2. The viscosity of pure sulfur is independent of the rate of heating and cooling and of the previous heat treatment of the sulfur. The viscosity cooling curve practically coincides with the heating curve.

3. It has been shown that the low viscosities given by preheated sulfur containing organic matter are due to the formation of hydrogen persulfides and that preheating has no effect on the values for pure sulfur.

4. Curves showing the lowering effect of hydrogen persulfide on the viscosity of sulfur are given.

5. The effect of gases on the viscosity of sulfur is described. Hydrogen sulfide through reaction with sulfur to form persulfides greatly reduces the viscosity of sulfur. The lowering effect by ammonia gas is due to minute formation of hydrogen sulfide and persulfides by reaction with the sulfur.

6. The presence of minute amounts of hydrogen persulfides and hydrogen sulfide in sulfur profoundly affects its viscosity and probably other physical properties. It is believed that traces of these substances are responsible for much of the lack of concordance in the physical data of sulfur.

7. The effect of the halogens on lowering the viscosity of sulfur is shown in detail. Because of the persistence of this effect, sulfur so treated can be used as a heat transfer medium.

NEW YORK, N. Y. RECEIVED SEPTEMBER 22, 1942

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Properties of Liquid Sulfur

BY RICHARD E. POWELL AND HENRY EYRING

Introduction.—It is well known that when molten sulfur is heated above about 160°, the mobile liquid changes into an extremely viscous liquid. The low-temperature liquid (S_λ) has been shown to consist of 8-membered puckered rings,[1] and there is considerable evidence that the high-temperature liquid (S_μ) is made up of long sulfur chains. The two forms are supposed to be in dynamic equilibrium. The recent investigation by Bacon and Fanelli[2] of the viscosity of specially purified sulfur has shown, in addition to other important results, that the equilibrium is rapidly and completely reversible. It is the purpose of this paper to formulate a quantitative theory for the equilibria and for the viscosity of molten sulfur, based upon the current picture of the behavior of long-chain polymers.

We shall assume that the equilibria in molten sulfur are given by the reaction

$$\frac{x}{8}\, S_{8\,(\text{ring})} \rightleftharpoons S_{x\,(\text{chain})} \quad 0 < x < \infty \qquad (1)$$

The polysulfur chains are not all of the same length, but there is a distribution of chain lengths. Among the experimental evidences for this model of polysulfur are the following which support the existence of long chains.

(a) S_μ, produced by chilling viscous sulfur or from the vapor above viscous sulfur, is insoluble in carbon disulfide.[3,4]

(b) The extremely high viscosity of S_μ is characteristic of long-chain polymers.[5,6,2]

(c) Chilled S_μ gives elastic threads, which may be stretched 800-fold, and give fiber-patterns upon X-ray analysis.[7,8,9,10]

(d) Liquid S_λ (120–150°) shows "structure-viscosity."[11]

(e) The Eötvös relation, applied to the surface tension of molten sulfur, indicates that S_λ is about S_6 while S_μ is about S_{18}.[12] (At the present time, this is to be interpreted as a segment length and not as the length of the molecule[13]).

The following are evidences for the existence of short chains:

(f) The molecular weight of sulfur in the vapor state indicates that the molecule is S_8 only at low

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(1) B. E. Warren and J. T. Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

(2) R. Bacon and R. Fanelli, THIS JOURNAL, **65**, 639 (1943).

(3) A. Smith, *et al.*, *Z. physik. Chem.*, **42**, 469 (1903); **52**, 602 (1905); **54**, 257 (1906); **57**, 685 (1907); **61**, 200, 209 (1908); **77**, 661 (1911).

(4) D. L. Hammick, W. Cousins and E. Langford, *J. Chem. Soc.*, 797 (1928).

(5) L. Rotinjanz, *Z. physik. Chem.*, **63**, 609 (1908).

(6) C. C. Farr and D. B. McLeod, *Proc. Roy. Soc. London*, **A97**, 80 (1920).

(7) J. Trillat and H. Forestier, *Bull. soc. chim.*, **51**, 248 (1932).

(8) J. D. Strong, *J. Phys. Chem.*, **32**, 1225 (1928).

(9) K. Sakurada and H. Erbring, *Kolloid. Z.*, **72**, 129 (1935).

(10) K. H. Meyer and Y. Go, *Helv. Chim. Acta*, **17**, 1081 (1934); K. H. Meyer, *Trans. Faraday Soc.*, **32**, 148 (1936).

(11) W. Ostwald and H. Malss, *Kolloid. Z.*, **63**, 305 (1933).

(12) A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).

(13) W. Kauzmann and H. Eyring, THIS JOURNAL, **62**, 3113 (1940).

temperatures. At higher temperatures it ranges from S_8 to S_1.[14]

(g) A fraction of the carbon disulfide extract ("S_π") is more soluble than rhombic sulfur.[15]

(h) The room-temperature vapor above S_μ has a molecular weight of $S_{7.0-7.9}$.[16]

(i) Decreased depolarization of the Tyndall light as the temperature increases from 120 to 265° is taken to indicate the presence of smaller particles than S_8.[17]

Calculation of the Equilibria.—The equilibrium constant for reaction (1) is

$$\frac{y_x}{(y^*)^{x/8}} = K_x = e^{-\Delta H/RT + (ax + b)/R} \qquad (2)$$

where x is the chain length, y_x the mole fraction of molecules of length x, and y^* the mole fraction of S_8 rings. The heat of the reaction, ΔH, is taken to be constant, since the net result of making a chain of any length out of rings is to break just one S–S bond. The entropy of the reaction is made up of two terms: a constant term b due to the end effects and a term proportional to chain length, ax. Equation (2) may be rewritten as

$$y_x = y^* K_8 e^{8\alpha} e^{-\alpha x} \qquad (3)$$

in which the coefficients of x have been collected into the one parameter α, defined by

$$-\alpha \equiv \frac{a}{R} + \frac{\ln y^*}{8} \qquad (4)$$

The number of chain molecules m is now given by

$$m = \sigma \int_0^\infty y_x \, dx = \frac{\sigma y^* K_8 e^{8\alpha}}{\alpha} \qquad (5)$$

where σ is the total number of molecules. The number of chain molecules is also evidently given by the total number less the number of rings

$$m = \sigma(1 - y^*) \qquad (6)$$

Upon equating Eq. (5) and (6), inserting the value of y^* from Eq. (4), and expanding the exponentials (α will be shown to be very small), we obtain

$$\alpha^2 = -\alpha \frac{a}{R} + \frac{K_8}{8} \qquad (7)$$

Since the equilibrium constant K_8 can be made as small as we please by going to lower temperatures, $-a/R$ is obviously a lower limiting value for α and will be written α_0.

The number average chain length Z is given by

$$Z = \frac{\int_0^\infty x y_x \, dx}{\int_0^\infty y_x \, dx} = 1/\alpha \qquad (8)$$

and the weight average chain length Z_w is given by

$$Z_w = \frac{\int_0^\infty x^2 y_x dx}{\int_0^\infty x y_x dx} = 2/\alpha = 2Z \qquad (9)$$

Henceforth $1/Z$ can be written for α and $1/Z_0$ for α_0. Thus Eq. (7) becomes

$$\frac{Z}{Z_0} = \frac{2}{1 + (1 + {}^1/_2 K_8 Z_0^2)^{1/2}} \qquad (10)$$

The weight fraction of sulfur which is in the form of chains is given by

$$\phi = \frac{\int_0^\infty x y_x dx}{8y^* + \int_0^\infty x y_x dx} \approx \frac{1 - \alpha_0/\alpha}{2 - \alpha_0/\alpha} = \frac{1 - Z/Z_0}{2 - Z/Z_0} \qquad (11)$$

Eq. (11) expresses an unusual and interesting result. The weight fraction of chains, ϕ, is near zero at low temperatures ($Z \approx Z_0$), and rises toward an upper limit of 50% at high temperatures ($Z \ll Z_0$).[18]

This is precisely the result which was found experimentally, and has hitherto been unexplained. Figure 1 presents the observed values for per cent.

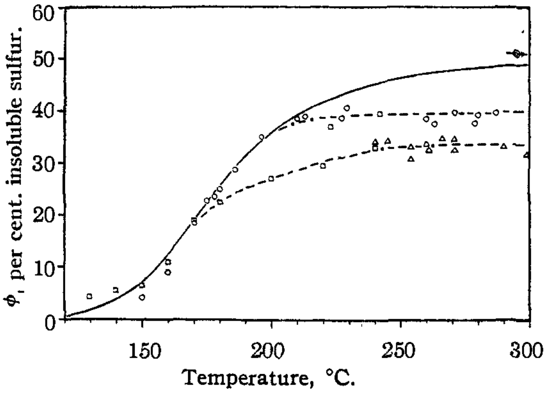

Fig. 1.—Equilibrium *vs.* temperature: □ Smith and Holmes, △ Hammick "fair droplets," ○ Hammick "good droplets," ◎ chilled stream of burning sulfur; solid line is calculated.

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[14] Mellor, "Comprehensive Treatise, "Longmans, Green Co., New York, N. Y., 1937, Vol. 10, p. 58..

[15] A. Aten, *Z. physik. Chem.*, **86**, 1 (1914).

[16] K. Neumann, *ibid.*, **A171**, 399 (1934).

[17] B. Lange and W. Cousins, *ibid.*, **A143**, 135 (1929).

[18] The exact form of Eq. (11) is

$$\phi = \frac{\exp(8/Z - 8/Z_0) - 1}{\exp(8/Z - 8/Z_0) - 1 - 8/Z} \qquad (11a)$$

It can be seen from Eq. (11a) that if sulfur could persist in the liquid state up to 800–900°, it would in that temperature range undergo another transition, with ϕ going to 100%. At those temperatures the number average chain length Z would be 8 and less.

insoluble sulfur, together with those calculated with the parameters ΔH = 27.5 kcal., $Z_0^2 \exp(\Delta S/R) = 10^{14}$. The experimental workers were unable to reach the asymptotic value at high temperatures since (as they realized and stated) some reversion always occurs on cooling the droplets. Hammick, *et al.*, who took pains to chill the droplets rapidly, obtained higher values than Smith did in his earlier work. Apparently the best experimental value (51%) was that obtained by suddenly chilling a stream of burning sulfur.

Calculated values of Z/Z_0 and of ϕ are also given in Table I.

TABLE I

Temp., °C.	Z/Z_0	ϕ	$\phi(Z/Z_0)^{1/2}$
120	0.9926	0.0074	0.0074
130	.9825	.0172	.0170
140	.9615	.0370	.0363
150	.9220	.0723	.0694
160	.8567	.1254	.1160
170	.7649	.1903	.1665
180	.6558	.2561	.2074
190	.5432	.3136	.2311
200	.4389	.3594	.2381
210	.3492	.3942	.2330
220	.2756	.4201	.2205
230	.2168	.4392	.2045
240	.1706	.4534	.1873
250	.1347	.4639	.1702
260	.1062	.4720	.1538
270	.0851	.4778	.1394
280	.0682	.4824	.1260
290	.0550	.4859	.1139
300	.0446	.4886	.1032

A possible source of error in the determination of ϕ might be that carbon disulfide extracted a considerable amount of the shorter chains. We can investigate this as follows: if everything below length W is soluble

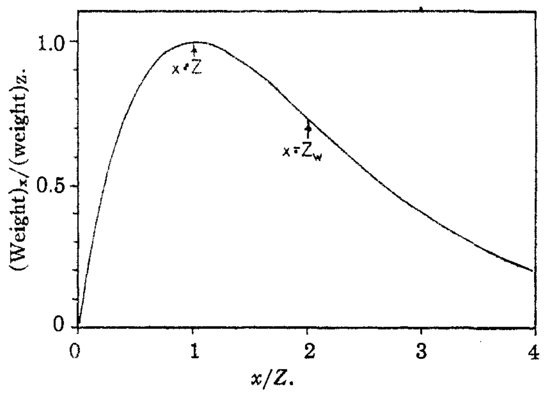

Fig. 2.—Distribution of chain lengths, calculated.

$$\frac{\text{Weight of insoluble chains}}{\text{Total weight of chains}} = \frac{\int_W^\infty xy_x\mathrm{d}x}{\int_0^\infty xy_x\mathrm{d}x} = e^{-W/Z}(1 + W/Z) \quad (12)$$

It is seen from Eq. (12) that for reasonable values of W/Z the error is negligible.

The distribution of chain lengths about the mean is given by

$$\frac{\text{Weight of length } x}{\text{Weight of length } Z} = \frac{xe^{-x/Z}}{Ze^{-Z/Z}} = \frac{x}{Z}e^{1-x/Z} \quad (13)$$

and is thus independent of temperature. The distribution is represented graphically in Fig. 2. It will be noted that the number-average chain length is also the most probable chain length.

Equilibria with Added Halogens.—Small amounts of added halogens (or H_2S) are markedly effective in reducing the viscosity of molten sulfur, probably because of the formation of chains such as S–S–S . . . S–S–X which are shorter than the original chains.[2] The equilibria under such conditions will now be derived.

Consider the reactions

$$(x/8)S_8 \rightleftharpoons S_x \quad (1)$$

$$(x/8)S_8 + Q \rightleftharpoons S_xQ \quad (14)$$

where Q is any admixed foreign atom. It will be assumed that Reaction (14) differs from Reaction (1) in having a different value of ΔF, therefore, a different value of K_8, which may be called K_8'. Upon formulating the equilibrium constants and solving as in the preceding section, one obtains

$$\alpha(\alpha - \alpha_0) = (K_8 + (Q)K_8')/8 \quad (15)$$

which is just Eq. (7) with a new and larger value of K_8. The concentration (Q) may now be eliminated, since the total amount of added Q is known. The ratio M of the number of Q atoms to the number of S atoms is

$$M = \frac{(Q) + \frac{y^*K_8'(Q)e^{8\alpha}}{\alpha}}{8y^* + \frac{y^*K_8e^{8\alpha}}{\alpha^2} + \frac{y^*K_8'(Q)e^{8\alpha}}{\alpha^2}} \quad (16)$$

Upon solving Eq. (15) and (16), the result is

$$\alpha = \alpha_i + 2M + \left[-M\frac{\alpha_0}{\alpha} + \left(\frac{K_8}{8\alpha} - \frac{K_8}{8\alpha_i}\right) + \frac{1}{K_8'}\left(\frac{K_8}{8} + \alpha\alpha_0 - \alpha^2\right)\right] \quad (17)$$

where α_i is the α without added Q. The quantities inside the square brackets are small and may be neglected to a first approximation giving

$$1/Z = 1/Z_i + 2M \text{ or } 1/Z_w = 1/Z_{wi} + M \quad (18)$$

Eq. (18) will be useful in the following section, where viscosity will be discussed. It is interesting

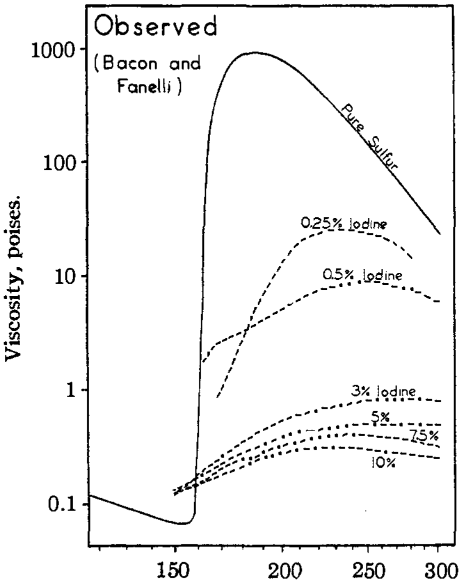

Fig. 3a.—Observed viscosity.

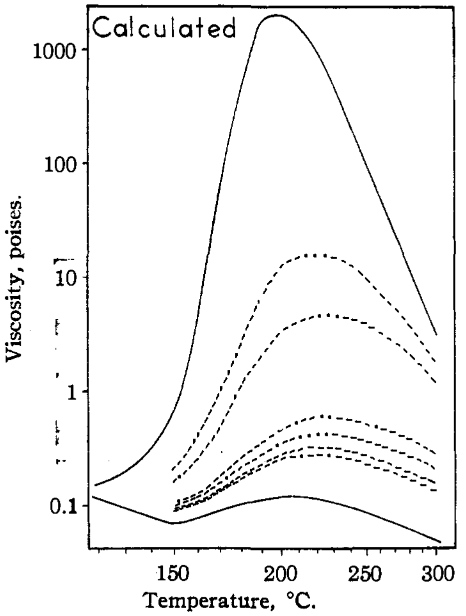

Fig. 3b.—Calculated viscosity. The lowest line is the hypothetical viscosity of a mixture of S_8 rings and S_8 chains.

that Eq. (18) could have been deduced intuitively, by saying that the number of "cuts" in a chain containing a mole of S atoms (*i. e.*, reciprocal of weight-average chain length) is equal to the number of "natural" cuts (*i. e.*, reciprocal of initial weight-average chain length) plus the number of cuts caused by admixed atoms (*i. e.*, number of atoms).

Viscosity.—The treatment of the viscosity of liquid sulfur will be based upon two assumptions. The first assumption is that the viscosity of polysulfur chains can be represented by an equation found by Flory[19] for molten polyesters, and discussed by Kauzmann and Eyring[18]

$$\eta_{\text{chains}} = \frac{Nh}{V} e^{-\Delta S^\ddagger/R + \Delta H^\ddagger/RT + BZ_{\text{w}}{}^{1/2}/R} \qquad (19)$$

where η is the viscosity, N is Avogadro's number, h is Planck's constant, V is the volume of a unit of flow, $\Delta S^\ddagger$ is the entropy of activation for viscous flow, $\Delta H^\ddagger$ is the heat of activation, B is a constant, and Z_{w} is the weight-average chain length.

The second assumption is that the viscosity of ring and chain mixtures can be expressed by

$$\eta_{\text{mixture}} = (\eta_{\text{rings}})^{1-\phi}\,(\eta_{\text{chains}})^{\phi} \qquad (20)$$

Eq. (20) is known to hold well for mixtures of simple liquids, and is probably of fairly general validity.[20]

The complete expression for viscosity is then

$$\ln \eta = \ln \frac{Nh}{V} + (1-\phi)\left[\frac{\Delta H_1^\ddagger}{RT} - \frac{\Delta S_1^\ddagger}{R}\right] + \phi \left[\frac{\Delta H_2^\ddagger}{RT} - \frac{\Delta S_2^\ddagger}{R}\right] + \phi\,\frac{BZ_{\text{w}}{}^{1/2}}{R} \qquad (21)$$

The viscosity data[2] from which the parameters of Eq. (21) are to be evaluated is presented graphically in Fig. 3a. We proceed as follows: Consider the viscosity values at any one temperature, both without added halogens (η_{i}) and with added halogens (η_{M}). The effect of added halogens in reducing Z has already been formulated in Eq. (18). The difference between ln η_{i} and ln η_{M} is now

$$\ln \eta_{\text{i}} - \ln \eta_{\text{M}} = \frac{\phi B Z_{\text{w}}{}^{1/2}}{R}\,(1 - 1/\sqrt{1 + MZ_{\text{w}}}) \qquad (22)$$

(Eq. (22) is exact as written in the high-temperature region, where ϕ is near 50%; in the actual computation, the appropriate small correction, *cf.* Eq. (21), was made for the effect of added halogen upon ϕ). Equation (22) contains two unknowns, B and Z_{w}; hence any two measurements of (ln η_{i} − ln η_{M}) may be solved simultaneously for the two unknowns. Values of η_{M} are available at six different values of M, so a check is available on the correctness of the calculations.

The chain length Z was determined in the above way, over a range of temperature of 200–300°. The results are plotted in Fig. 4, together with the line calculated from Table I with Z_0 = 27,000.

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(19) P. J. Flory, THIS JOURNAL, **62**, 1057 (1940).

(20) R. E. Powell, W. E. Roseveare and H. Eyring, *Ind. Eng. Chem.*, **33**, 430 (1941).

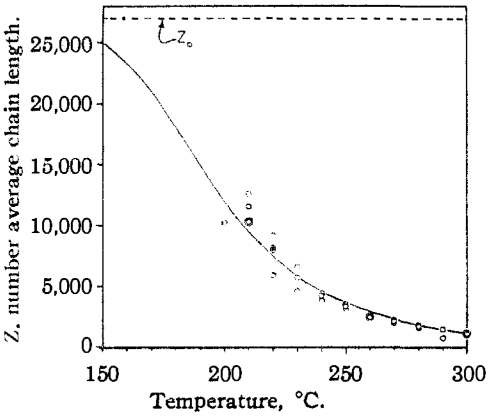

Fig. 4.—Chain length *vs.* temperature: O single circles, one computation; ◎ double circles, average of ten computations; solid line is calculated.

To determine B, ($\ln \eta_i - \ln \eta_M$) was plotted against $Z_w^{1/2}(1 - 1/\sqrt{1 + MZ_w})$ in Fig. 5, using data from 200–300°. The points fall reasonably well on a straight line, the slope of which gives $B = 0.35$.

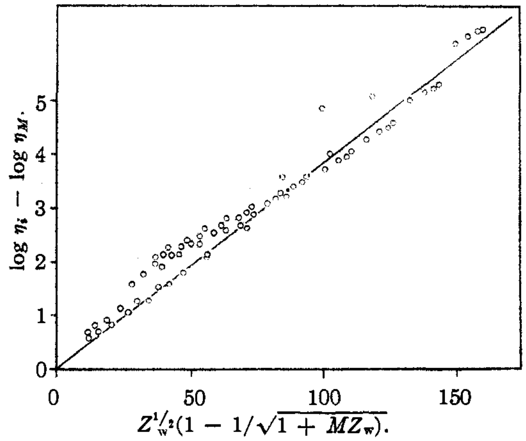

Fig. 5.—Viscosity *vs.* chain length.

Since B and Z_w are now known, the term for the effect of chain length on viscosity can be subtracted from Eq. (21), leaving the first three terms. The result (plotted as the lowest curve in Fig. 3b), is the hypothetical viscosity of the mixture of S_8 rings and S_8 chains, in the absence of long S_x chains. This curve was fitted with the parameters chosen by trial: $V = 128$ cc. (volume of S_8), $\Delta H_1^\ddagger = 8.3$ kcal., $\Delta S_1^\ddagger = 2.0$ E. U., $\Delta H_2^\ddagger = 9.0$ kcal., $\Delta S_2^\ddagger = 0$. It is worth pointing out that if sulfur did not form long chains, it would be a liquid with a normal viscosity of the order of 10 centipoises. The rapid increase of viscosity (at about 160°) to 20,000 times this value occurs simultaneously with the rapid growth of the amount of chains: the viscosity passes through a maximum at about the temperature at which $\phi Z^{1/2}$ is a maximum (*cf.* Table I): and the viscosity decreases above 200° as the rising temperature causes the chain length to decrease.

Effect of Pressure on Viscosity.—It has been suggested[21] that the effect of pressure on the viscosity of liquid sulfur would be of interest. From the model of liquid sulfur derived in the present paper, together with the known expressions for the effect of pressure on equilibria and on viscosity, some general conclusions can be drawn as to the viscosity of sulfur at high pressures. (1) Since S_8 rings become S_8 chains with a decrease in volume,[22] pressure will favor chains. This will result in an increase of viscosity. (2) Since short chains become long chains with a decrease in volume, pressure will favor the longer chains. This also will produce an increase of viscosity. (3) In the expression for viscosity, $\Delta F^\ddagger_{p=0} = \Delta H^\ddagger_{p=0} - T\Delta S^\ddagger_{p=0}$ should be replaced by $\Delta F^\ddagger_{p=P} = \Delta F^\ddagger_{p=0} + \int_0^P \Delta V^\ddagger \, dp = \Delta F^\ddagger_{p=0} + P\Delta V^\ddagger$. Here P is the pressure and $\Delta V^\ddagger$ is the volume change of activation, which may be taken to be about $^1/_7$ the volume of an S_8 molecule — the flowing unit.[23] This effect also gives an increase of viscosity. Thus higher pressure exerts three separate effects, each contributing to a higher viscosity.

To obtain a quantitative estimate of the viscosity under pressure, we proceed as follows. The equilibrium constant for Reaction (1) is now

$$K_x = e^{-\Delta F/RT} = e^{-\Delta F_{p=0}/RT - P(ux + v)/RT} \quad (23)$$

where u is the change in volume per chain atom, and v is the change in volume due to end effects. The value of u is estimated to be -0.1 cu. cm. per gram atom; the value chosen for v has almost no effect on the final result, but it is probably of the order of 1 cu. cm. per mole.

Eq. (23) is now solved just as Eq. (2) was, and the viscosity is obtained by inserting the new values of ϕ, Z, and $\Delta H^\ddagger$ into Eq. (21). The calculated results are presented graphically in Fig. 6 for pressures of 10, 100, and 1000 atmospheres.

According to these results, molten sulfur under moderate pressure should attain a viscosity typical of solid substances (10^{13} poises and upwards).

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[21] L. E. Copeland, W. D. Harkins and G. E. Boyd, *J. Chem. Phys.*, **10**, 357 (1942).

[22] Mellor, "Comprehensive Treatise," Vol. X, p. 63.

[23] D. Frisch, H. Eyring and J. F. Kincaid, *J. App. Phys.*, **11**, 75 (1940).

The actual numerical values of Fig. 6 must of course be regarded as approximations, but the direction and magnitude of the pressure effect is clear.

In experiments by Bridgman,[24] sulfur has been subjected to about 300,000 atmospheres of pressure, and X-ray pictures taken. It is stated that "the lines of the original material entirely disappeared, and a few broad lines replaced them. Either sulfur was rendered amorphous . . . . or else there was a permanent change." This is the only experimental result known to us on the behavior of sulfur under pressure, and the pressure used is far above the range we have considered.

Discussion.—The numerical parameters evaluated in this paper are assembled in Table II.

TABLE II

$$K_x = e^{-\frac{27,500}{RT} + \frac{23.84}{R} - \frac{x}{27,000}}$$

$$\eta_{\text{rings}} = \frac{Nh}{128} e^{-\frac{2.0}{R} + \frac{8,300}{RT}}$$

$$\eta_{\text{chains}} = \frac{Nh}{128} e^{-\frac{9,000}{RT} + \frac{0.35 Z_w^{1/2}}{R}}$$

The treatment of the equilibrium might be refined by including in the equilibrium constant K_x additional factors for the effect of changing environment, along the lines developed by recent workers.[25,26] Since the present simple treatment appears to be quite satisfactory, and the additional terms would introduce more disposable parameters, and since the molecular environment changes only slightly during the transition, such a refinement is unwarranted at present.

The analogy between polysulfur chains and long hydrocarbon chains can be seen in the entropies of the reactions of formation[27]

$$(x/8)\mathrm{S}_{8\ \text{ring}} \longrightarrow \mathrm{S}_{x\ \text{chain}} \qquad \Delta S = 23.84 - 0.0000735x$$

$$(x/6)\ \text{cyclohexane} \longrightarrow (\mathrm{CH}_2)_x \qquad \Delta S = 25.0 - 0.5x$$

The heat of the reaction, ΔH, is 27.5 ± 5 kcal. (In fact, this value cannot be much larger if the reaction is to take place rapidly at 200°.) This low heat is to be contrasted with the bond strength of the S–S bond, 63.8 kcal., given by Pauling.[28] The explanation of this discrepancy probably lies in the fact that because of the accessibility of *d* states each sulfur atom may, from electronic considerations,[29] form a double bond with one or even with both of its neighbors. The resonance energy of these structures is apparently large. The reaction from which the bond strength of 63.8 kcal. was deduced is

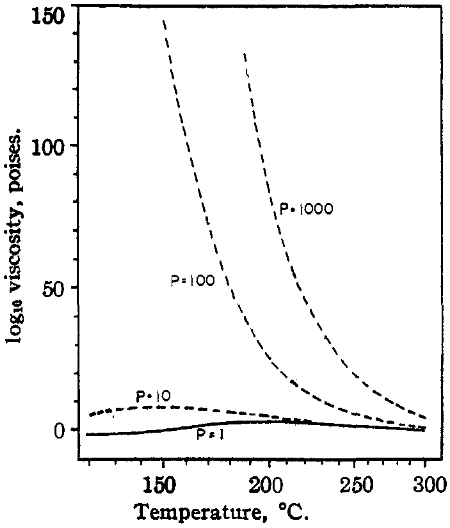
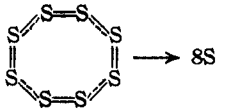
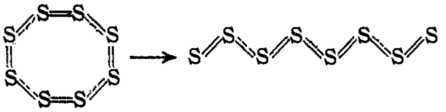


Fig. 6.—Effect of pressure on viscosity, calculated.



while the reaction leading to polysulfur is



The former reaction destroys all of the resonance energy, the latter retains much of it. The suggested double-bondedness of sulfur is also in accord with its general chemical behavior.

The two assumptions made in the treatment of viscosity are probably only approximately true for this case. However, each of these assumptions has been demonstrated useful for other substances, and each has some theoretical justification. The imperfection of fit of the calculated to the observed viscosities is probably to be ascribed to the inaccuracy of the second assumption. It is to be remarked that no other choice of any of the parameters in Table II will improve the agreement between calculated and observed viscosities. The deficiency in the assumed theory is therefore real, although what modification is required is not clear.

The viscosity of ring sulfur may be compared

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(24) P. W. Bridgman, *J. App. Phys.*, **12**, 461 (1941).

(25) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(26) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942).

(27) G. Parks and H. Huffman, "Free Energies of Some Organic Compounds," Chem. Catalog Co., New York, N. Y., 1932.

(28) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

(29) G. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

with the viscosity of another ring molecule, naphthalene

$$\eta_{C_{10}H_8} = \frac{Nh}{112} e^{-6.7/R + 6{,}300/RT}$$

Both substances have rather high heats of activation, and positive entropies of activation.

The viscosity of polysulfur may be compared with the viscosity of a polyester

$$\eta_{\text{polyester}} = \frac{Nh}{500} e^{-6.8/R + 8{,}200/RT + 0.5\, Z_w{}^{1/2}/R}$$

Both substances have rather high heats of activation, and the two values of B are similar.

All of the above results provide a general confirmation, as well as a detailed description, of the postulated chain structure of polysulfur.

Acknowledgment.—The authors wish to express their appreciation to Drs. Bacon and Fanelli for permission to use their data in advance of publication, and for valuable discussion.

Summary

1. The available measurements of the equilibria between 8-membered sulfur rings and sulfur chains of all lengths are interpreted in terms of a quantitative thermodynamic theory.

2. Using the values of molecular composition so determined, the viscosity is formulated in terms of current theories and the calculated and experimental values compared. The decreases in viscosity due to impurities, observed by Bacon and Fanelli, are compared with theory.

PRINCETON, NEW JERSEY RECEIVED SEPTEMBER 18, 1942

[DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

Raman Spectrum and Molecular Vibrations of Nitric and Deuteronitric Acids

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The interpretation of vibration spectra has been considerably lagging behind the rapid accumulation of experimental data. While the Raman spectra of many hundreds of compounds have been recorded, a complete or nearly complete correlation of frequencies and vibration forms has been ascertained for only a small number of substances.

The Raman spectrum of few compounds has been investigated as frequently as that of nitric acid.[2] In addition, solutions of various concentrations have been examined by many authors.

Among the various attempts of interpretation,[3] that of Chédin is outstanding. This author made full use of all available methods, namely, Placzek's polarization rules, the comparison with the spectra of the nitrate ion, organic nitrates and nitro compounds, and Bjerrum's force systems. Nevertheless, even Chédin's results are far from complete and sufficiently certain. It was obvious that entirely new experimental data were necessary for any further progress.

New data may be obtained by an investigation of deuteronitric acid. The ratio of the corresponding frequencies of the hydrogen and deuterium compound, which will be called the "isotopic quotient" and denoted by q, is a measure of the extent to which the hydrogen participates in the vibration. The isotopic quotient assumes the value 1 if the hydrogen does not oscillate, and the value $\sqrt{2}$ if the vibration is carried out by the hydrogen alone. Thus the isotopic quotients furnish sometimes an immediate criterion of interpretation.

In addition, the regrouping of the lines in the spectrum of the deuterium compounds is sometimes instrumental in the discovery of anomalies of a purely experimental nature (superposition of lines) as well as in the frequencies themselves (Fermi resonance[4]).

Several authors made successful use of the so-called product formula, derived independently by Teller and by the senior author.[5] This formula furnishes relations between the vibration frequencies of isotopic molecules, the atomic masses

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