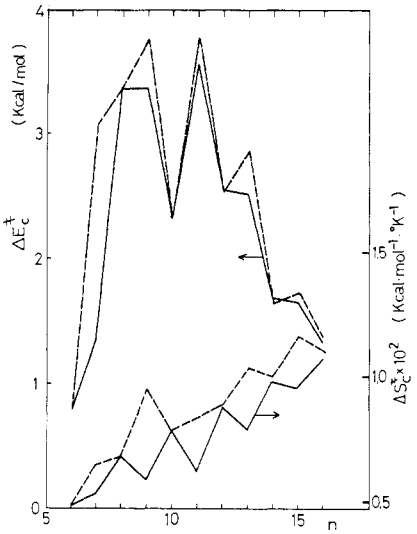

Figure 6. Conformational energies and entropies of activation at 350°K, calculated by treatment 3: r_0 = 1.75 (———), and 1.5 (– – – –).

be increased several times. It should be pointed out that the cyclization constants calculated assuming Gaussian distribution of end-to-end distance[30] were found to be extremely large compared with the observed values. As Morawetz, and Goodman[5] stated, the Gaussian treatment cannot apply to these short chains.

Conformational Energy and Entropy of Activation. To explain the relative ease of the cyclization reaction thermodynamically, the activation energies, $\Delta E_c^{\ddagger}$, and entropies, $\Delta S_c^{\ddagger}$, derived from conformational consideration were calculated by eq 5–8, for treatment 3. The results are plotted in Figure 6. Here, the total average energies were calculated in accordance with the total partition functions, that is, for chains shorter than n = 13, all conformations having no skeletal overlaps were constructed and then total average energies were calculated. For chains longer than n = 14, eq 13–18 were used without modification. As seen in Figure 6, the relative ease of the reaction is explained in terms of conformational energy of activation. On the other hand, the conformational entropy of activation showed rather monotonous dependence on the chain length. Therefore, as far as treatment 3 is concerned, the relative ease of the cyclization reaction is determined mainly by the conformational energy of activation. It was also found that the alternating properties in the conformational entropy were reversed going from r_0 = 1.50 to 1.75. This change can be understood in terms of diamond lattice model, in which r_0 = 1.75 corresponds to taking second, first, and zeroth neighbors of an end group as the reactive conformations and r_0 = 1.50 corresponds to taking first and zeroth neighbors. So, the trend in activation entropies may result from the fact that there can be only even-membered cyclic chains on a diamond lattice.[21–24] On the other hand, energetic consideration shows both values of r_0 lead to the preferred reactivity at even-membered chains.

In this paper, the intramolecular reaction was satisfactorily analyzed in terms of the statistical properties of a chain connecting the two functional groups. Using appropriate energy parameters and introducing long-range interactions, the absolute cyclization constants were estimated. Further, the conformational energies of activation were found to be the origin of the relative ease of cyclizations.

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(30) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 10.

On Swelling of Natural Rubber in Organic Solvents

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ABSTRACT: Functions of mixing are considered on the basis of available experimental data in terms of two statistical theories of solutions; the comparison made clearly establishes superiority of the more recent theory developed by Flory and involving three kinds of terms. In elastic contribution to the free energy of swelling, the number ν of network chains per unit volume of rubber appears independent of swelling liquid. A set of relations describing the swelling process involving the more accurate mixing contributions is discussed.

Absorption of liquids by natural rubber was studied experimentally by a number of authors, including careful investigations of Gee and his collaborators[1,2] and also measurements of Mullins.[3] These authors interpreted thermodynamic functions of mixing in terms of an approach usually referred to in the literature as the Flory–Huggins theory; for a description of this approach see ref 4.

Now a more recent theory of liquids and solutions formulated by Flory[5] appears to describe fairly successfully equilibrium properties of pure liquids as well as excess functions of

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(2) G. Gee, J. B. M. Herbert, and R. C. Roberts, *ibid.*, **6**, 541 (1965).
(3) L. Mullins, *J. Appl. Polym. Sci.*, **2**, 1 (1959).
(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter 12.
(5) P. J. Flory, *J. Amer. Chem. Soc.*, **87**, 1833 (1965).

mixing for a number of systems.[6] Only one system, however, involving natural rubber—namely that with benzene[7]—has been interpreted in terms of the new theory. It is our objective to find out whether, as compared to the earlier approach, the new theory does or does not give significant improvement in description of rubber-containing systems.

Elastic properties of rubber change on swelling simultaneously with mixing of components; we turn therefore to the statistical theory of rubber elasticity. According to basic assumptions of this theory, the two processes under consideration proceed simultaneously but independently. The increase of the Helmholtz free energy on swelling, A^{W}, is then

$$A^{W} = A^{M} + A^{Z} \tag{1}$$

where A^{M} represents the mixing contribution and A^{Z} the elastic term, with the cross-term A^{MZ} absent.

Apparent deviations from the theory of rubber elasticity have been reported in the literature. Shen[8] has found, however, that considerable experimental errors occur at small extension ratios, *i.e.*, at the range of extensions where deviations were supposed to appear. For natural rubber containing varying amounts of *n*-hexadecane, Shen has determined the relative energetic contributions to the tensile force f_e/f; $f = (\partial A^{Z}/\partial L)_{T,\phi}$ while $f_e = f - T(\partial f/\partial T)_{L,\phi}$, with L denoting length, T thermodynamic temperature, and ϕ concentration; the values of f_e/f obtained were independent of the degree of swelling. We shall thus assume eq 1 as our starting point.

The A^{Z} term depends, among other factors, on the number, ν, of elastically active polymer chains in the sample. We shall consider in particular the dependence of ν on solvent used.

I. Functions of Mixing

The model of the liquid state proposed by Flory[5,6] leads to the following partition function

$$Q = \Omega[\xi e^{3}v^{*}(\tilde{v}^{1/3} - 1)^{3}]^{Nrc}e^{Nrs\eta/2vkT} \tag{2}$$

where ξ is a geometric factor, v^{*} is the characteristic (hard-core) volume per segment, $\tilde{v}$ is the reduced volume, *i.e.*

$$\tilde{v} = v/v^{*} \tag{3}$$

N is the number of molecules; r, c, s, and η, appropriately averaged over concentration, characterize respectively the number of segments in a molecule, the number of intersegmental degrees of freedom, the surface of an interacting segment, and the interaction energy. The formulas for thermodynamic functions used below are obtainable from (2), with the combinatorial contribution Ω for a binary mixture $i + j$ assumed to be given by

$$\Omega = \phi_i^{-N_i}\phi_j^{-N_j} \tag{4}$$

with segment or hard-core volume fractions

$$\phi_i = r_iN_i/(r_iN_i + r_jN_j) \tag{5}$$

The applicability of equations such as (4) has been recently called into question by Bellemans and Van Craen,[9] who have found discrepancies between some exact results for rigid rectilinear r-mers on the square lattice and approximate results obtained using an equation similar to (4). There are, however, reasons that we can still use (4) in the present work. First, the approximate entropy equation studied by Bellemans and Van Craen contains, apart from terms coming from (4), additional terms involving the coordination number z directly and also indirectly through parameters

$$q_i = (r_i(z - 2) + 2)/z \tag{6}$$

We certainly agree with Bellemans and Van Craen that the closed rings, when present, should be accounted for; this does not concern segment fractions directly and is connected with the problem of using instead of (6) another equation for q_i.[10] Secondly, while the quasilattice model is certainly convenient for dealing with combinatorial problems, the two-dimensional square lattice is hardly a good approximation for real liquids. Bellemans and Van Craen say themselves[9] that "it is almost certain that the soundness of expression ... is much better in three than in two dimensions."

Parameters of the theory have been calculated in the following order. First, from (2) we have the formula

$$\tilde{v} = \left[\frac{\alpha T}{3(1 + \alpha T)} + 1\right]^{3} \tag{7}$$

applicable to single substances as well as to mixtures; α is the isobaric expansivity $V^{-1}(\partial V/\partial T)_{P,\phi}$. Using (7), the reduced volumes of pure components (or the hard-core volumes, *cf.* eq 3) were computed from the respective molar volumes V and from the isobaric expansivities taken at pressure $P = 0$. Subsequently, the reduced temperatures (or hard-core temperatures) of components were obtained from the relation

$$\tilde{T} = T/T^{*} = (\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} \tag{8}$$

Hard-core pressures were calculated from the limiting value at $P = 0$ of $\gamma = (\partial P/\partial T)_{v}$ as

$$P^{*} = \gamma T\,\tilde{v}^{2} \tag{9}$$

After obtaining thus the necessary quantities for pure components, we computed the reduced volumes for the mixtures, assuming first the additive value $\tilde{v}^{I}$, *i.e.*

$$\tilde{v} \approx \tilde{v}^{I} = \phi_i\tilde{v}_i + \phi_j\tilde{v}_j \tag{10}$$

As experimental data of Gee, *et al.*,[1,2] were actually expressed in terms of volume fractions ϕ_i', they were converted to segment fractions ϕ_i as defined by eq 5 through the relation

$$\phi_i = \frac{V_{i_{sp}}^{*}}{\left(\frac{1}{\phi_i'} - 1\right)\frac{V_{i_{sp}}}{V_{j_{sp}}}V_{j_{sp}}^{*} + V_{i_{sp}}^{*}} \tag{11}$$

where the index sp refers to the specific quantity per gram.

Two more parameters were necessary, X_{ij}, which characterizes the difference between "mixed" interaction energy η_{ij} and the "pure" energies η_{ii} and η_{jj}, and the ratio of surface parameters, s_i/s_j, or else for any given segment concentration ϕ_i the surface concentration θ_i

$$\theta_i = \frac{\phi_i}{\phi_i + (s_j/s_i)\phi_j} \tag{12}$$

There are at least three ways of dealing with s_i/s_j ratio. First, this ratio may be obtained along with the X_{ij} parameter from experimental values of the chemical potential difference

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(7) B. E. Eichinger and P. J. Flory, *Trans. Faraday Soc.*, 64, 2035 (1968).
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$(\mu_i - \mu_{ii})^R/N_A kT$ for the solvent. The single and double subscripts refer respectively to the component in solution and in the pure state, N_A is Avogadro's number, and the superscript R refers to the residual quantity, defined[5] generally as

$$F^R = F^M - F^\Omega \tag{13}$$

F is a thermodynamic function, F^M denotes a function of mixing, and F^Ω denotes the contribution coming from terms displayed in eq 4. As mentioned by Flory,[5] the advantages of using residual functions may be seen by considering the special case of $r_i = r_j$. From (4), (5), and the formula for ideal entropy of mixing, S^I, we then obtain $F^R = F^M - F^I = F^E$, where F^E is an excess function of mixing; we thus have this special case as a certain reference state: if r_j becomes greater than r_i, then F^R becomes different from F^E. The necessary formula for $(\mu_i - \mu_{ii})^R$ is obtainable also from (2). Rearranging it so as to have an explicit equation for X_{ij} we write

$$X_{ij} = \frac{\left[1 + \left(\frac{s_i}{s_j} - 1\right)\phi_i\right]^2 \tilde{v} D}{\phi_j^2} \tag{14}$$

where, using the quantities per mole

$$D = \frac{(\mu_i - \mu_{ii})^R}{V_i^*} - p_i^*\left(3\tilde{T}_i \ln \frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \tilde{v}_i^{-1} - \tilde{v}^{-1}\right) \tag{15}$$

For n experimental points for a given system at a given temperature, the set of n eq 14 in two unknowns, X_{ij} and s_i/s_j, may be solved; actually, by a simple algebraic transformation an equation linear with respect to ϕ_i and containing two unknowns, $X_{ij}^{-0.5}$ and $X_{ij}^{-0.5}[(s_i/s_j) - 1]$, is obtained, and a set of n such equations is solved by the method of least squares. Now the hard-core pressure for the mixture may be calculated

$$p^* = p_i^*\phi_i + p_j^*\phi_j - X_{ij}\theta_j\phi_i \tag{16}$$

and in turn the hard-core temperature for the mixture is obtainable

$$T^* = \frac{p^*}{(p_i^*/T_i^*)\phi_i + (p_j^*/T_j^*)\phi_j} \tag{17}$$

Further, using eq 8, a new value of $\tilde{v}$ for the mixture may be calculated, one that does include the excess reduced volume $\tilde{v}^E$. The new $\tilde{v}$ value may be used instead of that obtained from eq 10, and the same procedure repeated. If the second set of values of X_{ij} and s_i/s_j differs only insignificantly from the first, the second set may be accepted, otherwise the procedure is to be repeated again. In our actual calculations, usually one repetition was found sufficient.

The second possibility of obtaining the s_i/s_j ratio consists in relying on a geometric scheme such as the group surface method. This is clearly more elegant, as we avoid determining X_{ij} and s_i/s_j as simultaneous adjustable parameters, but we have to remember that geometric schemes are approximate. The third—the simplest—possibility is to assume $s_i/s_j = 1$; this has been done recently by Patterson and his colleagues.[11] We shall reconsider the problem later on, in the light of numerical results for all three cases.

To proceed toward comparison of the two theories of solutions, let us notice that the earlier theory[4] expression for the mixing contribution to the chemical potential $(\mu_i - \mu_{ii})^M$ contains, apart from combinatorial terms, only one more term, namely of the energetic type. The characteristic parameter in this term may be related to $(\mu_i - \mu_{ii})^R$ by[7]

$$\chi = (\mu_i - \mu_{ii})^R/N_A kT\phi_j^2 \tag{18}$$

We have calculated the values of χ from (18). First, parameters $(\mu_i - \mu_{ii})^M$ were obtained from experimental data in Tables 1 and 5 of ref 1; then the combinatorial contribution was subtracted according to eq 4, giving $(\mu_i - \mu_{ii})^R$; *cf.* definition 13. Values of χ so obtained differ from those of Gee and his colleagues, as we have used segment fractions instead of volume fractions. The behavior of $\chi(\phi')$ and $\chi(\phi)$ is similar, however, and we discuss $\chi(\phi)$ for each system below. In the new theory the energetic term contains the characteristic parameter X_{ij}. If we have at disposal a value for s_i/s_j, we can use eq 14 to compute a value of X_{ij} for each individual point.

Now consider in turn results obtained for systems with various solvents.

Acetone and Rubber. Booth, *et al.*,[1] have obtained activities for this system by the differential manometry method at 273.15 and 298.15°K. At the former temperature, the necessary equation of state data of pure components, if accessible, would be less accurate; moreover, the experimental activities are for four concentrations only, with the numerical values probably affected by partial crystallinity of rubber. We have therefore performed calculations for 298.15°K. The respective parameters for rubber were accessible from ref 7, with the density of the rubber sample accepted by Eichinger and Flory[7] sufficiently close to that of Booth, *et al.*[1] The parameters for acetone were calculated as described above from the density expansion $\rho(T)$ as given in ref 12 and the value of isothermal compressibility $\kappa = -V^{-1}(\partial V/\partial P)_{T,\phi}$ of Newitt and Weale;[13] the small difference between κ at $P = 0$ and κ at the atmospheric pressure ought not affect our results. Both the experimental values used and the characteristic parameters of components calculated therefrom are listed below in Table I.

Denoting for this, as well as for subsequent systems, the solvent by index 1 and rubber by index 2, the experimental values of $(\mu_1 - \mu_{11})^M/N_A kT$ and $(\mu_1 - \mu_{11})^R N_A kT$ are given in Table II. Using these and assuming eq 10, the value of X_{12} which resulted from eq 14 was 87.4 J cm^{-3}. In the second round of calculations performed as described above (*i.e.*, with $\tilde{v}^E$ now $\neq 0$, solving n equations in two unknowns), values $X_{12} = 87.0$ J cm^{-3} and $s_2/s_1 = 0.437$ were obtained. Using the latter pair of parameters, theroetical values of $(\mu_1 -$

TABLE I
CHARACTERISTIC PARAMETERS OF PURE COMPONENTS

	Rubber	Acetone	Methyl ethyl ketone	Ethyl acetate
V_{sp}, cm^3 g^{-1}	1.0951	1.2748	1.2502	1.1180
$\alpha \times 10^3$, °K^{-1}	0.654	1.440	1.309	1.373
γ, J cm^{-3} °K^{-1}	1.272	1.162	1.142	1.158
$\tilde{v}$	1.1722	1.3314	1.3077	1.3195
V_{sp}^*, cm^{-3} g^{-1}	0.9342	0.9575	0.9560	0.8473
T^*, °K	6775	4362	4556	4457
p^*, J cm^{-3}	519	614	582	601

(11) J. Biroš, L. Zeman, and D. Patterson, *Macromolecules*, 4, 30 (1971).

(12) "International Critical Tables," Vol. 3, McGraw-Hill, New York, N. Y., 1923, p 27.

(13) D. M. Newitt and K. E. Weale, *J. Chem. Soc.*, 3092 (1951).

TABLE II
ACETONE + RUBBER AT 298.15°K

		Experimental		Calculated			
		$(\mu_1 - \mu_{11})^M$	$(\mu_1 - \mu_{11})^R$	$(\mu_1 - \mu_{11})^R$			
ϕ_2'	ϕ_2	N_Akt	N_Akt	N_Akt	χ	X_{12}, J cm^{-3}	X_{12}', J cm^{-3}
0.805	0.824	−0.001	0.914	0.909	1.338	87.7	58.3
0.846	0.862	−0.044	1.074	1.073	1.444	87.1	62.8
0.868	0.882	−0.085	1.170	1.172	1.506	86.9	65.4
0.916	0.925	−0.255	1.415	1.420	1.659	86.6	72.1
0.947	0.953	−0.509	1.596	1.607	1.770	86.3	76.7
0.955	0.960	−0.583	1.681	1.660	1.800	88.3	79.9

$\mu_{11})^R/N_AkT$ were obtained, as shown in the fifth column of Table II. Then values of χ from eq 18 and experimental $(\mu_1 - \mu_{11})^R$ were computed. Further, using $s_2/s_1 = 0.437$, also from each of the experimental values of $(\mu_1 - \mu_{11})^R$ and using eq 14 and 15, values of X_{12} were calculated; these are listed in column 7 of Table II; their average is $X_{12} = 87.1$ J cm^{-3}.

We have alternatively used the group surface method of Bondi[14] to determine s_2/s_1. The necessary Bondi value for rubber, s_2', was obtained indirectly through the formula

$$\frac{s_2'}{s_1'} = \left(\frac{s_2}{s_B}\right)'' \frac{V_1^*}{V_B^*} \frac{s_B'}{s_1'} \tag{19}$$

where the subscript B denotes benzene; $(s_2/s_B)'' = 0.90$ as given by Eichinger and Flory[7] was accepted, while s_B' and s_1' were computed according to the method of Bondi.[14] The value of s_2'/s_1' resulting from (19) was 1.00. It might be mentioned that the Bondi method has already been found to overestimate the s_2/s_1 values for the rubber + benzene system; *cf.* the remarks in ref 7. Values of X_{12}', obtained using $s_2'/s_1' = 1$ in eq 14 and 15 and experimental values of $(\mu_1 - \mu_{11})^R$, are listed in column 8 of Table II.

Inspection of the data in the table shows that the experimental and calculated values of $(\mu_1 - \mu_{11})^R/N_AkT$ are fairly close to one another, the difference being practically within the limits of accuracy of the respective experiments. The applicability of the earlier polymer solution theory may best be assessed by considering the energetic parameter χ. The dependence of χ on concentration is fairly well pronounced, in spite of the fact that the concentration range covered by experiments is only 0.150 in volume fractions. On the other hand, the energetic parameter of the new theory, X_{12}, is remarkably stable and for all purposes concentration independent—provided $s_2/s_1 = 0.437$ is used. For the surface ratio parameter taken from the group surface method, the energetic parameter which we have denoted for distinction by X_{12}' is clearly concentration dependent. We note, however, that it is possible to obtain X_{12} from X_{12}', namely

$$\lim_{\phi_1 \to 0} X_{12}' = X_{12}$$

From eq 14, we see that with $s_i/s_j = 1$ the explicit term with s_i/s_j cancels out, but it is in taking the limit that the implicit dependence of the energetic parameter on the surface ratio disappears also.

Booth, *et al.*, also give a single value of the partial molar excess heat of mixing of acetone, H_1^E, at swelling equilibrium. From (2) we can obtain an expression for the excess energy of mixing, U^E. With the volumes of mixing, V^E, of rubber with a solvent being not larger than 1 cm^3 mol^{-1}, at atmospheric pressure PV^E does not exceed 0.1 J mol^{-1}. Thus, safely $H^E \approx U^E$, and consequently

$$H_1^R = p_1^* V_1^* \left[\tilde{v}_1^{-1} - \tilde{v}^{-1} + \frac{\alpha T(\tilde{T}_1 - \tilde{T})}{\tilde{v}\tilde{T}}\right] + (1 + \alpha T)V_1^* D \tag{20}$$

αT for the mixture may be obtained from $\tilde{v}$ using eq 7. By definition (*cf.* eq 13) $H_1^R = H_1^E = H_1^M$.

Calculations according to (20) at $\phi_2 = 0.824$ give $H_1^E = 1597$ J mol^{-1}, as compared to the "experimental" value of 979 J mol^{-1}. On one hand, we have to remember that (20) has been obtained from (2) by two differentiations. On the other hand, however, the "experimental" value has been obtained using three derivatives: $\partial f/\partial N_1$, $\partial N_1/\partial T$, and $\partial N_1/\partial L$. Two of these are known within one significant figure only, so that a large error is necessarily involved in experimental H_1^E values. In view of this, the agreement is as good as could be expected. We would be inclined, under the circumstances, to give more weight to the value calculated from eq 20.

Methyl Ethyl Ketone + Rubber. Activities for this system have been determined by Booth, *et al.*,[1] at 298.15 and 318.15°K. The relevant parameters for methyl ethyl ketone were accessible for 298.15°K,[15] so we again performed calculations for this temperature. The respective experimental and characteristic hard-core parameters are listed in Table I.

Calculations were made in the same way as for the acetone-containing system. The relevant values from eq 14 are $X_{12} = 51.5$ J cm^{-3} and $s_2/s_1 = 0.537$. The Bondi method with eq 19 gives $s_2'/s_1' = 0.812$, again a typical overestimate. The experimental values and the calculated quantities including X_{12}, X_{12}', and X_{12}'' (corresponding respectively to the surface ratios 0.537, 0.812, and 1.00) are listed in Table III.

The conclusions reached for the acetone system are reiterated for the present one. This applies equally to the agreement between experimental and theoretical $(\mu_1 - \mu_{11})^R/N_AkT$ values, to the dependence of χ on concentration, and to the independence of X_{12} on ϕ. As the concentration range covered by the experiments is twice as large as it was for acetone + rubber, the $\chi(\phi)$ variations are even more evident. One notices that the value of χ at the saturation point is about one-half of the value at the other end of the concentration interval.

Again, a single value of H_1^E at the saturation ($\phi_2 = 0.578$) has been given by Booth, *et al.* It is 347 J mol^{-1}, while eq 20 gives $H_1^R = 50$ J mol^{-1}. The reasons for the difference are clearly the same as discussed for the previous system.

Ethyl Acetate + Rubber. Experimental activities in this

(14) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).

(15) P. J. Flory, and H. Höcker, to be published.

TABLE III
METHYL ETHYL KETONE + RUBBER AT 298.15°K

		Experimental		Calculated				
		$(\mu_1 - \mu_{11})^M$	$(\mu_1 - \mu_{11})^R$	$(\mu_1 - \mu_{11})^R$				
ϕ_2'	ϕ_2	N_Akt	N_Akt	N_Akt	χ	X_{12}, J cm^{-3}	X_{12}', J cm^{-3}	X_{12}'', J cm^{-3}
0.551	0.578	−0.007	0.278	0.280	0.839	50.8	33.0	27.4
0.613	0.639	−0.009	0.370	0.367	0.901	50.9	35.5	30.2
0.622	0.647	−0.012	0.383	0.381	0.908	50.7	35.8	30.6
0.684	0.707	−0.039	0.483	0.491	0.981	49.3	36.6	32.1
0.725	0.746	−0.058	0.567	0.577	1.035	49.6	38.1	33.9
0.778	0.796	−0.104	0.691	0.704	1.110	49.7	39.9	36.4
0.874	0.886	−0.319	0.964	0.990	1.263	49.4	43.4	41.2
0.924	0.931	−0.595	1.152	1.176	1.355	50.0	46.2	44.7
0.959	0.963	−1.014	1.323	1.322	1.426	51.4	49.2	48.4
0.967	0.970	−1.183	1.364	1.360	1.444	51.7	49.8	49.1

TABLE IV
ETHYL ACETATE + RUBBER AT 298.15°K

		Experimental		Calculated				
		$(\mu_1 - \mu_{11})^M$	$(\mu_1 - \mu_{11})^R$	$(\mu_1 - \mu_{11})^R$				
ϕ_2'	ϕ_2	N_Akt	N_Akt	N_Akt	χ	X_{12}, J cm^{-3}	X_{12}', J cm^{-3}	X_{12}'', J cm^{-3}
0.625	0.652	−0.013	0.392	0.375	0.880	39.9	35.9	26.0
0.697	0.721	−0.069	0.488	0.495	0.951	36.7	33.6	25.8
0.740	0.762	−0.099	0.574	0.579	0.997	37.0	34.2	27.3
0.794	0.813	−0.183	0.680	0.697	1.055	36.1	33.9	28.3
0.871	0.884	−0.374	0.894	0.897	1.149	37.3	35.8	31.9
0.880	0.892	−0.431	0.902	0.922	1.159	36.3	34.9	31.4
0.949	0.954	−0.982	1.151	1.144	1.256	37.8	37.2	35.5
0.983	0.985	−1.906	1.302	1.367	1.306	38.9	38.6	38.1
0.999	0.999	−4.693	1.321	1.327	1.329	37.2	37.2	37.1
0.999	0.999	−4.689	1.325	1.327	1.329	37.3	37.3	37.3

section are also taken from the paper of Booth, *et al.*,[1] measured for ten concentrations at 298.15°K and for four concentrations at 323.15°K. We have obtained values of V, α, $\tilde{v}$, and T^* for ethyl acetate at 298.15°K from the temperature expansion of the density given in ref 12. The same source contains values of isothermal compressibility of the ester for a number of temperatures, measured at the pressure interval between 0.1 and 0.2 J cm^{-3}. We have obtained the necessary value of κ by temperature interpolation using a formula from an earlier paper.[16] The straight line in the figure in ref 16, drawn using the same experimental data as employed presently, indicates that the formula is well obeyed; thus the temperature interpolation does not introduce errors. On the other hand, the value so obtained is not strictly true for $P = 0$. The behavior of the thermodynamic functions in which we are interested, however, can be affected only slightly, and so the approximation in γ can hardly be consequential for our conclusions. The respective parameters are listed in Table I.

Thermodynamic functions were calculated as for previous systems. $X_{12} = 37.4$ J cm^{-3} and $s_2/s_1 = 0.592$ were obtained from the experimental data. The Bondi method gives $s_2'/s_1' = 0.664$; the agreement is thus better than for the previous system, but we still have an overestimate. The respective values including X_{12}, X_{12}', and X_{12}'' (for the surface ratio of unity) are listed in Table IV. Again χ varies considerably with composition. Values of X_{12} calculated in turn for each individual point, given in the last column of the table, are again composition independent, except for scatter due to experimental errors (the accuracy of the measurements seems to be somewhat lower for the present system than for the previous ones). Owing to the closeness of the s_2/s_1, and s_2'/s_1' ratios, variations of X_{12}' with concentration are fairly small for the present system, and in any case much smaller than those of χ. For the surface ratio of unity, *i.e.*, for X_{12}'', we have evident concentration dependence, but at $\phi_1 = 0.001$ all three energetic parameters are equal.

For the swelling equilibrium, Booth, *et al.*, give the experimental value $H_1^E = 276$ J mol^{-1}. The respective value from eq 20 is 634 J mol^{-1}.

Other Systems. According to Mullins,[3] a single value of $\chi = 0.42$ fits the data for rubber + *n*-decane at 298.15°K. It is conceivable that in the case of nonpolar hydrocarbon the earlier theory gives better agreement with experiment than for the systems we have dealt with above. For lack of appropriate numerical values in ref 3, we are unable to perform the same analysis as previously.

As for the system involving benzene, Gee, *et al.*,[2] have already discussed deviations from the earlier theory. Indeed, new results of Eichinger and Flory show clearly variations of χ with composition; see Figure 3 in ref 7. This variation has been explained in terms of the new theory.

We conclude this paragraph with reconsidering the determination of X_{ij} and s_j/s_i. All sets of numerical data show that, whatever the choice of the s_j/s_i ratio, values of X_{ij} tend to the proper value when $\phi_i \to 0$. Actually, evaluation of X_{ij} may be done still more simply. From eq 14 and 15, we have

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TABLE V
NUMBERS OF NETWORK CHAINS FOR DIFFERENT SOLVENTS

Solvent	$\nu \times 10^{-19}$, cm^{-3} Eq 24a	Eq 24b
Acetone	12.7	12.5
Methyl acetate	12.7	12.3
Methyl ethyl ketone	10.2	9.6
Ethyl acetate	10.3	9.6
Methyl propyl ketone	12.3	11.3

$$X_{ij} = \frac{\tilde{v}_j}{V_i^*} \lim_{\phi_i \to 0} (\mu_i - \mu_{ii})^R + p_i^*\left(1 - \frac{\tilde{v}_j}{\tilde{v}_i} - 3\tilde{v}_j\tilde{T}_i \ln \frac{\tilde{v}_i^{1/3} - 1}{\tilde{v}_j^{1/3} - 1}\right) \quad (21)$$

Thus, in distinction to fitting procedures, eq 21 determines uniquely the value of X_{ij}, on the basis of characteristic parameters of pure components plus one limiting value, so that measurements over wide concentration ranges are not necessary. In actual calculations, eq 21 gives, *e.g.*, for the rubber + ethyl acetate system $X_{12} = 37.2$ J cm^{-3}, while the average of values in column 7 of Table IV is 37.4 J cm^{-3}.

As for the s_i/s_j ratio, we can—until geometric schemes are improved—determine it from any experimental point for a mixture using the known X_{12} parameter.

II. Elasticity Contribution

Consider now the second term of eq 1. The approach to the theory of elasticity developed by Flory[17] gives for the elastic contribution

$$A^Z = \frac{\nu kT}{2}(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3 - \ln \lambda_x\lambda_y\lambda_z) \quad (22)$$

where ν is the number of chains bound by cross linkages in the network, x, y, and z are Cartesian coordinates while λ's are the extension ratios: $\lambda_x = L_x/L_{0x}$, where L_x and L_{0x} are the lengths along the coordinate x respectively after and before swelling.

We turn now to the expression for A^Z employed by Booth, *et al.*,[1] as it is their data that we use. In our notation their equation is

$$A^Z = C'(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) + C''(\lambda_x^{-2} + \lambda_y^{-2} + \lambda_z^{-2} - 3) \quad (23)$$

where C' and C'' are constants. The contribution of the second term in (22) decreases when approaching the point of swelling equilibrium. As discussed by Bashaw and Smith,[18] the origin of C'' is unknown, while it is possible to associate the statistical formula 22 with the first term in (23); then

$$\nu = 2C'/kT \quad (24a)$$

Let us note that the values of ν resulting from the last equation represent the *effective* numbers of networks chains. Mullins[3] has found that the "physical" values of ν (or of the molecular weight M_c inversely proportional to ν) calculated from C' are different from the "chemical" values of M_c obtained by chemical analysis. The two sets of values have been reconciled by including corrections for chain entanglements and also for chain ends.

From the values of C' given by Booth, *et al.*, we have calculated values of ν for rubber from the same sample swollen in five different solvents. The resulting parameters per 1 cm^3 of rubber are listed in Table V. We expected the numbers to be independent of solvent; the values obtained show that this is approximately the case. The differences observed might be caused solely by limited accuracy of experiments and/or concentration extrapolation; Booth, *et al.*, state that C' is sensitive to L_0 and that it is difficult to assess the accuracy of their results. The average value from Table V is 11.6×10^{19} cm^{-3}.

Tobolsky and Shen[19] have proposed an alternative equation of state for rubber elasticity. For the parameter under consideration instead of (24a) we would then have

$$\nu = 2C'(\phi_2')^\epsilon/kT \quad (24b)$$

The case for $\epsilon \neq 0$ is supported by experimental evidence,[8] and one now expects it to apply to many polymers. We have therefore tried the alternative, using $\epsilon = -0.1$ as suggested by Shen.[8] The resulting values are also listed in Table V. The conclusion is the same as from the use of eq 24a. The average value is slightly smaller, namely 11.0×10^{19} cm^{-3}.

Applicability of eq 2 and its consequences allow us, on the basis of eq 1, to combine formulas of section I with those of the present section. A variety of relations describing the swelling process follows then immediately. It is not our intention to write them out here, except for a single example. For the parameter D as defined by (15), denoting the volume of unswollen rubber sample by V_{22}, for the case of isotropic swelling ($\lambda_x = \lambda_y = \lambda_z$) and at saturation ($\mu_1 = \mu_{11}$), we have, using eq 22

$$D = \frac{N_A kT}{V_1^*}(\ln \phi_1 + \phi_2) - p_1^*\left(3\tilde{T}_1 \ln \frac{\tilde{v}_1^{1/3} - 1}{\tilde{v}^{1/3} - 1} + \tilde{v}_1^{-1} - \tilde{v}^{-1}\right) - \frac{\tilde{v}_1 \nu kT}{V_{22}}\left[(\phi_2')^{1/3} - \frac{\phi_2'}{2}\right] \quad (25)$$

III. Some Concluding Remarks

The results of section I indicate clearly that the statistical theory of Flory described in ref 5 and 6 represents a vast improvement over the earlier approach for rubber-containing systems. While we have to bear in mind approximations involved in assuming the partition function 2 and combinatorial contribution 4, independence of X_{12} of composition is remarkable, particularly against the background of considerable variations of χ with concentration. In the present context, it might be worth noting that the new Flory theory has been found, on one hand, to describe such a subtle quantity as excess isothermal compressibility of a mixture of hydrocarbons,[20] while, on the other hand, it has been found to describe, in an approximate way, even excess functions of mixing alcohols.[21]

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