

## Thermodynamic Properties of Liquids, Including Solutions. X. Prediction of Polymer Solution Properties\*

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**ABSTRACT:** A comprehensive theory of the thermodynamic properties of solutions must deal with the dependence of the Gibbs free energy, the enthalpy, and the entropy on concentration, temperature, and the chemical compositions of the components. The author's new theoretical approach, which appears to satisfy the requirements considerably better than previous approaches, is used as a basis of a discussion of the prediction of the thermodynamic properties of solutions from parameters previously determined for other solutions, with a minimum of new data. Procedures for making predictions expected to be relatively accurate and (using a smaller amount of new experimental data) for making approximate predictions are both dealt with.

**KEY WORDS** Thermodynamics / Polymer Solutions / Contact Energy /  
Contacting Surface Area /

This paper deals with the problem of the prediction of the thermodynamic properties of solutions, with the aid of the theory described in preceding papers of this series.<sup>1-9</sup>

The properties of interest are those concerned with equilibria between two phases: two liquid solutions, a liquid solution and a gas or a gel or a crystalline solid. In polymer science, such properties as the solubility of polymers in different solvents, the volatility of solvents, the solubility of polymers in different solvents, compatibility of plasticizers, and the fractionation of mixtures of polymer molecules of different molecular weight and/or chemical composition depend primarily on these equilibria.

We should like to predict these properties from previously determined properties of the solution components and other related solutions. If additional experimental data on the solution of interest are required, we should like to minimize the amount of such data and to obtain it as simply as possible.

Since only a small number of solutions have so far been treated quantitatively with the new theory, a considerable amount of extrapolation and speculation is necessary. It would certainly

be safer to postpone dealing with this subject in print until a later date, after tentative procedures had been tried and evaluated. On the other hand, consideration of the general problem now may help to guide future theoretical and experimental work.

### THERMODYNAMIC BASIS

The properties of interest can all be related by known thermodynamic equations to the molal Gibbs free energy ( $\bar{G}$ ) or, equivalently, to the activities ( $a_1, a_2$ ) of the solution components. These activities are related to  $\bar{G}$  by the equations

$$\bar{G}_1 = \left( \frac{\partial \bar{G}}{\partial N_1} \right)_{N_2} = RT \ln a_1 \quad (1)$$

$$\bar{G}_2 = \left( \frac{\partial \bar{G}}{\partial N_2} \right)_{N_1} = RT \ln a_2 \quad (2)$$

$N_1$  and  $N_2$  denote the numbers of moles of solvent and solute, respectively.

Our general problem is to predict, for a given system, the dependence of  $\bar{G}$  (or of  $a_1$  and  $a_2$ ) on the composition, *e.g.*, on the mole fractions ( $x_1, x_2$ ), volume fractions ( $\phi_1, \phi_2$ ), or segment fractions ( $x_{\alpha}, x_{\beta}$ ), and on the temperature. We must be guided by the related principles: (1)

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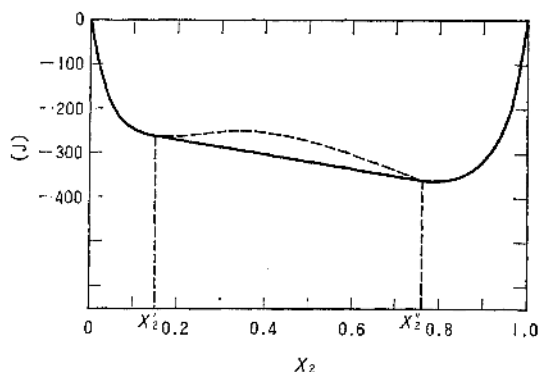


Figure 1. Gibbs free energy for  $s_d=5300$  J,  $r_0=1.2$ ,  $K=1$ , and  $\bar{S}^b=0$ . (Reprinted from ref 6.)

that, for any system in equilibrium, the total Gibbs free energy is a minimum, and (2) that, for equilibrium between two phases, the activity of each component must be the same in both phases.

The second of these principles leads directly to the result that the partial pressure of a volatile component of a solution is proportional to the activity of that component in the solution.

The first principle requires, for example, that, if the curve representing the dependence of the Gibbs free energy of a solution on mole fraction has a common tangent at two points (see Figure 1), the solution will separate into two liquid phases, over the composition range between these points. Within these limits, the total Gibbs free energy will be less for the two phase system (given, in the figure, by the sloping

straight line) than it would be for a single phase solution (given by the curve).

Similarly, it can be shown that the solubility of a non-swelling crystalline solute is given by the intersection of the sloping straight line in Figure 2 with the Gibbs free energy curve. (The ordinate of the point  $G_2$  on the right hand axis is minus the molal heat of fusion of the solute.)

The molal Gibbs free energy change ( $\Delta\bar{G}^M$ ) on mixing the components of a solution is related to the corresponding enthalpy change ( $\Delta\bar{H}^M$ ) and entropy change ( $\Delta\bar{S}^M$ ) by the exact equation

$$\Delta\bar{G}^M = \Delta\bar{H}^M - T\Delta\bar{S}^M \quad (3)$$

It is convenient to treat the enthalpy and entropy changes separately. Moreover, at ordinary pressures the enthalpy and energy changes are practically equal; for our purposes the minute differences between them can be neglected.

Experimentally, the entropy changes cannot be measured directly. They must be calculated from the Gibbs free energy and enthalpy changes by means of eq 3. Theoretically, equations have been deduced for  $\Delta\bar{H}^M$  and  $\Delta\bar{S}^M$  separately. If the parameters in these equations are known, substitution into eq 3 yields the desired  $\Delta\bar{G}^M$ .

Although  $\Delta\bar{H}^M$  and  $\Delta\bar{S}^M$  are not precisely independent of temperature, they are often approximately so. Neglecting any temperature dependence of these quantities,

$$\left(\frac{\partial\Delta\bar{G}^M}{\partial T}\right)_P = -\Delta\bar{S}^M \quad (4)$$

Hence, if the theoretical equations and param-

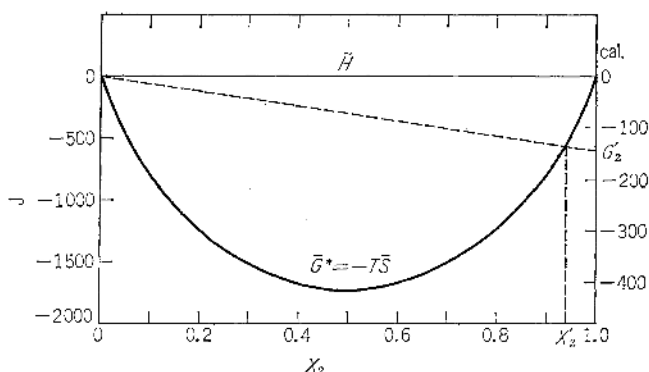


Figure 2. Gibbs free energy for an ideal solution at 25°C. (Reprinted from ref 6.)

eters for the concentration dependence of  $\Delta\bar{H}^M$  and  $\Delta\bar{S}^M$  are sufficiently accurate, they will give, not only (by eq 3) the concentration dependence of the Gibbs free energy at one temperature, but also (by eq 4) the approximate concentration dependence at other temperatures.

#### ENTHALPY AND VOLUME CHANGES OF MIXING<sup>1</sup>

I assume a liquid to behave thermodynamically as if its molecules were each composed of one or more chemically uniform segments, with these segments having surfaces in mutual contact. For each type of segment ( $\alpha, \beta$ ) I assume the average contacting surface area ( $\sigma_\alpha^0, \sigma_\beta^0$ ) per mol to be constant at a given temperature. For each type of contact I assume the average contact energy per unit contact area ( $\varepsilon_{\alpha\alpha}, \varepsilon_{\beta\beta}, \varepsilon_{\alpha\beta}$ ) to be constant at a given temperature. The relative total contact areas for the different types ( $\sigma_{\alpha\alpha}, \sigma_{\beta\beta}, \sigma_{\alpha\beta}$ ) I assume to be governed by equilibrium constants. This minimizes the free energy. If there are only two types of segment, hence three types of contact,

$$K = \frac{\sigma_{\alpha\beta}^2}{4\sigma_{\alpha\alpha}\sigma_{\beta\beta}} \quad (5)$$

For perfectly random mixing,  $K$  is unity.

From these assumptions I have deduced equations for the excess energy (or enthalpy) of a solution in terms of segment and intersegment parameters, including the equilibrium constant or constants. For the special case of a mixture of two types of single segment molecules, the molal enthalpy change on mixing, sometimes called the excess enthalpy of mixing, is

$$\bar{H}^E = \varepsilon_A x_1 z_\beta g_K \quad (6)$$

where

$$\varepsilon_A = \sigma_\alpha^0 \Delta\varepsilon / 2 = \sigma_\alpha^0 (2\varepsilon_{\alpha\beta} - \varepsilon_{\alpha\alpha} - \varepsilon_{\beta\beta}) / 2 \quad (7)$$

$$z_\beta = 1 - z_\alpha = r_\alpha x_2 / (x_1 + r_\alpha x_2) \quad (8)$$

$$r_\alpha = \sigma_\beta^0 / \sigma_\alpha^0 \quad (9)$$

$$g_K = - \frac{2}{z_\alpha z_\beta K} [1 - (1 + K' z_\alpha z_\beta)^{1/2}] \quad (10)$$

$$K' = 4(K^{-1} - 1) \quad (11)$$

If there are only two types of segment, the equations involve three parameters: One is the

equilibrium constant ( $K$ ) just mentioned. Another is the ratio ( $r_\alpha$ ) of the average contacting surface area of a  $\beta$  segment to that of an  $\alpha$  segment. The third measures the energy (or enthalpy) change when contacts between like segments are replaced by contacts between unlike segments. (See eq 7.)

The magnitude of  $K$  determines the spread or fatness of the curve obtained when the excess enthalpy ( $\Delta\bar{H}^E = \Delta\bar{H}^M \approx \Delta E^M$ ) per mol (Avogadro's number) of segments is plotted against the segment fraction ( $x_\beta = N_\beta / (N_\alpha + N_\beta)$ ). If each component molecule consists of a single segment, one mol of segments is the same as one mol of molecules, and  $x_\beta = x_2$ . Comparison of curves 1, 2, and 3 in Figure 3 shows the effect of changing  $K$ , while keeping the other parameters constant.

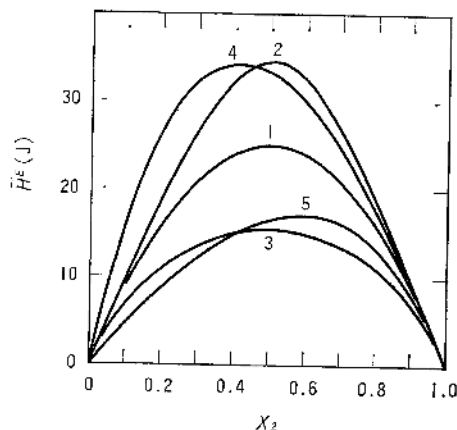
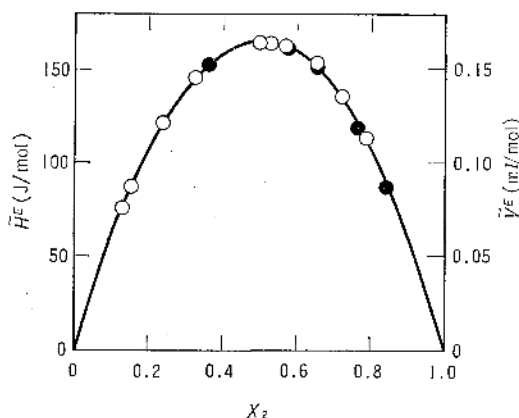


Figure 3. Theoretical enthalpy of mixing curves, for  $\varepsilon_A = 100$  J: curve 1,  $r_\alpha = 1, K = 1$ ; curve 2,  $r_\alpha = 1, K = 5$ ; curve 3,  $r_\alpha = 1, K = 0.2$ ; curve 4,  $r_\alpha = 2, K = 1$ ; curve 5,  $r_\alpha = 0.5, K = 1$ . (Reprinted from ref 6.)

The magnitude of  $r_\alpha$  determines the dissymmetry or skewness of the curve. Compare curves 1, 4, and 5. The other parameter,  $\varepsilon_A$ , is a scaling parameter. Multiplying a given value of  $\varepsilon_A$  by any constant multiplies the magnitudes of  $\bar{H}^E$  at all concentrations by that constant.

I have derived theoretical equations for the excess volume that are like those for the excess enthalpy, except for the replacement of the scaling parameter  $\varepsilon_A$  by  $v_A$ , which measures the

change in volume when contacts between like segments are replaced by contacts between unlike segments. (See ref 4, p 275. A more detailed treatment of the relation between  $\bar{H}^E$  and  $\bar{V}^E$  is planned for another paper or papers.) Since the  $K$  and  $r_\sigma$  parameters are the same for the two properties, a graph showing both plotted against  $x_\beta$ , with vertical scales adjusted to give agreement at one concentration, should show agreement at all concentrations. In other words, the curve shapes should be the same. Figure 4 exemplifies this for the cyclohexane + carbon tetrachloride system.<sup>10</sup>



**Figure 4.** Excess enthalpies (○) and volumes (●) for cyclohexane—carbon tetrachloride solutions at 20°C. Experimental data by Kehlen and Sackmann.<sup>10</sup> The curve is theoretical, applicable to both properties:  $r_\sigma=0.974$ ;  $K=0.835$ ;  $\epsilon_d=703.5$ ;  $v_d=0.6993$ .

This means that the two important parameters,  $K$  and  $r_\sigma$ , can be determined from accurate measurements of the volume change on mixing. With those parameters known, a single heat of mixing measurement will suffice to give the dependence of enthalpy on concentration over the whole range.

In general, these three parameters should be practically the same for all solutions involving the same segment types, regardless of the numbers of segments of each type in each type of molecule. Studies of mixtures of normal alkanes, for example, agree with this expectation. The same parameters should also apply, with others, to mixtures containing other types of segments

also. Comparison of some pairs of ditonic systems (each containing the same two types of segments) do show some differences between the parameters. They may result, for example, from differences in accessibility of the segments or, for long chain molecules, from differences in the amount of intramolecular contacting. More studies of ditonic systems containing the same two segment types are obviously needed.

#### ENTROPY CHANGES ON MIXING<sup>4</sup>

The molal entropy change on perfectly random mixing of two kinds of equal sized molecules is

$$\Delta\bar{S}^{M*} = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (12)$$

a result which, if the heat of mixing is zero, leads to Raoult's law. If the molecules are rigid, but of unequal size, my new theory<sup>4</sup> leads to

$$\Delta\bar{S}^M = -R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \quad (13)$$

for perfectly random mixing. The part of the excess entropy of mixing (defined as the excess over the Raoult's law entropy) that results from the size difference, is therefore

$$\begin{aligned} \bar{S}_{rm}^E &= \Delta\bar{S}^M - \Delta\bar{S}^{M*} \\ &= -R[x_1 \ln(\phi_1/x_1) + x_2 \ln(\phi_2/x_2)] \quad (14) \end{aligned}$$

if the mixing is perfectly random.

If the equilibrium constant  $K$  is not 1, the mixing is not perfectly random, since the probabilities of the three contact types are not equal. The theoretical equation for the correction to the excess entropy to allow for this is (for a mixture of single-segment molecules of two types)

$$\begin{aligned} \bar{S}_{cc}^E &= -\frac{k_B \sigma_\alpha^*}{4} \{x_1 [(1-z_\beta g_K) \ln(1-z_\beta g_K) \\ &\quad - z_\alpha \ln z_\alpha - z_\beta \ln(z_\alpha z_\beta)] \\ &\quad + r_\sigma x_2 [(1-z_\alpha g_K) \ln(1-z_\alpha g_K) \\ &\quad + z_\alpha g_K \ln(z_\alpha z_\beta g_K^2) - z_\beta \ln z_\beta] \} \quad (15) \end{aligned}$$

where  $k_B$  represents the Boltzmann constant.

This correction involves, in addition to  $K$  and  $r_\sigma$  (see eq 8, 10, and 11), a parameter  $\sigma_\alpha^*$ , which measures the average contacting surface area (or the average number of contacts) per Avogadro's number of  $\alpha$  segments in a hypothetical solution in which each unit area (or each contact) is completely independent of others. (The defini-

tion of  $\sigma_\alpha^0$  in ref 1 did not require independence of contacts. For the enthalpy of mixing theory the magnitude of  $\sigma_\alpha^0$  did not need to be evaluated. If contact independence were required for  $\sigma_\alpha^0$ , its value, as used in eq 11, would equal the value of  $\sigma_\alpha^*$ , as used in eq 15.)

Another contribution to the entropy of mixing comes from the concentration dependence of the entropy associated with the oscillations and rotations of the molecules and their parts. For nonrigid molecules, such as many polymers, this contribution includes the change in entropy associated with the change in randomness of orientation of each rigid segment relative to its neighbors. It is thus related to the concentration dependence of molecular flexibility. Assuming the oscillational, rotational and orientational randomness to change rectilinearly with the average fraction of contacting surface of each segment that makes contact with segments of the other kind, the theoretical equation (for a system containing only two segment types) is

$$\bar{S}_{or}^E = R x_2 \ln(1 + k_s' z_\alpha g_K) \quad (16)$$

Again the  $K$  and  $r_\sigma$  parameters are involved, through  $z_\alpha$  and  $g_K$ , and again a new parameter,  $k_s'$ , is required. This parameter measures the average change in randomness when the contacts made by a segment of one type change from all of one type to all of the other type. Relations to molecular structure and flexibility and to the relative magnitudes of the interaction energies for different types of contact will doubtless become evident as  $k_s'$  values for more systems become available.

#### DETERMINATION AND ESTIMATION OF PARAMETERS

Examples of the procedures used in the determination of the parameters from experimental data have been presented in preceding papers of this series. Let us now consider the general problem of determining or estimating them for new systems.

As already noted,  $K$  and  $r_\sigma$  can be deduced from accurate measurements of the shape of either the  $\bar{H}^E$  or the  $\bar{V}^E$  curve. If  $K$  is equal to (or close to) unity, the correction ( $\bar{S}_{cc}^E$ ) for nonrandomness of mixing is zero (or negligible).

The two additional parameters needed,  $\epsilon_A$  and  $k_s'$ , can be determined from one  $\bar{H}^E$  measurement and one  $\bar{G}^E$  measurement or from two measurements of  $\bar{G}^E$  at different (not too close) concentrations. If  $K$  is not equal to, or close to, unity,  $\sigma_\alpha^*$  is also needed and another data point is required. One good  $\bar{H}^E$  value at any concentration, plus two good  $\bar{G}^E$  values at two (not too close) concentrations, should suffice to give all the parameters and so all of the enthalpy, entropy and Gibbs free energy curves.

As our knowledge of the parameter values for different systems accumulates, it should be possible to relate them more and more closely to molecular compositions and structures. It should thus become possible to estimate them for new systems. These estimates need not always be accurate. For example, if it is known that the contribution of  $-T\bar{S}_{cc}^E$  to  $\Delta\bar{G}^M$  is relatively small compared with other contributions to  $\Delta\bar{G}^M$ , a crude estimate of  $\sigma_\alpha^*$  may suffice. Likewise, if it is known that the contribution of  $-T\bar{S}_{or}^E$  to  $\Delta\bar{G}^M$  is relatively small compared to other contributions to  $\Delta\bar{G}^M$ , a crude estimate of  $k_s'$  may be sufficient.

The parameter  $r_\sigma$  for an  $\alpha\beta$  system can of course be calculated from the  $r_\sigma$  values for  $\alpha\gamma$  and  $\beta\gamma$  systems, because of the definitions of these ratios. See eq 9.

In previous papers of this series and in this paper, so far, no use has been made of a possible relation between the parameters  $K$  and  $\epsilon_A$ . In ref 1, however, the expected form of such a relation was given. Let us now consider the matter further.

The relation proposed was

$$K = A \exp(-\Delta\epsilon/kT) = A \exp(-2\epsilon_A/\sigma_\alpha^0 kT) \quad (17)$$

where  $k$  is a constant having an unknown magnitude depending on the arbitrary choice of the magnitude of  $\sigma_\alpha^0$ , and  $A$  is an unknown function depending on the relative accessibilities of the two types of segment surfaces for contacts with other segment surfaces. Other factors are doubtless also involved.

If  $\sigma_\alpha^0$  is redefined as the average number of unit areas (or the average number of contacts) per mol of  $\alpha$  segments in an equivalent hypothetical system in which each unit segment surface makes contact independently with other

segment surfaces (the type of contact being unrelated to the types of neighboring contacts), then it seems reasonable to identify  $\sigma_{\alpha}^0$  with  $\sigma_{\alpha}^*$  and to put  $k$  equal to the Boltzmann constant,  $k_B$ . We thus arrive at the equation

$$K = A \exp(-2\varepsilon_A/\sigma_{\alpha}^* k_B T) \quad (18)$$

$$\ln K = \ln A - \left( \frac{2\varepsilon_A}{\sigma_{\alpha}^* k_B} \right) \frac{1}{T} = \ln A - \left( \frac{2}{\sigma_{\alpha}^* k_B T} \right) \varepsilon_A \quad (19)$$

If  $A$ ,  $\sigma_{\alpha}^*$ , and  $\varepsilon_A$  were strictly independent of temperature, for a given solution type, a plot of  $\ln K$  against  $1/T$  should be rectilinear. Also, if  $A$  and  $\sigma_{\alpha}^*$  had the same values for different systems at the same temperature, a plot of  $\ln K$  against  $\varepsilon_A$  should be rectilinear. Actually, one cannot reasonably expect the parameters  $A$  and  $\sigma_{\alpha}^*$  to be the same for different systems, but it would not be surprising to find that a plot of known values of  $\ln K$  against the corresponding known values of  $\varepsilon_A$  would approximately fit a smooth curve, probably one that does not depart much from rectilinearity. Such a result would seem more likely the more similar are the solution components in the systems included in the plot.

Data are not now available for a good test of this suggested relation, but a plot of the  $\ln K$  and  $\varepsilon_A$  values deduced for the four polymer-solvent systems so far studied shows fair agreement. Within the probable error of the data points, the relation is rectilinear. If future results show similar or better agreement, we shall have a means of predicting approximate  $\varepsilon_A$  values from  $K$  values, or *vice versa*.

If, also, the  $\sigma_{\alpha}^*$  and  $k_e'$  parameters can be approximated for a new system from their known values for old systems, the  $\Delta\bar{H}^M$ ,  $\Delta\bar{S}^M$  and  $\Delta\bar{G}^M$  curves (and so the thermodynamic properties dependent on them) can all be deduced from the theoretical equations, plus, as new data, only measurements of the excess

volume of mixing (to obtain  $K$  and  $r_2$ ). How accurate such approximations and the values of the properties obtained thereby will be remains to be seen.

## POLYMER SOLUTIONS

For simplicity I have, in this paper, treated the solution components as if they were simple small molecules. The same principles (with a few minor modifications) and similar equations apply to more complex low-molecular solutions and to polymer solutions. The appropriate equations for polymer solutions, involving no new parameters, have been published in preceding papers.<sup>2,3,5,7,8</sup> Those for more complex low-molecular systems will be published in future papers.

## CONCLUSION

I have discussed the problem of the prediction of thermodynamic properties of solutions with the aid of my new theory, showing how, in my opinion, accurate predictions are possible with only a small amount of new data, and (better after more empirical parameter values have been accumulated) how approximate predictions can be made more easily—perhaps even with no new data other than solution volumes.

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