SOME THERMODYNAMIC PROPERTIES OF HIGH POLYMERS, AND THEIR MOLECULAR INTERPRETATION

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1. *Introductory*

THE past decade has witnessed a rapid growth in the understanding of the thermodynamic properties of polymers and their solutions. This has been achieved largely by the development of statistical theories of rubber-like elasticity and of the free energy of mixing of polymers with liquids. A number of reviews are available, dealing with portions of this field of work, but for the most part they are addressed to specialist workers. The object of this Review is to survey in broad outline a number of related topics, without entering into detailed discussion of statistical theories. The emphasis will therefore be laid on the experimental thermodynamic data which form the basis for these theories, and on their physical significance. An attempt will be made to develop the argument so far as possible in physical terms, although it must be realised that this is essentially a field in which we are concerned with quantitative measurements and their mathematical inter-relations.

One fundamental experimental difficulty which is common to nearly all the problems to be discussed below is that of ensuring that the system under investigation has reached a state of equilibrium. The significance of the concept of equilibrium in measurements on polymers has recently been very clearly discussed by A. R. Ubbelohde.[1] The difficulty arises from the fact that many processes in a polymer take place so slowly that they may to a good approximation be said not to occur at all during the time involved in an experiment. When this is the case, it is clear that the system cannot be assumed to reach a state of equilibrium with respect to this particular process. It is indeed quite common to find that certain properties of a polymer are very dependent on the previous history of the specimen ; examples will be given later. Even when this is the case, the system may still be in equilibrium with respect to other possible changes, and it is therefore permissible to apply the thermodynamic criteria of equilibrium.* Care is needed in relating the experimental results to theories, in order to make sure that the theory is not based on the assumption of equilibrium with respect to changes which are in fact so slow as to be virtually negligible. The usefulness of considering partial equilibria in this

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[1] Faraday Society, General Discussion on " Swelling and Shrinking ", Sept. 1946.

* This behaviour is, of course, not confined to polymeric systems, although it is more frequent there than in systems containing only components of low molecular weight. Familiar examples are furnished by the existence of supercooled liquids in equilibrium with vapour, and the stability of mixtures of oxygen and hydrogen.

way depends on the possibility of choosing a time scale for the experimental work long enough to permit the rapid processes to be complete, and at the same time short enough to exclude other, slower, processes.

2. *Crystallisation of Polymers*

The most comprehensive study of the crystallisation of a polymer is the work on natural rubber; this has been summarised by L. A. Wood.[2] The phenomena encountered are very much more complicated than in the freezing of a liquid. Apart from the possible occurrence of supercooling, the latter is a sharp phase change occurring at a perfectly definite temperature. Crystallisation is accompanied by the evolution of the latent heat L, and a volume change $-\Delta V$. The freezing point T_c can be altered by the application of a hydrostatic pressure P, in accordance with the familiar equation :[3]

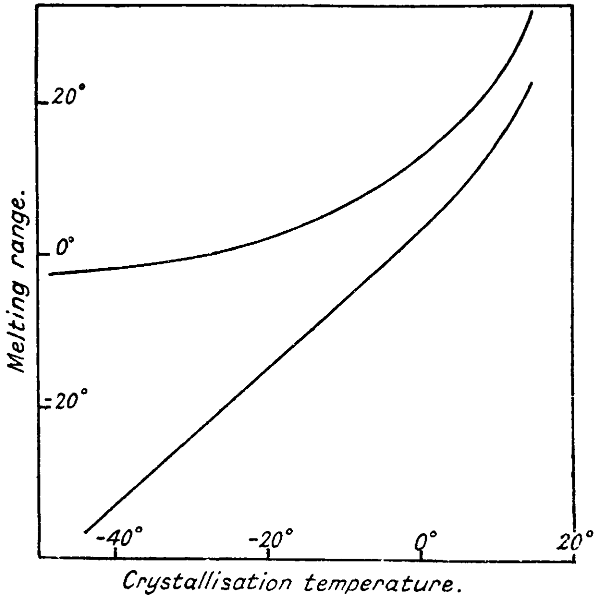

FIG. 1

Melting range of natural rubber as a function of the crystallisation temperature.

$$dT_c/dP = T\Delta V/L \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In contrast with this simple behaviour, a polymer cannot be said to have any single freezing point. The crystallisation of an amorphous polymer by cooling is very dependent on the rate of cooling. If a polymer is allowed to crystallise and then heated, melting takes place over a temperature range, and this range depends on the temperature at which crystallisation was

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[2] "Advances in Colloid Science", Interscience Publishers, 1946, pp. 57—93.

[3] E. A. Guggenheim, "Modern Thermodynamics", Methuen, 1933, p. 55.

carried out. Figs. 1[4] and 2[5] illustrate some of the resulting complexities in the melting of crystalline natural rubber. Fig. 1 shows that after crystallisation at a given temperature, it is necessary to raise the temperature by some 5° in order to cause melting to start, and by as much as 20—30° to complete it. It must be emphasised that a time factor is involved in the data thus represented. It is clear from Fig. 1 that crystallisation is possible within the temperature range in which melting occurs, and it is only possible to obtain such data because melting is a much faster process than crystallisation. If crystallisation is carried out at — 30° and the temperature then raised to 0°, the crystals will melt, but further crystallisation will then slowly occur, producing crystals which do not melt completely until the temperature is raised to 15°. Another possibility implicit in Fig. 1 is the co-existence of two sets of crystals having different melting ranges. This possibility has been verified experimentally as shown in Fig. 2. A sample of " stark " rubber which had crystallised slowly at room temperature had a melting range of 32—39°. A sample was allowed to crystallise further at 2°; on warming, the crystals were found to melt in two discrete ranges, between 5° and 15°, and then between 32° and 39°.

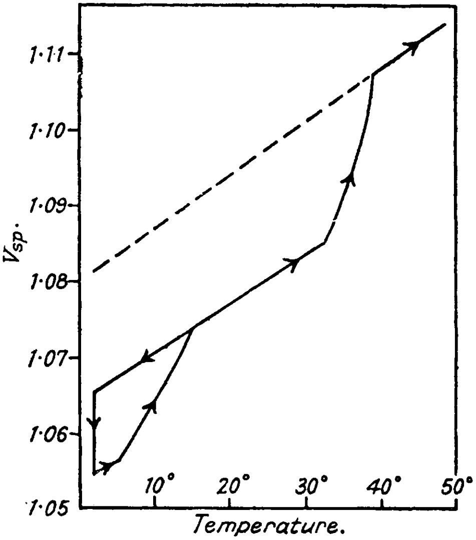

FIG. 2

Double melting range in the melting of the sample of " stark " rubber. Arrows indicate the direction of temperature changes. V_{sp}. *is the specific volume.*

The phenomena observed in the melting of polythene are much simpler, and provided that measurements be made slowly, a reversible volume-temperature relation is found,[6] as shown in Fig. 3. The three curves refer

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[4] From the data of N. Bekkedahl and L. A. Wood, *J. Chem. Physics*, 1941, **9**, 193.

[5] From the data of L. A. Wood, *op. cit.*, ref. 2, p. 70.

[6] E. Hunter and W. B. Oakes, *Trans. Faraday Soc.*, 1945, **41**, 49.

to three different samples of polythene, and it will be noted that, although there is a sharp break at the point where crystals first appear on cooling the amorphous material, the volume does not change discontinuously at this point. The interpretation placed on the region in which an abnormally large coefficient of expansion is observed is that it is a range in which the degree of crystallisation varies continuously with the temperature. Similar behaviour is shown by the heat content,[7] and R. B. Richards [8] has estimated from these data the fraction θ in the amorphous state, as shown in Fig. 4.

It will be noted from Fig. 4 that crystallisation is never complete, an observation which is readily understood in terms of the molecular picture of the crystallisation of a polymer. The individual crystallite is shown by X-ray evidence to be small, of the order of 200—500 A. side in the case of stretched natural rubber.[9] It follows that the units from which the crystallites are built are almost certainly not whole molecules, but portions of molecules, and that a single molecule may pass through several crystallites, as indicated in Fig. 5.[10] It is clear that if crystallisation commences from a number of points simultaneously, growth from these centres must leave amorphous regions which cannot be incorporated into crystals without a very large-scale reorganisation involving the temporary melting of many crystallites. Such a process would be so slow as to be quite negligible.

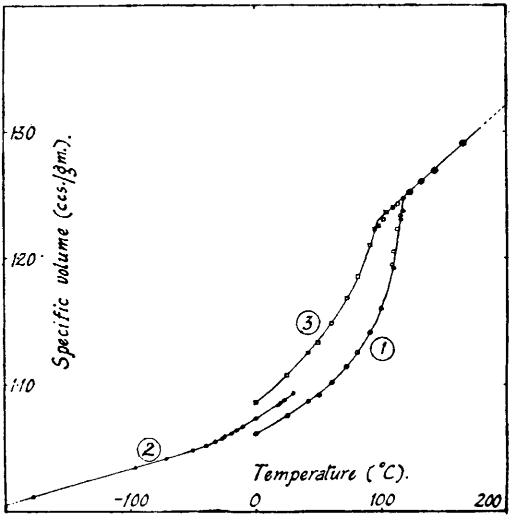

FIG. 3

Volume–temperature curves for three samples of polythene.

(*Reproduced by permission from* Transactions of the Faraday Society, 1945, **41**, 51.)

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[7] H. C. Raine, R. B. Richards, and H. Ryder, *ibid.*, p. 57. [8] *Ibid.*, p. 127.

[9] J. Hengstenberg and H. Mark, *Z. Krist.*, 1928, **69**, 271 ; S. D. Gehman and J. E. Field, *Ind. Eng. Chem.*, 1940, **32**, 1401.

[10] L. R. G. Treloar, *Rep. Prog. Physics*, 1943, **9**, 118.

In considering how to apply thermodynamic methods to the crystallisation of polymers two different problems are involved. The first is that of the equilibrium of an individual crystallite in its own environment. There is no difficulty in writing down equations, analogous to (1), for the effect of the various stresses which may be imposed on the crystallite by its environment, and it is evident that when the material is in a steady state at a fixed temperature, each individual crystallite must be in equilibrium with the stresses on it. A qualitative development of this idea provides

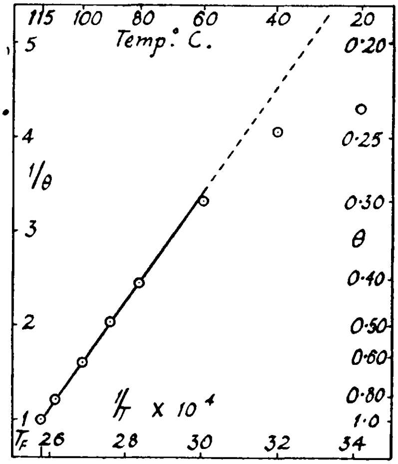

Fig. 4

Crystallinity of polythene as a function of temperature.

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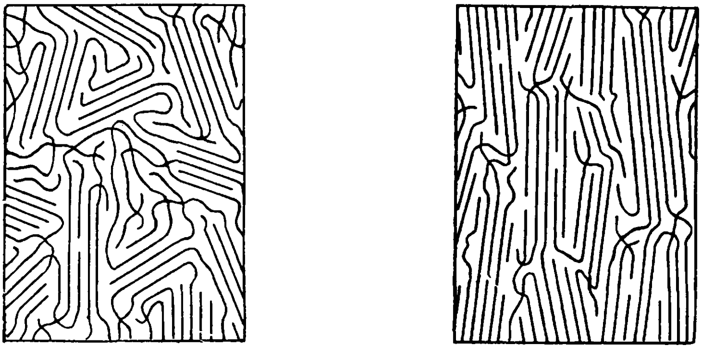

(*a*) (*b*)

Fig. 5

Molecular structure of a crystalline polymer : (a) *unstretched,* (b) *stretched.*

(*Reproduced by permission from* Reports of Progress in Physics, 1942—43, **9**, 118.)

a ready explanation of the phenomena which have been described above. If a polymer is cooled quickly to a temperature at which crystallisation is possible, a number of crystallites will start to grow at points where chains are suitably oriented. Growth will then take place by the incorporation of neighbouring chains, but these can only be brought into suitable positions by the slow process of diffusion. The high viscosity of the polymer and the mechanical entanglement of the chains retard growth, not only by the slowness of diffusion, but also by setting up stresses which are only slowly relieved. At any stage of the growth, therefore, the crystallite is *nearly* in equilibrium with its environment to any *rapid* change of temperature. Hence, if, at any stage in the crystallisation, the temperature is raised a few degrees (rapidly) the crystallite will start to melt under the influence of the existing stresses. Furthermore, since melting involves no bulk transport of matter, it is a rapid process, and a considerable rise of temperature, assisted by the stresses in the environment, may therefore cause complete melting, even at a temperature at which crystallisation is still possible. This is believed to provide an acceptable explanation of the phenomena represented in Figs. 1 and 2, and of the very striking fact[11] that the melting range shown in Fig. 1 is independent of the extent of crystallisation. The fact that such phenomena have not been reported for polythene is to be ascribed to the higher temperatures involved and the lower viscosity of the material; the whole time scale is therefore greatly contracted, and the stresses in the individual crystallites due to the surrounding amorphous region decay in times comparable with the period of observation. In these circumstances the individual crystallites will grow until they begin to interfere with one another's growth. Thermodynamically this is represented by a system of stresses between the crystallites; incorporation of more amorphous material into the crystallites involves an increase in these stresses and lowers the melting point.[12] An approximate quantitative treatment of this problem has been attempted by E. M. Frith and R. F. Tuckett [13] and by R. B. Richards.[8] The basis of the treatment is the assumption that on the average each chain is partly in an amorphous region and partly in a crystalline region. Growth of the crystallites restricts the freedom of the amorphous portions, and thus diminishes the configurational entropy of the system.* It is found possible in this way to account semi-quantitatively for the melting range of polythene shown in Fig. 4. It is clear from the foregoing argument that this theory should not be applied to the melting of natural rubber, where the equilibrium assumed in the theory is not attained experimentally.

The second thermodynamic problem involved in the crystallisation of polymers is the inter-relation of such quantities as can be measured experimentally. In this case we are not concerned with individual crystallites or stresses within the material, but simply with observations made on the

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[11] *Op. cit.*, ref. 2, p. 66.

[12] T. Alfrey and H. Mark, *Rubber Chem. Tech.*, 1941, **14**, 525.

[13] *Trans. Faraday Soc.*, 1944, **40**, 251.

* Compare § 5.

polymer in bulk. Although only a limited equilibrium condition is achieved, measurements of the changes of volume and heat capacity accompanying crystallisation under specified conditions do refer to definite thermodynamic processes, even though it may not be possible physically to describe precisely what these are. As an illustration we may consider the application of equation (1) to the crystallisation of natural rubber. The melting point * of a sample of stark rubber was found [14] to be increased by pressure according to the equation

$$\log_{10}(p + 1300) = 5{\cdot}9428 - 875/T$$

where p is the pressure in bars. Putting $p = 1$, we find $T = 311$ and $dT/dP = 0{\cdot}037$ deg./bar. The latent heat of fusion L of a different sample of stark rubber having a melting point of 284° K. was estimated [15] to be 4·0 cals./g. = 167 bars c.c./g. Equation (1) then gives for the expansion on melting

$$\Delta V = 167 \times 0{\cdot}037/284 = 0{\cdot}022 \text{ c.c./g.}$$

This is in accord with the values found experimentally for similar samples of rubber.[10] Thus the overall process of crystallisation can be treated thermodynamically as if it were a simple phase change, ignoring the physical complexities of the process.

3. *Transitions of the Second Order*

If the volume or heat capacity of a polymer is plotted as a function of temperature, there may or may not be a region in which occurs a phase change of the type described in the previous section. Quite generally, a point is found at which the slopes of these curves change sharply, as indicated in Fig. 6. This discontinuity is described as a transition of the second order, and is characterised by sudden changes in the specific heat and the coefficient of expansion. Second-order transition temperatures for a number of polymers are listed in Table I, taken from a recent review of this subject by R. F. Boyer and R. S. Spencer.[16] This transition point is usually accompanied by a change in the physical properties of the polymer, from a brittle, glassy state below the transition temperatures to an elastic or plastic, extensible state above it. It has been generally considered that above this temperature certain new degrees of freedom become effective, and indeed it would seem that this must be true.

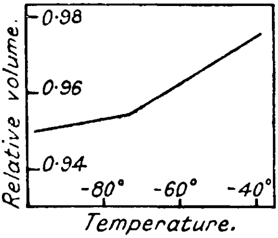

FIG. 6

Volume-temperature relation for amorphous natural rubber in the neighbourhood of the second-order transition.

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[14] L. A. Wood, N. Bekkedahl, and R. E. Gibson, *J. Chem. Physics*, 1945, **13**, 475.

[15] N. Bekkedahl and H. Matheson, *J. Res. Nat. Bur. Stand.*, 1934, **13**, 411 ; 1935, **15**, 503.

[16] *Op. cit.*, ref. 2, pp. 1—55.

* The temperature at which melting was complete.

TABLE I

Second-order transition points for some hydrocarbon polymers

Material.	Temp.	Material.	Temp.
Poly*iso*butylene . . .	− 74°	Polystyrene	81°
Natural rubber . . .	− 73	Polyindene	85
GR-S rubber	− 61		

Recently, doubt has been thrown on the validity of considering this transition as a thermodynamic singularity. It has been shown [17] that the transition temperature of polystyrene can be very greatly lowered by allowing more time for the attainment of equilibrium in studying the effect of temperature on volume. When the temperature is lowered, say, from 80° to 75° a rapid contraction occurs, apparently complete within the time required for thermal equilibrium, giving a thermal expansivity of *ca.* $2{\cdot}7 \times 10^{-4}$ deg.$^{-1}$. If the temperature is maintained at 75° for several hours a further slow contraction occurs, the final volume change giving a thermal expansivity of *ca.* $4{\cdot}5 \times 10^{-4}$ deg.$^{-1}$, equal to the value found above the transition point. In other words, by reducing the rate of cooling, the transition point can be lowered from 81° to below 75°. By proceeding sufficiently slowly, R. S. Spencer and R. F. Boyer [17] were able to reach a temperature of 20° without encountering a transition point. Similar observations have been recorded for a number of other polymers, and these authors have therefore concluded that the transition points are not true thermodynamic singularities at all. The Reviewer considers this to be a misleading conclusion. It is obvious that the transition is very dependent on the rate of measurement, but as we have seen, the existence of processes slow compared with the time of an experiment does not preclude the application of thermodynamic reasoning to the limited equilibrium attained under these conditions. Exactly the same considerations apply here ; at a specified rate of heating there is clearly an abrupt change in the mechanism of expansion at a certain temperature, or at any rate within a small temperature range. This temperature can quite properly be regarded as a thermodynamic singularity, in spite of its dependence on rate. As an illustration of the usefulness of this method of approach, consider the effect of pressure on the transition temperature. Equation (1) is not directly applicable to this problem, since ΔV and L are both zero. In order to evaluate the ratio $\Delta V/L$, suppose the transition from one state to the other to occur at a temperature ΔT above the equilibrium transition point. ΔV would then be given by $V.\Delta\alpha.\Delta T$, where V is the molar volume of the material and $\Delta\alpha$ the difference in expansivities above and below the transition. Similarly, the latent heat of the transition would no longer be zero but $\Delta C_p.\Delta T$, where ΔC_p is the difference in the specific heats above and below the transition. Combining these, we have

$$\Delta V/L = V\Delta\alpha/\Delta C_p \quad . \quad . \quad . \quad . \quad . \quad (2)$$

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[17] *J. Appl. Physics*, 1946, **17**, 398.

Since this is independent of ΔT, it will also be true at the transition point. Hence, from (1)

$$\partial T/\partial P = TV.\Delta\alpha/\Delta C_p \qquad . \quad . \quad . \quad . \quad (3)$$

This equation has been used by W. H. Keesom [18] in discussing the second-order transition between helium I and helium II; it does not appear to have been applied to polymers. A. H. Scott [19] found that the transition point of a sulphur vulcanisate of natural rubber containing 19·5% of combined sulphur was increased from 36° to 45° by applying a pressure of 800 bars. Thus for this material $\partial T/\partial P = 0{\cdot}011$ deg./bar. Values of $\Delta\alpha$ and ΔC_p for rubber hydrocarbon can be obtained from the data of N. Bekkedahl and of Bekkedahl and H. Matheson.[15] These give

$$V.\Delta\alpha = 0{\cdot}0004 \text{ c.c./g. deg.}; \quad \Delta C_p = 5 \text{ bars c.c./g. deg.}$$

Hence $\partial T/\partial P = 200 \times 0{\cdot}0004/5 = 0{\cdot}016$ deg./bar. This is of the same order as the value found by Scott for the vulcanisate.

4. *Rubber-like Elasticity*

It is a simple matter to extend the usual discussions of the thermodynamic properties of a material to take account of the work done on the body when a force is applied to it.[20] In general, experiments on the elastic extension of materials are carried out isothermally and at atmospheric pressure; in these circumstances, the force f required to produce a simple extension of the length l is related to the Gibbs free energy of the material as follows:

$$f = \left(\frac{\partial G}{\partial l}\right)_{T,P} \qquad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This increase in the Gibbs free energy which occurs on stretching can be divided in the usual way into changes in heat content (H) and entropy (S). To do this it is necessary to study the effect of temperature on the force required to maintain a fixed length l. We then have

$$\left(\frac{\partial S}{\partial l}\right)_{P,T} = -\left(\frac{\partial f}{\partial T}\right)_{P,l} \qquad . \quad . \quad . \quad . \quad (5)$$

$$\left(\frac{\partial E}{\partial l}\right)_{P,T} \simeq \left(\frac{\partial H}{\partial l}\right)_{P,T} = f - T\left(\frac{\partial f}{\partial T}\right)_{P,l} \qquad . \quad . \quad . \quad . \quad (6)$$

To a very good approximation for materials in a condensed phase, changes of heat content during processes at normal pressures may be equated to the corresponding changes of internal energy (E); this approximation will be made throughout the following discussion.

Equations (4), (5), and (6) are perfectly general and apply to any elastic material. Very different values are, however, found when these equations are applied on the one hand to metals, and on the other to rubber-like polymers.

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[18] Leiden Communications, Supplement 80*b*; cf. J. K. Roberts, " Heat and Thermodynamics ", 1940, p. 331.

[19] *J. Res. Nat. Bur. Stand.*, 1935, **14**, 99.

[20] G. Gee, *Trans. Faraday Soc.*, 1946, **42**, 585.

Some typical data are plotted in Fig. 7 [21] for steel and in Figs. 8 [20] * and 9 [22] for pure gum vulcanisates of natural rubber, using as variable, not the length l, but the extension ratio α, equal to l/l_0, where l_0 is the unstretched length. Comparing the two figures, a number of striking differences are apparent: (1) The great difference of extensibility, *viz.*, *ca.* 1% for steel up to 1000% for rubber. (2) The very much larger modulus of elasticity of steel (*ca.* 10^5 times larger than for a typical rubber). (3) The relative importance of the entropy and energy contributions. The extension of steel is accompanied by a considerable increase of entropy, the rate of increase being practically constant, and the force may be said to be due in the main to the increase of internal energy. Sufficiently small exten-

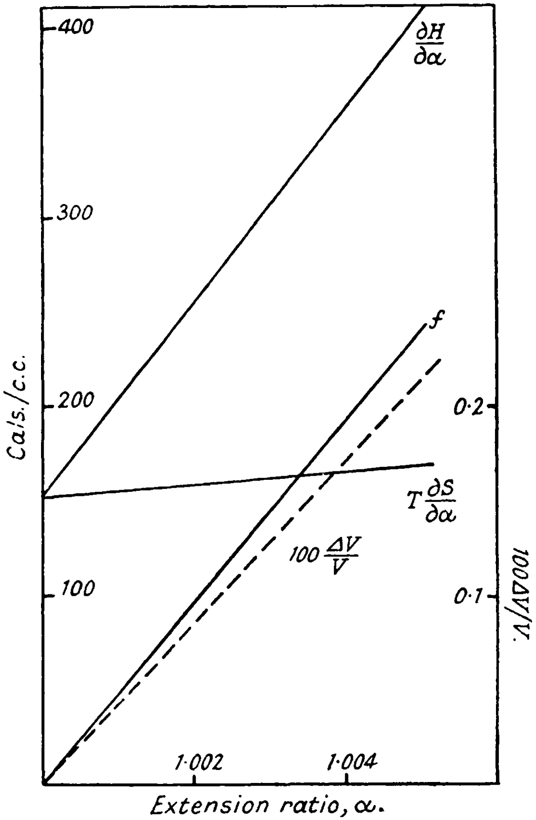

FIG. 7

Thermodynamics of the elastic extension of steel.

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[21] Data from " Physical and Chemical Constants " (G. W. C. Kaye and T. H. Laby), Longmans, 1935, pp. 29 and 30.

[22] L. A. Wood and F. L. Roth, *J. Appl. Physics*, 1944, **15**, 781.

* A numerical slip in the original has been corrected.

sions of natural rubber also involve increases of both entropy and internal energy, but at larger extensions the contribution of internal-energy changes to the force becomes relatively unimportant. Over most of the extension range, the entropy of extension is negative, and makes the major contribution to the observed force. (4) The extension of steel is accompanied by a considerable bulk expansion (ΔV),[*] reflected in its low Poisson's ratio. Small elongations of natural rubber take place with only very small volume

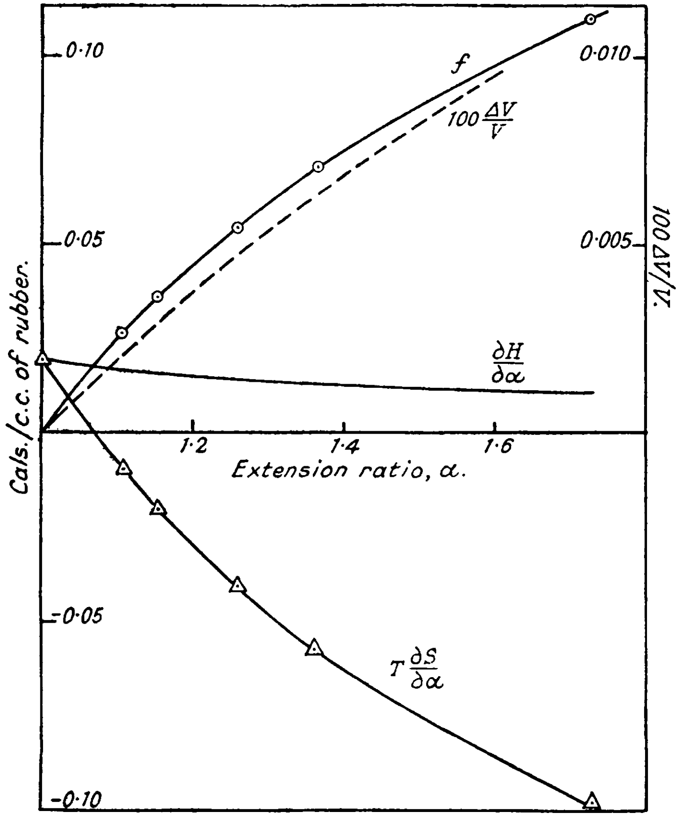

FIG. 8

Thermodynamics of the elastic extension of rubber.

changes (increase) but at large extensions there is a considerable bulk contraction.

Taking these observations in this order, we shall now consider what qualitative conclusions can be drawn as to the molecular mechanisms involved. It is clear in the first place, from the very high extensibility and low modulus of elasticity, that the processes involved in the deformation

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[*] Note that ΔV is the *total* expansion ; the other quantities in Figs. 7—9 are all differentials.

of rubber-like polymers differ fundamentally from those operative in metals. In the latter, extension involves essentially the separation of atoms without change of their relative positions ; the possible movement is small, and the opposing forces large. The large deformations possible in rubber-like materials must necessarily involve considerable relative movements of molecules, and the forces applied are too small to produce appreciable changes of interatomic or intermolecular distances.

The most striking thermodynamic feature of the extension of rubber is the large decrease of entropy which occurs over a wide range of deformation. This has been interpreted in terms of the decreased freedom of the individual molecules. Rubber-like polymers are essentially linear in structure, and their molecules possess a high measure of flexibility. In general, most or all of the links in the chain are single C–C bonds about which rotation can occur more or less freely. As a result, the chain takes up a series of ever-changing configurations. Of all these configurations, only one will give the chain its maximum outstretched length, whereas in most configurations the chain will be extensively kinked, with its ends much closer together. The overall shape and length (*i.e.*, end-to-end distance) of any individual molecule will tend to change randomly, but it is evident that a molecule must have some statistically most probable length. In a piece of rubber, the molecules are not altogether free, their motions being restricted by the presence of neighbouring chains to which they are held by van der Waals forces. Vulcanised rubbers possess in addition a number of cross links, where molecules are joined chemically. Qualitatively, these restrictions do not affect the essential features of the picture. In the undeformed rubber, the molecules will tend to be highly kinked ; extension of the rubber will involve a net straightening of molecules, which are thus constrained to take up less probable configurations. It is this process which accounts for the observed decrease in entropy on extension.

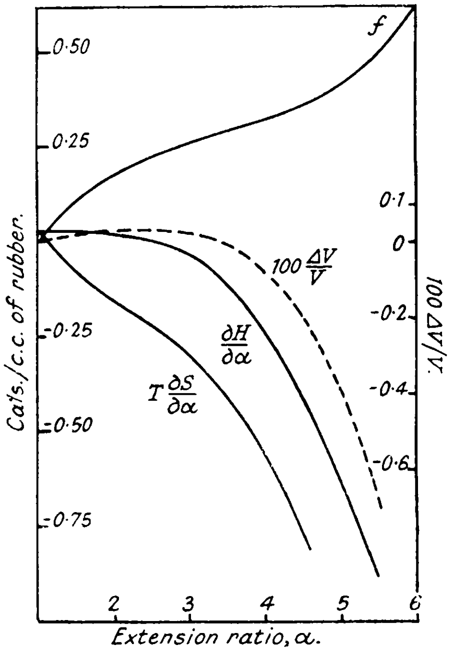

FIG. 9

Thermodynamics of the elastic extension of rubber.

The expansion of a material when stretched is a normal feature of the elastic behaviour of all isotropic materials. Its origin may be understood physically by considering the applied force as made up of two shears and a hydrostatic tension. So long as the material is isotropic, the effect of a tensile force is the same as that of two shear stresses which change the shape of the material without affecting its volume, and a hydrostatic tension which causes the material to expand.[23] The hydrostatic component is equal in magnitude to one-third of the tensile stress. Hence if Y is the Young's modulus of the material $[= (\partial f/\partial l)_{P,T}]$ and K its compressibility $[= -(\partial V/\partial P)_T/V]$ the relative expansion $\Delta V/V$ produced by a small extension (in the ratio α) is given by

$$\Delta V/V = \tfrac{1}{3}YK(\alpha - 1) \quad . \quad . \quad . \quad . \quad (7)$$

In terms of the Poisson's ratio σ we have the familiar expression

$$2\sigma = 1 - \tfrac{1}{3}YK \quad . \quad . \quad . \quad . \quad . \quad (8)$$

The very small expansions accompanying the extension of rubber ($\sigma \approx 0{\cdot}4999$) are thus directly related to its low Young's modulus.

The contraction observed at larger elongations is evidence that the material is no longer isotropic. The large contraction observed in natural rubber at elongations greater than about 300% arises from crystallisation, and may indeed be employed as a relative measure of the extent of crystallisation.[10]

In these volume changes, the packing of the molecules is changed, and work is done by or against the intermolecular forces. Consequently, changes occur in the entropy and internal energy of the material, an expansion being accompanied by increases of both quantities. The effects of these changes on the free energy nearly cancel, thus leaving the force required to stretch the rubber almost the same as it would have been had the volume been maintained constant by applying a hydrostatic pressure.[20] To a first approximation, the increase of internal energy on stretching produced in this way will be equal to the increase resulting from the application to the unstretched material of a hydrostatic tension sufficient to produce the same expansion. This will be strictly true for small elongations of any isotropic material. Now this quantity can be calculated thermodynamically, and it can thence be shown that

$$\left(\frac{\partial E}{\partial l}\right)_{P,T,f=0} \approx \left(\frac{\partial H}{\partial l}\right)_{P,T,f=0} = \tfrac{1}{3}Y\beta T \quad . \quad . \quad . \quad (9)$$

where β is the coefficient of cubical expansion. This is a perfectly general relationship, holding, *e.g.*, both for steel (Fig. 7) and for natural rubber (Fig. 8). Two consequences may be noted : (*a*) Experimental data *on an isotropic material* which do not agree with equation (9) must necessarily be wrong. (*b*) The observed increase of energy and entropy for *small* extensions of rubber are completely unrelated to the mechanism of deformation.

K. H. Meyer and A. J. van der Wyk [24] have recently pointed out that measurements of the shear modulus of rubber are free from the complications arising from these volume changes, since a shear stress has no hydro-

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[23] A. E. H. Love, " The Mathematical Theory of Elasticity ", Cambridge, 1934, p. 83.

[24] *Helv. Chim. Acta*, 1946, **29**, 1842.

static component. It is indeed easy to show that if ω is the amount of shear, then for any isotropic body

$$(\partial H/\partial \omega)_{P,T,f\to 0} = 0 \qquad . \quad . \quad . \quad . \quad . \quad (10)$$

5. *The Elasticity of an Ideal Network*

The main conclusion from the thermodynamic data of Figs. 8 and 9 is that the restoring force in a stretched rubber arises from the decreased entropy associated with the straightening out of the randomly-kinked molecules. Several attempts have been made to calculate the force by applying the methods of statistical mechanics to an idealised model of the system.[25] To do this, it is necessary to compute the number of configurations g_0 of the system before stretching and the reduced number g_1 after stretching. The deformation being assumed to take place without change of volume or internal energy, the entropy increase ΔS_{d} is then given, by the application of Boltzmann's equation, by

$$\Delta S_{\text{d}} = \boldsymbol{k} \ln (g_1/g_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The model employed in all the treatments published hitherto represents the molecule by a series of equal links, joined end to end and oriented at random. No account is taken of the volume of the links, and impossible configurations in which two links occupy the same position in space are not excluded from the computation. These chains are linked together at a number of points so as to constitute a three-dimensional network, in which the length of a segment, *i.e.*, the distance measured along a chain from any junction point to the next, is constant. For not too large extensions, the force per unit area of the unstrained rubber at an extension ratio α is given by an expression of the form

$$f = B(\alpha - 1/\alpha^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

More generally, the work W done in deforming a unit cube to a block of sides λ_1, λ_2, λ_3 (where $\lambda_1\lambda_2\lambda_3 = 1$) is found to be

$$W = \tfrac{1}{2}B(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The quantity B has been variously estimated: we shall adopt here the value given by F. T. Wall,[25] which may be put in the alternative forms

$$B = N\boldsymbol{k}T = \rho \boldsymbol{R}T/M_c \qquad . \quad . \quad . \quad . \quad . \quad (14)$$

where N is the number of chain segments, M_c is the " molecular weight " of a segment, and ρ is the density of the rubber. Equations (12) and (13) are valid only for small deformations; if any of the chains approach their fully stretched-out length, (12) must be replaced by a more complex expression, due to Guth and James,[25] which may be written

$$f = \tfrac{1}{3}B\alpha_0 \left\{ \mathrm{L}^{-1}\left(\frac{\alpha}{\alpha_0}\right) - \alpha^{-3/2}\mathrm{L}^{-1}\left(\frac{\alpha^{-1/2}}{\alpha_0}\right) \right\} \quad . \quad . \quad . \quad (15)$$

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[25] A systematic treatment, with brief reference to the contributions made by other workers, is given by E. Guth, H. M. James, and H. Mark, *op. cit.*, ref. 2, pp. 253—298; cf. also L. R. G. Treloar, *Trans. Faraday Soc.*, 1945, **41,** 83.

where α_0 is the limiting extensibility of the network, and L^{-1} denotes the inverse Langevin function, defined by

$$L(x) = \coth x - \frac{1}{x} = y \qquad . \quad . \quad . \quad . \quad . \ (16)$$

$$L^{-1}(y) = x \qquad . \quad . \quad . \quad . \quad . \quad . \ (17)$$

It will be noted that equations (13) and (14) define the entire elastic behaviour of a rubber at not too large deformation in terms of a single molecular parameter, which measures the extent to which the rubber is cross-linked. To take account of large deformations, it is necessary to introduce, as a second parameter, the ultimate extensibility. L. R. G. Treloar [25] has related this also to the degree of cross-linking, thus leaving only one adjustable parameter available to fit the whole stress–strain curve.

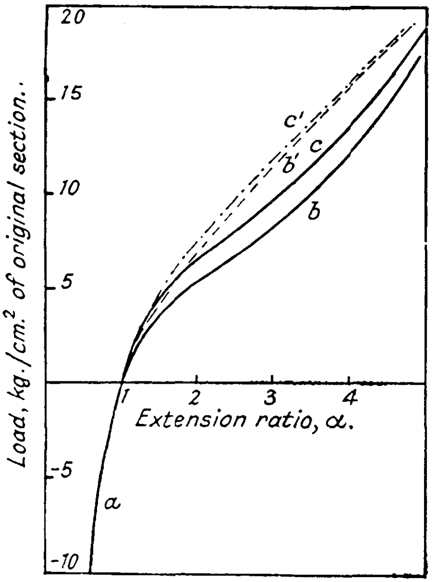

Fig. 10

Stress–strain data for natural rubber vulcanisates in (a) *compression,* (b) *simple elongation,* (c) *shear. Broken curves calculated.*

These theoretical stress–strain curves may be compared with experiment in a variety of ways. L. R. G. Treloar [26] has examined the validity of the form of equation (13) by measuring, on a single specimen of rubber, stress–strain curves in (1) elongation, (2) compression, (3) shear, and (4) a combination of (1) and (3). Some of his results are shown in Fig. 10; the most striking feature of them is the way in which a single parameter describes the elastic behaviour in four different types of measurement. The agreement between theory and experiment is not quantitatively accurate, but the Reviewer has shown [20] that a considerably closer fit is obtained if experiments are carried out on rubber highly swollen with a liquid. The elastic behaviour can be more accurately described by the two-constant equation deduced by H. Mooney [27] on more general mathematical grounds, not involving any molecular model.

Equation (15) leads to a stress–strain curve in qualitative agreement with Fig. 9, f becoming infinite at $\alpha = \alpha_0$. By treating α_0 as an adjustable parameter, the stress–strain curve of a pure gum natural rubber has been reproduced almost exactly up to 400% elongation.[28] The value of α_0

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[26] *Ibid.*, 1943, **39,** 59.

[27] *J. Appl. Physics*, 1940, **11,** 582; R. Rivlin, *ibid.*, 1947, **18,** 444; L. R. G. Treloar, *Proc. Physical Soc.*, in the press.

[28] H. M. James and E. Guth, *J. Chem. Physics*, 1943, **11,** 455.

required is, however, considerably less than that calculated by L. R. G. Treloar from the degree of cross-linking.[25] As we shall see below, the form of the curve at high elongations is in any case highly dependent on crystallisation; equation (15) would not be applicable in such circumstances.

The final test to be applied concerns the significance of the degree of cross-linking. K. H. Meyer and A. J. Van der Wyk [29] have recently argued that the elastic behaviour of rubber is not determined by cross-linking, as equation (14) requires, but their data, obtained by applying very small deformations for short times, hardly seem to constitute an appropriate test. P. J. Flory [30] has shown that the values of M_c deduced from the elastic behaviour of a series of butyl rubber vulcanisates are in satisfactory agreement with values deduced from their solubility. A similar conclusion has been reached by the Reviewer [31] by comparing M_c with the amount of sulphur combined in a series of sulphur vulcanisates of natural rubber.

The statistical theory of an ideal network thus appears to give a very satisfactory semi-quantitative account of the equilibrium elastic behaviour of real rubbers, relating the elastic moduli to a definite molecular property of the rubber.

6. *Crystallisation of Stretched Polymers*

The crystallisation of polymers on stretching presents two thermodynamic problems: (*a*) the effect of a tension on the melting point of a polymer and (*b*) the effect of crystallisation on its elastic behaviour. The first is closely analogous to the effect of a hydrostatic pressure, already discussed in § 2. It may be shown [32] that the effect of a tension f is given by

$$\left(\frac{\partial T}{\partial f}\right)_P = \frac{T.\Delta l}{L_f + f.\Delta l} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

where Δl is the increase in length of a specimen (held under constant tension, temperature, and pressure) consequent upon the occurrence of a small amount of crystallisation, and L_f is the latent heat of fusion of this same amount of crystalline polymer. There do not appear to be any data available for comparison with this equation, but a very simple argument shows that Δl must be positive. If we consider an amorphous polymer held at constant length, crystallisation will only occur if the Gibbs free energy is thereby reduced. Since the tension f is equal to $\partial G/\partial l$, it follows that f must be reduced by any spontaneous process. The reduction of tension on slow crystallisation is, in fact, a well-known phenomenon; under certain conditions, f may actually fall below zero, as shown by a tendency for the material to become bowed.[33] With the experiment in mind, it is easily seen that probable values of Δl and L_f may well make $\partial T/\partial f$ of the order of 1 deg./kg. for a specimen of 1 cm.^{2} cross-section. This is consistent with the observation that natural rubber can be made to crystallise by stretching, even at temperatures nearly 100° above its normal melting

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[29] *J. Polymer Science*, 1946, **1**, 49.

[30] *Ind. Eng. Chem.*, 1946, **38**, 417.

[31] *J. Polymer Science*, in the press.

[32] G. Gee, unpublished work.

[33] W. L. Holt and A. T. McPherson, *Rubber Chem. Tech.*, 1937, **10**, 412.

point.[34] The molecular explanation of this rise of melting point on stretching is, of course, to be found in the improved alignment thus produced.

The effect of crystallisation on the elastic behaviour of a polymer is complex. We have already noted that crystallisation reduces the tension in a sample held at constant length. On the other hand, once crystallites are formed they increase the modulus of elasticity because they act effectively as cross links, surviving unchanged during further elongation of the rubber, although by their presence they prevent the rubber from taking up its most stable state. This behaviour is due, of course, to the extreme improbability of the co-operative process needed to permit the crystallites to melt and then re-form in more favourable configurations. The extension of a polymer when crystallisation is occurring is thus not an equilibrium process, and the statistical equations noted in § 5 should not be applied to it.

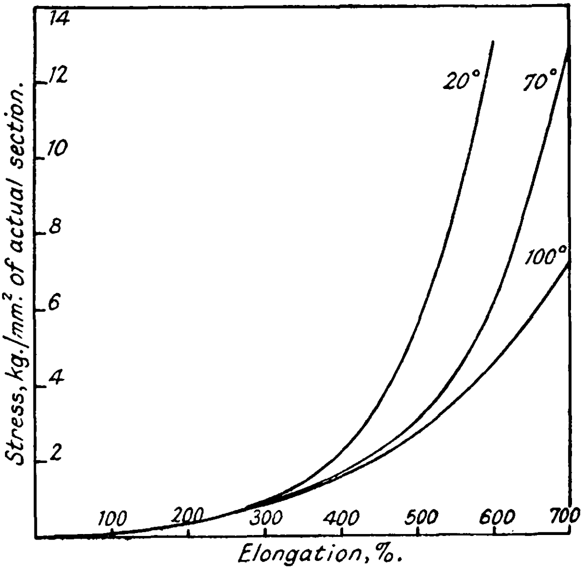

FIG. 11

Stress–strain curves for a natural rubber vulcanisate at three temperatures.

The considerations set out in the last paragraph have an important bearing on the experimental problem of studying the thermoelastic behaviour of crystallisable polymers. If a series of complete stress–strain curves are plotted at different temperatures, the elongation at which crystallisation commences increases progressively with rise of temperature, with the result that at high temperatures the polymer tends to be more highly extensible, and its stress–strain curve is generally below that found at lower temperatures ; some typical results for natural rubber [35] are given in Fig. 11. At

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[34] J. E. Field, *J. Appl. Physics*, 1941, **12**, 23.

[35] G. Gee and T. A. Sharpley, unpublished.

the same time, if the length of the specimen is fixed, while the temperature is varied, $\partial f/\partial T$ is found (at nearly any elongation) to be positive. The explanation of this discrepancy is that in comparing complete stress–strain curves measured at different temperatures, we are in effect comparing two different materials; the apparent temperature coefficient obtained from such a comparison has no thermodynamic significance.

7. *The Absorption of Vapours by Polymers*

Vapour-pressure curves of swollen polymers fall broadly into two types, represented by the data for benzene in rubber[36] and agar-agar in water,[37] illustrated in Fig. 12. The former are everywhere convex towards the vapour-pressure axis, while the latter are sigmoid, with the opposite curvature at low vapour pressures. Thermodynamically, the vapour pressure is related to the Gibbs free energy of dilution, denoted by the symbol ΔG_0. This is defined as the increase in the Gibbs free energy of the whole system when one mole of liquid is transferred from a reservoir of pure liquid to a large bulk of the swollen polymer. Alternatively, we may say that ΔG_0 is equal to the difference of chemical potential of the liquid in the swollen polymer and in the pure liquid. It may be shown[36] that for any polymer liquid system

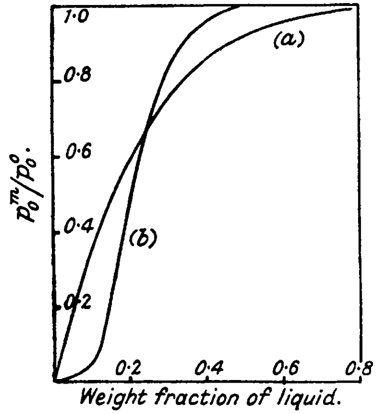

FIG. 12

Vapour pressure curves of (a) *benzene in rubber*, (b) *agar-agar in water.*

$$\Delta G_0 = RT \ln (p_0^m/p_0^0) \quad . \quad . \quad (19)$$

where p_0^m and p_0^0 are the vapour pressures of the swollen polymer and of the pure liquid. The only assumption involved in the derivation of equation (19) is that the vapour behaves as a perfect gas. This is usually a fairly good approximation, which can be corrected if necessary by replacing the vapour pressures by fugacities. No assumptions are made about the nature or structure of the polymer, and the equation is in fact valid for solutions generally.

The free energy of dilution can be separated into the heat ΔH_0 and entropy ΔS_0 of dilution, if vapour-pressure data are available at different temperatures, the necessary relationships being

$$\left.\begin{aligned} \Delta S_0 &= -(\partial \Delta G_0/\partial T)_{P,\,n_0} \\ \Delta H_0 &= \left(\partial \frac{\Delta G_0}{T} \Big/ \partial \frac{1}{T}\right)_{P,\,n_0} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (20)$$

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[36] G. Gee and L. R. G. Treloar, *Trans. Faraday Soc.*, 1942, **38**, 147; G. Gee and W. J. C. Orr, *ibid.*, 1946, **42**, 507.

[37] R. Friche and J. Lüke, *Z. Elektrochem.*, 1930, **36**, 309.

The temperature coefficients must be measured at constant *weight* composition of the swollen polymer, and it is important to note that they are frequently sufficiently small for vapour pressures to require correction for departure from perfect-gas behaviour.

When this type of analysis is applied to the data of Fig. 12, very different results are obtained, as shown in Fig. 13. The heat and entropy of dilution of rubber by benzene are both positive, and this is generally found to be the case for non-polar polymers.[38] Highly exothermic swelling is characteristic of the absorption of water by polymers in which it is appreciably soluble. These invariably contain polar groups to which water molecules could attach themselves by hydrogen bonding, and there is little doubt that this is the reason for the large heat evolution observed. In attempting a quantitative statistical treatment of the absorption of vapours, these two types of system require separate consideration.

The positive heat and entropy of dilution found for nearly all non-aqueous systems affords strong evidence that absorption results simply from the tendency of the solute molecules to diffuse into the polymer by virtue of their thermal energy. The observed entropy of dilution is thus taken to represent the increase of configurational entropy consequent upon mixing the small molecules with the large ones. Another way of looking at this is to say that the most probable way in which the available space can be occupied by the polymer and the liquid * is a random distribution of the two components. This method of approach lends itself to quantitative treatment, since it permits the use of the Boltzmann relation between the entropy and probability (W) of a state :

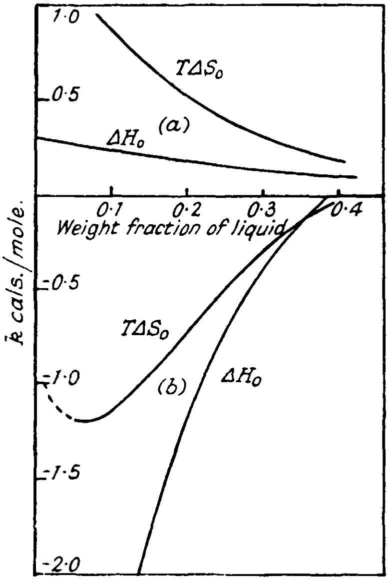

FIG. 13

Heats and entropies of dilution :
(a) *benzene in rubber ;*
(b) *agar-agar in water.*

$$S = k \ln W \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

If W_1 and W_2 are the probabilities of the random mixture and a state of complete separation, the increase of entropy ΔS on mixing is thus given by

$$\Delta S = k \ln (W_1/W_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

The problem of evaluating W_1/W_2 has been approached by considering the

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[38] G. Gee, *J.*, in the press ; *op. cit.*, ref. 2, pp. 145—195.

* The vapour molecules when dissolved in the polymer are, of course, to be considered as in the liquid state, since they are closely surrounded by neighbouring molecules, but yet able to diffuse.

solution to be arranged on a regular lattice, so defined that each molecule of liquid occupies one, or a small number of lattice points, while the polymer occupies a large number of points forming a continuous succession of nearest neighbour sites. The method has been outlined recently[38, 39] and only the simplest form of the final result will be quoted here. If the liquid molecule is sufficiently large or flexible to require several lattice points, the entropy of mixing calculated is found to be nearly independent of the particular lattice chosen. If x is the ratio between the molecular volumes of the polymer and liquid, and v_r the volume fraction of the polymer, then

$$\Delta S_0 \simeq -R\{\ln(1-v_r)+v_r(1-1/x)\} \quad . \quad . \quad . \quad (23)$$

Except in dilute solutions the term $1/x$ is generally negligible, and the equation then takes a very simple form, completely free from any molecular parameters. In other words, according to this theory, the entropy of dilution of any polymer by any liquid should be the same.

The molecular origin of the heat of mixing lies in the change of intermolecular contacts. Mixing involves the separation of polymer chains to make room for a molecule of liquid, which has to break loose from its neighbours before it is free to take up the vacant site. Once there, it is strongly held, and in general the energy of the polymer–liquid contacts does not differ widely from that of the contacts they replace. It is this which makes the problem of calculating the heat of mixing so difficult. Indeed, the existence of different kinds of intermolecular force would seem to preclude the possibility of any simple theory of general applicability. Fortunately, for nearly all but hydroxylic compounds, much the most important forces are the dispersion forces, and by neglecting all others, a very simple treatment can be given. This method was widely and successfully applied by J. H. Hildebrand[40] to liquid mixtures, and may also be used for polymer–liquid systems.[41] This treatment gives the heat of dilution in terms of the cohesive energy densities (C.E.D.) of the components. The C.E.D. is the energy needed to separate all the molecules in 1 c.c. of a substance; for a liquid it is equal to the latent heat of evaporation at constant volume (per c.c.). Denoting the C.E.D.s of liquid and polymer by e_0, e_r, the calculated heat of dilution is

$$\Delta H_0 = V_0(\sqrt{e_0}-\sqrt{e_r})^2 v_r^2 \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where V_0 is the molar volume of the liquid. The C.E.D. of the polymer is not so readily obtained. An approximate estimate can be made from the chemical structure of the polymer, but this would scarcely be sufficiently precise to use in equation (24). A method of deducing it from the swelling of a non-linked polymer has been described;[41] this is based on the assumption that equation (24) is valid, or at least that $\Delta H_0 = 0$ when $e_0 = e_r$. In general, equation (24) is not quantitatively accurate for liquid mixtures, and in most discussions of polymer–liquid mixtures, it has simply been assumed that ΔH_0 is proportional to v_r^2. By combining a term of this form

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[39] G. Gee, *Trans. Faraday Soc.*, in the press.

[40] " Solubility ", Reinhold, 1936.

[41] G. Gee, *I.R.I. Trans.*, 1943, **18**, 266.

with equation (23), M. L. Huggins [42] obtained for the free energy of dilution :

$$\Delta G_0 = RT\{\ln(1 - v_r) + v_r(1 - 1/x) + \mu v_r^2\} \quad . \quad . \quad (25)$$

Except for dilute solutions, v_r/x may be neglected, and combination of (19) and (25) gives the vapour-pressure isotherm

$$p_0^m = p_0^0(1 - v_r)\exp.(v_r + \mu v_r^2) \quad . \quad . \quad . \quad (26)$$

This equation has proved astonishingly successful in representing vapour-pressure data over a wide concentration range, with a single value of μ. Recently, however, it has been pointed out [39] that systems of limited miscibility show a systematic deviation, represented by a decrease in μ as the amount of vapour absorbed approaches the saturation value. The importance of this in the determination of two-phase equilibria will be discussed below. It should also be stressed that at least part of the success of the isotherm arises from a compensation of errors. The form of equation (24) is based on a model which requires each segment of polymer molecule in an infinitely dilute solution to be completely surrounded by solvent molecules. For polymers with flexible chains this will clearly not be true : random linking of the chain will result in many intramolecular contacts. The effect of this will be to reduce $\Delta H_0/v_r^2$ in dilute solutions ; this has been demonstrated experimentally for rubber in benzene,[36] and is believed to be a general phenomenon ; μ remains relatively unchanged because there is a compensating reduction in ΔS_0.

The above treatment is based on an assumed randomness of the solution, but the existence of a finite heat of mixing tends to favour the states of lower energy. It has been shown [43] that this effect is negligible for the heats of mixing normally encountered in relatively non-polar systems. The sorption of water by a highly polar polymer represents the other extreme of behaviour. It is now generally recognised that the first amount of water to be taken up is exothermally attached to specific polar groups,[44] the order thus imposed on the system being reflected in the negative entropy of dilution. There is still much discussion as to the mechanism of absorption of the remainder,[45] and it would be out of place in such a review as this to attempt to hold the balance between the different points of view. The various isotherms which have been deduced generally contain three adjustable parameters, and not unnaturally they can be made to fit a simple curve such as that shown in Fig. 12 very well. Some of the possible complications of the systems studied will be referred to below.

[42] *Ann. N.Y. Acad. Sci.*, 1942, **43**, 1.

[43] W. J. C. Orr, *Trans. Faraday Soc.*, 1944, **40**, 320 ; E. A. Guggenheim, *Proc. Roy. Soc.*, 1944, *A*, **183**, 203, 213.

[44] F. T. Pierce, *J. Textile Inst.*, 1929, **20**, T 133.

[45] A. B. D. Cassie, *Trans. Faraday Soc.*, 1945, **41**, 450, 458 ; " Fibrous Proteins ", Society of Dyers and Colourists, 1946, p. 96 ; P. H. Hermans, *ibid.*, p. 92 ; G. A. Gilbert, *ibid.*, p. 96 ; A. J. Hailwood and S. Horrabin, Faraday Soc. Discussion (see ref. 1).

8. *The Osmotic and Swelling Pressures of Polymer Solutions and Gels*

This problem is very intimately related to the preceding one, the osmotic or swelling pressure Π being given by

$$\Delta G_0 = -\Pi \bar{V}_0 \qquad (27)$$

where $\bar{V}_0$ is the partial molar volume of the liquid in the solution. In general, osmotic pressures are only measured in solutions sufficiently dilute to justify replacing $\ln(1 - v_r)$ in equation (25) by $-v_r - \frac{1}{2}v_r^2$. Combination with (27) gives for the osmotic pressure

$$\Pi \simeq \frac{RT}{\bar{V}_0}\left\{\frac{v_r}{x} + (\tfrac{1}{2} - \mu)v_r^2\right\} \qquad (28)$$

This equation has been widely used in interpreting osmotic data for polymer solutions,[42] but is open to criticism on the grounds that dilute solutions are not accurately described by the present theory. Attempts [46] to formulate a more precise statistical theory of dilute solutions have not yet made very much progress. For the purpose of determining the molecular weight of a polymer from osmotic data, the precise form of equation (28) is immaterial, the important conclusion being that at infinite dilution the only remaining term is the first, $\frac{RT}{\bar{V}_0}.\frac{v_r}{x}$, equivalent to the familiar van't Hoff form RTc/M, where c is the concentration and M the molecular weight of the solute. It can be shown [47] by a very general argument that this must necessarily be the case for solute particles of any size or shape. Hence the molecular weight can always be determined by extrapolating osmotic data to infinite dilution, this being most conveniently done from the approximately linear plot of Π/c against c.

9. *The Solubility of Polymers in Liquids*

The conditions for the co-existence of two condensed phases in equilibrium in a binary system of polymer + liquid may be put in the form

$$\left.\begin{aligned}\mu_0^r &= \mu_0^0\\ \mu_r^r &= \mu_r^0\end{aligned}\right\} \qquad (29)$$

where μ_0, μ_r are the chemical potentials of liquid and polymer and the indices 0, r refer to the phases which are respectively dilute and concentrated with respect to polymer. These conditions are, of course, identical with those for two phases in any binary system, but the polymer–liquid system is peculiar in that, in nearly all circumstances, one phase is experimentally indistinguishable from pure liquid; the second equilibrium condition is then meaningless and μ_0^0 is the chemical potential of the pure liquid. In these circumstances the two equations (29) may be replaced by

$$\Delta G_0 = 0 \qquad (30)$$

where ΔG_0 is the Gibbs free energy of dilution of the concentrated phase.

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[46] P. J. Flory, *J. Chem. Physics*, 1945, **13**, 453; W. J. C. Orr, *Trans. Faraday Soc.*, 1947, **43**, 12.

[47] G. Gee, *ibid.*, 1944, **40**, 261.

Thus a polymer will be completely miscible with a liquid if ΔG_0 is negative at all concentrations. This is equivalent to considering the equilibrium as an osmotic equilibrium (with $\Pi = 0$) in which the polymer is unable to enter the dilute phase. If the polymer is cross-linked, this method is precise ; for linear polymers it is adequate for most purposes. The observation which justifies this simplification means that in general a liquid is either miscible with a polymer in all proportions, or does not disperse it to any measurable extent ; [48] this behaviour is readily predictable from equation (25).

According to the theory of non-polar systems outlined in § 7, the factor tending to make ΔG_0 positive, and thus leading to separation into two phases, is a large positive ΔH_0. Equation (24) suggests that this will be found in the case of a polymer and liquid differing appreciably in C.E.D. Although this is not an invariable rule, it has proved very useful.[38] In selecting a solvent for a given polymer, the most likely choice would usually be one having a C.E.D. close to that of the polymer.

This analysis is readily extended to the solubility of polymers in mixed liquids.[49] If there are two liquids, there are three equilibrium conditions, analogous to (29), but as in the case of a single liquid, one of these may usually be omitted. The remaining two are more complicated this time, since in general the liquid absorbed by the polymer differs in composition from the liquid in equilibrium with it, and express the fact that there must be no change of Gibbs free energy on a small transfer of either liquid component from one phase to the other.

There are six types of intermolecular contact to consider in a ternary mixture, and the heat of mixing of the two liquids influences the solvent power of the mixtures very considerably. It may be shown [49] that, if this heat of mixing is large, the solvent power of the mixture will exceed that of the components separately. This behaviour seems very natural on a crude physical picture, the large heat of mixing of the components tending to drive them away from one another, which is only possible if they both mix with the polymer. The conditions for enhancement of solvent power on mixing are readily formulated in terms of the C.E.D.s of the liquid and polymer ; it is necessary that the C.E.D. of the polymer be intermediate between those of the liquids. This prediction has been verified by using it to select pairs of liquids which, though individually non-solvents for a given polymer, would dissolve it when mixed ; Table II gives some typical results.

The solubility of crystalline polymers presents some new features of interest and practical importance. The two-phase equilibrium in a saturated solution of a completely crystalline material is of a different type from that previously considered, since the solvent is absent from the solid phase. There is therefore only one equilibrium condition to be satisfied ; this may be put in the form

$$\Delta G_s = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where ΔG_s is the molar increase of Gibbs free energy accompanying the

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[48] J. N. Brønsted, *Z. physikal. Chem.*, 1931, Bodenstein Festband, p. 257.

[49] G. Gee, *Trans. Faraday Soc.*, 1944, **40**, 463, 468.

TABLE II

Solubility of GR-S *in mixed liquids*

Solvents.		Non-solvents.		Solvent mixtures.	Non-solvent mixtures.
(*a*) *n*-Hexane	55	(*d*) *n*-Pentane	50	(*d*) + (*e*)	
(*b*) Ethyl ether . . .	58	(*e*) Ethyl acetate	80	(*d*) + (*f*)	(*e*) + (*f*)
(*c*) *iso*Butyl acetate . .	69	(*f*) Methyl acetate	89		

The number following the name of each liquid is its C.E.D. ; the estimated C.E.D. of GR-S is 63 cals./c.c.

dissolution of crystalline solute in the solution. Since the dissolved material is essentially liquid, the process of solution may be considered to take place in two stages, involving, first, melting of the crystals, and then mixing of the liquid with the solvent. If the free-energy changes in these two steps are ΔG_f and ΔG_r, the former must be positive, since the crystals are stable with respect to their melt. This positive contribution to ΔG_s has to be balanced by an equal negative term ΔG_r ; if ΔG_f is large the saturated solution will therefore be dilute. For a substance of low molecular weight ΔG_f is simply related to the melting point T_f and molar latent heat of fusion L_f :

$$\Delta G_f = L_f(1 - T/T_f) \quad . \quad . \quad . \quad . \quad (32)$$

Combination of this expression with the value of ΔG_r appropriate for ideal solutions gives an equation for the solubility in terms of L_f and T_f ; this has been found very successful for relatively non-polar systems involving solutes of low molecular weight (cf. J. H. Hildebrand [40]).

When the solute is a polymer, the problem becomes much more complex, as will be evident from the discussion of crystallisation, in § 2. The polymer is never wholly crystalline, and the crystalline and amorphous regions are so intimately related structurally, that practically no molecules will be free to disperse in the liquid until almost the whole of the crystallites have melted. At this point the polymer becomes amorphous and its solubility is determined by the factors already discussed. The essential new feature to be investigated therefore is the effect of a liquid on the melting point of the polymer. R. B. Richards [8] has included this problem in the statistical mechanical treatment of crystallisation. The effect of the liquid on the crystalline–amorphous equilibrium is calculated by introducing the entropy of mixing of the liquid with the amorphous regions, using an equation equivalent to (23). The final expression for the melting point is somewhat complex, and contains three more or less adjustable constants, but it is very successful in reproducing the general effect of additions of low-molecular substances to polythene : the melting range is lower and melting becomes still more gradual.

It is well known that fractional solution or precipitation may be employed to separate heterogeneous polymers into fractions more or less homogeneous in molecular weight. The whole subject of polymer fractionation has been recently reviewed,[50] and only a few points need to be noted here. In general, fractionation is carried out by using critical mixtures of solvent and non-solvent, the molecular weight which just dissolves having been found experimentally [51] to be simply related to the fraction p of precipitant:

$$1/M = A + Bp \qquad \ldots \qquad (33)$$

An equation of this form can be derived,[52] with certain approximations, from the statistical theory outlined in § 7. The thermodynamic formulation of the two-phase equilibrium existing when a part of the polymer has been precipitated from solution is complex. Even if the distribution of molecular sizes is replaced by two species, there are four equilibrium conditions to be satisfied, one for each component of the system. In this case, since we are concerned with solutions of finite concentration, none of these is negligible.

In order to treat the problem statistically, the theory described in § 7 must be extended to the mixing of two polymers. This has been carried out by E. A. Guggenheim,[43] whose solution gives for the entropy of mixing ΔS_m of $n_i, n_j \ldots$ moles of polymer in the volume ratio $v_i, v_j \ldots$

$$\Delta S_m = -k\sum_i n_i \ln v_i \qquad \ldots \qquad (34)$$

The heat of mixing of homologous polymers may be assumed to be zero, and their heats of solution in a given liquid proportional to their molecular weights. It is thus a straightforward matter to express the thermodynamic equilibrium conditions in terms of molecular quantities, but the resulting set of simultaneous equations has not yet been solved in any complete way. In the Reviewer's opinion, it is doubtful whether the present status of the statistical theory justifies the labour involved in numerical solutions.

A rather simpler problem is presented by the mutual solubility of polymers. A. Dobry [53] has shown that, in general, if solutions of two different polymers in the *same* solvent are mixed, two phases are formed. The higher the concentration of the solutions, the more completely do the two polymers separate in the two phases. Of 35 pairs of polymers examined, only four formed single-phase systems over the whole concentration range studied. Dobry has sought to explain this behaviour in terms of complex formation, but in the Reviewer's opinion, a phenomenon of such generality must almost certainly have a simple general explanation. In fact, such an explanation is implicit in the order of magnitude of the entropy of mixing given by equation (34).

Let us consider various binary mixtures of two liquids each of molar volume 100 c.c. and two polymers each of molar volume 100,000 c.c. The

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[50] L. H. Cragg and H. Hammerschlag, *Chem. Reviews*, 1946, **39**, 79.

[51] G. V. Schulz, *Z. physikal. Chem.*, 1937, *A*, **179**, 321; R. A. Blease and R. F. Tuckett, *Trans. Faraday Soc.*, 1941, **37**, 571.

[52] G. Gee, *Ann. Reports*, 1942, **39**, 7.

[53] *J. Chim. physique*, in the press; read at Strasbourg Polymer Conference, Nov. 1946.

increases of entropy (XT) on mixing 1 c.c. of each of two components at room temperature are approximately :

(a) Two liquids	8·3 cals.
(b) Liquid + polymer	4·15 cals.
(c) Two polymers	0·0083 cal.

This entropy of mixing of two polymers is so small that even a very small positive heat of mixing would result in almost complete immiscibility. Since for most pairs of polymers ΔH_m is likely to be positive and of the same order of magnitude as for liquid mixtures,* it appears certain that most pairs of polymers will be immiscible. The high viscosity of polymers makes this very difficult to test directly with dry polymers, but Dobry's work affords convincing evidence of its truth. The presence of a common solvent for the two polymers will, of course, tend towards the formation of a single phase. The three equilibrium conditions defining the two-phase systems described by Dobry are easily formulated in terms of the statistical theory of polymer solutions, but do not appear to be explicitly soluble, and have not yet been examined numerically. It can be said with confidence that they are in qualitative agreement with the experimental observations.

10. *The Swelling of Polymers in Liquids*

This problem is of course only the limiting case of the absorption of vapours by polymers, when the vapour is saturated. Owing to its practical importance and experimental simplicity, it has been the subject of a good deal of work, and therefore merits special reference here. In this section, attention is confined to polymers which are totally insoluble in the liquid concerned, so that the equilibria to be discussed are osmotic equilibria defined by the single thermodynamic condition

$$\Delta G_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

For a linear polymer, combination of this condition with the statistical expression (25) for ΔG_0, gives (v_r/x being neglected)

$$\ln (1 - v_r) + v_r + \mu v_r^2 = 0 \quad . \quad . \quad . \quad . \quad (35)$$

It is convenient for the purpose of this section to re-write this in terms of the volume of liquid Q_m imbibed by unit volume of polymer at saturation :

$$\ln (1 + 1/Q_m) = (Q_m + 1)^{-1} + \mu(Q_m + 1)^{-2} \quad . \quad . \quad (36)$$

This has a positive solution if $\mu > 0·5$, so that a polymer–liquid combination having $\mu > 0·5$ should not be completely miscible. Doubt has recently been cast on this conclusion by some data on polystyrene in diethyl ketone and n-butyl acetate. E. C. Baughan[54] has reported that the vapour pressures of these systems give μ values of 0·67 and 0·82 respectively, yet both liquids are solvents for polystyrene. For these systems then, μ is not independent of concentration, and it will be shown below that there is evidence of similar discrepancies in the swelling of natural vulcanisates in poor swelling agents.

Despite this apparent limitation, the mean value of μ remains a most

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[54] Faraday Soc. Discussion (ref. 1).

* Cf. the argument leading up to equation (24).

useful parameter by which to characterise a polymer–liquid combination, and its evaluation, by means of equation (36), from the observed maximum swelling, offers the simplest method by which it may be estimated. We shall show below how the method may be extended to values of $\mu < 0{\cdot}5$ when cross-linked polymers are available. It is convenient to anticipate at this stage in order to describe swelling data which throw light on the factors determining μ. According to equation (24), μ would be equal to $V_0(\sqrt{e_0} - \sqrt{e_r})^2/RT$, and although this seldom holds quantitatively, there is strong evidence that this quantity exercises the controlling effect in the relative swelling of a given polymer in a range of liquids, provided the systems be chosen so as to exclude obvious specific interactions, and especially hydrogen bonding. This evidence has been reviewed recently,[38] but we may repeat here one of its most strikingly successful applications.[41] Fig. 14 shows the equilibrium swelling of five different natural rubber vulcanisates in a range of aliphatic liquids as a function of $\sqrt{V_0}(\sqrt{e_0} - \sqrt{e_r})$. The experimental points refer to the top curve, and show how different chemical types all lie nearly on a single curve ; similar agreement was found for the

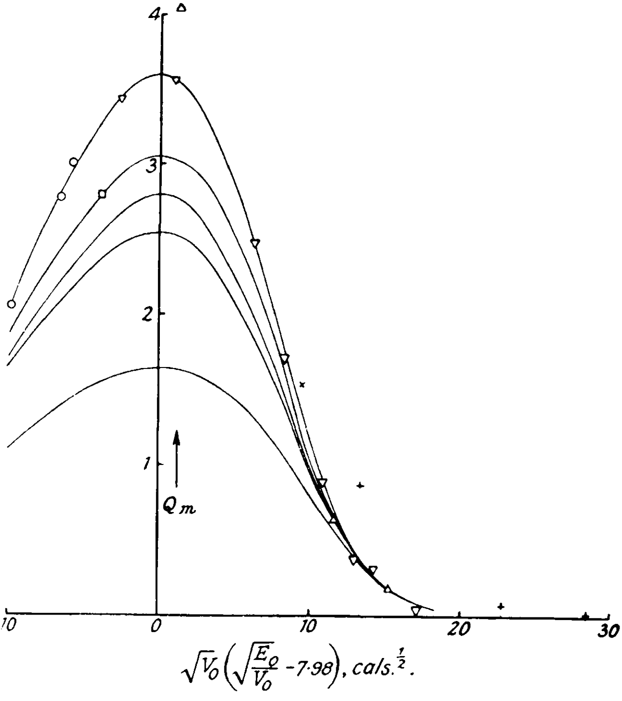

FIG. 14

Swelling of natural rubber vulcanisates in a range of aliphatic liquids.

(Hydrocarbons, ○ ; *ketones,* △ ; *esters,* ▽ ; *aldehydes,* × ; *ethers,* □ ; *nitriles,* +.)

other four vulcanisates. To fit one of these curves quantitatively, it is necessary to write empirically

$$\mu = \mu_0 + kV_0(\sqrt{e_0} - \sqrt{e_r})^2 \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where μ_0 is a constant, but k is still slightly dependent on $\sqrt{V_0}(\sqrt{e_0} - \sqrt{e_r})$. A range of aromatic liquids gave similar results, but with different k (more nearly 1). The estimation of μ values from cohesive energy densities is therefore only qualitatively successful, but within this limitation is of great use in correlating the swelling powers of a range of liquids.

The next problem to be considered is the effect of mechanical restraints on the swelling of a given polymer in a given liquid. Restraints may be either external or internal, *i.e.*, due to the structural rigidity of the material, and in general only the former can be discussed by thermodynamic methods. A linear polymer which is amorphous and not brittle behaves essentially as a liquid to continuous stresses, and cannot therefore support permanently any type of stress other than hydrostatic. A hydrostatic pressure may be applied either to the polymer only, some form of porous membrane being used to effect equilibrium with the liquid, or to both components. The former case is simply the familiar osmotic or swelling pressure, and the effect of a pressure P on ΔG_0 is given by

$$\left(\frac{\partial \Delta G_0}{\partial P}\right)_{T,Q} = \bar{V}_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

where $\bar{V}_0$, the partial molar volume of the liquid in the compressed polymer, is usually very near to the molar volume V_0 of the free liquid, at least for fairly small pressures. Thus application of an excess pressure P raises the free energy of dilution by $\bar{V}_0P$. To calculate the resulting decrease of swelling, use may be made of the mathematical identity

$$-\left(\frac{\partial Q}{\partial P}\right)_{T,\Delta G_0} = \left(\frac{\partial \Delta G_0}{\partial P}\right)_{T,Q} \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_{T,P} \quad . \quad . \quad . \quad (39)$$

whence

$$-\left(\frac{\partial Q}{\partial P}\right)_{T,\Delta G_0} = \bar{V}_0 \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_{T,P} \quad . \quad . \quad . \quad . \quad . \quad (40)$$

Here Q is the degree of swelling of the polymer ($= 1/v_r - 1$), not necessarily at saturation, and the left-hand side represents the change of swelling with pressure if the vapour pressure is kept constant. The derivation of this equation has involved no assumptions about the nature of the polymer; it is indeed equally applicable to liquids. The chemical nature and structure of the polymer will of course control the magnitude of $\partial \Delta G_0/\partial Q$ and hence also of $(\partial Q/\partial P)_{\Delta G_0}$.

If the pressure is applied to both phases, (38) has to be replaced by

$$(\partial \Delta G_0/\partial P)_{T,Q} = \bar{V}_0 - V_0 \quad . \quad . \quad . \quad . \quad . \quad (41)$$

In view of the approximate quality of $\bar{V}_0$ and V_0, the effect of a hydrostatic pressure applied both to liquid and to polymer may be in either sense, but will usually be unimportant. In aqueous systems, however, $\bar{V}_0$ is generally less than V_0, and for these a hydrostatic pressure will increase the maximum swelling.

A precisely analogous method may be employed to calculate the effect of any other applied stress on the swelling of any body capable of sustaining the stress. An example in which we shall be interested is that of a polymer constrained (by unidirectional tension or compression) to a length l in a specified direction. If f is the force required, and l_0 the unstrained length and cross-section in the dry state, it is found [39] that, at constant T and P

$$l_0\left(\frac{\partial Q}{\partial l}\right)_{\Delta G_0} = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l \quad . \quad . \quad . \quad (42)$$

In this case we cannot at once evaluate $(\partial f/\partial Q)_l$, but it is evident physically that swelling a stretched polymer will generally have the effect of diminishing the tension. If this is so, extending a piece of swollen polymer will, according to (42), diminish its vapour pressure, and increase its swelling capacity.

In order to carry out experiments on the effect of applied stresses, it is necessary to work with a polymer possessing structural rigidity even when swollen. This internal structure also imposes restraints on the swelling of the polymer, and may thus affect both the entropy and the heat of swelling. If the structure is such as to leave the polymer macroscopically homogeneous, there is no thermodynamic method of evaluating its effect. In certain cases, however, the structure is sufficiently coarse to enable its constituents to be considered separately. An obvious example of this type is found in a reinforced plastic, where the reinforcing layers (which may themselves be swollen) restrain the swelling of the plastic interlayers.[55] An extremely interesting and thorough analysis of the swelling of wood has been made by W. W. Barkas, along similar lines.[56] A typical wood cell has the form of a hollow cylinder, with a thin elastic sheath. Swelling occurs almost exclusively perpendicular to the axis, and is restrained by the elastic reaction of the sheath, which is comparatively little swollen. The very detailed discussion of this problem given by Barkas could probably be applied to other materials.

Attempts which have been made to calculate the effect of internal structure on the swelling of wool and keratin [57] rest on a much more questionable basis. It is assumed that the work done by the water in swelling the structure is the same as would have to be expended in order to produce the same dimensional changes by applying external forces. This is certainly not true in general, and would require strong justification before it could be accepted in any particular case. In the Reviewer's opinion, the restoring forces of the structure are very greatly over-estimated by this procedure.

The effect of cross-linking on the swelling of rubber-like polymers is another example of a restraint imposed by an internal structure. This has been analysed on the basis of the statistical mechanics of an ideal network (cf. § 5), the problem being to calculate the elastic reaction of the network

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[55] F. T. Barwell and K. W. Pepper, *ibid.*

[56] Forest Products Research Special Report No. 6, H.M.S.O., 1945.

[57] A. B. D. Cassie, *loc. cit.*, ref. 45.

when swollen by a liquid. It is clear from the model that this restraint takes the form of a negative contribution to the entropy of swelling. This contribution has been estimated by James and Guth and by P. J. Flory [25] for the cases of isotropic swelling and of swelling with the polymer restrained in one direction. After introduction of these terms into equation (25), the free energy of dilution becomes

(*a*) Isotropic swelling,

$$\Delta G_0 = RT\left\{\ln\left(1+\frac{1}{Q}\right) - (1+Q)^{-1} + \mu(1+Q)^{-2} + \frac{\rho_r V_0}{M_c}(1+Q)^{-1/3}\right\} \quad . \quad (43)$$

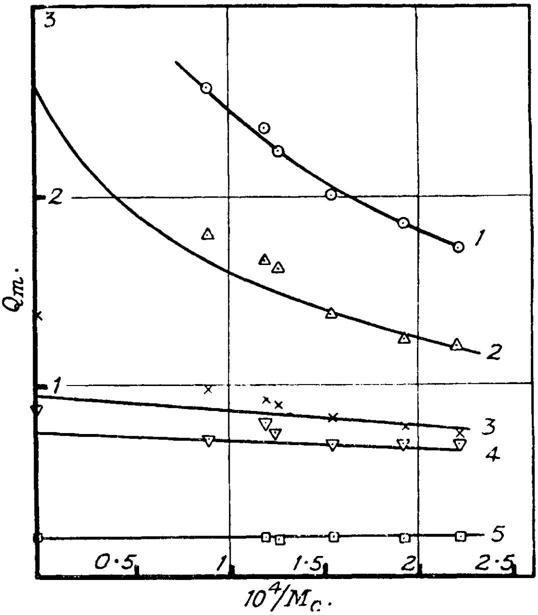

FIG. 15

Effect of vulcanisation on swelling of natural rubber compounds : 1, *light petroleum* (*b.p.* 40—60°) *;* 2, n-*propyl acetate ;* 3, *ethyl acetate ;* 4, *methyl ethyl ketone ;* 5, *acetone.* (*Curves theoretical.*)

(*Reproduced by permission from* Transactions of the Faraday Society, 1946, **42**, *B*, 36.)

(*b*) Swelling at length *l*,

$$\Delta G_0 = RT\left\{\ln\left(1+\frac{1}{Q}\right) - (1+Q)^{-1} + \mu(1+Q)^{-2} + \frac{\rho_r V_0}{M_c}\cdot\frac{l_0}{l}\right\} \quad . \quad . \quad (44)$$

where ρ_r and M_c are the density and molecular weights between junction points of the polymer, V_0 is the molar volume of the liquid, l_0 is the length dry and unstrained, l is the length swollen and strained.

These equations permit μ to be calculated from the swelling of polymers of known degrees of cross-linking, and also give values for $\partial \Delta G_0/\partial Q$ which may be substituted into equations (40) and (42). An interesting feature of (44) is that, as $l \longrightarrow \infty$, the negative entropy contribution vanishes, leaving

ΔG_0 equal to the value for an uncross-linked polymer. It can thus be seen that cross-linking should reduce the swelling capacity, while extension should increase it towards its original value.

These predictions have been tested by using a series of natural rubber compounds,[39] some of the results being shown in Figs. 15—17. Values of M_c were estimated from the elastic moduli of the rubbers when swollen, and are therefore not really independent quantities. Two points are to be observed : (*a*) the very good quantitative account of the effects of network structure on swelling in good swelling agents which can be given by this theory, and (*b*) the systematic departure found for poor swelling agents. Analysis of the latter by means of equation (42) shows that it is accounted for almost wholly by the term $\partial \Delta G_0/\partial Q$. The conclusion drawn is that polymer–liquid systems with a relatively small mixing tendency cannot be adequately characterised by a single value of μ, but that, as saturation is approached, μ falls considerably. This phenomenon, which appears to be quite general, is illustrated by the vapour-pressure data for natural rubber hydrocarbon in ethyl acetate,[32] shown in Fig. 18. It represents a defect in the current statistical theory of polymer–liquid systems which has not yet been satisfactorily explained.

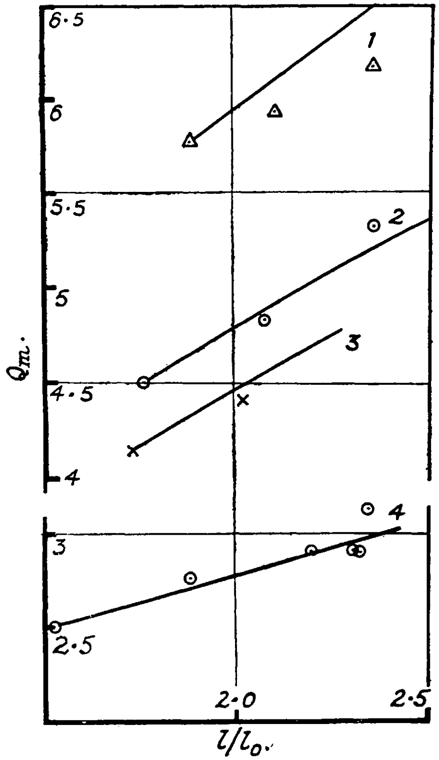

Fig. 16

Effect of extension on swelling : (1) *chloroform,* (2) *benzene,* (3) *toluene,* (4) *light petroleum* (*b.p.* 40—60°). (*Curves theoretical.*)

(*Reproduced by permission from* Transactions of the Faraday Society, 1946, **42**, *B*, 37.)

11. *The Solubility of Gases in Polymers*

This problem differs from that of the absorption of liquids only in that the reference state of the solute is the gas (usually at 1 atm. pressure) instead of the liquid. Just as the dissolution of crystalline materials may be divided into (*a*) fusion and (*b*) mixing, so the solution of gases may be supposed to proceed through a preliminary liquefaction. This is not in all cases a physically possible route, since we may be concerned with gases which are above their critical temperatures. This objection is more apparent than real, since even in the case of unsaturated vapours the process of liquefaction

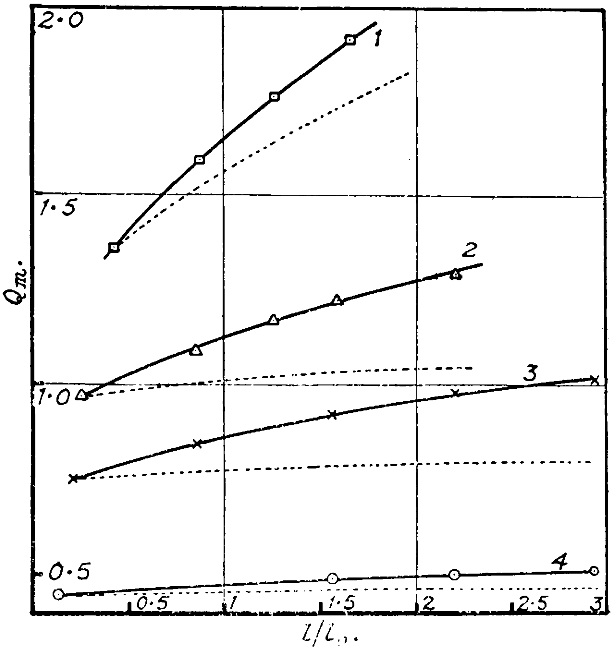

FIG. 17

Effect of extension on swelling : (1) n-propyl acetate (add 0·5 to ordinates), (2) ethyl acetate, (3) methyl ethyl ketone, (4) ethyl formate. (Broken curves theoretical.)

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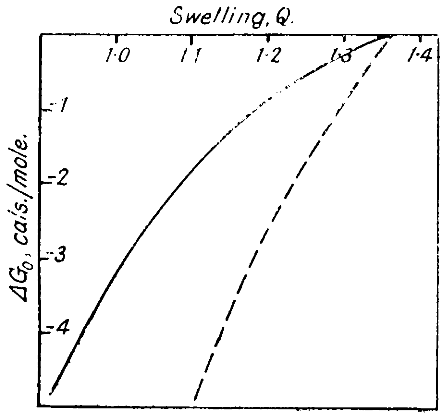

FIG. 18

Free energy of dilution of natural rubber by acetone.

[*Broken curve calculated from equation* (25), *with* $\mu = 0{\cdot}713$.]

is an unnatural one, involving an increase of Gibbs free energy. The only additional difficulty in the case of permanent gases is concerned with the extrapolation required in estimating the free energy of condensation. Writing the Gibbs free energy of solution ΔG_s of gas at 1 atm. pressure in the solution as the sum of ΔG_c and ΔG_0, the Gibbs free energies of condensation and dilution, we have for equilibrium

$$\Delta G_c + \Delta G_0 = 0 \quad . \quad . \quad . \quad . \quad . \quad (45)$$

The problem is now seen to be very much simpler than that of the solution of crystalline polymers, since ΔG_c is connected only with the properties of the gas. If T_b is the condensation temperature and L_b the molar latent heat of condensation, assumed independent of T,

$$\Delta G_c = L_b(T/T_b - 1) \quad . \quad . \quad . \quad . \quad (46)$$

ΔG_0 is given by equation (25), but in the case of gas solutions v_r is invariably close to 1, so that, to a good approximation

$$\Delta G_0 \simeq RT\{\ln(1 - v_r) + 1 + \mu\} \quad . \quad . \quad . \quad (47)$$

The solubility is usually expressed as the volume of gas (c.c. at N.T.P.) dissolving in 1 c.c. of polymer under a pressure of 1 atm. Denoting this by σ, its relation to v_r is

$$\sigma = 22{,}400(1 - v_r)/V_0 \quad . \quad . \quad . \quad . \quad (48)$$

where V_0 is the molar volume of the liquefied gas at the temperature of the experiment; this can only be estimated by extrapolation. Combination of equations (45) to (48) gives finally

$$- \ln \sigma \simeq \frac{L_b}{RT_b}\left(1 - \frac{T_b}{T}\right) - \ln\left(\frac{22{,}400}{V_0}\right) + 1 + \mu \quad . \quad . \quad (49)$$

L_b/T_b is the entropy of evaporation, which may be taken as 20 cals./mole/° c. while a typical value of ln $(22{,}400/V_0)$ is about 6·5. Hence (49) reduces to

$$- \ln \sigma \simeq 4{\cdot}5 + \mu - 10T_b/T \quad . \quad . \quad . \quad . \quad (50)$$

This argument has been set out in some detail as it has not been published elsewhere, and the final result is particularly simple and striking. It is to be emphasised that the low solubility of permanent gases is due, on this view, to their very large positive free energy of condensation at ordinary temperature. Since this is determined largely by the difference between their condensation temperatures and the experimental temperatures, it is natural to find a term T_b/T in equation (50). The value of μ is relatively unimportant for permanent gases; this is in accord with the observation that the solubilities of say air in a range of polymers do not differ widely. Without knowing μ it is not possible to compare equation (50) with experiment exactly, but it is found that even if we set $\mu = 0$ the calculated solubilities of hydrogen, nitrogen, oxygen, and methane agree within a factor of 3 with the observed solubilities in natural rubber.[58] A further test of the validity of this method of approach is to use it to calculate the heat of solution, which is obviously given by

$$\Delta H_s = \mu RT - 20T_b \quad . \quad . \quad . \quad . \quad . \quad (51)$$

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[58] G. J. van Amerongen, *J. Appl. Physics*, 1946, **17**, 972.

Eliminating μ between (50) and (51), we have

$$\Delta H_s \simeq -RT(4{\cdot}5 + \ln \sigma) \quad . \quad . \quad . \quad . \quad . \quad (52)$$

Table III gives the values of μ needed to fit some experimental solubilities to equation (50), and a comparison of the observed heats of solution with those calculated from equation (52); the agreement is only approximate, but is as good as would be expected from such a crude analysis.

TABLE III

Solubilities of gases in natural rubber at 25° C.

Gas.	T_b, K.	$-\ln \sigma$.	μ, eqn. (50).	ΔH_s (cals./mole).	
				Exptl.	Eqn. (52).
H_2	20°	3·25	− 0·58	900	− 740
N_2	77	2·92	1·00	650	− 940
O_2	90	2·31	0·82	150	− 1300
CH_4	112	1·38	0·65	− 1900	− 1850
CO_2	200	0·06	2·30	− 2600	− 2640
NH_3	240	− 1·93	1·65	− 5400	− 3800
SO_2	263	− 3·12	1·23	− 7000	− 4500