

## The Thermodynamics of High Polymer Solutions. V. Phase Equilibria in the Ternary System: Polymer 1—Polymer 2—Solvent

Robert L. Scott

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We may obtain  $\phi_1$ ,  $\phi_2$  and the ratio  $\phi_1/\phi_2$  as functions of  $\phi_1^0$ ,  $\phi_2^0$ , and  $\phi_3$ :

$$\phi_1 = (\phi_1^0 + \epsilon)(1 - \phi_3) = \phi_1^0 - \phi_3 \left[ \phi_1^0 + \frac{\mu_{13} - \mu_{23} + \mu_{12}(\phi_1^0 - \phi_2^0)}{1 - 2\mu_{12}\phi_1^0\phi_2^0} \right] + \dots \quad (54a)$$

$$\phi_2 = (\phi_2^0 - \epsilon)(1 - \phi_3) = \phi_2^0 - \phi_3 \left[ \phi_2^0 + \frac{\mu_{23} - \mu_{13} + \mu_{12}(\phi_2^0 - \phi_1^0)}{1 - 2\mu_{12}\phi_1^0\phi_2^0} \right] + \dots \quad (54b)$$

$$\frac{\phi_1}{\phi_2} = \frac{\phi_1^0 + \epsilon}{\phi_2^0 - \epsilon} = \frac{\phi_1^0}{\phi_2^0} \times \left( 1 - \phi_3 \frac{[\mu_{13} - \mu_{23} + \mu_{12}(\phi_1^0 - \phi_2^0)]}{(1 - 2\mu_{12}\phi_1^0\phi_2^0)} + \dots \right). \quad (37)$$

We have noted that Gee,<sup>21</sup> although starting with equations entirely equivalent to our Eq. (35ab)

did not obtain an equation equivalent to our Eq. (39), but rather a single liquid approximation equivalent to our Eq. (36).

This discrepancy is apparently due to the introduction of a variable  $r$  (analogous to our  $\epsilon$ ), and in the subsequent expansion retaining no powers of  $r$  higher than the first. This is tantamount to dropping the  $\phi_3\epsilon$  and  $\epsilon^2$  terms from Eq. (51). But since  $\epsilon \sim \phi_3$ , there is no justification for dropping these terms unless the  $\phi_3^2$  term is dropped also. If one solves Gee's Eq. (14), retaining terms in  $r^2$ , one obtains an equation entirely equivalent to our Eq. (36), if  $V_1 = V_2$  (i.e., setting Gee's variable  $l = 1$ ).

Gee's treatment of solubility<sup>19</sup> depends upon his assumption that the  $\phi_3^2$  term in  $\pi$  vanishes at the critical solubility limit (an assumption which we have proved to be correct). Since he inadvertently calculated  $a_2^*$ , rather than  $a_2$ , his results, while in qualitative agreement with ours, are not exactly equivalent, to the extent that  $a_2^* \neq a_2$ .

## The Thermodynamics of High Polymer Solutions. V. Phase Equilibria in the Ternary System: Polymer 1—Polymer 2—Solvent\*

ROBERT L. SCOTT†

*Department of Chemistry, University of California, Berkeley, California*

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A thermodynamic analysis of phase equilibria similar to that developed in Part IV when applied to the ternary system of two polymers and a solvent leads to an explanation of the usual incompatibility of different high polymers in solution. Unless their heat of mixing is virtually zero or negative, two high polymers are always immiscible in the absence of a solvent; the primary role of the solvent is non-specific, merely one of diluting the polymer mixture and decreasing the heat of interaction of the polymers. The recent experiments of Dobry and Boyer-Kawenoki show reasonable agreement with these theoretical conclusions. Osmotic pressures of mixed polymers are discussed; such measurements would permit determination of  $\mu_{12}$ , the interaction constant of the two polymers.

### INTRODUCTION

THE incompatibility of certain high polymers in solution is a phenomenon long familiar to polymer chemists, especially in the fields of paints and varnishes. Recently, Dobry and Boyer-Kawenoki<sup>1</sup> have examined phase separation for a large number of three-component systems, and find incompatibility of two polymers in the same solvent to be the normal situation. The application of thermodynamic analysis to the ternary systems

involving one polymer and two liquids<sup>2</sup> suggests the extension of such a treatment to the corresponding system of two polymers and one solvent.

### THE TWO POLYMER SYSTEM

First let us consider a mixture of two chain polymers in the absence of a solvent. (We ignore the mechanical problems involved and assume that equilibrium is reached somehow.) Flory,<sup>3</sup> Scott and Magat,<sup>4</sup> and Guggenheim<sup>5</sup> have derived expressions for the free energy of mixtures of polymers of different molecular weight. The equations of Flory and of Scott and Magat, although based

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† Present address: Department of Chemistry, University of California, Los Angeles 24, California.

<sup>1</sup> A. Dobry and F. Boyer-Kawenoki, *J. Polymer Sci.* 2, 90 (1947).

<sup>2</sup> R. L. Scott, *J. Chem. Phys.* 17, 268 (1949).

<sup>3</sup> P. J. Flory, *J. Chem. Phys.* 12, 425 (1944).

<sup>4</sup> R. L. Scott and M. Magat, *J. Chem. Phys.* 13, 172 (1945) (Article I of this series).

<sup>5</sup> E. A. Guggenheim, *Proc. Royal Soc. A* 183, 203, 213 (1944).

upon somewhat different assumptions, are in this particular case identical; to them we add a term for the heat of mixing of the two different polymers:

$$\Delta \bar{F}_1 = RT \left[ \ln \phi_1 + \left( 1 - \frac{m_1}{m_2} \right) \phi_2 + m_1 \mu_{12} \phi_2^2 \right], \quad (1a)$$

$$\Delta \bar{F}_2 = RT \left[ \ln \phi_2 + \left( 1 - \frac{m_2}{m_1} \right) \phi_1 + m_2 \mu_{12} \phi_1^2 \right], \quad (1b)$$

where  $\phi_1$  and  $\phi_2$  are volume fractions, and  $m_1$  and  $m_2$  are essentially degrees of polymerization, relating the molal volumes  $V_1$  and  $V_2$  of the polymers to a fictitious molal volume  $V_0$  of one submolecule of polymer.

$$m_1 = V_1/V_0, \quad m_2 = V_2/V_0.$$

$\mu_{12}$  is a constant related to the heat of interaction of submolecules of the two polymers.

The introduction of the  $m$ 's in terms of an arbitrary  $V_0$  is unnecessary here, but will prove desirable later when we identify  $V_0$  with the molal volume of the solvent in the three-component system. The constant  $\mu_{12}$  is in this case entirely due to the heat interaction. The contribution of an entropy term,  $\mu^s$ , while usually considerable, is for two long chains entirely negligible.

For long chains, and small values of  $\mu_{12}$ , the more complex equations of Guggenheim<sup>6</sup> reduce to Eqs. (1a) and (1b).

We may obtain the critical conditions by the familiar requirement that the first and second derivatives of either  $\Delta \bar{F}_1$  or  $\Delta \bar{F}_2$  be zero. Solving such equations, we find that when the two polymers are at their critical solution temperatures:

$$(\mu_{12})_c = \frac{1}{2} \{ (1/(m_1)^{\frac{1}{2}}) + (1/(m_2)^{\frac{1}{2}}) \}^2, \quad (2)$$

$$(\phi_1)_c = (m_2)^{\frac{1}{2}} / \{ (m_1)^{\frac{1}{2}} + (m_2)^{\frac{1}{2}} \}, \quad (3)$$

$$(\phi_2)_c = (m_1)^{\frac{1}{2}} / \{ (m_1)^{\frac{1}{2}} + (m_2)^{\frac{1}{2}} \}. \quad (4)$$

In the "critical phase," the low molecular weight material predominates. For  $m_1 = 1$ , these equations reduce to the familiar ones for a polymer-solvent system<sup>6-8</sup> (in this case, however,  $\mu_{12}$  includes a significant entropy term).

We see that for two polymers, both of high molecular weight, the critical value of  $\mu_{12}$  is several orders of magnitude smaller than that for two normal liquids ( $\mu_{12} = 2$ ) or for a polymer-solvent system ( $\mu_{12} = \frac{1}{2}$ ). Polymers of infinite molecular weight would be incompatible if there were any positive heat of mixing (per submolecule) at all.

<sup>6</sup> M. L. Huggins, J. Chem. Phys. 9, 440 (1941); Ann. N. Y. Acad. Sci. 43, 1 (1942).

<sup>7</sup> P. J. Flory, J. Chem. Phys. 9, 660 (1941); 10, 51 (1942).

<sup>8</sup> R. L. Scott, J. Chem. Phys. 13, 178 (1945) (Article II of this series).

## TWO POLYMERS—ONE SOLVENT

We may now proceed to consideration of the ternary system of two polymers and one solvent. For the partial molal free energies of the polymers (subscripts 1 and 2) and the solvent (subscript 0), we write:

$$\Delta \bar{F}_0 = RT [\ln \phi_0 + (1 - (1/m_1)) \phi_1 + (1 - (1/m_2)) \phi_2 + \mu_{10} \phi_1^2 + \mu_{20} \phi_2^2 + (\mu_{10} + \mu_{20} - \mu_{12}) \phi_1 \phi_2], \quad (5a)$$

$$\Delta \bar{F}_1 = RT [\ln \phi_1 + (1 - m_1) \phi_0 + (1 - (m_1/m_2)) \phi_2 + m_1 \{ \mu_{10} \phi_0^2 + \mu_{12} \phi_2^2 + (\mu_{10} + \mu_{12} - \mu_{20}) \phi_0 \phi_2 \}], \quad (5b)$$

$$\Delta \bar{F}_2 = RT [\ln \phi_2 + (1 - m_2) \phi_0 + (1 - (m_2/m_1)) \phi_1 + m_2 \{ \mu_{20} \phi_0^2 + \mu_{12} \phi_1^2 + (\mu_{20} + \mu_{12} - \mu_{10}) \phi_0 \phi_1 \}], \quad (5c)$$

where  $\mu_{10}$  = the interaction constant for the binary system polymer 1—solvent.

$\mu_{20}$  = the interaction constant for the binary system polymer 2—solvent.

$\mu_{12}$  = the interaction constant for the binary system polymer 1—polymer 2.

$\mu_{12}$ , as noted for the two polymer system, is entirely a heat contribution, but  $\mu_{10}$  and  $\mu_{20}$  will have sizable contributions from entropy terms  $\mu^s$ , as is normal for polymer-solvent systems.

If two phases exist at equilibrium, the free energies of each component must be the same in both phases. Denoting the two phases by single and double primes, we may write:

$$\Delta \bar{F}_0' = \Delta \bar{F}_0'', \quad (6a)$$

$$\Delta \bar{F}_1' = \Delta \bar{F}_1'', \quad (6b)$$

$$\Delta \bar{F}_2' = \Delta \bar{F}_2'', \quad (6c)$$

Normally these equations will be soluble only by long and tedious successive approximation methods. Fortunately, we shall be able to obtain useful qualitative results without such labor.

## THE SPECIAL SYMMETRICAL CASE

For the special case in which  $\mu_{10} = \mu_{20} = \mu$ ,  $m_1 = m_2 = m$ , the equations become symmetrical, and we may calculate a phase diagram without difficulty. Substituting the above conditions into Eqs. (5abc) and making the necessary substitutions into Eqs. (6abc), we obtain:

$$\ln \phi_0' + (1 - (1/m))(1 - \phi_0') + \mu(1 - \phi_0')^2 - \mu_{12} \phi_1' \phi_2' = \ln \phi_0'' + (1 - (1/m))(1 - \phi_0'') + \mu(1 - \phi_0'')^2 - \mu_{12} \phi_1'' \phi_2'', \quad (7a)$$

$$\ln \phi_1' + (1 - m) \phi_0' + m \{ \mu(\phi_0')^2 + \mu_{12}(\phi_2')^2 + \mu_{12} \phi_0' \phi_2' \} = \ln \phi_1'' + (1 - m) \phi_0'' + m \{ \mu(\phi_0'')^2 + \mu_{12}(\phi_2'')^2 + \mu_{12} \phi_0'' \phi_2'' \}, \quad (7b)$$

$$\ln \phi_2' + (1 - m) \phi_0' + m \{ \mu(\phi_0')^2 + \mu_{12}(\phi_1')^2 + \mu_{12} \phi_0' \phi_1' \} = \ln \phi_2'' + (1 - m) \phi_0'' + m \{ \mu(\phi_0'')^2 + \mu_{12}(\phi_1'')^2 + \mu_{12} \phi_0'' \phi_1'' \}. \quad (7c)$$

A solution of these equations will be

$$\phi_0' = \phi_0'', \quad (8)$$

$$\phi_1' = \phi_2'', \quad (9a)$$

$$\phi_1'' = \phi_2'. \quad (9b)$$

Substituting these conditions into Eq. (7b), we obtain

$$\ln \phi_1' + m\mu_{12}\phi_2' = \ln \phi_2' + m\mu_{12}\phi_1'. \quad (10)$$

The identical equation is obtained from (7c), of course. Equation (10) is easily solved, but the nature of the solution will be clearer if we make a further substitution, defining a new variable  $\theta$ , corresponding to the relative concentrations of the two polymers:

$$\theta_1' = \phi_1' / (\phi_1' + \phi_2') = \phi_1' / (1 - \phi_0), \quad (11a)$$

$$\theta_2' = \phi_2' / (\phi_1' + \phi_2') = \phi_2' / (1 - \phi_0) = 1 - \theta_1'. \quad (11b)$$

Transforming Eq. (10) into the new variables, we find:

$$\ln \theta_1' + m\mu_{12}(1 - \phi_0)(\theta_2')^2 = \ln \theta_2' + m\mu_{12}(1 - \phi_0)(\theta_1')^2. \quad (12)$$

This is entirely equivalent to the solution of a binary system of two molecules of equal size.<sup>9</sup> We see, therefore, that the function of the solvent is merely that of diminishing the value of the heat constant  $\mu_{12}$ . The tie lines of the ternary system are all parallel to the 1,2 axis, and we may regard each cross section as a binary system for which the constant is  $m\mu_{12}(1 - \phi_0)$ . We may obtain the plait point by applying the familiar critical conditions for symmetrical binary systems.

$$m\mu_{12}(1 - \phi_0) = 2, \quad (13)$$

$$\theta_1 = \theta_2 = \frac{1}{2}, \quad (14)$$

or, rearranging,

$$\phi_0 = 1 - (2/m\mu_{12}), \quad (15)$$

$$\phi_1 = \phi_2 = 1/m\mu_{12}. \quad (16)$$

The striking feature of this calculation is that the position of the phase boundary is independent of the value of  $\mu$ , the polymer-solvent interaction.<sup>10</sup> Figure 1 shows phase diagrams calculated for  $m\mu_{12} = 4, 8$ , and 20. For an  $m$  of 1000 (molecular weight of polymer about 100,000), these would mean  $\mu_{12}$ 's of 0.004, 0.008, and 0.02, very small indeed compared with normal heat interactions. We see, therefore, that for large molecular weight

polymers, incompatibility should be the rule rather than the exception. Only when the two polymers are so nearly alike in chemical nature that  $\mu_{12}$  is vanishingly small will they be compatible.

### PLAIT POINTS

For the general case, no exact analytical solution is possible. Each individual system must be calculated after substituting particular values of the parameters,  $\mu_{10}$ ,  $\mu_{20}$ ,  $\mu_{12}$ ,  $m_1$ , and  $m_2$ . We may attempt to determine the plait point of the ternary system by the methods outlined in the preceding paper,<sup>2</sup> but even here we must approximate. Fortunately, a good approximation is available. If  $|\mu_{10} - \mu_{20}| \ll 1$ , and  $m_1^{\frac{1}{2}} < m_2 < m_1^2$ , as will usually be the case,<sup>11</sup> we may write:

$$\phi_0 \cong 1 - (1/2\mu_{12}) \{ (1/m_1)^{\frac{1}{2}} + (1/m_2)^{\frac{1}{2}} \}^2, \quad (17a)$$

$$\phi_1 \cong (1/2\mu_{12})(m_2)^{\frac{1}{2}} / \{ (m_1)^{\frac{1}{2}} + (m_2)^{\frac{1}{2}} \} \times \{ (1/m_1)^{\frac{1}{2}} + (1/m_2)^{\frac{1}{2}} \}^2, \quad (17b)$$

$$\phi_2 \cong (1/2\mu_{12})(m_1)^{\frac{1}{2}} / \{ (m_1)^{\frac{1}{2}} + (m_2)^{\frac{1}{2}} \} \times \{ (1/m_1)^{\frac{1}{2}} + (1/m_2)^{\frac{1}{2}} \}^2, \quad (17c)$$

The tie lines are still nearly parallel to the 1-2 axis, and any dependence on the values of  $\mu_{10}$  and  $\mu_{20}$  shows up only in the higher terms of the approximation. For purposes of comparison, we transform Eq. (17abc) as follows:

$$\mu_{12} = \frac{1}{2} \{ (1/m_1)^{\frac{1}{2}} + (1/m_2)^{\frac{1}{2}} \}^2 \{ 1/(1 - \phi_0) \}, \quad (18)$$

$$\theta_1 = (m_1)^{\frac{1}{2}} / \{ (m_1)^{\frac{1}{2}} + (m_2)^{\frac{1}{2}} \}, \quad (19)$$

$$\theta_2 = (m_2)^{\frac{1}{2}} / \{ (m_1)^{\frac{1}{2}} + (m_2)^{\frac{1}{2}} \}, \quad (20)$$

Comparison of Eqs. (18)–(20) with Eqs. (2)–(4) reveals a striking similarity. Here, as in the special symmetrical case, we conclude that the main contribution of the solvent is purely that of lowering

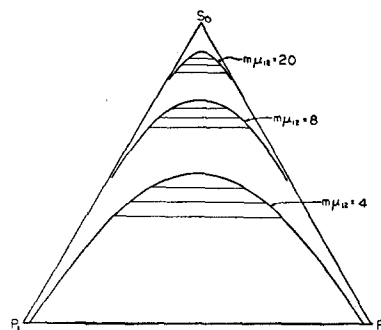


FIG. 1.

<sup>9</sup> See, for example, J. H. Hildebrand, *Solubility of Non-Electrolytes* (Reinhold Publishing Corporation, New York, 1936), second edition, pp. 51–54, 144–152.

<sup>10</sup> For values of  $\mu$  large enough so that the polymers are immiscible with the liquid, this is, of course, not exactly true, since there are tie lines along the 1-0 and 2-0 axes. However, we confine ourselves here to the case where the liquid is a solvent for both polymers.

<sup>11</sup> The significance of these conditions is as follows: The entropy contribution,  $\mu_s$ , to the polymer-solvent  $\mu$ 's is about 0.3, while if we required the liquid to be a solvent for both polymers, the  $\mu$ 's cannot exceed about 0.5; hence the maximum value for  $|\mu_{10} - \mu_{20}|$  will be around 0.2, which is very much smaller than 1. The second condition is essentially that the polymer of shorter length be more like the other polymer in size than like the solvent.

the critical solution temperature by dilution; the exact nature of the solvent is of only secondary importance.

It remains to show the magnitude of the incompatibility. For many non-polar systems we may write:

$$\mu_{12} = V_0/RT(\delta_1 - \delta_2)^2, \quad (21)$$

where  $V_0$  is the molecular volume of the solvent, and the  $\delta$ 's are the square roots of the internal pressures or "cohesive energy densities" of polymers 1 and 2.

If we assume  $V_0 = 100$  cc,  $T = 300^\circ\text{K}$ ,  $\Delta\delta = 0.2$ ,  $m_1 = m_2 = 10,000$  (molecular weight about 1,000,000), then  $\mu_{12} = 0.0067$ , and we find for the plait point:

$$\phi_1 = \phi_2 = 0.015, \quad \phi_0 = 0.97.$$

Phase separation in such a case sets in at 3 percent total polymer; for molecular weights around 100,000, phase separation would occur around 30 percent total polymer.

A  $\delta$ -difference of 0.2 is small (about the difference between benzene and toluene or between hexane and octane), and most polymer pairs, unless they are very similar in chemical composition, will exhibit much larger  $\mu_{12}$ 's and correspondingly greater incompatibility than the case calculated above. Hence, it is not surprising that most polymer pairs are very incompatible even if the solvent is a "good" solvent for both.

### THE DILUTION APPROXIMATION

The discovery that the main effect of the solvent is merely to dilute the polymer mixture, and in so doing decrease the heat interaction, encourages us to make an attempt to calculate the phase diagram by what we might call the "dilution approximation." We assume that the volume fraction of solvent  $\phi_0$  is the same in both conjugate phases, and that we may write by analogy to Eq. (12) for the symmetrical case:

$$\begin{aligned} \ln\theta_1' + (1 - (m_1/m_2))\theta_2' + m_1\mu_{12}(1 - \phi_0)(\theta_2')^2 \\ = \ln\theta_1'' + (1 - (m_1/m_2))\theta_2'' \\ + m_1\mu_{12}(1 - \phi_0)(\theta_2'')^2, \end{aligned} \quad (22a)$$

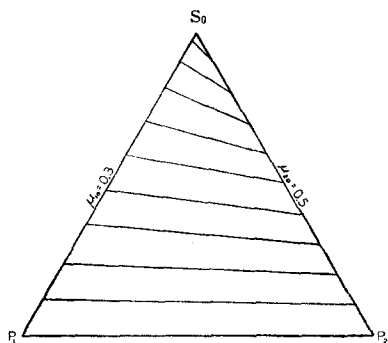


FIG. 2.

$$\begin{aligned} \ln\theta_2' + (1 - (m_2/m_1))\theta_1' + m_2\mu_{12}(1 - \phi_0)(\theta_1')^2 \\ = \ln\theta_2'' + (1 - (m_2/m_1))\theta_1'' \\ + m_2\mu_{12}(1 - \phi_0)(\theta_1'')^2. \end{aligned} \quad (22b)$$

The problem essentially reduces, therefore, to a binary system of two polymers such as discussed in the first section, which is relatively easy to determine.<sup>12</sup> The tie lines of the ternary system are all parallel to the 1,2 axis, and each represents a binary system for which  $\mu = \mu_{12}(1 - \phi_0)$ . As in the binary system, we expect displacement of the plait point and the whole solubility curve in the direction of the low molecular weight polymer (see Fig. 3).

### THE COMPLETE IMMISCIBILITY APPROXIMATION

We may obtain another approximate idea of the phase diagram by the approximation of complete immiscibility introduced in the preceding article.<sup>2</sup> If we assume that one phase consists solely of solvent and polymer 1, and the other solely of solvent and polymer 2, we may equate the free energy of the solvent in the two phases:

$$\begin{aligned} \ln\phi_0' + (1 - (1/m_1))(1 - \phi_0') + \mu_{10}(1 - \phi_0')^2 \\ = \ln\phi_0'' + (1 - (1/m_2))(1 - \phi_0'') \\ + \mu_{20}(1 - \phi_0'')^2. \end{aligned} \quad (23)$$

For given values of the constants  $m_1$ ,  $m_2$ ,  $\mu_{10}$  and  $\mu_{20}$ , we can calculate conjugate values of  $\phi_0'$  and  $\phi_0''$ . Obviously this approximation is correct only when  $\mu_{12}$  is very large, and it will be more nearly correct in those regions where the incompatibility of the polymers is largest,—i.e., at high polymer concentrations. Figure 2 shows such a diagram for the extreme case  $m_1 = 100$ ;  $\mu_{10} = 0.3$ ;  $m_2 = 10,000$ ;  $\mu_{20} = 0.5$ . If we assume, in addition,  $\mu_{12} = 0.2$ , the approximate equations (17abc) yield a plait point at  $\phi_0 \cong 0.96975$ ,  $\phi_1 \cong 0.0275$ ,  $\phi_2 \cong 0.00275$ . Shown in Fig. 3 is the dilution approximation for the same conditions (coordinates in volume percent—only upper part of diagram shown). The true diagram will lie somewhere between these extremes.

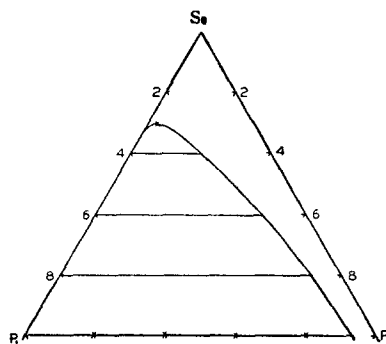


FIG. 3.

<sup>12</sup> It should be pointed out that Eqs. (22a) and (22b) are formally equivalent to a polymer-solvent system, as well,

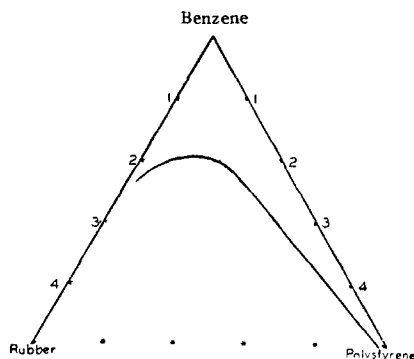


FIG. 4.

Coordinates in weight percent

## COMPARISON WITH EXPERIMENT

Let us now examine the experimental data of Dobry and Boyer-Kawenoki<sup>1</sup> in the light of the preceding theory. Their conclusions may be summarized as follows:

(a) Of the 35 pairs of high polymers tested, only three or four (nitrocellulose-polyvinyl acetate, nitrocellulose-polymethyl methacrylate benzylcellulose and polystyrene, and perhaps nitrocellulose-cellulose acetate in acetic acid) do not show separation. In view of the stringent limits on  $\mu_{12}$ , this is hardly surprising. With two polar polymers, of course, a negative  $\mu_{12}$  is not excluded. Unfortunately, the only system investigated for which all three components were completely non-polar is the system polystyrene-rubber-benzene shown in Fig. 4.

(b) When two high polymers are incompatible in one solvent, they are generally incompatible in all other solvents. This is in agreement with our conclusion that the primary dependence is upon the molecular weights and the interaction constant  $\mu_{12}$  of the two polymers, the exact nature of the solvent being only of secondary importance. The limit of phase separation appears to vary somewhat, the plait points in acetic acid, mesityl oxide, and dioxane being greater than for the others; this departure from the theoretical expectation may perhaps be attributed to specific interactions of the polar molecules.

(c) The molecular weight of the polymers is of great importance; the higher it is, the greater is the incompatibility. Figure 5 shows this effect for two fractions of cellulose acetate ( $M=16,000$  and  $56,000$ ) and two fractions of polyvinyl acetal ( $M=39,000$  and  $97,000$ ). In addition to the greater incompatibility with higher molecular weights, the theory predicts a displacement toward the lower molecular weight material (the cellulose acetate), the greatest asymmetry occurring for the 97,000-16,000 pair. All these qualitative conclusions are confirmed by Fig. 5.

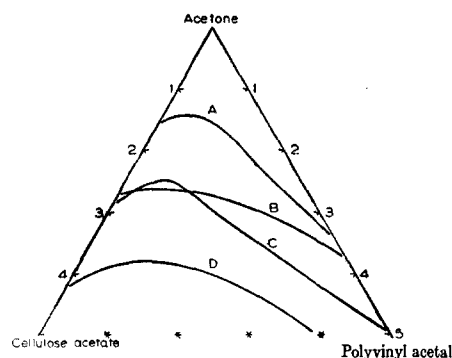


FIG. 5.

Coordinates in weight percent

(d) There is no obvious relationship between the compatibility of two polymers and the chemical nature of their monomers. The explanation probably rests upon a satisfactory treatment of the thermodynamics of polar solutions. Measurement of the heat of mixing of the corresponding monomer pairs would be instructive.

Unfortunately, only a few tie-lines were obtained, and no plait points. From theory one deduces that the plait points are close to the limits of phase separation (maximum  $\phi_0$ ), but experimental confirmation is lacking.

## OSMOTIC PRESSURES WITH POLYMER MIXTURES

The problem of osmotic pressures with two polymers and one solvent is not the complicated one which we have encountered in the case of mixed solvent,<sup>2</sup> since only one component is diffusible. We may obtain the osmotic pressure of a solution of mixed polymers directly from Eq. (5a):

$$\pi V_0 = -\Delta \bar{F}_0 = -RT[\ln \phi_0 + (1 - (1/\bar{m}_1))\phi_1 + (1 - (1/\bar{m}_2))\phi_2 + \mu_{10}\phi_1^2 + \mu_{20}\phi_2^2 + (\mu_{10} + \mu_{20} - \mu_{12})\phi_1\phi_2]. \quad (24)$$

With the use of the variables  $\theta_1$  and  $\theta_2$ , we may transform Eq. (24):

$$\pi = -(RT/V_0)[\ln \phi_0 + (1 - (1/\bar{m}_n))(1 - \phi_0) + \mu^*(1 - \phi_0)^2], \quad (25)$$

where  $\bar{m}_n$  is the number average  $m$ :

$$1/\bar{m}_n = (\theta_1/m_1) + (\theta_2/m_2), \quad (26)$$

and

$$\mu^* = \mu_{10}\theta_1 + \mu_{20}\theta_2 - \mu_{12}\theta_1\theta_2. \quad (27)$$

If we define a volume fraction of total polymer  $\phi_p = \phi_1 + \phi_2$ , and expand Eq. (25) in powers of  $\phi_p$ , we obtain

$$\pi = + (RT/V_0)[(\phi_p/\bar{m}_n) + (\frac{1}{2} - \mu^*)\phi_p^2 + \dots]. \quad (28)$$

This is the familiar equation for the osmotic pressure of a high polymer solution except for the substitution of  $\bar{m}_n$  for  $m$  and  $\mu^*$  for  $\mu$ . We may transform from volume fractions to concentrations (grams per cc) by noting that  $c = \phi\rho$  where  $\rho$  is the density in grams per cc. We then obtain:

$$\pi = RT[(c_p/\bar{M}_n) + (\frac{1}{2} - \mu^*/V_0\bar{\rho}^2)c_p^2 + \dots], \quad (29)$$

where  $\bar{M}_n$  is the number average molecular weight, defined as

$$(c_p/\bar{M}_n) = (c_1 + c_2/\bar{M}_n) = (c_1/M_1) + (c_2/M_2), \quad (30)$$

and  $\bar{\rho}$  is the harmonic mean of the densities if expressed as a function of concentration, or the arithmetic mean taken as volume fractions:

$$\begin{aligned} \bar{\rho} &= c_1 + c_2/(c_1/\rho_1) + (c_2/\rho_2) = \phi_1\rho_1 + \phi_2\rho_2/\phi_1 + \phi_2 \\ &= \theta_1\rho_1 + \theta_2\rho_2. \end{aligned} \quad (31)$$

By the usual technique of plotting  $\pi/c$  against  $c$ , we may use the slope of the line to determine the coefficient of  $c^2$  and, hence,  $\mu^*$ . Since  $\mu_{10}$  and  $\mu_{20}$  are known, we can use the variation of  $\mu^*$  with  $\theta$  (Eq. (27)) to determine  $\mu_{12}$ , which cannot be determined directly.

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## The Kinetics of the Thermal Decomposition of Propylene

M. SZWARC

*Department of Chemistry, The University of Manchester, Manchester, England*

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The thermal decomposition of propylene was investigated for temperatures ranging from 680°C up to 870°C and with percentages of decomposition from 0.01 percent up to about 2 percent. The reaction was shown to be a homogenous gas reaction of the first order, the first-order constant being given by an expression  $1.1 \cdot 10^{13} \exp(-72,000/RT)$ . Two mechanisms are discussed, both of which account for the observed kinetics and products of decomposition. It is demonstrated that the first step in the thermal decomposition of propylene is the splitting of the C—H bond leading to the formation of H atoms and allyl radicals. The problem of the value of  $D(C-H)$  in propylene is discussed in the light of the two suggested mechanisms. An attempt is made to account for the variety of the reactions between H atoms and propylene molecules as observed by various investigators.

ALTHOUGH several investigations of the pyrolysis of propylene have been carried out within the last twenty years, we still lack a full understanding of the mechanism of this process. In particular, the first steps of this decomposition are not definitely known, and the present research was an attempt to clarify this problem. We shall start with a brief summary of the results obtained by previous investigations, confining our discussion to those processes which are homogenous gas reactions.\*

Frey and Smith<sup>1</sup> studied the decomposition of propylene in a silica vessel at 575°C and atmospheric pressure, using a flow method and a time of contact of 1–4 minutes. They found that this process was a homogenous gas reaction. Analysis of the gases showed  $CH_4$  and  $C_2H_4$  to be the main products of the decomposition, in addition to smaller quantities

of  $H_2$ ,  $C_2H_6$ , and higher hydrocarbons. Assuming that the  $C_2H_6$  resulted from the hydrogenation of a part of the originally formed  $C_2H_4$ , we find from the data of these authors that the  $CH_4/C_2H_4$  ratio is 1:1 ( $CH_4 = 10.7$  percent,  $C_2H_4 = 8.0$  percent, and  $C_2H_6 = 1.9$  percent). This is the ratio which we might expect on the basis of the mechanism suggested later in the discussion of our results. Assuming also that the hydrogenation of  $C_2H_4$  to  $C_2H_6$  and  $C_3H_6$  to  $C_3H_8$ \*\* consumed a part of the  $H_2$  originally formed, we find the  $CH_4/\text{total } H_2$  ratio as 2:1. This is the  $CH_4/H_2$  ratio found in the present research.

Kinetic studies of the thermal decomposition of propylene were provided by Hurd and Meinert,<sup>2</sup> who investigated this reaction between 600°C and 700°C under atmospheric pressure in a flow system.

\* A review of the earlier literature is given by G. Egloff and E. Wilson, *Ind. Eng. Chem.* **27**, 917 (1935).

<sup>1</sup> F. E. Frey and D. F. Smith, *Ind. Eng. Chem.* **20**, 948 (1928).

\*\* Frey and Smith found, indeed, that under their experimental conditions the hydrogenation of  $C_2H_4$  and  $C_3H_6$  by  $H_2$  occurs easily.

<sup>2</sup> C. D. Hurd and R. N. Meinert, *J. Am. Chem. Soc.* **52**, 4978 (1930).