[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Equilibrium Polymerization of Sulfur

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A simple and unified theory is presented describing the ring-chain equilibrium over the entire liquid range of sulfur. One single formula is given describing the number average degree of polymerization at any temperature in that range, and the ΔH and ΔS values for the initiation and propagation reactions are given.

In previous papers,[1-3] a theory describing equilibrium polymerization in the presence of an initiator was developed and successfully applied to the polymerization of ε-caprolactam by water. The reversibility of the viscosity–temperature curve of sulfur[4] indicates that here also an equilibrium polymerization is involved, differing, however, from caprolactam by the absence of an external initiator. The conditions at equilibrium at any temperature for the polymerization of sulfur may be derived as

$$\mathrm{M} \underset{}{\overset{K'}{\rightleftarrows}} \mathrm{M}^*; \quad K' = \frac{M^*}{M}; \quad M^* = K'M \tag{1}$$

where M is an S_8 ring, and M* an S_8 diradical.

$$\mathrm{M}^* + \mathrm{M} \overset{K_3'}{\rightleftarrows} \mathrm{M_2}^*; \; K_3' = \frac{M_2^*}{M^*M}; \; M_2^* = K_3'M^*M = K_3'K'M^2 \tag{2}$$

$$\mathrm{M_2}^* + \mathrm{M} \overset{K_3'}{\rightleftarrows} \mathrm{M_3}^*; \; K_3' = \frac{M_3^*}{M_2^*M}; \; M_3^* = K_3'M_2^*M = K_3'K'M^3 \tag{3}$$

$$\mathrm{M}_{n-1}^* + \mathrm{M} \overset{K_3'}{\rightleftarrows} \mathrm{M}_n^*; \; M_n^* = K_3'^{\,n-1}K'M^n \tag{4}$$

Let N = total concentration of polymer molecules.

$$N = \sum_{n=1}^{\infty} M_n^*$$

$$N = K'M[1 + K_3'M + (K_3'M)^2 + (K_3'M)^3 + \ldots\ldots]$$

$$N = \frac{K'M}{1 - K_3'M} \tag{5}$$

Let W = total concentration of monomer segments (S_8 units) incorporated in the polymer.

$$W = \sum_{n=1}^{\infty} nM_n^*$$

$$W = K'M[1 + 2K_3'M + 3(K_3'M)^2 + 4(K_3'M)^3 + \ldots\ldots]$$

$$W = \frac{K'M}{(1 - K_3'M)^2} \tag{6}$$

It is obvious that $W/N = P$, where P is the number average chain length (in terms of S_8 units).

$$P = \frac{W}{N} = \frac{1}{1 - K_3'M} \tag{7}$$

We also know that

$$M_0 = M + W = M + \frac{K'M}{(1 - K_3'M)^2} \tag{8}$$

and inserting equation 7 into equation 8, we get the useful calculational equation

$$M_0 = \frac{P-1}{PK_3'} + \frac{K'}{K_3'} \times P(P-1) \tag{8a}$$

from which the entire chain-length *vs.* temperature curve may be calculated by knowing only the parameters K' and K_3' (which are temperature dependent, and subject to the usual laws governing equilibrium constants) and M_0 which equals 3.90 moles/kg. (We employ this concentration unit rather than moles/liter because of the temperature dependency of the density of sulfur and because of the density change when monomer is converted to polymer, which may also be temperature dependent, and for which no precise data seem to be available.) It must be emphasized that in deriving equation 8a, no assumptions were made which restrict the validity of the formula to any temperature region; it should be applicable in the entire liquid range. Furthermore, the derivation does not take into account the probable formation of rings larger than S_8, nor does it depend on the detailed mechanism by which equilibrium is reached (this is shown for a similar case in reference 3. Appendix II). The probable presence of S_6 rings is also not taken into account, since their effect on the equilibrium is believed to be negligible.

As has been stated, only a knowledge of K' and K_3' for any temperature is required for the determination of P and M at that temperature, and, conversely, if P and M are known, K' and K_3' can be determined. Unfortunately, neither P nor M can be determined experimentally with high precision. Hammick, Cousins and Langford[5] attempted to determine M by measuring the percentage of sulfur of small quenched droplets insoluble in solvent. This is perhaps the most direct estimate of the percentage of polymer in the liquid, yet it is clearly not ideal, due, *inter alia*, to the difficulty of quenching the liquid quickly enough to obtain true equilibrium values. No experimental estimate of the molecular weight or the chain length appears to be available.

The molecular complexity of liquid sulfur was investigated on a theoretical basis by G. Gee[6] in an important pioneering contribution. We shall use his theoretical results as primary data in the absence of comprehensive experimental data. Gee's theories are necessarily quite cumbersome because he had to draw together very sparse experimental data and very ingenious assumptions to obtain a comprehensive semi-quantitative description of the sulfur equilibrium. His description does satis-

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[1] A. V. Tobolsky, *J. Polymer Sci.*, **25**, 220 (1957).

[2] A. V. Tobolsky, addendum to above, in press.

[3] A. Eisenberg and A. V. Tobolsky, THIS JOURNAL, **81**, in press (1959).

[4] R. F. Bacon and R. Fanelli, *ibid.*, **65**, 539 (1943).

[5] Hammick, Cousins and Langford, *J. Chem. Soc.*, 797 (1929).

[6] G. Gee, *Trans. Faraday Soc.*, **48**, 515 (1952).

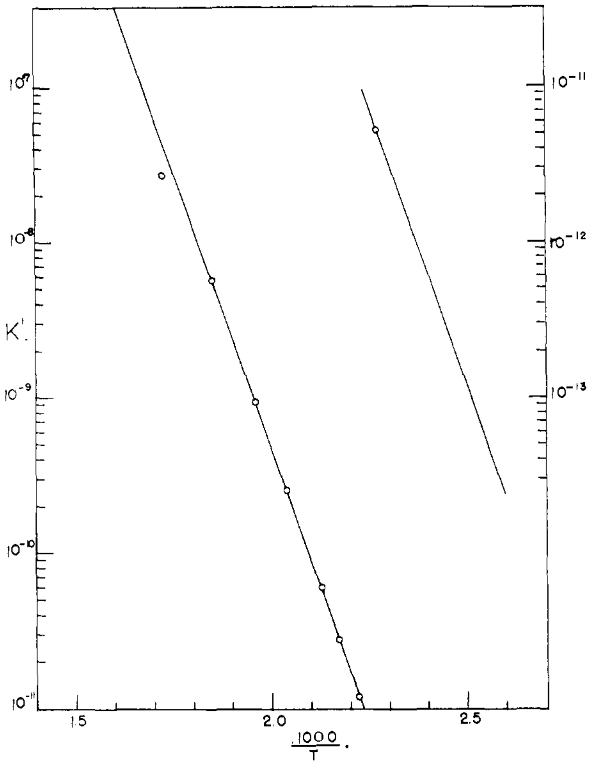

Fig. 1.—K' *vs.* $1/T$.

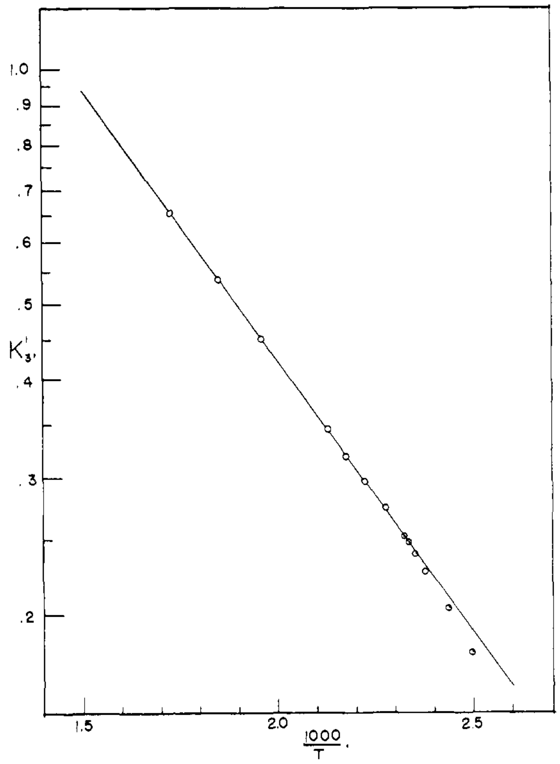

Fig. 2.—K_3' *vs.* $1/T$.

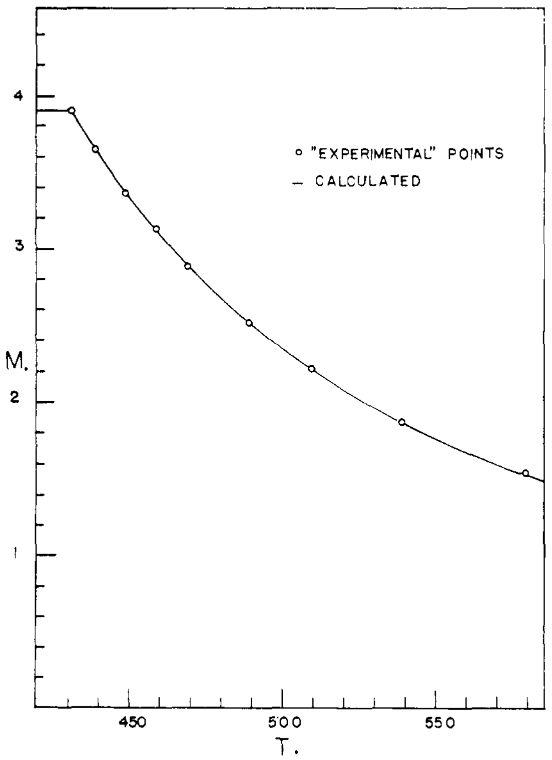

Fig. 3.—M *vs.* T.

factorily incorporate all the known experimental facts as far as these exist.

On the other hand, an example of the complexity of Gee's theory is that he had to use two quite distinct treatments below and above the "transition temperature" at 432°K., neither of which is valid in the immediate vicinity of 432°K.

The theory given in equations 1–8, on the other hand, does give a satisfactory explanation of all of Gee's results on the basis of a single, simple treatment which is valid over the entire liquid range as far as we can determine.

Gee's results, which we use in the sense of primary experimental data, are given in equations 9 through 12

$$\phi = 1 - \exp\left[\frac{H_4}{R}\left(\frac{1}{T\phi} - \frac{1}{T}\right)\right] \qquad (9)$$

$$\ln P = \ln P_m + \frac{H_5}{2R}\left(\frac{1}{T} - \frac{1}{T_m}\right) + \frac{1}{2}\ln\frac{\phi}{\phi_m} \qquad (10)$$

$$\phi_m = -\frac{H_4}{H_5 - H_4} \qquad (11)$$

applicable above the "transition temperature" T_ϕ (at which polymer seems to appear suddenly), and

$$\ln\left(1 - \frac{1}{P_\phi}\right) - \ln\left(1 - \frac{1}{P}\right)\frac{H_4}{8R}\frac{1}{T_\phi} - \frac{1}{T} \qquad (12)$$

applicable below T_ϕ, where ϕ is the weight fraction of polymer in the liquid, H_4 refers to the reaction $S_i^* \rightleftarrows S_{i-8}^* + S_8$, P_m is the maximum chain length (taken as 10^6 atoms), T_m is the temperature at which P_m is reached and ϕ_m is the corresponding weight fraction of the polymer, H_5 refers to the reaction $S_i^* \rightleftarrows S_{i-x}^* + S_x^*$, and P_ϕ is the chain length at the transition temperature. In a later publication[7] a final set of numerical values of the constants used in equations 9 through 12 were

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(7) F. Fairbrother, G. Gee and G. T. Merrall, *J. Poly. Sci.*, **16**, 459 (1955).

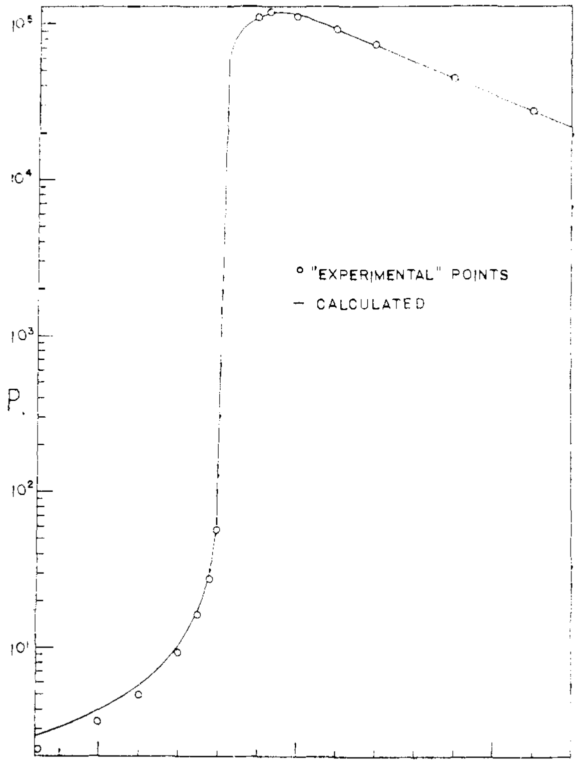

Fig. 4.—P *vs.* T.

given

H_4 = − 3200 cal./mole
T_ϕ = 432°K.
H_5 = 24,000–35,000 cal./mole (we used 30,000 cal./mole)

which yield

ϕ_m = 0.0964
T_m = 442.8°K.

(T_m and ϕ_m are related by equation 9).

Using the above constants in equations 9 through 12, expressions for P and M (where $M = M_0(1 - \phi) = 3.90(1 - \phi)$) can be obtained as explicit functions of temperature.

Once P and M are known at a given temperature, K' and K_3' can be calculated by equations 7 and 8. A list of numerical values of P and M obtained from Gee's formulas and the corresponding values of K' and K_3' are given in Table I.

It is of course not surprising that one can compute values of K' and K_3' from P and M at a single temperature. The check on the validity and usefulness of our approach is that the values of K' and K_3' at different temperatures should follow van't Hoff's law, and give sensible values for $\Delta H'$ and $\Delta H_3'$.

TABLE I

No.	Temp., °K.	P^a	M	K'	K_3'
1	385	2.21			0.1402
2	400	3.38			.1805
3	410	5.02			.2050
4	420	9.44			.2293
5	425	16.4			.2405
6	428	27.6			.2470
7	430	57.9			.2525
8	440	112,300	3.65	5.32×10^{-12}	.2736
9	450	113,900	3.36	1.22×10^{-11}	.2970
10	460	94,500	3.14	2.71×10^{-11}	.3185
11	470	75,800	2.89	6.09×10^{-11}	.3460
12	490	46,000	2.52	2.59×10^{-10}	.3976
13	510	28,400	2.21	9.45×10^{-10}	.4514
14	540	13,870	1.86	5.69×10^{-9}	.5366
15	580	5,750	1.52	2.71×10^{-8}	.6527

[a] The number average chain length as obtained from formula 10 or 12 refers to the number of S atoms in the chain. In this table, as also throughout this article, P is defined as the number average chain length in terms of S_8 units. Therefore, the values for P obtained from Gee's formulas were divided by 8 to yield the values given in Table I.

Plots of log K' *vs.* $1/T$ and log K_3' *vs.* $1/T$ obtained from Table I are shown in Figs. 1 and 2. Straight lines are obtained over most of the "experimental" range taken from Gee's computations. We assume that the correct values of K' and K_3' follow the van't Hoff law over the entire liquid range. The equations for the straight lines shown in Figs. 1 and 2 are

$$K' = 1.137 \times 10^5 \exp\left[-\frac{16{,}520}{T}\right];\quad \Delta S' = 23.0\,\frac{\text{cal.}}{\text{deg. mol.}}$$

$$\Delta H' = 32{,}800\,\frac{\text{cal.}}{\text{mole}} \tag{13}$$

$$K_3' = 10.43 \exp\left[-\frac{1596}{T}\right];\quad \Delta S_3' = 4.63\,\frac{\text{cal.}}{\text{deg. mole}}$$

$$\Delta H_3' = 3{,}170\,\frac{\text{cal.}}{\text{mole}} \tag{14}$$

where the entropies and enthalpies refer to a standard state of 1 mole/kg.

Using equations 13 and 14 as absolutely valid and substituting numerical values of K' and K_3' in equations 7 and 8, theoretical values of P and M can be obtained at all temperatures. These are plotted in Figs. 3 and 4 and compared with Gee's values. The comparison shows excellent agreement.

In summary, we have completely predicted the sulfur equilibrium curve by a simple and unified theoretical treatment, completely comprised in equations 7, 8, 13 and 14. Furthermore, equations 13 and 14 are merely the simplest expression of van't Hoff's law, with a non-temperature dependent ΔH^0 and ΔS^0.

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