

piperazine, in diphenyl ether are shown by the upper curves in Fig. 134.<sup>19</sup> Consider a mixture having a polymer concentration less than that at the critical intersection of the liquidus and solidus curves.\* Let the mixture initially be at a temperature high enough to allow complete homogeneity. Then when it is cooled, liquid-liquid phase separation, observed visually and indicated by the open circles, will precede crystallization. On further lowering of the temperature, crystallization (also observed visually in this more dilute range) occurs at the same (critical) temperature independent of the proportion of diluent within this range. This constancy is, of course, required by the phase rule since two liquid phases are present in addition to the crystalline phase being formed.

Recalling the previous assertion that efficient fractionation requires liquid-liquid phase separation, we conclude that nitrobenzene and amyl acetate should be satisfactory solvents from which to fractionate polyethylene by successively lowering the temperature and that the better solvent xylene should be avoided for this purpose. The character of the phase diagram may, in fact, be used as a criterion of the efficacy of a given solvent for fractionation (see Chap. VIII, p. 344). If the curve representing the precipitation temperature plotted against concentration rises monotonically, crystalline separation is clearly indicated; if it passes through a maximum at a low concentration, liquid-liquid separation is virtually assured, and the solvent may be assumed to be a satisfactory one to use for fractionation.

The curves of Figs. 133 and 134 may be regarded as plots of solubilities against temperature. It must be borne in mind however, that the dissolved phase is interspersed with the crystalline phase when polymer is present in excess of its solubility limit. Even in the more dilute solutions from which the crystalline polymer may settle out, the "precipitate" will contain some amorphous polymer and diluent. In short, these curves are useful primarily in defining the maximum amount of polymer which may be totally dissolved as a function of the temperature.

### 3. SWELLING OF NETWORK STRUCTURES

A three-dimensional network polymer such as vulcanized rubber, although incapable of dispersing completely, may nevertheless absorb a large quantity of a suitable liquid with which it is placed in contact.

\* The critical concentration at the maximum of the liquid-liquid curve in Fig. 134 occurs at a higher concentration than in the other systems discussed (Fig. 121, p. 547, and Fig. 133) owing, in part at least, to the comparatively low molecular weight of the polyamide.

Swelling occurs under these conditions for the same reason that the solvent mixes spontaneously with an analogous linear polymer to form an ordinary polymer solution; the swollen gel is in fact a solution, although an elastic rather than a viscous one. Thus an opportunity for an increase in entropy is afforded by the added volume of the polymer throughout which the solvent may spread. This mixing tendency, expressed as the entropy of dilution, may be augmented ( $\chi_1 < 0$ ) or diminished ( $\chi_1 > 0$ ) by the heat (or first neighbor interaction free energy) of dilution. As the network is swollen by absorption of solvent, the chains between network junctions are required to assume elongated configurations, and a force akin to the elastic retractive force in rubber consequently develops in opposition to the swelling process. As swelling proceeds, this force increases and the diluting force decreases. Ultimately, a state of equilibrium swelling is reached in which these two forces are in balance.

A close analogy exists between swelling equilibrium and osmotic equilibrium. The elastic reaction of the network structure may be interpreted as a pressure acting on the solution, or swollen gel. In the equilibrium state this pressure is sufficient to increase the chemical potential of the solvent in the solution so that it equals that of the excess solvent surrounding the swollen gel. Thus the network structure performs the multiple role of solute, osmotic membrane, and pressure-generating device.

**3a. Theory of Swelling.**<sup>27,28</sup>—The free energy change  $\Delta F$  involved in the mixing of pure solvent with the initially pure, amorphous, unstrained (i.e., isotropic) polymeric network is conveniently considered to consist of two parts: the ordinary free energy of mixing  $\Delta F_M$ , and the elastic free energy  $\Delta F_{el}$  consequential to the expansion of the network structure. Thus we may write

$$\Delta F = \Delta F_M + \Delta F_{el} \quad (33)$$

A suitable expression for  $\Delta F_M$  may be obtained from Eq. (XII-22), bearing in mind that the number  $n_2$  of polymer molecules is to be equated to zero owing to the absence of individual polymer molecules in the network structure. Thus

$$\Delta F_M = kT(n_1 \ln v_1 + \chi_1 n_1 v_2) \quad (34)$$

By analogy with the deformation of rubber, the deformation process during swelling, considered apart from the actual mixing with solvent, must occur without an appreciable change in internal energy of the network structure. Hence  $\Delta F_{el}$  may be equated to  $-T\Delta S_{el}$  where  $\Delta S_{el}$ , representing the entropy change associated with the change in



configuration of the network, is given by Eq. (XI-41). If we let  $\alpha_s$  represent the linear deformation factor (see Chap. XI), then by the condition of isotropy  $\alpha_x = \alpha_y = \alpha_z = \alpha_s$ , and according to Eq. (XI-41)

$$\Delta F_{el} = (kTv_e/2)(3\alpha_s^2 - 3 - \ln \alpha_s^3) \quad (35)$$

where  $\nu_e$  is the effective number of chains in the network.

The chemical potential of the solvent in the swollen gel is given by

$$\mu_1 - \mu_1^0 = N(\partial\Delta F_M/\partial n_1)_{T,P} + N(\partial\Delta F_{el}/\partial\alpha_s)_{T,P}(\partial\alpha_s/\partial n_1)_{T,P} \quad (36)$$

where  $N$  is Avogadro's number. In order to evaluate  $(\partial\alpha_s/\partial n_1)$ , we note that

$$\alpha_s^3 = V/V_0$$

where  $V_0$  is the volume of the relaxed network, i.e., the volume occupied by the polymer when the cross-linkages were introduced into the random system (see Chap. XI), and  $V$  is the volume of the swollen gel. Ordinarily the cross-linkages will have been introduced in the unswollen polymer. Assuming this to have been the case,  $V_0$  will represent the volume of the unswollen polymer, and  $V_0/V = v_2$ . Assuming further that mixing occurs without an appreciable change in the total volume of the system (polymer plus solvent)

$$\alpha_s^3 = 1/v_2 = (V_0 + n_1V_1/N)/V_0 \quad (37)$$

It follows that

$$(\partial\alpha_s/\partial n_1)_{T,P} = V_1/3\alpha_s^2 V_0 N$$

Evaluating the other two derivatives occurring in Eq. (36) by differentiating Eqs. (34) and (35) and expressing  $\nu_e$  in moles, we obtain<sup>28</sup>

$$\mu_1 - \mu_1^0 = RT[\ln(1 - v_2) + v_2 + \chi_1 v_2^2 + \nu_1(\nu_e/V_0)(v_2^{1/3} - v_2/2)] \quad (38)$$

The first three terms occurring in the right-hand member of Eq. (38), represent  $\partial\Delta F_M/\partial n_1$ ; they correspond to  $\mu_1 - \mu_1^0$  according to Eq. (XII-26) for a polymer of infinite molecular weight (i.e.,  $x = \infty$ ). The last member introduces the modification of the chemical potential due to the elastic reaction of the network structure.\* The activity  $a_1$

\* Until recently<sup>28</sup> the last term in the brackets in Eq. (38) was given erroneously as  $(\nu_1\nu_e/V_0)v_2^{1/3}$ . This error resulted from the use of incorrect elastic entropy and free energy expressions in which the  $\ln\alpha_s^3$  term of Eq. (35) was omitted. This term takes account of the entropy of distribution of the  $\nu_e/2$  effective cross-linkages over the volume  $V_0\alpha_s^3 = V$ .

The treatment given here, like that of rubber elasticity in Chapter XI, is developed for a network in which the ends of the chains are united tetrafunctionally,

of the solvent is specified also by Eq. (38) through the relationship  $\ln a_1 = (\mu_1 - \mu_1^0)/RT$ .

If the chemical potential difference  $\mu_1 - \mu_1^0$  calculated according to Eq. (38) is plotted against  $v_2$ , it will be found that, owing to the positive contribution of the elastic term (with  $\nu_e > 0$ ), the chemical potential  $\mu_1$  exceeds  $\mu_1^0$  for the pure solvent for all concentrations below a certain polymer concentration  $v_{2m}$ . In other words, the activity  $a_1$  would exceed unity for compositions with  $v_2 < v_{2m}$ . This region therefore represents an unstable one, which, if somehow formed, would spontaneously exude pure solvent until the concentration in the gel increased to  $v_{2m}$ , at which the activity equals unity. The swollen gel would then be in equilibrium with the surrounding pure solvent. Hence,  $v_{2m}$ , defined as the concentration ( $> 0$ ) at which the activity of the solvent is unity, or at which  $\mu_1 = \mu_1^0$ , represents the composition at *swelling equilibrium*. To locate this composition we equate  $\mu_1 - \mu_1^0$  of Eq. (38) to zero, obtaining thereby<sup>28</sup>

$$-[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] = \nu_1(\nu_e/V_0)(v_{2m}^{1/3} - v_{2m}/2) \quad (39)$$

or, adopting the terminology used in Chapter XI (see Eqs. XI-28 and XI-30')

$$-[\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] = (\nu_1/\bar{v}M_c)(1 - 2M_c/M)(v_{2m}^{1/3} - v_{2m}/2) \quad (39')$$

where  $M_c$  is the molecular weight per cross-linked unit and  $M$  is the primary molecular weight. The factor  $(1 - 2M_c/M)$ , it will be recalled, expresses the correction for network imperfections resulting from chain ends. For a perfect network ( $M = \infty$ ) it reduces to unity. The left-hand member in these equations represents the lowering of the chemical potential owing to mixing of polymer and solvent; that on the right gives the increase from the elastic reaction of the network. The latter corresponds to the increase  $\pi\nu_1$  in the chemical potential resulting from an osmotic pressure  $\pi$  at equilibrium.

It is customary to employ the *swelling ratio*  $q$  equal to the ratio  $V/V_0$  of the volumes of the swollen and unswollen structures. Thus,  $q = 1/v_2$ . At swelling equilibrium, we may replace  $1/v_{2m}$  by  $q_m$ , the subscript  $m$  indicating maximum, or equilibrium, swelling. At low degrees of cross-linking, i.e., at large  $M_c$  values of 10,000 or more,  $q_m$  in a good solvent will exceed ten. Then  $v_{2m}^{1/3}$  is considerably greater than  $v_{2m}/2$ , and we may as a first approximation neglect the latter com-

i.e., by conventional cross-linkages. For networks in which the junctions are  $f$ -functional, it is necessary merely to replace  $v_2/2$  in Eq. (38) with  $2v_2/f$ .<sup>28</sup>



pared with the former. To a similar approximation the higher terms in the series expansion of the left-hand member of Eq. (39) may be neglected. The swelling equilibrium equation may then be solved for  $v_{2m} = 1/q_m$  with the following result:<sup>27</sup>

$$q_m^{5/3} \cong (V_0/\nu_e)(1/2 - \chi_1)/\nu_1 \quad (40)$$

or, from Eq. (39')

$$q_m^{5/3} \cong (\bar{\nu}M_c)(1 - 2M_c/M)^{-1}(1/2 - \chi_1)/\nu_1 \quad (40')$$

These simplified relationships offer a clearer insight into the dependence of the equilibrium swelling ratio  $q_m$  on the quality of the solvent as expressed by  $\chi_1$ , and on the extent of cross-linking. Because of the nature of the approximations introduced to obtain Eqs. (40) and (40'), their use as quantitative expressions must be limited to networks of very low degrees of cross-linking in good solvents.

It has been shown in Chapter XI that the force of retraction in a stretched network structure depends also on the degree of cross-linking. It is possible therefore to eliminate the structure parameter ( $\nu_e/V_0$ ) by combining the elasticity and the swelling equations, and thus to arrive at a relationship between the equilibrium swelling ratio and the force of retraction at an extension  $\alpha$  (not to be confused with the swelling factor  $\alpha_e$ ). In this manner we obtain from Eq. (XI-44)\* and Eq. (39)

$$\tau_\alpha = -RT(\alpha - 1/\alpha^2) [\ln(1 - v_{2m}) + v_{2m} + \chi_1 v_{2m}^2] / \nu_1 (v_{2m}^{1/3} - v_{2m}/2) \quad (41)$$

where  $T$  refers to the temperature of the stress measurement. If the equilibrium swelling is very large ( $v_{2m} \ll 1$ ), we may introduce approximations corresponding to those which yielded Eq. (40). Then

$$\tau_\alpha \cong RT(\alpha - 1/\alpha^2)(1/2 - \chi_1)/\nu_1 q_m^{5/3} \quad (42)$$

This equation calls attention to the well-established inverse relationship between the degree of equilibrium swelling of a series of rubber vulcanizates in a given solvent and the forces of retraction, or "moduli," which they exhibit on stretching. The indicated approximate dependence of  $q_m$  on the inverse three-fifths power of the "modulus" has been confirmed.<sup>29,30</sup>

In using Eq. (XI-44) to derive Eq. (41), we have, in effect, accepted the former as a valid representation of the dependence of the force of retraction on the extension. Experiments cited in Chapter XI showed

\* The total volume  $V$  occurring in Eq. (XI-44) is to be identified with the present  $V_0$  inasmuch as the volume was assumed to remain constant during elastic deformation.

this theoretical relationship to be disturbingly inaccurate. The resulting quantitative limitations of Eqs. (41) and (42) must not be overlooked. Better agreement with experiment could be expected through the use of the semiempirical stress-strain relation, Eq. (XI-50), instead of Eq. (XI-44) in the derivation of Eq. (41).

**3b. Experimental Results on the Swelling of Nonionic Network Systems.**—The degree of swelling observed at equilibrium in a good solvent invariably decreases with increasing degrees of cross-linking.<sup>29,30,31,32</sup> It also decreases with increase in the primary molecular weight  $M$  as should be expected according to Eqs. (39') and (40'); as a matter of fact, quantitative proportionality between  $q_m^{5/3}$  and the network imperfection factor  $(1 - 2M_c/M)$  has been verified.<sup>29</sup> The dependence of the equilibrium swelling ratio on the network structure need not be pursued further. Instead, we shall focus the discussion on the connection between  $q_m$  and the force of retraction  $\tau$ . The relationship of the latter quantity to the network structure, as embodied in  $\nu_e/V_0$  or in  $M_c$  and  $M$ , was discussed in detail in Chapter XI. Hence the relationship between  $q_m$  and the structure is implicit in the discussion of the quantitative connection between  $q_m$  and  $\tau$ , and its separate treatment would represent an unnecessary duplication.

The results shown in Fig. 135 for a series of multilinked polyamides<sup>33</sup> illustrate the relationship between the equilibrium swelling ratio and the equilibrium force of retraction  $\tau_\alpha$  for the stretched unswollen specimen. Swelling measurements were made in *m*-cresol at 30°C; and the forces of retraction were measured on the unswollen polymers at 241°C at the several extension ratios  $\alpha = 1.4, 2.0,$  and  $3.0$  as indicated. The range in the degree of cross-linking ( $\nu_e$ ) covered by these data is about sixfold. The log-log plot is suggested by the approximate Eq. (42). Although the points describe straight lines within experimental error in accordance with this relation, the negative slopes are somewhat greater than the value 5/3 it prescribes. The lines drawn actually are slightly curved, for they have been calculated from the more accurate relationship given by Eq. (41) rather than from Eq. (42).

Because of the previously mentioned inadequacy of the function  $\alpha - 1/\alpha^2$ , a different value for the parameter  $\chi_1$  is required for the set of points (Fig. 135) at each elongation  $\alpha$ . These values are  $-0.90, -0.73,$  and  $-0.56$  for  $\alpha = 1.4, 2.0,$  and  $3.0$ , respectively. If the function  $\alpha - 1/\alpha^2$  were replaced by an empirical representation of the shape of the stress-strain curve, a single value of  $\chi_1$  would suffice to represent all of the data within experimental error. This limitation of Eq. (41) relates to an unexplained feature of the stress-strain curve and is