85.

molecules escaping into solution (as in methyl ethyl ketone) while not preventing a return to random orientation following the deformation which accompanies swelling.

It was naturally of interest to make a comparison with Kratky's data, but it is best not to stress any apparent discrepancy until the preliminary results we have presented here have been replaced by the more accurate values which we hope to obtain.

THE INTERACTION BETWEEN RUBBER AND LIQUIDS.

X. SOME NEW EXPERIMENTAL TESTS OF A STATISTICAL THERMODYNAMIC THEORY OF RUBBER-LIQUID SYSTEMS.

By Geoffrey Gee.

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In recent years a number of papers have been published, in which the thermodynamic properties of rubber liquid systems have been deduced by statistical methods. These theoretical treatments have on the whole been highly successful, but their critical evaluation is rendered difficult by the almost complete lack of reliable experimental data. Any reasonably comprehensive attempt to fill this gap would be extremely laborious. By concentrating attention on points where, if at all, weaknesses were likely to be found, it has been possible to review fairly quickly the present position.

Calculations of the Gibbs free energy of dilution ΔG_0 of a polymer liquid mixture by the liquid have been based on a lattice model of the system. A lattice point is assumed capable of accommodating either a molecule of solvent or a "segment" of the polymer chain equal in volume to a solvent molecule. An approximate treatment [1, 2] leads to a result of the form

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

where v_r is the volume fraction of rubber in the mixture, and μ is a parameter given by

$$\mu = A + B/RT \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where A and B are constants, and Bv_r^2 is the heat of dilution, ΔH_0. The only extensive data at present available to test this result are those for the system rubber and benzene.[3, 4] The results at 25° C. are represented by equation (1) with only small variations of μ over the whole range of composition, but A and B are both strongly dependent on v_r, especially when this is low.[4] Huggins [5] has shown that equation (1) describes the rather fragmentary data for a number of rubber-liquid systems at a single temperature. As a result there is a growing tendency to employ μ as a quantity characterising a particular polymer liquid mixture. The simplicity of such a procedure makes it very attractive; but it is clearly desirable to apply some critical experimental tests of its validity. This is the purpose of the present paper and an experimental study has therefore been made of some two-phase equilibria.

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[1] Flory, *J. Chem. Physics*, 1942, **10**, 51.

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

[3] Gee and Treloar, *Trans. Faraday Soc.*, 1942, **38**, 147.

[4] Gee and Orr, *ibid.* (in press).

[5] Huggins, *Ind. Eng. Chem.*, 1943, **35**, 216.

The experimental work to be described is largely concerned with vulcanised natural rubber. It is assumed that the introduction of a few cross links into the rubber will have a negligible effect on the heat and entropy of mixing. There will, however, be an additional term to be added to equation (1) representing the decrease of entropy resulting from the network deformation consequent upon imbibition of liquid. The correction has been evaluated by Flory and Rehner [6] in terms of the molecular weight M_c between junction points of the network. For isotropic swelling they obtain

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

where ρ_r is the density of the rubber, and V_0 the molar volume of the liquid. If a piece of rubber is constrained to a length l, compared with an initial length l_0 dry and unstrained, equation (3) must be replaced by

$$\Delta G_0 = RT\,\{\ln(1 - v_r) + v_r + \mu v_r^2 + \rho_r V_0 l_0/lM_c\} \quad . \quad . \quad (4)$$

The elastic tension f in the swollen rubber is given by [6, 7]

$$f = \rho_r A_0 RT(l/l_0 - l_0^2/l^2 v_r)/M_c \quad . \quad . \quad . \quad (5)$$

where A_0 is the cross-section of the dry unstrained rubber. Equation (5) has been shown [8] to hold for highly swollen rubbers, although it is less satisfactory when v_r is large. If, therefore, M_c is estimated from the tension in a highly swollen rubber, there is good reason to expect the last term of equations (3) and (4) to be accurate for small v_r. Since this term is only important when v_r is small, it is considered that data on vulcanised rubbers may safely be used to test equation (1).

The quantity measured in the experiments reported below is the equilibrium volume of liquid Q_m imbibed by unit volume of the rubber, and three types of measurement are included. These give the dependence of Q_m on the degree of cross-linking, on the degree of extension l/l_0 of the rubber, and on the temperature. Equations (3) and (4) readily lead to the following expressions for these quantities when the equilibrium condition $\Delta G_0 = 0$ is inserted.

For isotropic swelling, the effect of M_c is given by

$$\ln(1 + 1/Q_m) - (Q_m + 1)^{-1} - \mu(Q_m + 1)^{-2} = \rho_r V_0/M_c(Q_m + 1)^{\frac{1}{3}}. \quad (6)$$

The effect of elongation is given by

$$\ln(1 + 1/Q_m) - (Q_m + 1)^{-1} - \mu(Q_m + 1)^{-2} = \rho_r V_0 l_0/lM_c. \quad . \quad (7)$$

Reference will also be made to some earlier data on the dependence of the tension f on the degree of swelling $Q(\doteq 1/v_r - 1)$; an expression for this is obtained from equation (5):

$$(\partial f/\partial Q)_l = \rho_r A_0 RT l_0^2/l^2 M_c. \quad . \quad . \quad . \quad . \quad (8)$$

In discussing the experimental data, use will be made of the following thermodynamic relations, derivations of which are given in Appendix I.

$$l_0\left(\frac{\partial Q_m}{\partial l}\right)_T = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l \quad . \quad . \quad . \quad . \quad (9)$$

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_{T,f=0} = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \left\{\frac{1}{l_0\partial Q_m/\partial l} - \tfrac{1}{3}(Q_m + 1)^{-\frac{2}{3}}\right\} \quad . \quad (10)$$

$$\Delta H_0 = T\Delta S_0 = -\frac{Q_m}{T}\left(\frac{\partial \Delta G_0}{\partial Q}\right)_T \cdot \frac{\partial \ln(\Delta w)}{\partial\, 1/T} \quad . \quad . \quad . \quad . \quad (11)$$

All the above are true only at $Q = Q_m$. In equation (11) Δw is the weight of liquid imbibed by a fixed amount of rubber.

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[6] Flory and Rehner, *J. Chem. Physics*, 1943, **11**, 521.

[7] James and Guth, *ibid.*, 1943, **11**, 455.

[8] Gee, *Trans. Faraday Soc.* (in press).

Equations (9) and (11) show that the dependence of the maximum swelling on either length or temperature is inversely proportional to $\partial \Delta G_e / \partial Q$. Although the dependence of Q_m on cross linking is not strictly a thermodynamic problem at all, a simple analysis leads to the conclusion that this also is inversely proportional to $\partial \Delta G_e / \partial Q$. In general, therefore, the variation of Q_m with internal or external parameters is determined by the *slope* of the free energy-composition curve in the neighbourhood of the two phase equilibrium. It is this fact which makes the ability of an equation to describe these phenomena such a severe test of the theory on which the equation is based.

Effect of Cross-linking on Swelling Capacity.—Several natural rubber vulcanisates were prepared; the compounds, whose compositions are given in Appendix II, being selected to cover a range of "cure." The estimation of M_e was made by allowing a strip of rubber, carrying a dead load, to swell to its maximum capacity in 40/60 petrol ether at 25° C.

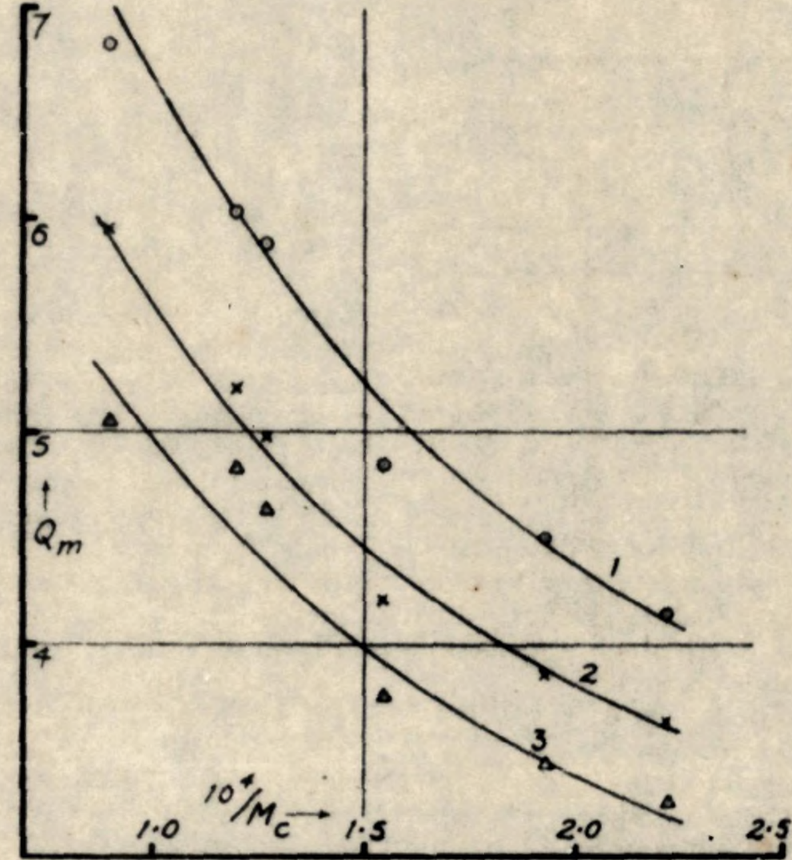

FIG. 1.—Effect of vulcanisation on swelling.

(*a*) Good swelling agents. 1. Carbon tetrachloride.
2. Carbon disulphide. 3. Benzene.
(Curves theoretical.)

When equilibrium was attained, the distance between two reference points on the strip was measured, and the degree of swelling estimated by cutting out the portion of the strip between the reference points and determining its petrol content. The value of $10^{-3} M_e$ obtained in this way are given in Appendix III; their reciprocals will be seen to run roughly parallel with the loads at 300 % estension as determined on a standard tensile testing machine (the so-called "modulus at 300 %"). Swelling measurements were carried out in a variety of liquids differing widely both in chemical type and in solvent power. Weighed samples of rubber (*ca.* 1 g.) were immersed in excess liquid and maintained at constant temperature for three days, by which time swelling was substantially complete, and then quickly surface dried and weighed. The results are shown in Fig.

1 and 2, in which Q_m is plotted as a function of $1/M_c$ for the various rubbers, with the addition, for the non-solvents, of unvulcanised rubber. Data for the two pairs of liquids, chloroform and carbon tetrachloride, benzene and toluene, were so similar that only one of each pair is shown. In order to fit the data to equation (6) a value of μ has to be selected to give the best general representation of the points, it being assumed that chemical differences among the rubbers would not be sufficient to affect μ significantly. The curves drawn in Fig. 1 and 2 were calculated from equation (6) by using the values of μ shown in Table I, and evidently give a fairly good representation of the data for the good swelling agents, bearing in mind the difficulty of making satisfactory comparisons of different rubbers. This is in agreement with the conclusion drawn by Flory[9] from his data on the swelling of a range of butyl rubbers in cyclohexane. The data for methyl ethyl ketone and ethyl acetate show a systematic deviation from the calculated curve, the effect of cross linking in reducing the swelling power being more marked than would be expected. It is difficult to estimate the quantitative discrepancy in δQ_m, the amount by which Q_m is lowered by cross linking, but it would seem that the experimental value for ethyl acetate is at least twice the calculated. It appears rather unlikely that any large part of this factor can arise from the term $\rho_r V_0/M_c(Q_m + 1)^{\frac{1}{3}}$, since it has previously been found that rubbers swollen by 100 % show nearly the theoretical behaviour in tension.[8] The tentative conclusion would therefore be that $\partial \Delta G_0/\partial Q$ for poor swelling agents is lower than would be expected on the basis of their swelling capacity; in other words, that equation (1) is only approximately true. The discrepancy involves only small deviations in the value of μ given by equation (6) when applied to different rubbers. Thus, e.g. Table I gives $\mu = 0{\cdot}78$ for ethyl acetate; the value calculated from the swelling capacity of raw rubber is $\mu = 0{\cdot}71$. Table I includes for comparison μ values calculated by Huggins[5] from vapour pressure data on raw rubbers, and the general order of agreement is fairly good, suggesting

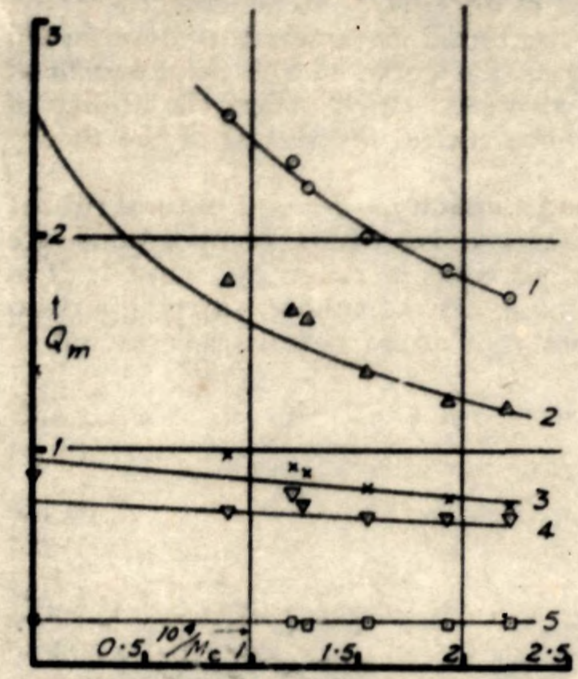

FIG. 2.—Effect of vulcanisation on swelling.

(*b*) Moderate and poor swelling agents. 1. 40/60 petrol ether. 2. *n*-Propyl acetate. 3. Ethyl acetate. 4. Methyl ethyl ketone. 5. Acetone. (Curves theoretical.)

TABLE I.—VALUES OF μ FROM EQUATION (6).

Liquid.	μ (from Q_m).	μ (Vap. Press.).
Carbon tetrachloride .	0·29	0·28
Chloroform . . .	0·34	0·37
Carbon disulphide . .	0·425	0·49
Benzene	0·395	0·43 *
Toluene	0·36	0·43-0·44
40/60 petrol ether . .	0·54	0·43 †
n-Propyl acetate . .	0·62	—
Ethyl acetate . . .	0·78	—
Methyl ethyl ketone . .	0·94	—
Acetone	1·37	—

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* Data of Gee and Orr give 0·41.

† Light petroleum.

[9] Flory, *Chem. Rev.*, 1944, **35**, 51.

that for good swelling agents equations (1) and (6) are probably both reasonably satisfactory.

Effect of Extension on Swelling.—The measurement of the effect of extension on swelling is in principle much more satisfactory than the comparison of different rubbers. In practice it turns out to be very difficult except for liquids of moderate swelling power. With good swelling agents, only very small extensions can be applied without breaking the specimen, and it becomes necessary to measure relatively small differences in Q_m. In some cases, notably chloroform and toluene, the difficulty is enhanced by failure to attain steady equilibrium values of Q_m, the result obtained increasing very markedly with time.[*] With acetone the effect of extension on Q_m was very small, but with intermediate liquids, such as ethyl acetate and methyl ethyl ketone, very satisfactory and reproducible results were obtained over a wide range of extensions. Most of the data reported were obtained by stretching rings over glass formers, but for the better swelling agents, there was found to be less danger of rupture if the rubber was stretched in the form of a strip. This latter procedure was more troublesome, as it was necessary to cut out the stretched portion when swollen to equilibrium and determine its swollen weight. The sample was then returned to the liquid to determine its weight when swollen and unstrained, while finally the dry weight was obtained by removing the liquid *in vacuo*. By this method $\partial Q_m/\partial l$ is certainly underestimated for liquids in which Q_m increases with time.

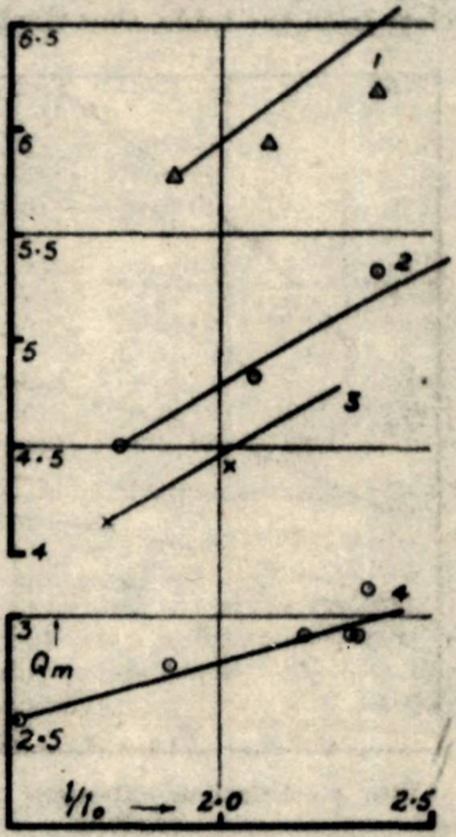

FIG. 3.—Effect of extension on swelling.
(*a*) Good swelling agents.
1. Chloroform. 2. Benzene.
3. Toluene. 4. 40/60 pet. ether.
(Curves theoretical.)

The results are shown in Fig. 3 and 4, in which the theoretical curves are calculated from equation (7), using values of μ chosen to give the observed swelling at $f = 0$. Bearing in mind the above note about chloroform and toluene, equation (7) is satisfactorily confirmed for good swelling agents (Fig. 3). For poor swelling agents, the effect of extension is far larger than predicted. Flory and Rehner[11] have shown that equation (7) describes accurately the effect of extension on the swelling of a sample of butyl rubber in xylene.

It is possible to determine whether the unexpectedly large dependence of Q_m on extension arises mainly from anomalies in the elastic behaviour or in the state of mixing, by making use of equation (9), but to do so it is necessary to estimate $(\partial f/\partial Q)_l$. Data have been reported previously[8] on the effect of toluene on the tension of stretched rubber strips; from these $(\partial f/\partial Q)_l$ is readily obtained by graphical interpolation. The resulting figures have been applied to the present data, this being justified by two facts: (*a*) that similar samples of rubber were used in the two investigations; and (*b*) that unpublished work[†] has shown that the

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[*] Scott[10] has reported that this is a normal feature of swelling, and has termed this relatively slow rise of Q_m the "increment". By working in nitrogen, and restricting the duration of experiments, no trouble has been encountered with most of the liquids used.

[†] Both by the author and by Dr. L. R. G. Treloar.

[10] Scott, *Trans. Inst. Rubber Ind.*, 1929, **5**, 95.

[11] Flory and Rehner, *J. Chem. Physics*, 1944, **12**, 412.

tension at constant length of swollen rubbers depends, to a first approximation, only on the degree of swelling, and not on the nature of the liquid. It must be emphasised that the figures will not necessarily be very precise, since a considerable amount of graphical interpolation has been necessary. Some typical results are given in Table II, in which

$$l_0\frac{\partial Q_m}{\partial l}, \quad -\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \quad \text{and} \quad \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l$$

are compared with values computed from the above statistical equations.

In considering these results, it must be borne in mind that $\frac{\partial Q_m}{\partial l}$ and $\left(\frac{\partial f}{\partial Q}\right)_l$ are both differential quantities, not measured directly, so that both are liable to considerable experimental error. None the less, it is clear from the table, that the high values of $\partial Q_m/\partial l$ arise mainly from very low values of $\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l$. An important observation is that these low values are not essentially dependent on extension, the discrepancy between theory and experiment being of the same order at different extensions. This conclusion is confirmed by extrapolating the data to $f = 0$, and employing equation (10) to calculate $\partial \Delta G_0/\partial Q$ for the unstretched rubber; the results are set out in Table III. The figures for methyl ethyl ketone and ethyl acetate are consistent with the observed relatively large effect of vulcanisation on the swelling in these two liquids (Fig. 2).

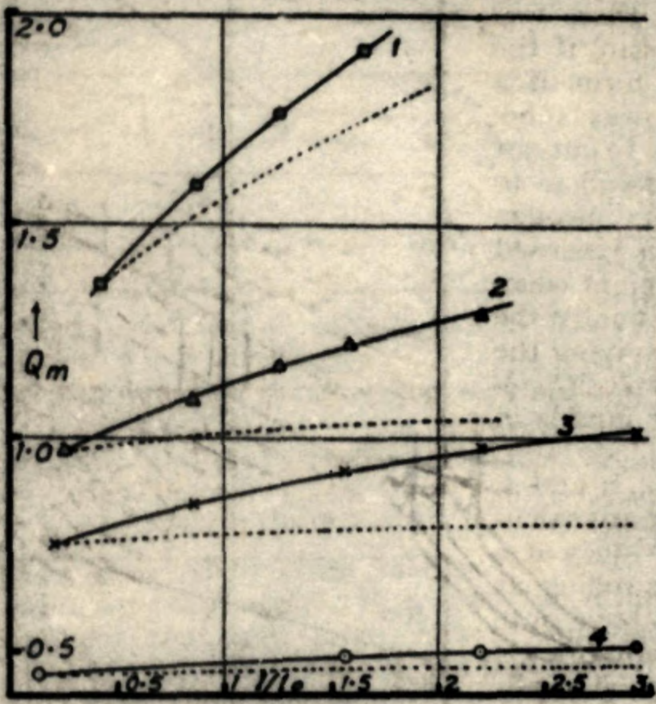

FIG. 4.—Effect of extension on maximum swelling.

(*b*) Poor swelling agents.

1. *n*-Propyl acetate (add 0·5 to ordinates).
2. Ethyl acetate. 3. Methyl ethyl ketone.
4. Ethyl formate.

(Dotted curves theoretical.)

By considering the magnitudes of the separate terms in equation (3) it is easily seen that $(\partial \Delta G_0/\partial Q)_{f=0}$ is determined essentially by the free energy of mixing, no important contribution arising from network deformation. It follows that the last column of Table III gives an estimate of the ratio between the true and calculated values of $(\partial \Delta G_0/\partial Q)_T$ for raw rubber at the values of Q shown in column 2. It is known by direct measurement that this ratio is close to unity for benzene,[3, 4] at all values of Q. The success of the statistical equations in describing both the elastic behaviour and the effect of extension on swelling for a series of good swelling agents shows that the same must be true of these. In contrast, the results of Table III suggest that as the limit of imbibition is approached for poor swelling agents, $\partial \Delta G_0/\partial Q$ falls below its calculated value. This has already been shown to be the case for methyl alcohol [12] where, in the neighbourhood of maximum swelling, $\partial \Delta G_0/\partial Q$ falls to not more than one-twentieth of the value to be expected from equation (4) and the

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[12] Ferry, Gee and Treloar, *Trans. Faraday Soc.*, 1945, 41, 340.

observed maximum swelling. Lens' data for acetone [13] are not sufficiently precise to estimate the ratio (observed/calculated) with any precision, but it is certainly low (≈ 0·05). These various observations are collected

TABLE II.—RELATION BETWEEN SWELLING, TENSION AND EXTENSION. (RUBBER A.)

Liquid.	Q_m (unstrained).	l/l_0.	$l_0 \frac{\partial Q_m}{\partial l}$.		$-\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l$ Cal./cc. Rubber.		$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l$ Cal./mole Liquid.	
			Expt.	Theory.	Expt.	Theory.	Expt.	Theory.
Ethyl formate	0·447	1·5	0·036	0·0105	0·052$_5$	0·0310	11$_7$	237
		2·0	0·025	0·0061	0·036$_5$	0·0175	11$_7$	230
		2·5	0·019$_5$	0·0040	0·027$_0$	0·0112	11$_1$	227
Methyl ethyl ketone	0·75	1·5	0·144	0·0348	0·043$_2$	0·0310	27	80·1
		2·0	0·119	0·0218	0·025$_9$	0·0175	22	75·8
		2·5	0·095	0·0138	0·017$_6$	0·0112	17	73·1
Ethyl acetate	0·96	1·5	0·22$_5$	0·074	0·039$_7$	0·0310	17	40·1
		2·0	0·18$_7$	0·047$_5$	0·022$_8$	0·0175	12	36·2
		2·5	0·15$_0$	0·032$_5$	0·015$_0$	0·0112	10	33·7
n-Propyl acetate	1·86	1·5	0·54	0·40	0·033$_6$	0·0310	7·$_2$	8·9$_6$
		2·0	0·45	0·30$_2$	0·018	0·0175	4·$_6$	6·6$_7$
		2·5	0·36	0·24$_6$	0·011$_5$	0·0112	3·$_7$	5·2$_6$

in Fig. 5, in which the ratio of observation to calculation at the point of maximum swelling is plotted as a function of Q_m. There is no reason to expect all the points to lie on a smooth curve, but it seems extremely probable that the curve drawn will furnish at least a rough estimate of the ratio for other liquids. *There is, in other words, strong evidence that equation* (1) *fails to give the correct dependence of the free energy of dilution on composition for liquids of limited swelling power.*

TABLE III.—EVALUATION OF $(\partial \Delta G_0/\partial Q)_{f=0}$ (RUBBER A).

Liquid.	Q_m.	l/l_0 $(=(Q_m+1)^{\frac{1}{3}})$.	$-\frac{1}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l$. Cal./cc. Rubber.	$l_0 \frac{\partial Q_m}{\partial l}$.	$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_{f=0}$. Cal./mole Liquid.		Ratio Expt./Theory.
					Expt.	Theory.	
Ethyl formate	0·447	1·13	0·075	0·04$_9$	120	242	0·50
Methyl ethyl ketone	0·75	1·20	0·062$_5$	0·15$_9$	34	83·9	0·41
Ethyl acetate	0·96	1·25	0·055	0·24$_5$	21	42·2	0·50
n-Propyl acetate	1·26	1·42	0·037$_5$	0·55	7·$_2$	8·1$_5$	0·88

The way in which this failure accounts for some of the anomalous effects of vulcanisation and extension on swelling is shown schematically in Fig. 6, which relates to a liquid in which raw rubber is swollen to $Q_m = 1{\cdot}00$. Curves 1 and 2 represent the "experimental" and

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[13] Lens, *Rec. trav. chim.*, 1932, **51**, 971.

calculated curves of ΔG_0 while 3 and 4 give (minus) the increment due to vulcanisation, unstretched and stretched to $l/l_0 = 2$. The points of intersection of curves 3 and 4 with 1 and 2 give for the maximum swelling of the vulcanised rubber:

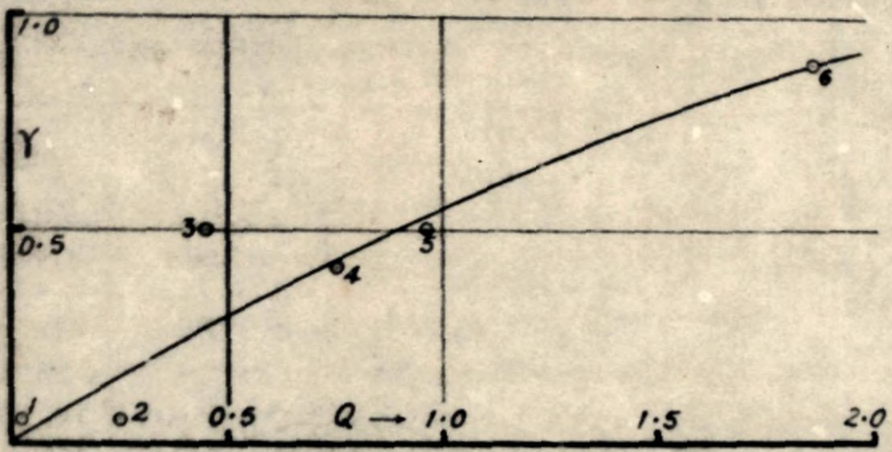

FIG. 5.—Ratio (γ) of experimental to theoretical values of $(\partial \Delta G_0/\partial Q)_T$.
1. Methyl alcohol. 2. Acetone.

unstretched,	experiment	0·828,	calculated	0·902
stretched,	experiment	0·876	calculated	0·930

(These figures are, of course, only illustrative, and have no quantitative significance.)

The Effect of Temperature on Swelling.—The temperature dependence of the maximum swelling of several natural rubber vulcanisates was determined in a range of liquids, employing the technique already described. In most cases measurements were carried out in duplicate, the first sample being allowed to swell successively at 0° C., 25° C., 0° C.; and the second sample at 25° C., 0° C., 25° C. In this way an adequate check was obtained on the attainment of equilibrium, and the absence of any important drift of Q_m with time. The results may be expressed in the form $-\partial \ln \Delta w/\partial(1/T)$, where Δw is the weight of liquid imbibed, but in order to use them to evaluate the heat of dilution from equation (11), it is also necessary to estimate $(\partial \Delta G_0/\partial Q)_T$. A statistical expression for this quantity obtained from equation (4) may be used for the good swelling agents. In general, it is necessary to introduce the factor γ

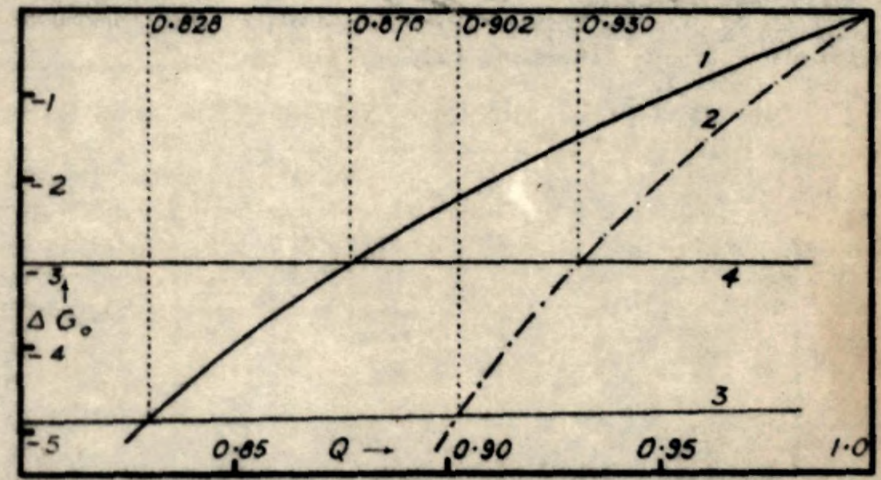

FIG. 6.—Theoretical and experimental dependence of Q_m on vulcanisation and extension.
1. ΔG_0 raw rubber (exptl.). 2. Do. (theoretical).
3. $-\partial \Delta G_0$ vulcanised rubber at $f = 0$. 4. Do. at $l/l_0 = 2$.

determined in the last section, as the ratio between the true and calculated values of $(\partial \Delta G_0/\partial Q)_T$. From equation (11), introducing the factor γ, and dividing by v_r^2 gives

$$\frac{\Delta H_0}{v_r^2} = \frac{\gamma R}{Q_m + 1}\left(-\frac{\partial \ln \Delta w}{\partial(1/T)}\right)\left\{1 + (1 - 2\mu)Q_m - \frac{\rho_r V_0}{3M_c}Q_m(Q_m + 1)^{5/3}\right\}. \quad (12)$$

where Q_m is the mean maximum swelling over the range of temperature considered and μ is determined by equation (6). The application of this equation to a single rubber in a range of liquids is illustrated in Table IV, values of γ being read from Fig. 5. Very similar results have been obtained for other rubbers.

TABLE IV.—HEAT AND ENTROPY OF DILUTION FROM TEMPERATURE DEPENDENCE OF SWELLING. (RUBBER B.)

Liquid.	Q_m.	$-\frac{\partial \ln \Delta w}{\partial(1/T)}$.	$\frac{\Delta H_0}{v_r^2}$. Cal./mole Liquid.	
			Eqn. (12).	Calorimetric[12] ($Q=0$).
Carbon tetrachloride	6·90	− 125	− 105	− 255
Chloroform	6·81	− 185	− 130	− 450
Carbon disulphide	5·87	35	15	95
Toluene	5·23	30	20	15
Cyclohexane	5·05	75	50	
Benzene	4·96	235	125*	310*
n-Butyl *n*-butyrate	3·25	100	65	
n-Heptane	2·90	75	35	135
di-*iso*propyl ketone	2·82	330	160	
n-Pentane	2·58	− 115	− 45	
n-Butyl acetate	2·39	75	120	
n-Propyl acetate	1·63	620	205	
Ethyl acetate	0·84	1010	230	
Methyl ethyl ketone	0·62	1000	215	
Methyl acetate	0·30	905	155	
Acetone	0·18	925	120	950

* Direct measurement on raw rubber[4] gives $\Delta H_0/r_r^2 = 310$ at $Q = 0$; 168 at $Q = 4{\cdot}96$.

Several features of this table call for comment. In the first place the results for the last two members of the series are very largely determined by γ, and it is clear from Fig. 5 that this may be quite seriously in error. For the next three members there are direct experimental measurements of γ; for the remainder $\gamma = 1$ is likely to be very nearly accurate.

At first sight the values of $\Delta H_0/v_r^2$ estimated here, do not agree at all well with those based on calorimetric data (compare columns 4 and 5). The discrepancy is always in the direction making the numerical value calculated from the temperature coefficient the smaller of the two. Now it has been shown by direct measurement[4] in the case of raw rubber and benzene that $\Delta H_0/v_r^2$ falls as the benzene content increases, and the value of *ca.* 168 cal./mole found at $Q = 4{\cdot}96$ is in fair agreement with the estimate of 125 obtained here.

For this system the calorimetric estimate, which was based on the heats of mixing of benzene with dihydromyrcene,[12] is equal to the experimental value[4] at $Q = 0$. Since both columns 4 and 5 are essentially experimental their disagreement is evidence that $\Delta H_0/v_r^2$ is not independent of the degree of swelling, i.e. that even if μ is independent of composition, the "constants" A and B of equation (2) are not.

Conclusions.

The general conclusion which emerges from these experiments is that the simple equation (1) proposed by Huggins is more limited in application than has been previously supposed. It gives correctly the isothermal dependence on composition of the free energy of a polymer-liquid mixture whose heat of mixing is small, μ being treated as an empirical parameter. It is therefore possible to calculate the colligative properties of the mixture at a fixed temperature with fair precision using only the one adjustable parameter. Since the independence of μ on v_r is found to arise only from an approximate cancellation of the concentration dependence of A and B (equation 2), the equation cannot be safely used to discuss heats and entropies of dilution. If there is an appreciable heat of mixing, equation (1) is no longer strictly accurate even at a fixed temperature. As the polymer approaches saturation, the dependence of ΔG_0 on composition becomes considerably less than expected. The direct consequence of this is that theoretical treatments based on equation (1) underestimate the extent to which the swelling capacity of a polymer depends on external conditions or structural changes.

Discussion of the origin of these anomalies requires a critical examination of the basis of equation (1) and of other statistical theories of polymer solutions. This lies beyond the scope of the present paper, and will be considered in a further communication.

Summary.

Experimental data are reported on the effects of vulcanisation, extension and temperature on the swelling of rubber. These, although in qualitative agreement with a simple equation derived from a statistical theory of polymer solutions, reveal quantitative discrepancies which are important in discussions of two-phase equilibria.

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APPENDIX I.

Thermodynamic Relations.

(i) **Dependence of Q_m on Extension.**—Considering a stretched, swollen rubber maintained at constant temperature and pressure; by mathematical identity

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l = -\left(\frac{\partial \Delta G_0}{\partial l}\right)_Q \left(\frac{\partial l}{\partial Q}\right)_{\Delta G_0} \quad . \quad . \quad . \quad (13)$$

and

$$\left(\frac{\partial \Delta G_0}{\partial l}\right)_Q = \left(\frac{\partial}{\partial l}\right)_Q \left(\frac{\partial G}{\partial n_0}\right)_l = \left(\frac{\partial}{\partial n_0}\right)_l \left(\frac{\partial G}{\partial l}\right)_Q = \left(\frac{\partial f}{\partial n_0}\right)_l, \quad . \quad (14)$$

where f is the tension in the rubber and n_0 the number of moles of liquid in the rubber.

Further,
$$n_0 = A_0 l_0 Q/V_0 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

whence,
$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_l = -\frac{V_0}{A_0 l_0}\left(\frac{\partial f}{\partial Q}\right)_l\left(\frac{\partial l}{\partial Q}\right)_{\Delta G_0} . \quad . \quad . \quad . \quad (16)$$

A particular case of equation (16) is obtained by putting $\Delta G_0 = 0$, when $Q = Q_m$ giving

$$l_0 \frac{\partial Q_m}{\partial l} = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \Big/ \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l \quad . \quad . \quad . \quad . \quad (9)$$

where the terms on the right are to be given their values at $Q = Q_m$.

(ii) **Swelling at Constant Tension and at Constant Length.**—Equation (9) may be used to derive the limiting value of $(\partial \Delta G_0/\partial Q)_l$ at $f = 0$. To obtain from this the slightly different function $(\partial \Delta G_0/\partial Q)_{f=0}$, we use the identity

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_{f=0} = \left(\frac{\partial \Delta G_0}{\partial Q}\right)_l + \left(\frac{\partial \Delta G_0}{\partial l}\right)_Q\left(\frac{\partial l}{\partial Q}\right)_{f=0} . \quad . \quad . \quad (17)$$

Now at $f = 0$, $l = l_0(Q+1)^{\frac{1}{3}}$, so that

$$\left(\frac{\partial l}{\partial Q}\right)_{f=0} = \tfrac{1}{3} l_0 (Q + 1)^{-\frac{2}{3}} . \quad . \quad . \quad . \quad . \quad (18)$$

Combining this with the value of $(\partial \Delta G_0/\partial l_0)_Q$ obtained from (14) and (15), and of $(\partial \Delta G_0/\partial Q)_l$ from (9), the final result is

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_{f=0} = -\frac{V_0}{A_0}\left(\frac{\partial f}{\partial Q}\right)_l \left\{\frac{1}{l_0(\partial Q_m/\partial l)} - \tfrac{1}{3}(Q_m + 1)^{-\frac{2}{3}}\right\} \quad . \quad (10)$$

where the quantities on the right are to be given their values at $f = 0$, $Q = Q_m$.

(iii) **Temperature Dependence of Q_m.**—Considering a swollen rubber at constant pressure, and free from mechanical restraint; by identity

$$\left(\frac{\partial \Delta G_0}{\partial Q}\right)_T = -\left(\frac{\partial \Delta G_0}{\partial T}\right)_Q \Big/ \left(\frac{\partial Q}{\partial T}\right)_{\Delta G_0} . \quad . \quad . \quad . \quad (19)$$

If w_0 is the weight fraction of liquid in the rubber, the entropy of dilution ΔS_0 is given by the well-known relation

$$\begin{aligned} -\Delta S_0 &= (\partial \Delta G_0/\partial T)_{w_0} \\ &= \left(\frac{\partial \Delta G_0}{\partial T}\right)_Q + \left(\frac{\partial \Delta G_0}{\partial Q}\right)_T\left(\frac{\partial Q}{\partial T}\right)_{w_0} \quad . \quad . \quad . \quad (20) \end{aligned}$$

by identity. If α_0 and α_r are the coefficients of thermal expansion of liquid and rubber, it is easily seen that

$$\left(\frac{\partial Q}{\partial T}\right)_{w_0} = (\alpha_0 - \alpha_r)Q . \quad . \quad . \quad . \quad . \quad (21)$$

Substituting in (26) and combining with (25)

$$\Delta S_0 = \left(\frac{\partial \Delta G_0}{\partial Q}\right)_T\left\{\left(\frac{\partial Q}{\partial T}\right)_{\Delta G_0} - Q(\alpha_0 - \alpha_r)\right\} . \quad . \quad . \quad (22)$$

In the particular case of maximum swelling, $\Delta G_0 = 0$, $Q = Q_m$ and

$$\Delta H_0 = T\Delta S_0 = T\left(\frac{\partial \Delta G_0}{\partial Q}\right)_T\left\{\frac{\partial Q_m}{\partial T} - Q_m(\alpha_0 - \alpha_r)\right\} . \quad . \quad . \quad (23)$$

In using experimental data obtained by weighing, it is simpler to evaluate the temperature coefficient of the weight increase Δw, and replace equation (23) by the equivalent expression

$$\Delta H_0 = T\Delta S_0 = -\frac{Q_m}{T}\left(\frac{\partial \Delta G_0}{\partial Q}\right)_{T,\, Q=Q_m} \cdot \frac{\partial \ln \Delta w}{\partial (1/T)} . \quad . \quad . \quad (11)$$

APPENDIX II.

COMPOSITION OF VULCANISED RUBBERS.

	A, A′.	B, B′, B″.	C.	D.
Smoked sheet	100	100	100	100
Sulphur	2	3	3	5
Selenium (Vandex)	—	—	2	—
Zinc oxide	2	2	2	2
Stearic acid	0·5	0·5	0·5	0·5
Nonox	0·5	0·5	0·5	0·5
M B T S	1	—	—	—
Z D C	—	1	1	1

APPENDIX III.

"CURE" OF RUBBERS.

	A.	A′.	B.	B′.	B″.	C.	D.
Cure (Min.)	30	30	60	15	30	60	60
at (°c.)	142	142	100	142	142	100	100
Modulus (300 %) (kg./cm.^{2})	9	—	24	14	13	28	30
$10^{-3} M_c$	8·0	11·1	6·4	7·9	8·3	$5{\cdot}1_6$	4·5
10^{-4} Modulus × M_c	(72)	—	155	110	110	145	135

A and A′ differed in the amount of milling received during mixing; A had a bare minimum and was of Mooney viscosity 75; A′ was heavily milled to a Mooney viscosity of 15.

GENERAL DISCUSSION *

Dr. R. F. Tuckett (*Welwyn*) said: Gee's results on the swelling of stretched rubber show that the Flory-Huggins equation with its single arbitrary constant μ is not adequate in the phase separation region where ΔH_0 is relatively large. This is not unexpected, and it is of interest to examine a system whose apparent properties correspond very closely to the simple model on which the whole theory is based. This is so if the polymer unit and the solvent molecules are geometrically and chemically almost identical so that the heat of dilution is zero; in such a system $B = 0$ and μ becomes independent of temperature, being a function of z only, where z is the co-ordination number of the lattice on which the molecules are arranged. As $\Delta G_0 = RT \ln p/p_0$, then, for long chains, the relation between p/p_0 and w_r, the weight fraction of polymer, can be calculated from Guggenheim's equation as a function of z only.[1] For such an "ideal" polymer-solvent system, the following theoretical figures for p/p_0 are obtained for three values of w_r.

z.	$w_r =$ 0·8.	$w_r =$ 0·65.	$w_r =$ 0·50.
	$p/p_0 =$	$p/p_0 =$	$p/p_0 =$
6	0·51	0·73	0·87
8	0·49	0·71	0·85
∞	0·45	0·67	0·82

$z = \infty$ corresponds to the simple Flory-Huggins expression (Gee's equation (1)) and $z = 6$ seems to be the smallest value of z which is physically satisfying. The table shows, therefore, the plausible limits inside which p/p_0 should fall.

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* On preceding paper.

[1] Guggenheim, *Proc. Roy. Soc. A*, 1944, **183**, 203.

The experimental polymer-solvent systems which conform most closely to the theoretical requirements are those in which the solvent is either the monomer or the saturated monomer of the second polymeric component. The system polyvinyl acetate-ethyl acetate is especially suitable as its heat of dilution has been shown to be zero by direct measurement.[2] Walling, Briggs and Mayo [3] also give kinetic and activity results from which the p/p_0-w_r relation can be obtained for the polystyrene-styrene system. Results, which will be reported more fully elsewhere, are as follows :

$\frac{w_r}{p/p_0}$.	·80.	0·65.	0·50.
Polyvinyl acetate-ethyl acetate . . .	0·59	0·83	0·93
Polystyrene-styrene .	0·60	0·80	0·93

These values fall quite outside those of the previous table ; to obtain agreement, z values of the order of three are necessary, which seem physically impossible. Similar discrepancies are found in the osmotic pressure region and have been explained by Flory [4] but his modified theory is restricted to very dilute solutions. It seems unlikely that any end effects are significant for really long chains, and the results suggest that the whole theory requires re-examination.

Prof. E. A. Guggenheim (*Reading*) said : Just as the experimenter, in choosing the materials and details of his research, is largely guided by matters of convenience, so the theoretician in his research wisely begins by considering the simplest possible models before attempting to tackle more complicated ones. It is important to bear this in mind when making a comparison between experimental data and theoretical formulæ.

Up to the present, all the theoretical formulæ are based on the following assumptions (1) Each type of molecule occupies a definite integral number of sites on a lattice. (2) The energy of interaction is the sum of terms contributed by each pair of neighbouring sites. (3) The energy of interaction contributed by each pair of sites depends only on what species occupies each of the sites and not on which element of a molecule occupies either site.

Assumptions (1) and (2) are probably good enough for the purpose of comparison with the available experimental data ; but in my opinion assumption (3), which means regarding each molecule as completely homogeneous, is seriously wrong. Unpublished experimental data from Professor Brønsted's laboratory in Copenhagen show that two different normal paraffins have small, but far from negligible, heats of mixing. Since the middle portion of two different normal paraffins are indistinguishable, it seems obvious that the heat of mixing must be due to the end groups. It is therefore my opinion that the next stage in improving the theory should be a study of arrangements on a lattice of molecules with distinguishable elements and I hope to attack this problem in the near future.

From these considerations it would at first appear that the models already investigated would at least be sufficient in the case of zero energy of mixing. This, however, is not necessarily true for it is conceivable that the energy of interaction between two molecules may be non-zero, but may change sign when one of the molecules is reversed. In this case, a resultant zero energy of mixing may well be due to a balance between equal positive and negative contributions from various pairs of sites.

Dr. M. Magat (*Paris*) said : I should like to comment on the determination of the heat of mixing from swelling experiments and to give a

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[2] P. Meares (private commnnnicatoin).

[3] Walling, Briggs and Mayo, *J. Amer. Chem. Soc.*, 1946, **68**, 1145.

[4] Flory, *J. Chem. Physics*, 1945, **14**, 453.