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Thermodynamics of Heterogeneous Polymers and Their Solutions¹

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The statistical mechanical treatment previously applied to homogeneous polymer solutions has been extended to heterogeneous polymers composed of numerous molecular species differing in polymer chain length. Entropies of mixing with solvent are derived with reference to three standard states: the oriented pure components, the disoriented pure components, and the disoriented mixture of species. The entropy of mixing with respect to the last-mentioned state is identical with that previously derived neglecting polymer heterogeneity. Upon introducing a van Laar heat of mixing term, expressions for the partial molal free energies are derived. These should be reasonably correct in view of the satisfactory agreement between observed solvent activities in polymer-solvent solutions and theory, as shown by Huggins. The relationships should be useful not only in dealing with solutions, but also in equilibria involving heterogeneous polymers in the absence of solvent. The thermodynamic equations are applied to the problem of equilibrium in the range of partial misci-

bility for solvent-heterogeneous polymer systems. The requisites for efficient fractionation of high polymers are discussed. The efficiency of separation depends on the ratio of the volumes of the supernatant and the precipitated phases. In order to attain a high value for this ratio, very dilute solutions must be employed. The higher the molecular weight at which separation occurs the greater the dilution required for the same sharpness of separation. The free energy expressions are also applied to the formulation of equilibrium constants to be employed in reversible polymerization-degradation processes. It is shown that concentrations should be expressed in moles per unit volume in the equilibrium constant. The equilibrium state for a polyfunctional condensation, considered as a reaction between functional groups, is not affected by the polymeric nature of the reacting species; the position of equilibrium should be the same as is found for analogous monofunctional reactants under the same conditions.

INTRODUCTION

SOLUTIONS of high polymers have been known for some time to behave anomalously²⁻⁴ with respect to the ideal solution laws as originally set up for solutions of simple molecules. These apparent anomalies in thermodynamic and related behavior have been largely cleared up by statistical mechanical treat-

ments⁵⁻⁷ of high polymer solutions which have appeared in the last few years. These treatments are based on the following physical approximation: The liquid mixture composed of long chain polymer and monomeric solvent molecules is assumed to conform to a pseudo-lattice structure, each cell of which may be occupied either by a molecule of solvent or by an element of the chain (segment) equal in size to a solvent molecule. Proceeding from this concept, it has been

¹ A preliminary report on this work was published previously, *J. Chem. Phys.* **12**, 114 (1944).

² W. Ostwald, *Kolloid Zeits.* **46**, 248 (1928).

³ K. H. Meyer and R. Lühdemann, *Helv. Chim. Acta*, **18**, 307 (1935).

⁴ K. H. Meyer, *Natural and Synthetic High Polymers* (Interscience Publishers, Inc., New York, 1942), pp. 582-595.

⁵ M. L. Huggins, *J. Phys. Chem.* **46**, 151 (1942); *Ann. N. Y. Acad. Sci.* **43**, 1 (1942); *J. Am. Chem. Soc.* **64**, 1712 (1942).

⁶ P. J. Flory, *J. Chem. Phys.* **10**, 51 (1942).

⁷ A. R. Miller, *Proc. Camb. Phil. Soc.* **39**, 54 (1943).

possible to derive by an approximate mathematical procedure the following expression⁶ for the entropy of mixing n solvent with N polymeric solute molecules (initially in random configurations in the pure state) where

$$\Delta S_{\text{mixing}} = -k[n \ln v_1 + N \ln v_2]; \quad (1)$$

v_1 and v_2 are the volume fractions of the components, solvent and polymeric solute, respectively. This expression differs from the one representing the so-called "ideal" solution in that *mole* fractions are replaced by *volume* fractions. Inasmuch as the ideal solution law can be derived theoretically only for solutions of equal-sized species, where volume fractions equal mole fractions, the conventional ideal solution is seen to be included as a special case of Eq. (1).

Although certain limitations on this statistical treatment as applied to polymer solutions have become apparent,⁸ sufficient agreement with experiment has been obtained^{5, 6, 9, 10} to encourage extension of this method of attack. It is the purpose of the present paper to extend the previous statistical mechanical method to heterogeneous polymers and their solutions in which the polymer constituent is actually a mixture of many species differing in length, or molecular weight. The resulting equations afford a basis for dealing with chemical equilibria involving interconversion of the polymer species. They can also be applied to the problem of fractionation of polymers, as, for example, by fractional precipitation from solution.

DERIVATION OF ENTROPIES OF MIXING

The procedure closely parallels that which has been given previously for a polymer consisting of a single species. The pseudo-lattice for the solution is to be filled by successively adding the polymer molecules to it, then filling in the vacant cells with molecules of solvent. Suppose that $j-1$ polymer molecules previously have been assigned locations in the lattice. The number of unoc-

cupied sites in the lattice will be given by

$$n_0 - \sum_{i=1}^{j-1} x_i$$

where n_0 is the total number of lattice sites and x_i is the number of segments in the i th molecule ($i < j$). This factor will represent the number of sites available to the terminal segment of the j th molecule to be added to the lattice. The cell to which this first segment is assigned will be surrounded by γ -sites for the second segment, where γ is a "coordination number" for the lattice. Some of these may be occupied by segments of molecules previously added to the lattice. The expected number of available sites for the second segment of the j th molecule can be expressed therefore as the product of γ into the fraction of all lattice sites which are not occupied by previously added segments of molecules;⁶ this product is given by

$$\gamma \left(n_0 - \sum_{i=1}^{j-1} x_i - 1 \right) / n_0.$$

Of the γ -lattice sites surrounding the second segment, one is occupied by the first segment. The expected number of sites available to the third segment, therefore, will be

$$(\gamma - 1) \left(n_0 - \sum_{i=1}^{j-1} x_i - 2 \right) / n_0.$$

Similarly for the ξ th segment of the j th molecule the expected number of available sites will be

$$(\gamma - 1) \left[n_0 - \sum_{i=1}^{j-1} x_i - (\xi - 1) \right] / n_0. \quad (2)^{11}$$

The number (or expected number) of configurations available to the j th molecule as a whole can be obtained by combining the factors given above for the expected numbers of sites available to each segment. The resulting ex-

⁸ Paper presented before the Division of Physical and Inorganic Chemistry at the Pittsburgh Meeting of the American Chemical Society, September 6, 1943. To be published shortly.

⁹ M. L. Huggins, Ind. Eng. Chem. **35**, 216, 980 (1943); Ann. N. Y. Acad. Sci. **44**, 431 (1943).

¹⁰ G. Gee and L. R. G. Treloar, Trans. Faraday Soc. **38**, 147 (1942).

¹¹ The term $(\xi - 1)$ in these expressions may be open to objections on the grounds that segments of the j th molecule are not to be considered the equivalent of segments of other molecules which may locate any place in the lattice. In any event, its contribution to the term is insignificant, and could be omitted entirely. It has been included here for the reason that it simplifies reduction of the subsequent equations.

pression becomes

$$\nu_j = \frac{1}{\sigma} \left[n_0 - \sum_{i=1}^{j-1} x_i \right] \left[\gamma / (\gamma - 1) \right] \\ \times \prod_{\xi=2}^{x_j} \left[\left(n_0 - \sum_{i=1}^{j-1} x_i - \xi + 1 \right) (\gamma - 1) / n_0 \right].$$

The symmetry number σ of the polymer molecules usually may be taken equal to two, in consideration of the equivalence of the ends of the molecule. Replacing $\gamma/(\gamma-1)$ by unity in the second factor in brackets in the equation given above,

$$\nu_j = [n_0 / \sigma (\gamma - 1)] \prod_{\xi=0}^{x_j-1} \\ \times \left[\left(n_0 - \sum_{i=1}^{j-1} x_i - \xi \right) (\gamma - 1) / n_0 \right] \\ = \frac{1}{\sigma} \left(\frac{\gamma - 1}{n_0} \right)^{x_j-1} \left(n_0 - \sum_{i=1}^{j-1} x_i \right)! / \\ \left(n_0 - \sum_{i=1}^j x_i \right)!. \quad (3)$$

The total number of configurations available to the system of N polymer molecules is given by

$$W = \left(1 / \prod_{x=1}^{\infty} N_x! \right) \prod_{j=1}^N \nu_j, \quad (4)$$

where N_x is the number of polymer molecules composed of x units. Substituting Eq. (3) in (4) and simplifying the product term in the numerator,

$$W = \left[1 / \left(\sigma^N \prod_{x=1}^{\infty} N_x! \right) \right] \left[(\gamma - 1) / n_0 \right]^{\sum_{j=1}^N (x_j - 1)} \\ \times \left[n_0! / \left(n_0 - \sum_{i=1}^N x_i \right)! \right].$$

Noting that

$$\sum_{j=1}^N x_j = \sum_{i=1}^N x_i = \sum_{x=1}^{\infty} x N_x,$$

and replacing n_0 with

$$n_0 = n + \sum_{x=1}^{\infty} x N_x$$

where n is the number of solvent molecules,

$$W = [1 / (\sigma^N \prod N_x!)] [(\gamma - 1) / (n + \sum x N_x)]^{\sum (x-1) N_x} \\ \times [(n + \sum x N_x)! / n!]. \quad (5)$$

In Eq. (5) and in those which follow, the limits on the summations are omitted inasmuch as they invariably run from $x=1$ to ∞ .

The entropy of mixing is given by $k \ln W$, where k is Boltzmann's constant. Or, if at this point n and the N_x 's are expressed in moles, rather than as numbers of molecules,

$$\Delta S_{\text{mixing}} = R \ln W.$$

Substituting for W from Eq. (5) and introducing Stirling's approximation for factorial terms,

$$\Delta S_{\text{mixing}} = -R \left\{ n \ln \left(\frac{n}{n + \sum x N_x} \right) \right. \\ \left. + \sum \left[N_x \ln \left(\frac{N_x}{n + \sum x N_x} \right) \right] \right. \\ \left. - \sum [(x-1) N_x] [\ln (\gamma - 1) - 1] + N \ln \sigma \right\} \quad (6)$$

or

$$\Delta S_{\text{mixing}} = -R \{ n \ln v_1 + \sum [N_x \ln (v_x / x)] \\ - \sum [(x-1) N_x] [\ln (\gamma - 1) - 1] + N \ln \sigma \}, \quad (6')$$

where v_1 and v_x are volume fractions of solvent and x -mer, respectively. In writing these equations the term for solvent (first term) could have been included with the first summation, the solvent being considered as a "polymer" composed of one segment. However, in consideration of possible heats of interaction between solvent molecules on the one hand and polymer segments on the other, it will facilitate formulation of free energy expressions to keep these terms separate.

In deriving Eqs. (6) and (6') the liquid structure has been approximated by a lattice composed of cells equal in size to one solvent molecule. This physical approximation has received due consideration in previous publications. In the case of heterogeneous polymers, however, it leads to a summation term¹² $\sum N_x \ln (v_x / x)$ which contains only integral values of x . In applying these and subsequent

¹² The other summation terms in Eqs. (6) and (6') represent merely total number of segments and of molecules.

equations to actual heterogeneous polymers it will be necessary to let this summation include the actual molecular species, for which x , the ratio of the molecular volumes of polymer molecule and solvent, will in general be non-integral. The additional approximation introduced by this extension will be negligible so long as the x values concerned are large. It should be borne in mind, however, that in subsequent equations the x values may not necessarily be integral.

The above expressions (6) and (6') refer to the entropy change on forming the solution from N_1 , N_2 , N_3 , etc. molecules of monomer, dimer, trimer, etc., each initially in an ordered (crystalline) state, and n molecules of solvent. This entropy change can be separated into three components: (a) the entropy of disorientation of the individual pure components, (b) the entropy of mixing these, and (c) the entropy of dilution of the mixture.

$$\Delta S_{\text{mixing}} = \Delta S_a + \Delta S_b + \Delta S_c. \quad (7)$$

The quantity ΔS_a is, of course, the sum of the entropies of disorientation of the individual polymer species.⁶ For the x -mer species

$$\Delta S_{a,x} = RN_x [\ln (x/\sigma) + (x-1) \ln (\gamma-1) - (x-1)].$$

Hence,

$$\Delta S_a = R \sum [N_x \ln (x/\sigma)] + R \sum [(x-1)N_x] [\ln (\gamma-1) - 1]. \quad (8)$$

Subtracting this entropy of disorientation from Eq. (6) and setting $n=0$,

$$\Delta S_b = -R \sum [N_x \ln (xN_x / \sum xN_x)]. \quad (9)$$

This equation represents the entropy of mixing together the previously disoriented individual polymer species.

Finally, for the entropy change on diluting the mixed, disoriented polymer molecules with n molecules of solvent

$$\begin{aligned} \Delta S_c &= \Delta S_{\text{mixing}} - \Delta S_a - \Delta S_b \\ &= -R \left\{ n \ln \left(\frac{n}{n + \sum xN_x} \right) + \sum \left[N_x \ln \left(\frac{\sum xN_x}{n + \sum xN_x} \right) \right] \right\} \quad (10) \\ &= -R(n \ln v_1 + N \ln v_2), \quad (10') \end{aligned}$$

where v_2 is the volume fraction of all polymer molecules; i.e.,

$$v_2 = \sum v_x.$$

Equation (10') is identical with the equation previously derived⁶ for the entropy of mixing N disoriented polymer molecules, all of the same size, with n solvent molecules. When dealing with situations in which no change in the distribution of polymer species is encountered, this equation may be employed as the basic entropy of mixing expression without reservations for heterogeneity. In the expression previously derived^{5,6} for partial molal quantities it is only necessary to replace the number of segments x with its number average \bar{x}_n . In short, heterogeneity can be disregarded, provided that the polymer is confined to one phase and that no polymerization and/or degradative steps are involved within that phase. For example, vapor pressures and osmotic pressures of polymer-solvent mixtures can be handled using ΔS_c , as previously published,^{5,6,9} without regard for heterogeneity of the polymer. It is necessary, however, that the number average molecular weight, rather than some other average, be employed.

When two phases containing polymer are in equilibrium, passage of polymer from one phase to another being permissible, the undiluted, heterogeneous mixture of polymer molecules of given distribution is no longer adequate as a reference state. For the treatment of certain problems, e.g., chemical equilibria between polymer species (i.e., condensation or addition reactions between polymer species, or equilibrium degradation of the polymer molecules), Eqs. (6) or (6') should be employed as the basic entropy of mixing expressions. The state in which the individual species are separate and oriented then represents the standard reference state.

In other cases it may be more convenient to employ the unmixed, disoriented species for the reference state. This reference state is sufficient for the treatment of the equilibria encountered in the fractionation of high polymers by fractional precipitation or solution. The entropy of mixing the separate, disoriented species with

solvent is given by

$$\Delta S_{\text{mixing}}^* = \Delta S_b + \Delta S_c$$

$$= -R \left\{ n \ln \left(\frac{n}{n + \sum x N_x} \right) + \sum \left[N_x \ln \left(\frac{x N_x}{n + \sum x N_x} \right) \right] \right\} \quad (11)$$

$$= -R [n \ln v_1 + \sum (N_x \ln v_x)]. \quad (11')$$

An equation of this form for the entropy of mixing in a heterogeneous polymer solution was predicted by Gee¹³ as an empirical extension of the entropy of mixing expression⁶ for a solution composed of a single polymer component.

PARTIAL MOLAL ENTROPIES

As has been pointed out above, depending on the application, any one of three standard reference states—the disoriented mixture of polymer species in the absence of solvent; the disoriented, separated polymer species; or the oriented pure components—may be preferable. If the first-mentioned reference state is to be employed (ΔS_c) the partial molal functions previously derived,^{5,6} wherein x is replaced by \bar{x}_n , will suffice. For the other two cases either ΔS^* of Eq. (11) or ΔS of Eq. (6) must be differentiated to obtain the partial molal entropies. These are given below.

For the partial molal entropy of the solvent per mole,

$$\begin{aligned} \Delta \bar{S}_1 &= \partial \Delta S / \partial n = \Delta \bar{S}_1^* = \partial \Delta S^* / \partial n \\ &= -R \left[\ln \left(\frac{n}{n + \sum x N_x} \right) + 1 - \frac{n}{n + \sum x N_x} - \frac{\sum N_x}{n + \sum x N_x} \right] \\ &= -R [\ln (1 - v_2) + v_2 - \sum (v_x/x)]. \end{aligned}$$

Or, since the number average molecular size \bar{x}_n is given by

$$\begin{aligned} \bar{x}_n &= \sum x N_x / \sum N_x = v_2 / \sum (v_x/x) \\ \Delta \bar{S}_1 &= \Delta \bar{S}_1^* = -R [\ln (1 - v_2) + v_2 (1 - 1/\bar{x}_n)], \end{aligned} \quad (12)$$

¹³ G. Gee, Rubber Chem. Tech. **17**, 672 (1944).

which is identical with the expression previously derived,^{5,6} except that x has been replaced by \bar{x}_n .

For the polymer constituents

$$\begin{aligned} \Delta \bar{S}_x &= \partial \Delta S / \partial N_x \\ &= -R \left\{ \ln \left(\frac{N_x}{n + \sum x N_x} \right) + 1 - \frac{x n}{n + \sum x N_x} - \frac{x \sum N_x}{n + \sum x N_x} \right. \\ &\quad \left. - (x-1) [\ln (\gamma-1) - 1] + \ln \sigma \right\} \\ &= -R [\ln (v_x/x) + v_2 x (1 - 1/\bar{x}_n) - (x-1) \ln (\gamma-1) + \ln \sigma]. \end{aligned} \quad (13)$$

Similarly

$$\Delta \bar{S}_x^* = -R [\ln v_x - (x-1) + v_2 x (1 - 1/\bar{x}_n)]. \quad (14)$$

PARTIAL MOLAL FREE ENERGIES

Assuming that the heat of mixing of solvents with polymer can be expressed in the van Laar form, then

$$\Delta H = B(V_1 n) \sum V_x N_x / (V_1 n + \sum V_x N_x),$$

where V_1 is the molar volume of solvent, V_x is the molar volume of the x -mer polymer species, B is a constant characteristic for each solvent-polymer pair, and the summations are over all polymer species. This can be written

$$\Delta H = B V_1 n \sum x N_x / (n + \sum x N_x) \quad (15)$$

since $V_x = x V_1$.

The partial molal heats of mixing are obtained by differentiation.

$$\Delta \bar{H}_1 = \partial \Delta H / \partial n = B V_1 v_2^2, \quad (16a)$$

$$\Delta \bar{H}_x = \partial \Delta H / \partial N_x = B x V_1 v_1^2. \quad (16b)$$

Combining these experiments with those given above for the partial molal entropies,

$$\begin{aligned} \Delta \bar{F}_1 &= \Delta \bar{F}_1^* = \Delta \bar{H}_1 - T \Delta \bar{S}_1 \\ &= RT [\ln (1 - v_2) + v_2 (1 - 1/\bar{x}_n) + \mu v_2^2], \end{aligned} \quad (17)$$

where $\mu = B V_1 / RT$. Similarly,

$$\begin{aligned} \Delta \bar{F}_x &= RT [\ln (v_x/x) + v_2 x (1 - 1/\bar{x}_n) \\ &\quad - (x-1) \ln (\gamma-1) + \ln \sigma + \mu x (1 - v_2)^2] \end{aligned} \quad (18)$$

and

$$\Delta\bar{F}_x^* = RT[\ln v_x - (x-1) + v_2x(1-1/\bar{x}_n) + \mu x(1-v_2)^2]. \quad (19)$$

Huggins^{5,9} has shown that the data available on solvent activities in solvent-polymer mixtures agree very well with Eq. (17) when μ is suitably chosen.^{14a} In accordance with theory, μ is found to be characteristic for a given solvent-polymer pair at a given temperature, quite independent of concentration. Huggins has tabulated μ values for various systems.

Only in one case have solvent activities been measured carefully over the entire concentration range, namely, the benzene-rubber system thoroughly investigated by Gee and Treloar.¹⁰ Huggins has shown that a single value of μ suffices to establish a good correlation between Eq. (17) and observed activities at all concentrations. Gee and Treloar also measured activities of the benzene-rubber system at different temperatures, thus enabling the separate evaluation of the partial molal entropy and partial molal heat of dilution. In dilute solutions the partial molal entropy is not in accord with Eq. (12), nor is the partial molal heat of dilution consistent with Eq. (16a) throughout the concentration range.^{8,10,13} The former quantity approaches the theory as the concentration of rubber is increased. When these two somewhat erroneous equations are combined, however, a satisfactory free energy function is obtained, as Huggins has shown.

The basis for this divergence between the present theory of polymer solutions and experimental entropies has become evident from further theoretical research into the nature of dilute polymer solutions.⁸ It is unnecessary to go into the causes for the discrepancies further than to point out that in the theory as here (and previously) developed it is assumed, with reference to the j th molecule to be added to the lattice, that all previously added molecules present a perfectly random distribution of cells occupied by polymer chain segments. This is not a satisfactory approximation in dilute solutions of high polymers. Here the occupied sites are

present in loose "clusters," each polymer molecule occupying a "cluster" of consecutively adjacent cells. Intervening regions between these "clusters" are completely vacant.

For present purposes it is sufficient to point out that the theory, as given in previous papers and as extended here, yields an expression for the partial molal entropy which when combined with the μ term gives a partial molal free energy of the solvent which agrees well with experiment. It is only necessary to modify the significance of μ to include, in addition to the heat term, contributions from other factors the origins of which are not yet clear.^{14b} With μ redefined in this way, Eq. (17) appears to depict the partial molal free energy of the solvent satisfactorily.

For the two-component system consisting of a single polymer species of size x dissolved in a solvent, the condition

$$\begin{aligned} (\partial\Delta\bar{F}_x/\partial n) &= (\partial\Delta\bar{F}_1/\partial N_x) \\ \text{or} \quad (\partial\Delta\bar{F}_x/\partial v_1) &= (xv_1/v_x)(\partial\Delta\bar{F}_1/\partial v_x) \end{aligned}$$

necessarily applies. This connection permits derivation of the concentration dependent terms of $\Delta\bar{F}_x$ from $\Delta\bar{F}_1$. Thus, since Eq. (17) accounts satisfactorily for experimentally observed partial molal free energies of the solvent in two component systems composed of polymer and solvent (in which case $v_x = v_2$ and $\bar{x}_n = x$), then it necessarily follows that

$$\Delta\bar{F}_x = RT[\ln v_x + v_2x(1-1/x) + \mu x(1-v_x)^2 + \text{const.}] \quad (18')$$

must be equally acceptable for the solute. Furthermore, Eq. (17) applies with approximately the same value of μ to all polymers of a given series regardless of molecular weight. Hence, Eq. (18') must also be applicable to polymers of different molecular weights.

These, then, are the experimental facts justifying the use of Eq. (17) and, for solutions of one polymer component, Eq. (18') as well. Returning to the theory, it will be recalled that

^{14b} Huggins' treatment, which differs slightly from that of the writer, leads to a theoretically derived μ which includes other terms in addition to the heat term. However, in the opinion of the writer these are trivial in comparison with the difference between the value of μ required to reproduce the observed activities and the value of $\Delta\bar{H}_1/RT$ obtained from temperature coefficients.

^{14a} The parameter μ in this paper corresponds to Huggins' μ_1 .

no significant new assumptions are required in the generalization of the treatment to apply to heterogeneous polymers. It is justifiable, therefore, to place equal confidence in the expression

$$\Delta \bar{F}_x = RT[\ln v_x + v_2 x(1 - 1/\bar{x}_n) + \mu x(1 - v_2)^2 + \text{const.}] \quad (18'')$$

for the partial molal free energy of x -mer in a solution of a heterogeneous polymer.

The terms of Eq. (18) which are replaced by an undetermined constant in Eq. (18'') originate from the entropy of disorientation. The limitations of the theory in accounting for entropies in dilute solution have nothing to do with the validity of these terms in the free energy function. This portion of the partial molal free energy expression (18) rests squarely upon the theory in its present state of development, and is neither supported nor contradicted by experimental results.

The above arguments have been presented rather in detail in an effort to show clearly the justification for using Eqs. (17) and (18), or (19), to represent the partial molal *free energies*, even in dilute solutions where the present theory fails to give correct *entropies*. In the following sections these equations will be applied as semi-empirical approximations to the actual free energy functions.

APPLICATION TO THE FRACTIONATION OF HIGH POLYMERS

Frequently it is desirable to separate a high polymer into a series of fractions differing in average molecular weight. This is usually accomplished by fractional precipitation. Either of two methods may be employed: Fractions of successively decreasing molecular weights may be obtained by adding a precipitant in suitably controlled increments to a dilute solution of the polymer maintained at constant temperature, the precipitate formed after each addition of precipitant being separated from the supernatant solution; or a simple solvent medium is employed from which precipitation is induced by lowering the temperature in suitable stages. It is necessary, of course, to assure equilibration after each addition of precipitant, or after each decrease in temperature. In a few instances fractional solu-

tion rather than fractional precipitation has been employed.

In all of these methods, separation of successive fractions depends on a controlled alteration of μ in the critical region for precipitation. This critical region occurs when μ exceeds one-half.⁶ Except in the case of polymers which precipitate in crystalline form, the precipitates so obtained are liquid phases containing large amounts of solvent, although the concentration of polymer therein exceeds considerably the concentration in the supernatant phase. Fractionation depends upon the partition of each polymer species between these two phases. Higher polymers preferentially occur in the more concentrated phase. It has been recognized that the resulting fractions are by no means sharp; each fraction contains a rather wide distribution of species, although it is less heterogeneous than the original polymer. The equations given above provide a means for calculating the degree of separation obtained in the fractionation of high polymers under various conditions. They may also be of assistance in clarifying the factors affecting the sharpness of separation.

As indicated above, it is assumed in the following analysis that no crystallinity, or related regular structure, occurs in the precipitated phase. Furthermore, all polymer species are assumed to possess the same composition and unit structure, their only differences residing in the lengths of their chains. This latter assumption assures that the same μ value applies to all species. It will be assumed further that μ possesses the same value in either phase. This last assumption in general will not be strictly true when the solvent medium comprises a mixture of solvent and precipitant. The two phases may contain different proportions of the precipitant. The magnitude of the differences in μ for the two phases which may arise from this source has not been investigated. However, introduction of different μ values for the two phases would not change the general nature of the results derived below. When a single liquid is used for the solvent medium and the fractions are obtained by successive decreases in temperature, this assumption becomes unnecessary.

For equilibrium between the two phases to exist it is necessary that the partial molal free

energy of each constituent be the same in both phases. Using primes to signify quantities referring to the precipitated phase, the conditions for equilibrium can be expressed as follows:

$$\Delta \bar{F}_1 = \Delta \bar{F}_1', \quad \Delta \bar{F}_x = \Delta \bar{F}_x'.$$

Substituting from Eqs. (17) and (19), or (18),

$$\ln(1-v_2) + v_2(1-1/\bar{x}_n) + \mu v_2^2 \\ = \ln(1-v_2') + v_2'(1-1/\bar{x}_n') + \mu v_2'^2, \quad (20)$$

$$(\ln v_x)/x + v_2(1-1/\bar{x}_n) + \mu(1-v_2)^2 \\ = (\ln v_x')/x + v_2'(1-1/\bar{x}_n') + \mu(1-v_2')^2. \quad (21)$$

Equation (21) can be written

$$\ln(v_x'/v_x) = \alpha x, \quad (22)$$

where

$$\alpha = v_2(1-1/\bar{x}_n) - v_2'(1-1/\bar{x}_n') \\ + \mu[(1-v_2)^2 - (1-v_2')^2]. \quad (23)$$

The quantity α can be regarded as a partition factor. The ratio of concentrations of a given species in the two phases varies exponentially with x .

An equation equivalent to Eq. (22) has been obtained by Schulz.¹⁵ In deriving his relationship Schulz assumed that partition between the two phases is governed solely by differences in heats of solution of polymer molecules in the two phases. He assumed that this difference should increase in proportion to the molecular weight; thus the larger molecules should be preferentially distributed in favor of the precipitated phase where their heat of mixing with the medium will necessarily be lower. He neglected entropy effects such as have been taken into account by the present theory. Nevertheless, Schulz's partition equation is equivalent to Eq. (22) above, and he has carried out significant calculations on the nature of the molecular weight distributions in fractionated polymers. The significance assigned by Schulz to the partition factor α must be revised, however. His definition of α in effect includes only the μ term of Eq. (23).

The application of Eq. (23) to fractionation problems can be indicated as follows. Let V and V' represent the volumes of the respective phases,

and let Q_x and Q_x' represent the absolute volumes of x -mer in them; thus $Q_x = Vv_x$ and $Q_x' = V'v_x'$. Also, let Q_x^0 equal the total volume of x -mer, i.e., $Q_x^0 = Q_x + Q_x'$, and let the ratio of volumes of precipitated and supernatant phases be represented by $r = V'/V$. Then according to Eq. (22),

$$Q_x = Q_x^0/(1+re^{\alpha x}), \quad (24)$$

$$Q_x' = re^{\alpha x} Q_x^0/(1+re^{\alpha x}). \quad (24')$$

Whereas the relative concentration of each species in the two phases is governed by α , their relative amounts depend also on r .

The conditions of fractionation depend jointly on α and r . Both the location of the mean molecular weight about which the polymer is divided between the two phases and the sharpness of the separation depend on the particular combination of these parameters. Let us characterize the location of the region of separation by the molecular weight, or x value, at which $Q_x = Q_x'$. Let this particular value of x be designated by x_a . Then according to Eqs. (24) and (24'),

$$\exp(\alpha x_a) = 1/r.$$

Further, as an index of the efficiency of the separation let us consider the slope of the curve representing the proportion of x -mer in the precipitated phase plotted against x , at the point $x = x_a$. According to Eq. (24') this quantity is given by

$$[d(Q_x'/Q_x^0)/dx]_{x_a} = \alpha/4.$$

The relative efficiency ϵ can be defined as the increase in Q_x'/Q_x^0 per unit relative change in x when $x = x_a$

$$\epsilon = [d(Q_x'/Q_x^0)/d \ln x]_{x_a}, \\ \epsilon = \alpha x_a/4 = (1/4) \ln(1/r). \quad (25)$$

Thus the relative efficiency of separation increases as the log of the reciprocal of r , and is independent of the molecular weight region in which separation occurs.¹⁵

From Eq. (25) it is clear that the volume of the supernatant phase relative to the volume of the precipitated phase should be made as great as possible. The importance of this point gains further emphasis from the fact that, according to Eqs. (24) and (24'), the concentration of

¹⁵ G. V. Schulz, *Zeits. f. physik. Chemie* **B46**, 137 (1940); *ibid.* **B47**, 155 (1940).

every species including the lowest is greater in the precipitated phase than in the more dilute phase, although for components well below the molecular weight region of separation these concentrations will be nearly equal. Efficient elimination of lower polymers from the precipitated phase is possible only in the presence of a very large supernatant phase. Consequently, the solution from which precipitation takes place should be very dilute.

From a consideration of the phase equilibrium diagram (Fig. 1) depicting the concentrations of the phases in equilibrium as a function of μ which in turn depends on temperature or amount of precipitant, it is obvious that the more dilute the solution the more concentrated will be the precipitated phase. Thus, dilution not only increases the volume of the supernatant phase, but it also produces a "deswelling" of the precipitated phase. Both of these changes contribute toward the desired decrease in r .

The phase equilibrium diagrams for high-polymer solutions are extremely unsymmetrical (Fig. 1). The critical concentration at which partial miscibility first develops with increasing μ occurs at a low concentration of polymer. This critical concentration for a homogeneous polymer is given⁶ by

$$v_{2(\text{critical})} = 1/(1 + \sqrt{x}).$$

It moves in the direction of more dilute solutions as the molecular weight (x) is increased. From an examination of the shift with molecular weight in the phase equilibrium curves shown in Fig. 1 for homogeneous polymers, it is clear that the greater the molecular weight, the greater the degree of swelling of the precipitated phase in equilibrium with a supernatant phase of given concentration. Therefore, with increase in the molecular weight at which precipitation occurs, it becomes increasingly important to use dilute solutions. In fact, if the concentration is not much less than v_2 (critical) as given above, very little fractionation is to be expected.

The above discussion indicates the nature of the dependence of fractionation characteristics on the parameters α and r . Unfortunately, these are not simple functions of externally controlled variables such as μ , which depends on the amount of precipitant or temperature. Equation (23)

gives an indication of the complexity of the dependence of α on the concentrations of polymer in the two phases, on the number average molecular weights and on μ ; the quantities other than μ on the right of Eq. (23) depend on the initial distribution and on the dilution. The following discussion is aimed at a simplification of these inter-relationships.

The ratio of the volumes of polymer (all species included) in the two phases, $\sum_x Q'_x / \sum_x Q_x$, must equal rv_2'/v_2 , from which it follows that

$$\frac{\sum [Q_x^0 e^{\alpha x} / (1 + re^{\alpha x})]}{\sum [Q_x^0 / (1 + re^{\alpha x})]} = \frac{v_2'}{v_2} \equiv \gamma, \quad (26)$$

where the symbol γ has been introduced to represent this ratio. Equation (26) relates r , α , and the initial polymer distribution (the V_x^0 's) on the one hand with the relative total polymer concentration v_2'/v_2 on the other.

The number average molecular weights are similarly related to these three quantities.

$$\bar{x}_n = \sum v_x / \sum (v_x/x) = v_2 / \sum (v_x/x).$$

The quantity v_2/\bar{x}_n which appears in the equation for α , and in subsequent equations is given by

$$v_2/\bar{x}_n = \sum (v_x/x) = (1/V) \sum [Q_x^0/x(1 + re^{\alpha x})]. \quad (27)$$

Similarly

$$v_2'/\bar{x}_n' = (1/V') \sum [(Q_x^0 re^{\alpha x})/x(1 + re^{\alpha x})]. \quad (28)$$

Replacing V' with rV and subtracting Eq. (27) from (28),

$$(v_2'/\bar{x}_n') - (v_2/\bar{x}_n) = (1/V) \sum [Q_x^0(e^{\alpha x} - 1)/x(1 + re^{\alpha x})].$$

It will be convenient to define a quantity δ as follows:

$$\delta = (1/v_2)[(v_2'/\bar{x}_n') - (v_2/\bar{x}_n)].$$

Since

$$V = \sum (Q_x/v_2) = (1/v_2) \sum [Q_x^0/(1 + re^{\alpha x})],$$

it follows that δ is given by the following function of the initial distribution, r and α :

$$\delta = \frac{\sum [Q_x^0(e^{\alpha x} - 1)/x(1 + re^{\alpha x})]}{\sum [Q_x^0/(1 + re^{\alpha x})]}. \quad (29)$$

Returning now to Eq. (23) and solving for μ ,

$$\mu = \frac{\alpha + (v_2' - v_2) - \delta v_2}{(v_2' - v_2)[2 - (v_2' + v_2)]} \quad (30)$$

Substituting this expression for μ into Eq. (20), which as yet has not been made use of, and rearranging,

$$\begin{aligned} [1 - (v_2' + v_2)/2] \ln [(1 - v_2)/(1 - v_2')] \\ = (v_2' - v_2) + \alpha(v_2' + v_2)/2 - \delta v_2. \end{aligned}$$

Series expansion of the logarithmic term followed by combination of terms resulting from multiplication by the factor in brackets ultimately leads to

$$\begin{aligned} [(v_2' - v_2)^3/2] \left[\frac{1}{2 \cdot 3} + \frac{(2v_2' + 2v_2)}{3 \cdot 4} \right. \\ + \frac{3v_2'^2 + 4v_2'v_2 + 3v_2^2}{4 \cdot 5} \dots \\ \left. + \frac{(n+1)v_2'^n + 2nv_2'^{n-1}v_2 + \dots + (n+1)v_2^n}{(n+2)(n+3)} + \dots \right] \\ = \alpha(v_2' + v_2)/2 - \delta v_2. \quad (31) \end{aligned}$$

The infinite series in braces is very nearly equal to $1/6(1 - v_2' - v_2)$ so long as v_2 and v_2' are small. Making this substitution in Eq. (31),

$$(v_2' - v_2)^3/12(1 - v_2' - v_2) = \alpha(v_2' + v_2)/2 - \delta v_2. \quad (32)$$

The percentage error introduced by the approximation will be of the order of $(v_2'^2/10)100$, since $v_2 < v_2'$. Letting the ratio of the polymer concentrations in the two phases be represented by $\gamma = v_2'/v_2$, Eq. (32) may be expressed alternatively as

$$\begin{aligned} (\gamma - 1)^3 v_2^2 = 12[1 - v_2(\gamma + 1)] \\ \times [(\gamma + 1)\alpha/2 - \delta]. \quad (32') \end{aligned}$$

The external variables associated with separation of heterogeneous polymers by fractional precipitation are the initial polymer distribution, the value of μ (determined by temperature and amount of precipitant), and the average polymer concentration, or concentration of polymer prior to separation into two phases. This average concentration is given by $(v_2 + \gamma v_2')/(1 + \gamma)$. The com-

plexity of the relationships derived above is such that it has not been possible to deduce α and r directly from these independent variables. However, it is possible to obtain solutions by assigning arbitrary values to the dependent variables r and α and then solving for the physically independent variables. Given the initial distribution (the V_x^0 's) and assumed values of r and α , $v_2'/v_2 = \gamma$ can be obtained by executing the sum-

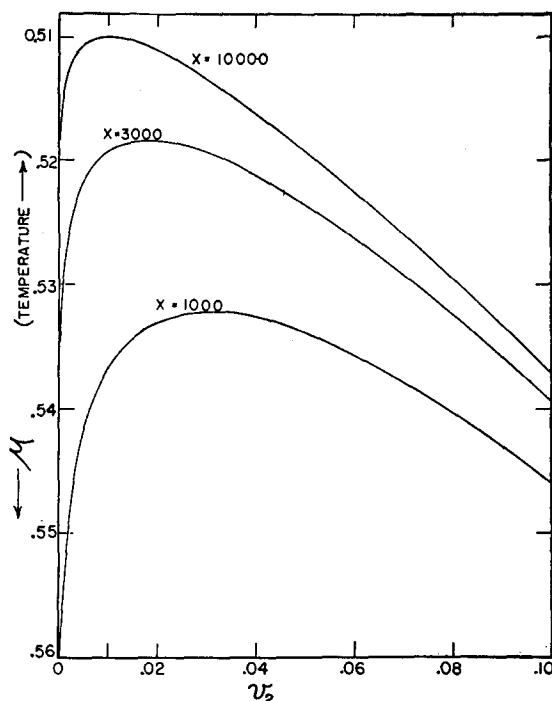


FIG. 1. Equilibrium phase compositions for solvent-homogeneous polymer mixtures in the region of partial miscibility for several values of x (relative molecular weight). Curves calculated from Eqs. (33) and (30). The pair of solutions for a given value of μ represent the calculated compositions of the phases in equilibrium. Since μ increases with decrease in temperature, the ordinate may be regarded as a temperature scale, and the curves should resemble temperature-composition diagrams for the binary liquid system.

mations of Eq. (26). Similarly, δ may be obtained from Eq. (29). Substituting these values of γ and δ into Eq. (32'), the resulting quadratic equation can be solved for v_2 . The value of v_2' is given by γv_2 . The average concentration can then be deduced, and μ can be computed from Eq. (30). This completes the deduction of the independent variables from the assumed values of r and α . Since the polymer distribution in each phase is governed, according to Eqs. (24) and

(25), by r and α and the initial distribution, the solution for this particular set of independent variables, the V_x 's, μ , and the average concentration, is complete.

Equation (32), or (32'), is useful also in deriving phase equilibria for homogeneous polymer-solvent systems. When only one polymer species composed of x segments is present, $v_2 = v_x$ and $v_2' = v_x'$. Hence

$$\alpha = (\ln \gamma)/x, \quad \delta = (\gamma - 1)/x$$

and Eq. (32') reduces to

$$(\gamma - 1)^2 v_2^2 = 12[1 - v_2(\gamma + 1)] \times [(\gamma + 1)(\ln \gamma)/2 - (\gamma - 1)]/x. \quad (33)$$

For any given value of x , this equation may be employed to obtain the concentrations of the two phases which are in equilibrium with one another. By substituting an arbitrary value for the ratio γ of these concentrations, solution of the quadratic equation (33) gives the concentration v_2 of the more dilute phase. Multiplication of v_2 by γ gives, of course, the concentration in the more concentrated phase. The corresponding value of μ can be found from Eq. (30). This procedure, based on the approximate equation (33), which is a modification of (32), is very much simpler than the method of successive approximations previously employed.⁶

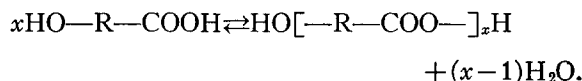
Solutions of Eq. (33) are shown in Fig. 1 plotted against μ , for several values of x . The ordinate scale is plotted in the direction of decreasing μ . Since μ decreases with increase in temperature, these plots should resemble temperature-composition diagrams for the binary liquid systems. The positive direction of the ordinate axis corresponds to an increase in temperature, or to a decrease in the proportion of precipitant at constant temperature.

CHEMICAL EQUILIBRIA IN POLYMERIC SYSTEMS

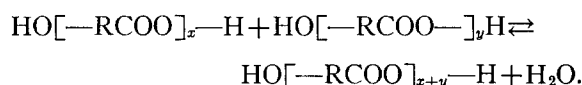
An appropriate formulation of an equilibrium constant for a chemical reaction involving polymer formation, condensation, or degradation can be secured with certainty only when the dependences of the partial molal free energies (or the activities) of the reacting components on their concentrations are known. This is obvious

from reference to the thermodynamic origins of the equilibrium constant. In this section the application of the above thermodynamic functions to the equilibria governing associative and degradative reactions of polymer molecules will be discussed.

Various condensation polymers which may be formed and degraded reversibly serve to illustrate the type of equilibria considered here. Polyesters, for example, are synthesized from their monomers by the reversible esterification reaction



The polymer molecules actually are not formed kinetically by the simultaneous condensation of x monomers; they are formed in an irregular stepwise succession of condensations, each of which is reversible,^{16,17}



Reactions of this character can be represented by the scheme¹⁸



where A and B are the functional groups which co-react to form the inter-unit linkage AB . In this process a molecule such as water may or may not be split out. The following treatment is also applicable, with minor modifications to the polymerization of a pair of bifunctional monomers $A-A$ and $B-B$, where the complementary functional groups reside in different monomers. Vinyl type polymerizations could be included, although these processes generally are not reversible in the thermodynamic sense.

As the standard reference state for each molecular species, a perfectly ordered hypothetical crystal will be chosen in which the molecules are arranged in perfect order. The standard states for the various species will possess similar structures insofar as the arrangement and packing of the units are concerned.

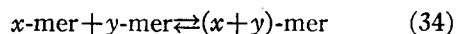
¹⁶ P. J. Flory, J. Am. Chem. Soc. **61**, 3334 (1939).

¹⁷ P. J. Flory, J. Am. Chem. Soc. **64**, 2205 (1942).

¹⁸ P. J. Flory, J. Am. Chem. Soc. **58**, 1877 (1936).

Furthermore, the packing density will be so chosen that the heat change in passing to the actual liquid state with randomly arranged molecules is zero. It should be remarked that these conditions are introduced as definitions of an arbitrary standard state, and not as assumptions.

We now assume that with the standard states so defined the standard free energy change in a reaction



is always the same regardless of x and y , and equal to ΔF^0 . In other words, it is assumed that the standard free energy change for a reaction leading to the formation of one AB linkage (e.g., one ester group) is invariably equal to ΔF^0 . This assumption can be expected to apply at all values of x and y when the functional groups A and B are separated sufficiently in the monomers so that the reactivity of A is influenced negligibly by previous reaction of the B group of the same unit, and vice versa. Furthermore, the intermolecular attractions of the A and B groups should not differ too much from that of the AB linking group. Even when these conditions are not met, the above assumption can be expected to apply satisfactorily except for low values of x and y .

The free energy of an x -mer admixed with other species, and possibly with a solvent as well, is given by

$$F_x = F_x^0 + \Delta \bar{F}_x,$$

where F_x^0 is its free energy in the standard state and $\Delta \bar{F}_x$ is the free energy change in transporting one mole of x -mer from the standard state to an infinite amount of the mixture, or solution. In other words, $\Delta \bar{F}_x$ is the partial molal free energy of the x -mer in the mixture with respect to the standard state, as given by Eq. (18). According to the definition of the standard states and the assumptions introduced above,

$$F_x^0 = xF_1^0 + (x-1)\Delta F^0, \quad (35)$$

where F_1^0 is the free energy of the monomer in the standard state and ΔF^0 , as previously defined, is the standard free energy change per mole of inter-unit linkages AB in the molecule. The

standard states have been defined with the purpose of view of obtaining an equation of the form of Eq. (35) wherein ΔF^0 is a constant. Hence,

$$F_x = x(F_1^0 + \Delta F^0) - \Delta F^0 + \Delta \bar{F}_x.$$

The total free energy of the mixture exclusive of inert solvent is given by

$$F = \sum N_x F_x = (F_1^0 + \Delta F^0) \sum x N_x - \Delta F^0 \sum N_x + \sum \Delta \bar{F}_x N_x. \quad (36)$$

When the polymerization (or degradation) reactions have reached a state of equilibrium, $dF=0$. Taking the differential of Eq. (36) and equating to zero,

$$\sum (\Delta \bar{F}_x - \Delta F^0) dN_x = 0, \quad (37)$$

since constancy of the total amount of material requires that

$$\sum x dN_x = 0, \quad (38)$$

and since $\sum N_x d(\Delta \bar{F}_x) = 0$, according to the Gibbs-Duhem equation. Equation (37) expresses the necessary condition for equilibrium.

If the process concerned is a simple one such as is expressed by Eq. (34), where only three species are involved, then

$$dN_x = dN_y = -dN_{x+y},$$

and for the equilibrium condition we have, according to Eq. (37),

$$\Delta \bar{F}_{x+y} - \Delta \bar{F}_x - \Delta \bar{F}_y + \Delta F^0 = 0.$$

After substituting from Eq. (18) for these partial molal free energies there is obtained

$$\ln K = -\Delta F^0/RT + \ln [(\gamma-1)\sigma], \quad (39)$$

where

$$K = \left(\frac{v_{x+y}}{v_x v_y} \right) \left(\frac{xy}{x+y} \right). \quad (40)$$

Alternatively

$$\ln K' = -\Delta F^0/RT + \ln [(\gamma-1)\sigma V_1], \quad (39')$$

where V_1 is the molar volume per structural unit $A-B$, and

$$K' = c_{x+y}/c_x c_y, \quad (40')$$

the c 's representing the respective concentrations in moles per unit volume. Inasmuch as γ

is a function of the liquid structure only and σ and V_1 are constants characteristic of the types of molecules concerned, evidently either K or K' should be an acceptable equilibrium constant.

It should be noted that use of mole fractions instead of molar concentrations in expressing the equilibrium constant (except, of course, when the equilibrium constant is dimensionless) is irreconcilable with the statistical mechanics of these mixtures.¹⁹ In the absence of diluent, conversion to mole fractions X_x through the substitutions

$$v_x = X_x \sum N_x / \sum x N_x,$$

etc., in Eq. (40) yields

$$[X_{x+y}/X_x X_y] = K \sum N_x / \sum x N_x = K \sum N_x / N_0,$$

where the total number of polymer segments, $\sum x N_x$, is replaced by N_0 . Since $\sum N_x$ varies with the degree of displacement of the reaction, the quantity in brackets should not be employed as an equilibrium constant.

Proceeding now to the more complex equilibrium between all possible species M_x , or $(A-B)_x$, where all values of x are considered, we will again employ the equilibrium condition as expressed by Eq. (37). According to Eqs. (18) and (38),

$$\sum \Delta \bar{F}_x dN_x = RT \sum \{ \ln (N_x v_2 / N_0) + \ln [(\gamma - 1)\sigma] \} dN_x. \quad (41)$$

Substituting Eq. (41) in (37)

$$\sum \left\{ \ln (N_x v_2 / N_0) + \ln [(\gamma - 1)\sigma] - \frac{\Delta F^0}{RT} \right\} dN_x = 0. \quad (42)$$

Solving Eqs. (38) and (42) by the Lagrange multiplier method,

$$N_x = (N_0 / v_2) e^{-\beta} e^{-\lambda x}, \quad (43)$$

where λ is the multiplier and

$$\beta = \ln [(\gamma - 1)\alpha] - \Delta F^0 / RT.$$

¹⁹ R. E. Powell and H. Eyring, J. Am. Chem. Soc. **65**, 648 (1943), in their analysis of the equilibria in liquid sulfur between ring (S_8) and chain forms have expressed equilibrium constants in terms of mole fractions. According to the present treatment their equilibrium "constants" are not to be regarded as constants.

It is found upon substituting Eq. (43) into the equation $\sum x N_x = N_0$, and carrying out the summation over integral values of x from 2 to ∞ , that

$$e^\beta = e^{-\lambda} / v_2 (1 - e^{-\lambda})^2. \quad (44)$$

Also, the total number of molecules $\sum N_x$ must equal $N_0(1 - p)$, where p is the "extent of reaction," or fraction of the initial A , or B , groups converted to AB . According to Eq. (43), after substituting Eq. (44) for e^β ,

$$\sum N_x = N_0(1 - e^{-\lambda}).$$

Hence, $e^{-\lambda}$ may be identified with the extent of reaction p . Making this substitution and introducing Eq. (44) in (43),

$$N_x = N_0(1 - p)^2 p^{x-1}, \quad (45)$$

which is the equation, previously derived^{17,18} by other methods, for the molecular size distribution in linear condensation polymers.

Tobolsky²⁰ has derived the above molecular size distribution equation by a similar procedure based on the same thermodynamic equations.⁶ He sought to introduce the effect of heat of polymerization into the equations, with particular reference to vinyl type polymerizations which invariably are exothermic. In so doing he erroneously employed the heat of reaction where a standard state free energy change obviously should be used. Consequently, an equilibrium constant derived from his treatment would depend on the former, rather than on the latter. The error can be corrected by substituting ΔF^0 for P (heat of reaction) in Tobolsky's equations. If pursued further, his treatment corrected in this manner would lead to conclusions equivalent to those reached here.

According to Eq. (44),

$$\beta = \ln [\sigma(\gamma - 1)] - \Delta F^0 / RT = \ln K, \quad (46)$$

where

$$K = p / v_2 (1 - p)^2. \quad (47)$$

Or

$$\ln K' = \ln [\sigma(\gamma - 1) V_1] - \Delta F^0 / RT, \quad (46')$$

where

$$K' = p V_1 / v_2 (1 - p)^2 = c_{AB} / c_A c_B. \quad (47')$$

c_{AB} , c_A , and c_B represent the concentrations of the respective functional groups in moles per unit

²⁰ A. V. Tobolsky, J. Chem. Phys. **12**, 402 (1944).

volume. Thus, polyfunctional condensations may be treated as reactions between functional groups without regard for the particular molecular species involved, a point of view set forth in previous publications.¹⁶⁻¹⁸ The entropies of mixing of long chain polymers are such as to require no revision in this postulate as applied to chemical equilibria between polymeric reactants.²⁰

It can be shown further that even the magnitude of the equilibrium constant should not be altered by the polymeric nature *per se* of the components in such equilibria. That is to say, the percentage esterification of a glycolbasic acid mixture at equilibrium should be about the same as is found between analogous mono alcohols and carboxylic acids under equivalent conditions of temperature and dilution. A monofunctional reaction of this type comes within the scope of the treatment of the reaction (34). If there are initially c_0 moles of each of the two reactants per unit volume, then

$$c_A = c_B = c_0(1 - p), \quad c_{AB} = c_0 p$$

and

$$c_0 = v_2 / (V_A + V_B),$$

where V_A and V_B are the molar volumes of the reactants. Substituting in Eq. (40')

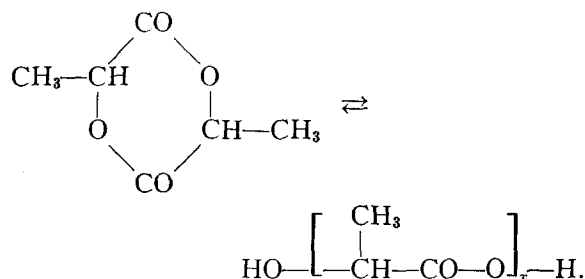
$$K' = p / (1 - p)^2 c_0 = p(V_A + V_B) / v_2(1 - p)^2,$$

which is identical with Eq. (47') for the bifunctional reaction, except for the obvious replacement of V_1 by $(V_A + V_B)$.

In the above discussion the role of a by-product of the polymerization reaction, such as the water formed during polyesterification, has been disregarded. It is obvious from the above discussion, however, that equilibrium constants for con-

densation processes from which a by-product is released may be written in an analogous manner, the concentration of the by-product appearing in the numerator.

These generalizations concerning equilibria in polymer reactions can be applied to the frequently encountered reversible ring-chain equilibria. For example, the six-membered lactide ring²¹ can be reversibly converted to a linear polyester



In this system two equilibria are to be considered: the ring-chain equilibria indicated above, and the polyesterification equilibrium, involving water as a by-product, which determines the average length of the chains. These chains will possess the size distribution given above, and this phase of the equilibrium may be treated as a reaction between functional groups. Other examples include numerous six-membered lactone rings which can be reversibly converted to chain polymers, the $(\text{PNCI}_2)_3 \rightleftharpoons (\text{PNCI}_2)_x$ reaction,²² aldehyde polymers, cyclic lactams, and the ring-chain sulfur transformation already referred to.¹⁹

²¹ W. H. Carothers, G. L. Dorough, and F. J. van Natta, J. Am. Chem. Soc. **54**, 761 (1932).

²² See K. H. Meyer, reference 4, p. 52.