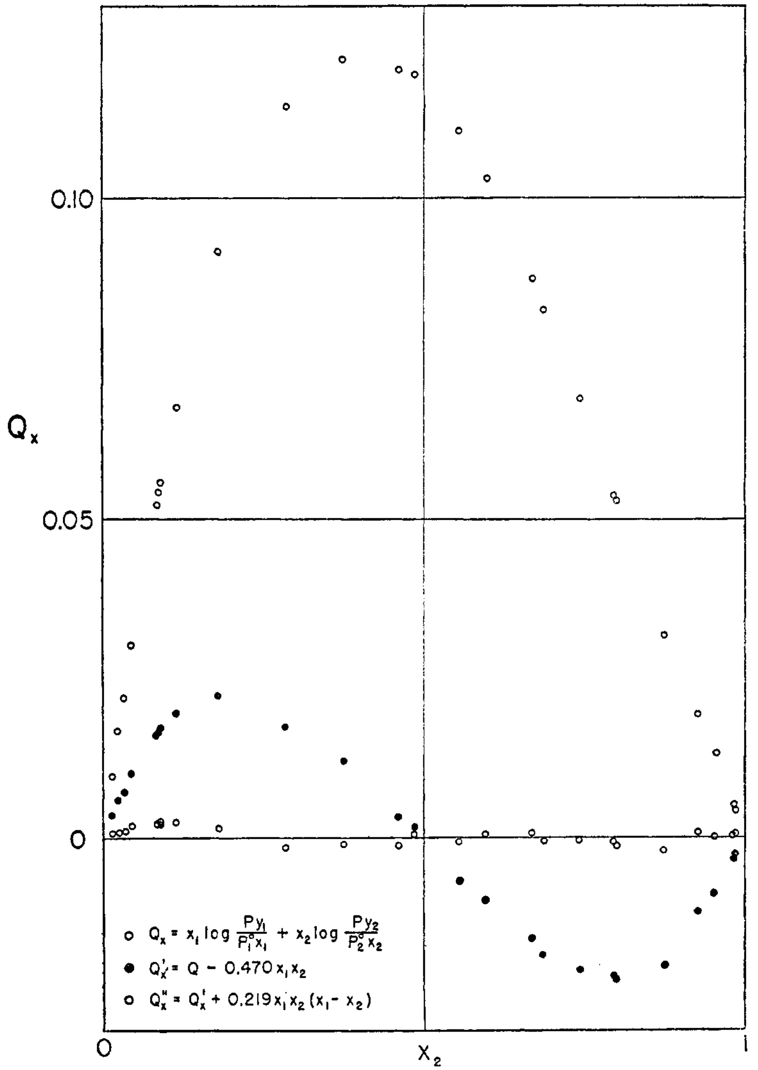

FIG. 7. Chloroform–ethanol: vapor pressures at 45°C.

The next term in the expansion with $\nu = 2$ is very small. The curves are drawn to give an approximate fit for $\nu = 3$ at $x = \frac{1}{8}$ and $\frac{7}{8}$ as well as at $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$. The curves at all temperatures are for the function

$$0.078x_1x_2(x_1 - x_2)[(x_1 - x_2)^2 - 0.25]$$

This term gives a considerable improvement in the fit at 35° and 45°C., but not much improvement at 55°C.

This analytical expression of the partial pressures is often called an integration of the Gibbs–Duhem equation. The Gibbs–Duhem equation is not sufficient because it also applies when the slope is infinite, as in the free energy of mixing. However, the measurements do give more than the excess free energy of mixing; they give the excess potential of each component. The consistency of the results may be determined by a reversal of Gibbs's method of determining the potentials as the intercept of the tangent to the curve of G_x *vs.* x_1 with the ordinates $x_1 = 1$ and $x_2 = 1$. If the measured value of $\bar{G}_1$ at $x_1 = x$ is plotted at $x_1 = 1$, the corresponding value of $\bar{G}_2$ at $x_2 = 1$ and the straight line drawn through them, the intercept with the ordinate $x_1 = x$ is the corresponding value of G_x and the line is the tangent to the curve of G_x *vs.* x_1 at that point. For a difference function we substitute the corresponding differences in the potentials. In practice it is simpler to calculate G_x algebraically as $x_1\bar{G}_1 + x_2\bar{G}_2$ and to draw

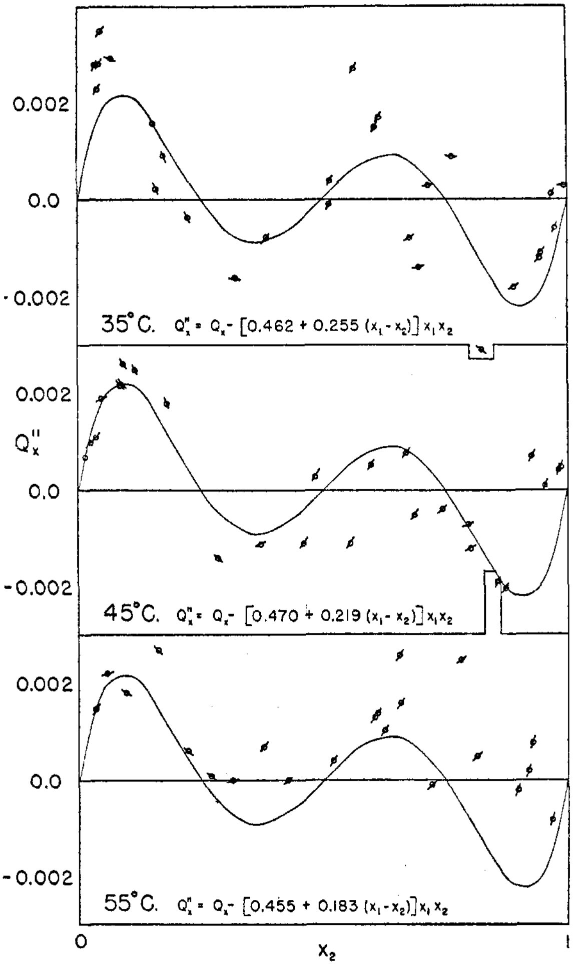

FIG. 8. Chloroform-ethanol: the curves represent $0.078x_1x_2(x_1 - x_2)[(x_1 - x_2)^2 - 0.25]$

a short segment of the line through G_x and one of the end points. The segments of straight lines should be tangent to the smooth curve through all the points. These lines are drawn in figure 8.

This method has the advantage over any other "test of the Gibbs–Duhem equation" which I know in that it involves no differentiation, but the measurements at each point are compared with the smooth curve through all the points. It shares the disadvantage of all such tests that we do not know how large an error in the measurements corresponds to a given deviation in slope. We can tell that the deviation of a single point from the smooth curve through the other points probably means an error in the pressure if the slope is correct but the position is in error, and probably an error in y if the position is correct and the slope in error. Deviations in both slope and position may indicate an error in x. A more exact comparison may be obtained by calculating P and y from the equation and comparing each with the corresponding measured quantity.

The scale of figure 8 is such that it should show the deviations of Q_x from an extensive property. At 45°C. the correction may be represented quite accurately by $F_x^E/2.3RT - Q_x = -0.01x_1x_2$, but the tangent does not give the corresponding values of the potentials. It would be hard to say, however, that the corrected points are more consistent than the uncorrected ones.

If only the liquid and vapor compositions have been determined, the coefficients can be determined from the equation

$$\log \alpha_{12} = \log y_1x_2/x_1y_2 \cong \frac{1}{2.3RT}\frac{\mathrm{d}F_x^E}{\mathrm{d}x_1} + \log\frac{P_{10}}{P_{20}}$$
$$= A - \Sigma_\nu Q_{12}^\nu[(x_1 - x_2)^{\nu+1} - 2\nu x_1x_2(x_1 - x_2)^{\nu-1}]$$

Redlich and Kister (15) have discussed the determination of the parameters of this equation. If we pin down the curve at $\frac{1}{4}$, $\frac{1}{2}$, and $\frac{3}{4}$, with the values y_1, y_2, y_3:

$$A = 2(y_1 + y_3 - y_2/2)/3$$
$$Q_{12}^0 = y_1 - y_3$$
$$Q_{12}' = 4(2y_2 - y_1 - y_3)/3$$

If only total pressures have been measured, the vapor pressures of the components and of one mixture are sufficient to give one constant. If the mixture is equimolal

$$\log P_{0.5} = \log (P_{10} + P_{20})/2 + Q_{12}^0/4$$

Further approximations must be made by trial and error. If the vapor pressures of the two components are approximately equal, two more constants can be obtained readily from the measurements at $x = \frac{1}{4}$ and $\frac{3}{4}$ in addition to the measurements used above.

If only one component is volatile, all the parameters contain the square of the mole fraction of the other component as a factor. There is therefore a great advantage in using measurements in solutions as dilute as possible. A plot of log Py/P_1x_1 minus an analytical function *vs.* x_2^2 will indicate the next function to choose.

The azeotropic pressure and composition are sufficient to determine two constants if the vapor pressures of the components at the same temperature are known. They may be determined from the equations

$$\log P_A/P_{10} = (1 - x_A)^2[Q^0_{12} + Q'_{12}(3 - 4x_A)]$$

$$\log P_A/P_{20} = x_A^2[Q^0_{12} + Q'_{12}(1 - 4x_A)]$$

in which P_A is the azeotropic pressure and x_A the mole fraction of component 1 in the azeotrope. The solubility of one solid component in the other will give one constant if the difference in potential of the solid and liquid is known from thermal measurements or from other solubility measurements. If the system is only partially miscible, the compositions of the two phases in equilibrium determine two constants (18).

When the deviations are large and positive it is always well to check that the equation does not demand separation into two liquid phases when there is none. This can be shown by the plot F_x^M, which shows an inflection if there is separation into two phases. Usually it is shown more clearly by plotting μ_1^M or μ_2^M, which show a maximum and minimum if there are two liquid phases and a horizontal inflection at the critical mixing point.

EFFECT OF DIFFERENCES OF VOLUME OR SURFACE

Expansion in power series of the mole fraction is not always the most economical expression of these functions. Eighteen years ago I showed (17) that for simple binary non-electrolyte mixtures, the excess free energy per unit volume should be expressed approximately by a constant times the product of the volume fractions of the components, that the constants should be calculable from the energies of evaporation of the components, and that the excess free energy of polycomponent solutions can be calculated with no new parameters. We have also shown in several papers that introduction of a second term is more effective with this expression than with mole fractions, although mixtures of a non-polar compound with an alcohol seem to be represented more simply by the mole fraction form. The simple one-parameter equation has since been much used by Hildebrand and his collaborators with solutions of small molecules and by many high-polymer chemists for the enthalpy of mixing. Professor Hildebrand discusses it more fully in this symposium (10). For a two-component system, if $\rho = V_2/V_1$,

$$F_x^E = \beta\frac{V_1x_1V_2x_2}{V_1x_1 + V_2x_2} = \frac{2\beta V_2x_1x_2}{\rho + 1}\,\frac{1}{1 - \dfrac{\rho - 1}{\rho + 1}(x_1 - x_2)}$$

$$= \frac{2\beta V_2}{\rho + 1}\,x_1x_2\Sigma_\nu\left(\frac{\rho - 1}{\rho + 1}\right)^\nu(x_1 - x_2)^\nu$$

So

$$F_{12}^{\nu} = \frac{2\beta V_2}{\rho + 1}\left(\frac{\rho - 1}{\rho + 1}\right)^{\nu}$$

The corresponding expressions for the chemical potentials are

$$\mu_1^E = \beta V_1\left(\frac{V_2 x_2}{V_1 x_1 + V_2 x_2}\right)^2 = \frac{4\beta V_1 \rho^2 x_2^2}{(\rho + 1)^2}\left(\frac{1}{1 - \frac{\rho - 1}{\rho + 1}(x_1 - x_2)}\right)^2$$

$$\mu_2^E = \beta V_2\left(\frac{V_1 x_1}{V_1 x_1 + V_2 x_2}\right)^2 = \frac{4\beta V_2 x_1^2}{(\rho + 1)^2}\left(\frac{1}{1 - \frac{\rho - 1}{\rho + 1}(x_1 - x_2)}\right)^2$$

The series F_{12}^{ν} converges for any finite value of ρ, and it converges rapidly if ρ is near unity, say between $\frac{1}{3}$ and 3. The mole fraction form is not a useful one for high polymers because of the slowness of convergence and because it fails to show simply that the enthalpy of mixing of a given mass of polymer is nearly independent of its molecular weight.

These relations hold equally well if ρ be defined differently, provided the product βV_2 be defined to correspond. The equation of Langmuir (13) is equivalent to defining ρ as $(V_2/V_1)^{2/3}$, and that used by van Laar (25) is equivalent to defining ρ as b_2/b_1, the ratio of van der Waals b's for the two components, which is almost the same as taking V_2/V_1. In the "van Laar equation" often used by chemical engineers, however, both ρ and βV_2 are determined empirically, usually as βV_2 and $\beta V_2/\rho$.

In my first treatment I assumed that simple non-polar solutions are regular, that is, that the entropy of mixing is the same as for an ideal solution. Almost everyone treating solutions was making this assumption, and the attempts to prove it were often more amusing than convincing. I accepted Hildebrand's justification (8) that solutions are regular when "orienting and chemical effects are absent and the distributions and orientations are random."

Since then the high-polymer chemists have shown that volume differences lead to an excess entropy of mixing. Starting with a quasi-crystal lattice model in which each solvent molecule and each polymer unit occupies one unit cell, Huggins (11) and Flory (3) arrived independently at expressions which may be written as

$$S_x^E = -R\,\Sigma_j x_j \ln V_j/V_x$$

This question has been treated more elegantly by Guggenheim (7). Although the original derivations apply to linear polymers which cannot coil back on themselves, Huggins suggests that the equation should apply to any mixture. Hildebrand (9) has recently reached the same conclusion, without using a quasi-crystal lattice, but with the assumptions that there is an entropy term proportional to the "free volume," and that the "free volume" per mole of a liquid is proportional to its total volume. This second assumption does not seem very probable to me.

For a binary mixture, the Flory–Huggins expression may be written:

$$-\frac{S_x^E}{R} = x_2 \ln \rho - \ln [1 + (\rho - 1)x_2]$$

The corresponding values for the partial molal entropies are

$$-\frac{\bar{S}_1^E}{R} = \ln \frac{1}{1 + (\rho - 1)x} + \frac{(\rho - 1)x}{1 + (\rho - 1)x}$$

$$-\frac{\bar{S}_2^E}{R} = \ln \frac{\rho}{1 + (\rho - 1)x} - \frac{(\rho - 1)(1 - x)}{1 + (\rho - 1)x}$$

In comparing other analytical expressions with the power series expansion, we may use two methods, both of which seem to me dangerous, however, when applied to curves from experimental measurements. The first is to determine the coefficients of the power series from the value of the other function and its derivatives at $x = 0.5$ by the relation

$$G_{12}^{\nu} = \frac{4}{2^{\nu}\nu!}\left(\frac{\mathrm{d}^{\nu} G_x}{\mathrm{d}x^{\nu}}\right)_{0.5}$$

taking G_{12}^0 as $4\left(\frac{\mathrm{d}^0 G_x}{\mathrm{d}x_1^0}\right)_{0.5}$. The second is to utilize the extrapolation of $\bar{G}_1^E$ to $(\bar{G}_2^E)_2$ at $x_2 = 1$ and of $\bar{G}_2$ to $(\bar{G}_2^E)_1$ at $x_1 = 1$ to give:

$$[(\bar{G}_1^E)_2 + (\bar{G}_2^E)_1]/2 = \Sigma G_{12}^{\nu} \text{ even}$$

$$[(\bar{G}_2^E)_2 - (\bar{G}_1^E)_1]/2 = \Sigma G_{12}^{\nu} \text{ odd}$$

Carlson and Coburn (2) use these two equations to determine two parameters from the extrapolation of experimental measurements. In the Margules equation their parameters are F_{12}^0 and F_{12}'; in the "van Laar equation" they are βV_2 and $\beta V_1 = \beta V_2/\rho$.

It is possible to determine any number of parameters from the derivatives at the midpoint and to check by extrapolation of the partial quantities to determine the residuals such as $\Sigma G_{12\text{ even}} - G_{12}^0$ or $\Sigma G_{12\text{ even}} - G_{12}^0 - G_{12}''$ and $\Sigma G_{12\text{ odd}} - G_{12}'$.

Figure 9 shows F_{12}'/F_{12}^0, F_{12}''/F_{12}^0, $(\Sigma F_{12\text{ odd}} - F_{12}')/F_{12}^0$ and $(\Sigma F_{12\text{ even}} - F_{12}^0 - F_{12}'')/F_{12}^0$ for the volume fraction expression given above, with F_{12}' and F_{12}'' determined from the derivatives at the midpoint. The dotted lines are F_{12}'/F_{12}^0 and F_{12}''/F_{12}^0 with F_{12}' and F_{12}'' determined from the values of F_{12}^0 and F_x^E at $x = \frac{1}{4}$ and $\frac{3}{4}$. The value of F_{12}^0 does not depend upon ρ.

Figure 10 shows the first four curves for the Flory–Huggins entropy. The value of F_{12}^0 does depend upon ρ, and is given as the broken curve with ordinates at the right. The Flory–Huggins entropy is more symmetrical than the volume fraction expression for the same value of ρ. It corresponds roughly to the latter at $\rho^{2/3}$.

The Flory–Huggins treatment gives too large an effect in many cases. Zimm (28) has assumed that high-polymer molecules are so much bigger than those of the solvent that the solvent may be treated as a continuous medium, and has made calculations for dilute solutions which are equivalent to the calculation of van der Waals' *b* for spherical molecules and for long cylinders. His results for long cylinders are larger than the simple Flory–Huggins result. The quantity $(\pi/RTc - 1)/c$, with π the osmotic pressure, is $\bar{V}_2 - \bar{V}_1/2$ for ideal solutions. Zimm obtains $l\bar{V}_2/d$ for cylinders with length, l, greater than ten times the diameter, d. By the Flory–Huggins assumptions this is $\bar{V}_2^2/\bar{V}_1$, which is twice their value for this term. For large spheres, however, Zimm obtains $4\bar{V}_2$, which is much smaller than the Flory–Huggins value.

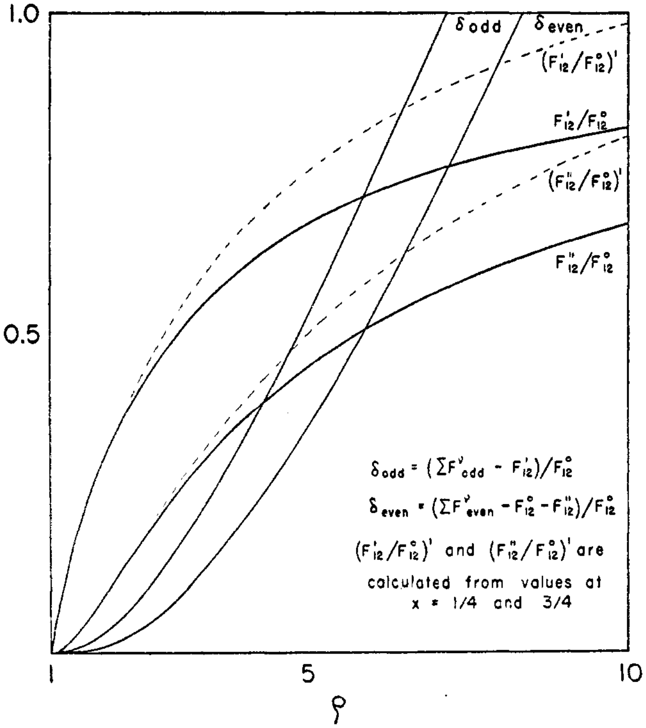

FIG. 9. Volume-symmetrical deviations

It is probable that the Flory–Huggins model represents mixtures of straight-chain hydrocarbons to a fair approximation, but most mixtures of small molecules cannot be pictured as fitting into a simple lattice. Nor can the size of one kind of molecules be neglected relative to that of another. In treating energy the lattice theory treats the number of contacts between the central molecule and those surrounding it. This should be represented approximately by the surface of the central molecule. It is not at all certain that the effective surface of a molecule is independent of the nature of the molecules around it, but it will be an improvement to make this assumption and take ρ as the ratio of surfaces instead of always the ratio of volumes. For long-chain molecules the surface is practically proportional to the volume, so ρ will still be the ratio of molal volumes. For molecules of different sizes but the same shape, the surface ratio is the two-thirds power of the volume ratio, corresponding to the formula proposed by Langmuir (13). To justify the use of a smaller ρ with the Flory–Huggins theory, we may assume that the "free volume" of a molecule is proportional to its surface, and follow Hildebrand (8) in the rest of his derivation.

This problem is of prime importance to the high-polymer and colloid chemist. Its relation to the association of small molecules is discussed later. With small molecules the place where I have found it most important is in the study of the effect of changing solvent on the rate of reaction, where the rate depends upon the ratio of the activity coefficients of the reactants to that of the critical complex.

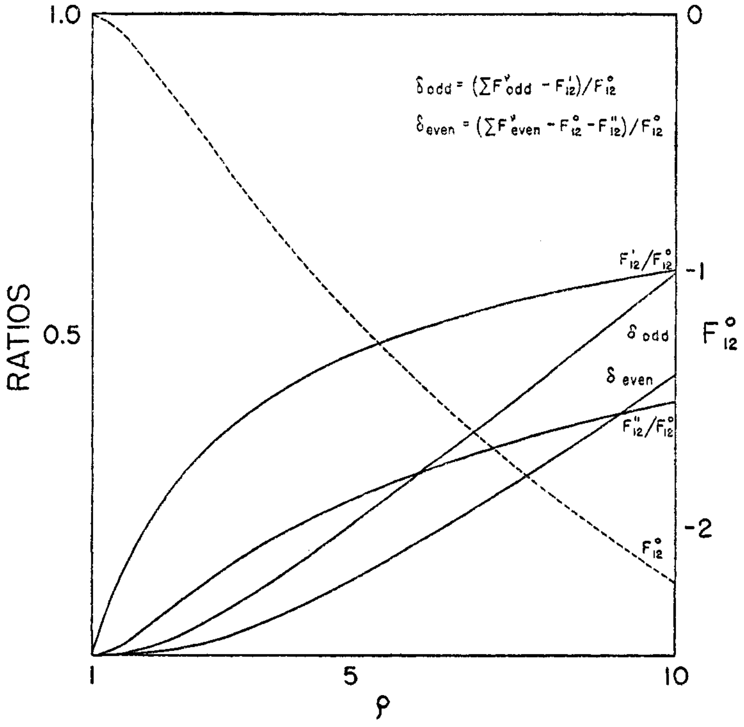

FIG. 10. Flory–Huggins deviations

The Flory–Huggins contribution is

$$\left(\ln \frac{f_A f_B}{f_x}\right)_{FH} = \ln \frac{\bar{V}_A \bar{V}_B}{\bar{V}_C V_x} + 1 - \frac{\bar{V}_A + \bar{V}_B - \bar{V}_C}{V_x}$$

If the volume of the critical complex is the sum of the volumes of the components, this becomes $-\ln V_x +$ const., which means that the rates should be compared in volume concentrations rather than in mole fractions. I have long insisted that the reverse is true, and experimental results have supported my thesis (22). If the volumes should be replaced by surfaces, the surface of the critical complex should be expected to be less than that of the reactants. If the difference is just the mean surface of a solvent molecule, the change with surface of solvent molecules is zero. It is possible that this relation is satisfied well enough so that the mole fraction expression holds approximately. It does seem a very complicated justification of a simple relation, and I am not happy about it.

EFFECTS OF VOLUME CHANGE ON MIXING

If distinction is to be made between the enthalpy and the minus temperature entropy product, it is important to consider the effect on these properties of the change of volume on mixing (19). This effect nearly cancels out in the free energy. The change in state considered in the foregoing theories, as in practically all other theories, is not the same as that treated experimentally, and it is important to consider the difference.

We shall limit ourselves to an isothermal change in state, $T = T_0$ throughout. We shall let N_A be the number of moles of component A initially at a pressure P_{A0}, with molal volume energy, entropy, enthalpy, work content, and free energy V_{A0}, E_{A0}, S_{A0}, H_{A0}, A_{A0}, and F_{A0}. The general isothermal change in state is

$$\underset{\text{unmixed}}{N_A A(P_{A0}, T_0) + N_B B(P_{B0}, T_0) + \cdots} \rightarrow \underset{\text{mixed}}{N_A A(P, T_0) + N_B B(P, T_0) + \cdots}$$

In the initial state

$$V_0 = N_A V_{A0} + N_B V_{B0} + \cdots\cdot,$$

$$E_0 = N_A E_{A0} + N_B E_{B0} + \cdots\cdot, \text{ etc.}$$

In the final state

$$V = V_0 + V^M$$

$$E = E_0 + E^M, \text{ etc.}$$

There are two special cases which are so important that we shall give them special subscripts. In both the initial pressures are all the same:

$$P_{A0} = B_{B0} \cdots\cdot = P_0$$

In the constant-pressure case

$$P = P_{A0} \qquad V = V_0 + V_p^M \qquad E = E_0 = E_p^M, \text{etc.}$$

In the constant total volume case

$$V = V_0 \text{ or } V_v^M = 0 \qquad E = E_0 + E_v^M, \text{etc.}$$

Most measurements with liquids are at constant pressure. Although in measurements of vapor–liquid equilibrium, P_{A0} is the vapor pressure of pure component A, P_{B0} is that of pure component B, and P is the vapor pressure of the mixture, the correction to constant pressure is easily made and is usually much smaller than the correction due to deviations from the gas laws.

All theoretical calculations are at constant total volume. The lattice treatment assumes tacitly that the initial pressures are such that a unit of each component occupies the same volume, which may require that P_{A0} is very different from P_{B0}. More general theories will permit that they are the same, or,

$$P_{A0} = P_{B0} = \cdots = P_0$$

In this case we can calculate some very interesting relations from thermodynamics alone.

$$P - P_0 = -\int_{V_0+V^M}^{V_0} \frac{dv}{\beta v} = \frac{1}{\beta} \ln (1 + V^M/V_0) \quad \text{since } dp = -\frac{dv}{\beta v}$$

$$F_v^M - A_v^M = (P - P_0)V_0 = \frac{V_0}{\beta} \ln (1 + V^M/V_0)$$

$$F_p^M - F_v^M = \int_{V_0}^{V_0+V^M} -\frac{dv}{\beta} = -\frac{V^M}{\beta}$$

$$F_p^E - A_v^E = F_p^M - A_v^M = \frac{V_0}{\beta} [\ln (1 + V^M/V_0) - V^M/V_0]$$

$$= -(V_0/2\beta)[(V^M/V_0)^2 + \cdots]$$

$$S_p^E - S_v^E = S_p^M - S_v^M = \int_{V_0}^{V_0+V^M} \left(\frac{\partial p}{\partial T}\right)_v dv$$

$$= \int_{V_0}^{V_0+V^M} \left[\left(\frac{\partial p}{\partial T}\right)_v + \frac{d(1/\beta)}{dT} \ln \frac{V_0 + V^M}{v}\right] dv$$

$$= V^M \left(\frac{\partial P_0}{\partial T}\right)_v + \frac{V_0 \, d \ln \beta}{\beta T \, d \ln T} [\ln (1 + V^M/V_0) - V^M/V_0]$$

$$H_p^M - E_v^M = V^M T \left(\frac{\partial P_0}{\partial T}\right)_v + \frac{V_0}{\beta}\left(1 + \frac{d \ln \beta}{d \ln T}\right) [\ln (1 + V^M/V_0) - V^M/V_0]$$

$$T \left(\frac{\partial P_0}{\partial T}\right)_v = T \frac{\alpha_0}{\beta_0} = \text{“Internal pressure”}$$

$$\alpha = \left(\frac{\partial \ln V}{\partial T}\right)_p, \quad \alpha_0 = \left(\frac{\partial \ln V_0}{\partial T}\right)_p, \quad \beta = \left(\frac{-d \ln V}{\partial p}\right)_T,$$

$$\beta_0 = \left(\frac{-d \ln V_0}{\partial p}\right)_T$$

The terms in $[\ln (1 + V^M/V_0 - V^M/V_0]$ are usually negligibly small, and there is no other term for $F_p^E - A_v^E$. The terms in $(\partial P_0/\partial T)_v$ in the entropy and enthalpy are far from negligible. For non-polar mixtures I have calculated (19) that $V_p^M = \beta_0 F_p^E$, so that

$$H_p^M - E_v^M = T\alpha_0 F_p^E$$

For most organic liquids, α_0 is about 10^{-3}, so $T\alpha_0$ varies from 0.25 to 0.5 at the temperatures which interest us most.

INTRAMOLECULAR COHESIVE ENERGY

I found eighteen years ago (17) that the cohesive energy density of a mixture of simple non-polar liquids, defined as the difference, E/V_0, between the energy per unit volume in the liquid state, E_l/V_0, and the energy of the same material in the perfect gas state at the same temperature, E_g/V_0, should be a quadratic function of the volume fractions of the components, and that the coefficient of each term is the product of the square roots of the cohesive energy densities of the two components involved in that term.

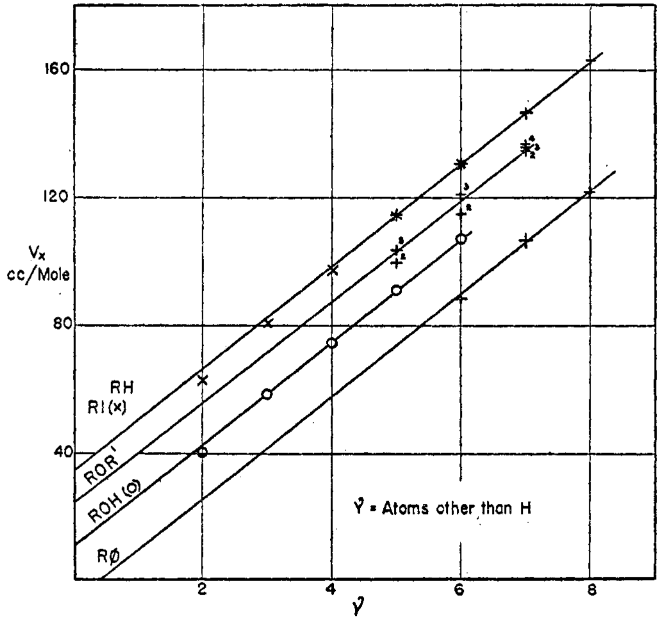

FIG. 11. Normal aliphatic compounds: volume

$$E/V_0 = (E_l - E_g)/V_0 = \Sigma_{jk} N_j V_{j0} N_k V_{k0} a_{jk}/V_0^2$$

$$= \Sigma_j N_j V_{j0} \sqrt{a_{jj}}\, \Sigma_k N_k V_{k0} \sqrt{a_{kk}}/V_0^2 = (\Sigma_j N_j V_{j0} \sqrt{a_{jj}}/V_0)^2$$

$$a_{jk} = \sqrt{a_{jj}\, a_{kk}} \qquad a_{jj} = E_j/V_{j0}$$

Last year[3] I made the suggestion that long flexible molecules should have an intramolecular cohesive energy in the perfect gas state, so that the energy available for interaction is larger than the difference between the liquid and the perfect gas.

---

[3] This section was presented at the 111th Meeting of the American Chemical Society in Atlantic City, April 17, 1947, but has not been previously published.

To study this effect let us first consider the different parts of a single molecule as components. Then members of a homologous series correspond to mixtures of different composition. Testing first the additivity of volumes, figure 11 shows the volumes of several normal aliphatic compounds plotted against ν, the number of atoms other than hydrogen. The lines are all drawn with slopes of 16 ml. per carbon atom, which appears to be the volume occupied at 20°C. by a CH_2 group in straight chains. This volume is also almost independent of the temperature, and the thermal expansion is almost entirely in the intercepts, which differ for different series. The top curve represents hydrocarbons and iodides, the second the ethers, the third alcohols and the fourth phenyl derivatives.

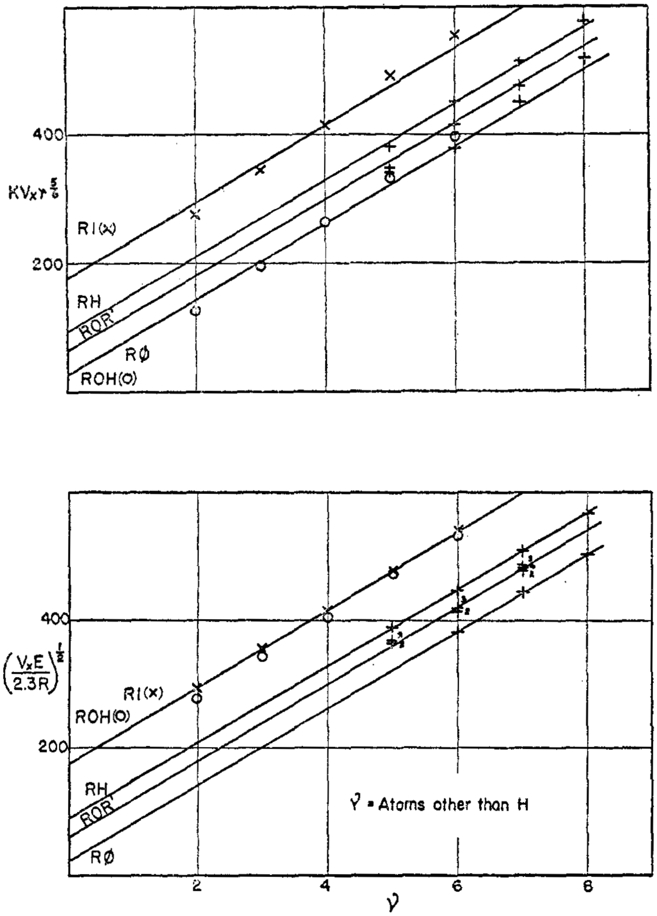

FIG. 12. Normal aliphatic compounds: (upper) refraction–volume; (lower) cohesive energy–volume.

The lower part of figure 12 shows $(V_0E/2.3)^{1/2}$ for these same substances. This should be a linear function of ν if the cohesive energy density is a quadratic function and $a_{jk} = \sqrt{a_{jj}\,a_{kk}}$, for

$$V_0E = V_0^2(E/V_0) = (\Sigma_j N_j V_{j0}\sqrt{a_{jj}})^2$$

The lines all have the slope of 60 units per carbon atom. The series are again characterized by the intercepts. The top curve represents the iodides, the second the hydrocarbons, the third the ethers, and the fourth the phenyl derivatives. The alcohols lie near the iodides and could be fitted by a straight line with slope slightly greater than that of the others. The slope would be increased if the interaction of the end groups, methyl and hydroxyl, with methylene groups is slightly greater than the geometric mean of the interaction of end groups with end groups and methylenes with methylenes.

The upper part of figure 12 shows the cohesive energy densities calculated from the refraction, $(n^2 - 1)/(n^2 + 2)$, for the sodium D line. The dispersion or London energy of two molecules depends upon the polarizabilities and is usually calculated as depending upon some other function of the mobility of the electrons. We shall assume that this part is also a function of the polarizability,

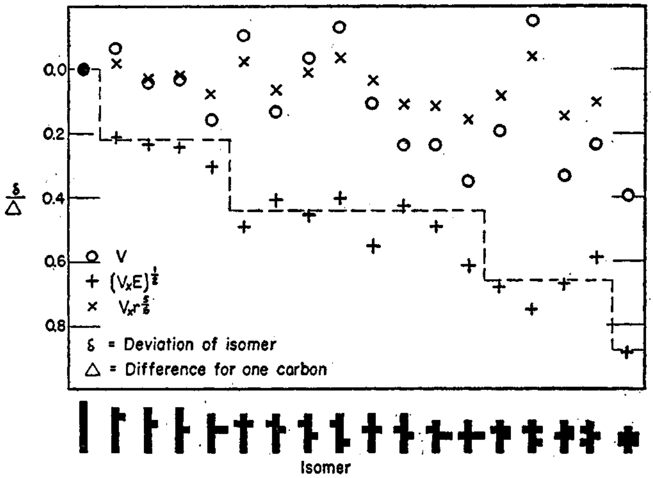

FIG. 13. Octanes: deviations from normal divided by change for one carbon

and that the cohesive energy density is proportional to some power of the refraction. Empirically I found the five-thirds power, and chose a coefficient to fit an average for the non-polar substances in this figure. The lines are taken directly from the lower figure.

We notice first that the alcohols have dropped from the top curve to the bottom. This is not surprising, since a large part of their cohesion comes from the exposed dipoles or hydrogen bonds. We notice next that every series indicates a slope slightly greater than that of the lines. This difference may be due to errors in our assumptions, but it cannot be corrected by a reasonable change of the exponent of the polarizations. If we assume that it is real, the difference indicates that the energy of evaporation gives too small a value for the cohesive energy of molecules long and flexible enough to show intramolecular cohesion in the perfect gas state.

Figure 13 shows the volume and the square root of the volume cohesive energy product calculated by the two methods for the isomeric octanes. The formulas of the isomers are given at the bottom, going from *n*-octane through 2-, 3-, and 4-methylheptanes, etc., to 2,2,3,3-tetramethylbutane. Except for this last substance the measurements are from Dr. Rossini's laboratory in the United States Bureau of Standards (27). Each function is represented by the difference from *n*-octane divided by the difference of *n*-nonane from *n*-octane.

The circles represent the volumes. I find little regularity except that a branch on the 2 carbon tends to increase the volume, and other branches tend to decrease it, particularly two branches on adjacent carbons. One might expect more regularity in these volumes. They are measured at atmospheric pressure, but an increase of only 0.01 per cent gives the volume under no external field with negligible differences between isomers.

The root energy–volume products calculated from refractions follow the volumes to a certain extent, but show a smaller deviation. The measured root energy–volume products show a very different behavior. The differences are greater and also more regular. The broken line in the figure drops an equal amount for each branch in the chain regardless of its position. It represents the experimental points to a fair approximation.

The evidence is clear that there is more intramolecular cohesive energy in the perfect gas state for branched chains, although it is not proven that this energy is available for intermolecular cohesion in the liquid. If it is available, the refractions should give a better measure of the behavior of solutions than the cohesive energies themselves. At the worst, the refractions should serve as an approximate measure of the cohesive energy density when direct measurements are impossible because of high melting point or decomposition on vaporization. For such substances the refraction, and if necessary the volume, may be measured in solution.

SORTING OF MOLECULES

Of course the distribution of the molecules in a solution will not be random if there is a change of energy when contact between two A molecules and that between two B molecules is replaced by two contacts between A and B molecules. The effect of this deviation on the thermodynamic properties has been calculated by Rushbrooke (16), by Kirkwood (12), and by Guggenheim (7) for spheres of equal volume with z nearest neighbors. Kirkwood's expression is

$$E^M_{vx} = B_{12}x_1x_2 - (2B_{12}^2/zRT)x_1^2x_2^2$$

with B_{12} independent of the temperature:

$$S^E_{vx} = -(B_{12}^2/zR)x_1^2x_2^2$$

If there were no other cause for deviation from the simple theory, we would have:

$$F^E_{xp} = B_{12}x_1x_2[1 - (B_{12}/zRT)x_1x_2]$$

In terms of the expansions used above we may say, since $x_1x_2 = \dfrac{1 - (x_1 - x_2)^2}{4}$, $E^0_{v12} = B_{12}(1 - B_{12}/2zRT)$, $E''_{v12} = B_{12}^2/2zRT$, $S^0_{v12} = -B^0_{12}/4zRT$, $S''_{v12} =$

$B_{12}^2/4zRT$, $F^0_{p12} = B_{12}(1 - B_{12}/4zRT)$, $F''_{p12} = B_{12}^2/4zRT$. The deviation is always negative. If B_{12} is positive and z is 8, the deviation is small until there is separation into two liquid phases when

$$\frac{B_{12}}{RT}\left(1 - \frac{B_{12}}{2zRT}\right) = 2$$

This treatment is based on the assumption that the energy of interaction is independent of the orientation. The theory of polar molecules would be advanced greatly if we had a similar treatment in which the interactions vary from spot to spot on the molecules. In the meantime we must be satisfied with treatments in terms of combination or association which do not distinguish between energy and enthalpy. By combination we mean interaction between unlike molecules which can be expressed by the law of mass action; by association we mean similar interaction between like molecules. Three types of association are important. In the first there is only one spot of special reactivity in each molecule, so the association is limited to dimers. We shall call this "acid-type association." In the second type, which we shall call "alcohol-type association," two active spots on each molecule permit the formation of linear chains of any length. In the third type, which we shall call "water-type association," four active spots on each molecule permit the formation of three-dimensional polymers. It is convenient to discuss the general case in which the number of reactive spots in each molecule is two or more. We shall discuss only the simplest type of combination, in which each molecule has but one spot which can react with a spot in a molecule of the other species.

We shall not make the assumption that chemical action is the only cause for deviations from the ideal solution laws. It has been known for many years (26) that no combination of reactions which obey the law of mass action can lead to separation into two liquid phases. We shall follow Redlich and Kister (14) in assuming that the non-chemical deviations do not depend upon the complexity of the molecules. It follows that the equilibrium constants do not depend upon the composition of the system.

We shall use the subscript A for the component which associates and B for the other; n_A and n_B are the numbers of formula weights of the components; x_A and x_B are the stoichiometric mole fractions, $x_A = n_A/(n_A + n_B)$; ν_g is the number of moles of the species g; and ξ_g and ξ_B are the "true" mole fractions, $\xi_g = \nu_g/(n_B + \Sigma_g \nu_g)$. The parts of the chemical potentials due to association, or combination, are

$$\mu_A^a/RT = \ln \gamma_A/\beta_A = \ln \xi_1/x_A\xi_1^0$$

$$\mu_B^a/RT = \ln \gamma_B/\beta_B = \ln \xi_B/x_B = \ln \xi_B/(1 - x_A)$$

in which γ_A and γ_B are the stoichiometric activity coefficients, β_A and β_B are those parts which are independent of the amount of chemical action, and ξ_1^0 is the value of ξ_1 when $x_A = 1$. The free energy per mole of components due to chemical action is

$$F_x^a/RT = x_A \ln \xi_1/x_A\xi_1^0 + (1 - x_A) \ln \xi_B/(1 - x_A)$$

It is convenient to work with one mole of total species, and very convenient to take ξ_1 as the independent variable.[4] Then it is necessary to determine ξ_1^0 as a function of K, and x_A and ξ_B as functions of K and ξ_1. We shall also use $Q_x = F_x^E/2.3RT$, etc. and common logarithms.

ACID-TYPE ASSOCIATION

In the acid-type association there are but three species, B and the monomers and dimers of A, and

$$\xi_2 = K\xi_1^2$$

$$n_A = \xi_1 + 2\xi_2 = \xi_1(1 + 2K\xi_1)$$

$$n_B = \xi_B = 1 - \xi_1(1 + K\xi_1)$$

$$x_A = \xi_1(1 + 2K\xi_1)/(1 + K\xi_1^2)$$

$$\xi_1^0 = (\sqrt{1 + 4K} - 1)/2K$$

So

$$Q_x^a = x_A \log \frac{(1 + K\xi_1^2)2K}{(1 + 2K\xi_1)(\sqrt{1 + 4K} - 1)} + (1 - x_A) \log (1 + K\xi_1^2)$$

The expression for x_A is a quadratic and it is possible to solve for ξ_1 and to express Q_x explicitly in x_A, but the expression is probably too complicated for general use.

Since

$$(\bar{Q}_A^a)_B = -\log \xi_1^0$$

and

$$(\bar{Q}_B^a)_A = \log (2 - \xi_1^0)$$

it is easy to obtain the results

$$\Sigma Q_{AB\ \text{even}} = \tfrac{1}{2} \log (2/\xi_1^0 - 1) = (1 - \xi_1^0)/2.3 + \cdots$$

and

$$\Sigma Q_{AB\ \text{odd}} = \tfrac{1}{2} \log \xi_1^0(2 - \xi_1^0) = (1 - \xi_1^0)^2/2.3 + \cdots$$

When $x_A = \frac{1}{2}$

$$\xi_1 = \sqrt{1 + 3K} - 1)/3K$$

So

$$Q_{12}^0 = 2 \log \frac{4}{27} \frac{(1 + 6K - \sqrt{1 + 3K})^2}{K(2\sqrt{1 + 3K} + 1)(\sqrt{1 + 4K} - 1)}$$

EXTENDED ASSOCIATION

For the alcohol type Redlich and Kister (14) follow previous workers in assuming that the association constant, K, for the reaction

$$A + A_{n-1} = A_n$$

---

[4] This is equivalent to taking temperature, pressure, and the potential (or activity) of component 1 as independent variables and closer to Gibbs than our usual procedures.

does not depend upon the order of the association. They obtain results which may be summed as

$$\bar{Q}^a_{\mathrm{A}} = \log\,[(1 - K\xi_1)^2 + K\xi_1^2](1 + K)$$

$$\bar{Q}^a_{\mathrm{B}} = \log\,[(1 - K\xi_1)^2 + K\xi_1^2]/(1 - K\xi_1^2)$$

$$Q^0_{\mathrm{AB}} = 4\log\left[1 + \frac{(\sqrt{1+K} - 1)^2}{K}\right] = 4\log\frac{2(\sqrt{1+K} - 1)}{K\sqrt{1+K}}$$

$$\Sigma Q_{\mathrm{AB\ even}} = \log\,(1 + K)$$

$$\Sigma \mathrm{Q}_{\mathrm{AB\ odd}} = 0$$

The symmetry of their results depends upon the expression of the equilibria in terms of mole fractions. The association polymers must give deviations due to different sizes of the different polymers. If we assume that the potentials are given by the Flory–Huggins expressions, the constants should be expressed in terms of volume fractions or concentrations (4).

We follow, in so far as we need to go, Stockmayer's method (24) of treating branched polymers. We consider a system of N monomer units of component A, existing as M molecules, and N_{B} molecules of component B which does not associate. We let f be the number of reactive spots on each unit, and α be the fraction of those spots which have reacted. From the assumption that there are no rings, $M = N(1 - \alpha f/2)$, and all of component A is in a single molecule when $\alpha f/2 = 1 - \frac{1}{N}$. From the assumption that every reactive group has the same probability of reacting, the number of monomer and dimer units, m_1 and m_2 are given by

$$m_1/N = (1 - \alpha)^f$$

$$m_2/N = f\alpha(1 - \alpha)^{2f-2}/2$$

Stockmayer finds that his expression for the number of a large polymer becomes invalid when $\alpha f/2 = f/2(f - 1)$, but there seems to be no reason why those parts which we have taken should not hold to the limit $\alpha f/2 = 1$.

We use the equilibrium expression for the formation of the dimer

$$\frac{m_2}{m_1^2} = \frac{f\alpha}{2N(1 - \alpha)^2}$$

But by the Flory–Huggins expression

$$\frac{m_2}{m_1^2} = \frac{k_2}{N + \rho N_{\mathrm{B}}} \quad \text{if } \rho = V_{\mathrm{B}}/V_1$$

To find k_2 we go to the limit $\alpha = \alpha_0$ when $N_B = 0$

$$k_2 = \frac{f}{2}\frac{\alpha_0}{(1-\alpha_0)^2}$$

$$\frac{N}{N+\rho N_B} = \frac{x_A}{1+(\rho-1)x_B} = \frac{\alpha(1-\alpha_0)^2}{(1-\alpha)^2\alpha_0}$$

It is convenient to use α_0 as the measure of the tendency to associate and to use α as the working variable. With the Flory–Huggins expression for the activity coefficients, we obtain

$$\bar{Q}^a_A = \log\left(\frac{1-\alpha}{1-\alpha_0}\right)^f - \log\,[(1+x_B(\rho-1)] + \frac{1}{2.3}\left[1-\alpha_0 f/2 - \frac{1-x_A\alpha f/2}{1+x_B(\rho-1)}\right]$$

$$\bar{Q}^a_B = \log\rho - \log\,[1+x_B(\rho-1)] + \frac{1}{2.3}\left[1-\rho\frac{1-x_A\alpha f/2}{1+x_B(\rho-1)}\right]$$

If $\rho = 1$, $\quad x_A = \dfrac{\alpha(1-\alpha_0)^2}{\alpha_0(1-\alpha)^2}$

$$\bar{Q}^a_A = \frac{f}{2}\left[\log\left(\frac{1-\alpha}{1-\alpha_0}\right)^2 + \frac{1}{2.3}(x_A\alpha-\alpha_0)\right]$$

$$\bar{Q}^a_B = \frac{f}{2}\frac{1}{2.3}x_A\alpha$$

$$Q^a_0 = 4\frac{f}{2}\left[\log\frac{1-\alpha_{0.5}}{1-\alpha_0} + \frac{1}{4.6}(\alpha_{0.5}-\alpha_0)\right]$$

$$\Sigma Q^a_{AB\ \mathrm{even}} = -\frac{f}{2}\log\,(1-\alpha_0)$$

$$\Sigma Q^a_{AB\ \mathrm{odd}} = \frac{f}{2}\left[\log\,(1-\alpha_0) + \frac{1}{2.3}\alpha_0\right]$$

If we assume the mole fraction form, on the other hand,

$$K = \frac{m_2}{m_1^2}(M+N_B) = \frac{f}{2}\frac{\alpha_0(1-\alpha_0 f/2)}{(1-\alpha_0)^2}$$

For $f = 2$, $\quad K = \dfrac{\alpha_0}{1-\alpha_0}$

$$Q^0_{AB} = 4\log 2(1-\sqrt{1-\alpha_0})$$

$$\Sigma Q_{AB\ \mathrm{even}} = -\log\,(1-\alpha_0)$$

$$\Sigma Q_{AB\ \mathrm{odd}} = 0$$

To show these relations graphically figure 14 gives $Q^0_{AB}2/f$, $-\Sigma Q_{AB\ \mathrm{odd}}2/f$ and $(\Sigma Q_{AB\ \mathrm{even}} - Q^0_{AB})2/f$ plotted against α_0 for the Flory–Huggins expression of extended association with $\rho = 1$. The broken lines show the corresponding

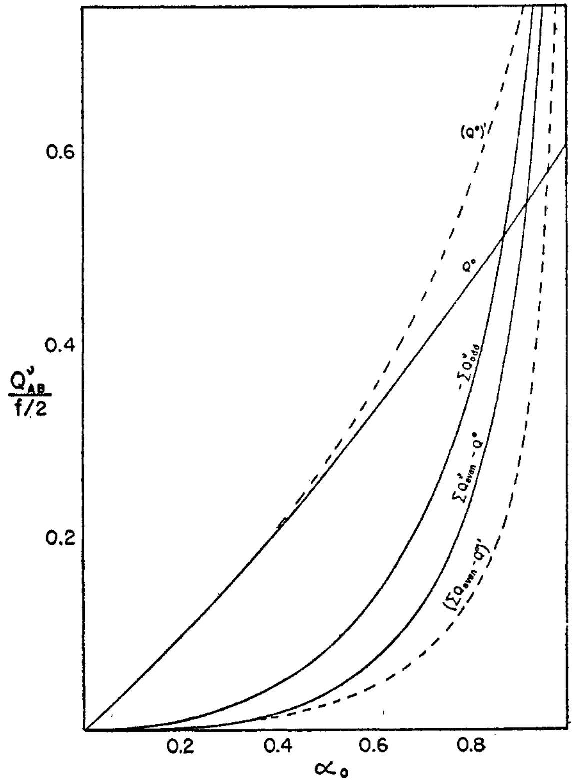

Fig. 14. Extended association

functions for the mole fraction expression for $f = 2$. In this case each Q_{odd} is zero.

Figure 15 shows the Q^0_{AB}, $-\Sigma Q_{\text{odd}}$, and $(\Sigma Q_{\text{even}} - Q^0_{\text{AB}})$ as functions of α_0 for the acid type of association in terms of mole fractions. The difference from figure 14 is not very great.

In figure 14 the curves for each value of f stop just before $\alpha_0 = 2/f$. Since $Q_0 2/f$ is approximately proportional to α_0, the value of Q_0 is about the same for all values of f at the same value of $\alpha_0 f/2$, that is, for an equal number of linkages per unit or an equal degree of association. The higher terms become relatively less important as f increases.

It is most interesting to note that the disappearance of the odd terms for the alcohol-type association depends upon the use of the mole fraction form, as well as upon the nature of the association. The quantitative values given in figures 14 and 15 are probably inaccurate because of the errors in the Flory–Huggins equations, but there must be enough truth in their picture to show that this type of association should not lead to symmetrical expressions. It must be remembered, moreover, that both treatments depend on the assumption that there is no ring formation. The probability of this assumption decreases as f increases, but it must be in error even for $f = 2$.

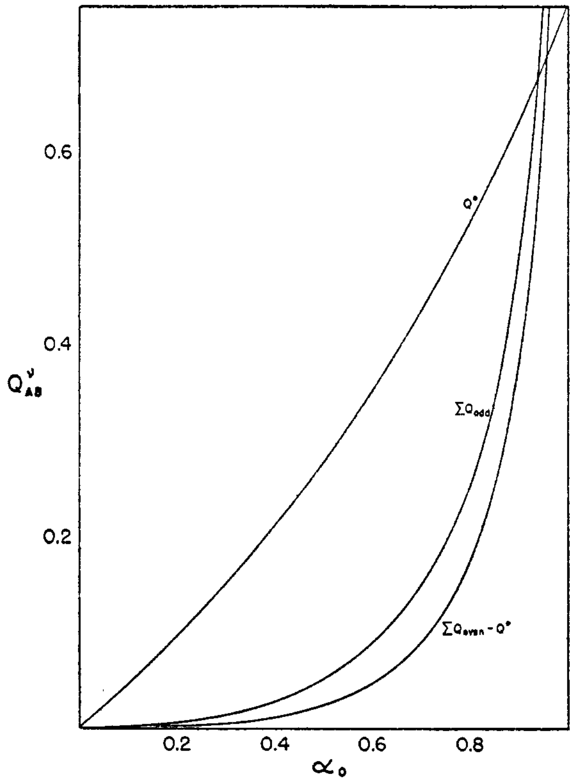

FIG. 15. Acid-type association

ONE-TO-ONE COMBINATION

If we have the reaction

$$A + B = C$$

$$\xi_C = K\xi_1\xi_B = 1 - \xi_1 - \xi_B = \frac{K\xi_1(1 - \xi_1)}{1 + K\xi_1}$$

$$\xi_B = \frac{1 - \xi_1}{1 + K\xi_1}$$

$$n_A = \xi_1 + \xi_C = \frac{\xi_1(1 + K)}{1 + K\xi_1}$$

$$n_B = \xi_B + \xi_C = 1 - \xi_1$$

$$x_A = \frac{\xi_1(1 + K)}{1 + 2K\xi_1 - K\xi_1^2}$$

$$Q^c_x = x_A \log \frac{1 + K\xi_1 - K\xi_1^2}{1 + K} + (1 - x_A) \log \frac{1 + 2K\xi_1 - K\xi_1^2}{(1 + K\xi_1)^2}$$

$$(\bar{Q}^c_A)_B = - \log (1 + K)$$

$$(\bar{Q}^c_B)_A = - \log (1 + K)$$

$$\Sigma Q^\nu_{AB\text{ even}} = -\log (1 + K) = - 2 \log (1 + \alpha_{0.5})(1 - \alpha_{0.5})$$

in which $\alpha_{0.5}$ is the fraction of groups reacted when $x = 0.5$. In the case of one-to-one combination, the deviations must obviously be symmetrical, so each Q_{odd} is zero. When $x_A = \frac{1}{2}$,

$$\xi_1 = \xi_B = (\sqrt{1 + K} - 1)/K$$

So

$$Q^0_{AB} = 4 \log 2(\sqrt{1 + K} - 1)/K = 4 \log (1 - \alpha_{0.5})$$

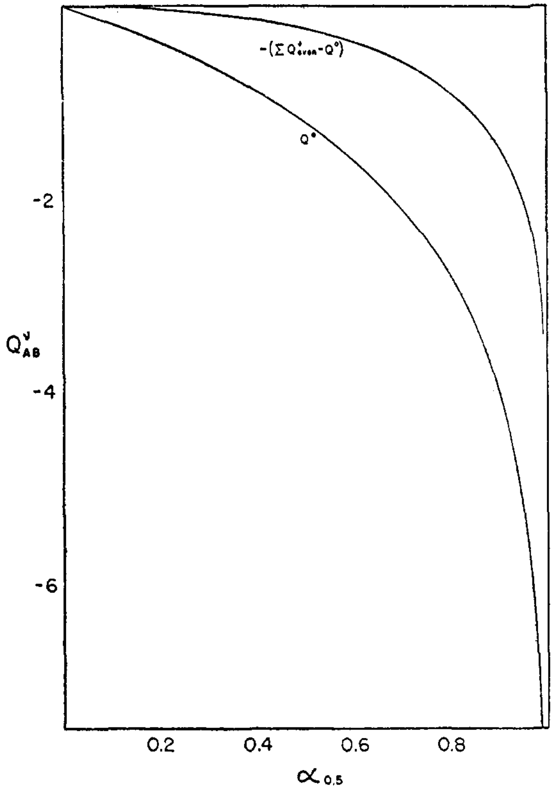

FIG. 16. One-to-one combination

Figure 16 shows Q^0_{AB} and $-(\Sigma Q_{AB\text{ even}} - Q^0_{AB})$ as a function of $\alpha_{0.5}$. The scale of the ordinates is ten times as large as in figures 14 and 15. Since the higher terms have the opposite sign to Q_0, the curve is more pointed than the parabola of a symmetrical solution.

If each type of molecule has a single reactive group, we should expect dimers of each component and the one-to-one compound. If either has more than one group, more complicated behavior may be expected. The free energies illustrated in figures 7 and 8 may be approximated by assuming the formation of two complexes $(C_2H_5OH)_2$ and $CHCl_3(C_2H_5OH)_3$, and doubtless could be approximated by linear chains of alcohol molecules branched, but with weaker links, at chloroform molecules. It is probable that the behavior of any completely miscible solutions can be expressed by chemical reactions obeying the law of mass action. However, it is certain that no partial miscibility can be explained in this way. Moreover, the assumption that the equilibrium constants are independent of the medium is a most improbable one, for the reactive groups such as hydroxyl must also interact with non-polar groups, and differently with different groups. Finally, all the other causes of deviations from ideal laws discussed earlier must also operate in systems in which there are chemical reactions. The best advice which comes from years of study of liquid mixtures is to use any model in so far as it helps, but not to believe that any moderately simple model corresponds very closely to any real mixture.

REFERENCES

(1) Benedict, M., Johnson, C. A., Solomon, E., and Rubin, L. C.: Trans. Am. Inst. Chem. Engrs. **41**, 371 (1945).
(2) Carlson, H. C., and Colburn, A. P.: Ind. Eng. Chem. **34**, 581 (1942).
(3) Flory, P. J.: J. Chem. Phys. **9**, 660 (1941); **10**, 51 (1942); **13**, 453 (1945).
(4) Flory, P. J.: J. Chem. Phys. **12**, 425 (1944).
(5) Gibbs, J. W.: Trans. Conn. Acad. Arts Sci. **3**, 115 (1875); *Collected Works*, Vol. I, p. 62.
(6) Guggenheim, E. A.: Trans. Faraday Soc. **33**, 151 (1937).
(7) Guggenheim, E. A.: Proc. Roy. Soc. (London) **A183**, 203, 213 (1944); Trans. Faraday Soc. **41**, 107 (1945).
(8) Hildebrand, J. H.: J. Am. Chem. Soc. **51**, 69 (1929).
(9) Hildebrand, J. H.: J. Chem. Phys. **15**, 225 (1947).
(10) Hildebrand, J. H.: Chem. Revs. **44**, 37 (1949).
(11) Huggins, M. L.: J. Chem. Phys. **9**, 440 (1941): J. Phys. Chem. **46**, 151 (1942); Ann. N. Y. Acad. Sci. **41**, 11 (1942); J. Am. Chem. Soc. **64**, 1712 (1942).
(12) Kirkwood, J. G.: J. Phys. Chem. **43**, 97 (1939).
(13) Langmuir, I.: Third Colloid Symposium Monograph, p. 3. The Chemical Catalog Company, Inc., New York (1925).
(14) Redlich, O., and Kister, A. T.: J. Chem. Phys. **15**, 849 (1947).
(15) Redlich, O., and Kister, A. T.: Ind. Eng. Chem. **40**, 345 (1948).
(16) Rushbrooke, G. S.: Proc. Roy. Soc. (London) **A166**, 296 (1938).
(17) Scatchard, G.: Chem. Revs. **8**, 321 (1931).
(18) Scatchard, G., and Hamer, W. J.: J. Am. Chem. Soc. **57**, 1805 (1935).
(19) Scatchard, G.: Trans. Faraday Soc. **33**, 160 (1937).
(20) Scatchard, G., and Raymond, C. L.: J. Am. Chem. Soc. **60**, 1278 (1938).
(21) Scatchard, G., Wood, S. E., and Mochel, J. M.: J. Phys. Chem. **43**, 119 (1939).
(22) Scatchard, G.: J. Chem. Phys. **7**, 657 (1939).
(23) Scatchard, G., Wood, S. E., and Mochel, J. M.: J. Am. Chem. Soc. **62**, 712 (1940).
(24) Stockmayer, W. H.: J. Chem. Phys. **11**, 45 (1943).
(25) van Laar, J. J.: Z. physik. Chem. **72**, 723 (1910); **83**, 599 (1913).
(26) Washburn, E. W.: Trans. Am. Electrochem. Soc. **22**, 330 (1912).
(27) Willingham, C. B., Taylor, W. J., Pignocco, J. M., and Rossini, F. D.: J. Research Natl. Bur. Standards **35**, 219 (1945).
(28) Zimm, B. H.: J. Chem. Phys. **14**, 164 (1946).