

is stable only above that temperature. Thus, sulfur exhibits the curious phenomenon of a "floor temperature" in contrast to organic polymerizations which exhibit "ceiling temperatures," i.e., temperatures above which high polymer is unstable. In the case of sulfur, as the temperature increases above 160°C, the number average degree of polymerization  $D$ , rises, reaches a maximum at  $\sim 170^\circ$ , and falls slowly as the temperature is raised. The equilibrium monomer concentration  $[M]$  below 160°C remains constant and essentially equal to that of the original monomer concentration  $[M_0]$  and begins to fall slowly above 160°C, more and more monomer being converted to polymer as the temperature rises.

$K(0)$ ,  $K_3(0)$ , and  $M_0(0)$  are known from the previous work.<sup>4a</sup> To proceed, the following quantities are needed:  $\beta_M$ ,  $\Delta V_P$ , and  $\Delta V_I$ .

A search through Gmelin's book and *Chemical Abstracts* revealed only two determinations of the compressibility of liquid sulfur, both below 160°C. Kleppa,<sup>6</sup> by ultrasonic means, determined the isothermal compressibility of liquid sulfur at 115°C as  $34.6 \times 10^{-6} \text{ bar}^{-1}$  and the adiabatic compressibility as  $30.4 \times 10^{-6} \text{ bar}^{-1}$ . Later, Baccareda and Butta<sup>7</sup> determined the adiabatic compressibility of liquid sulfur in the range 120°–143°C, also by ultrasonic means, and found it to be  $29.98 \times 10^{-12} \text{ cm}^2/\text{dyn}$ . Due to the excellent agreement in the two values for the adiabatic compressibility at different temperatures, the isothermal compressibility is taken as  $35 \times 10^{-6} \text{ atm}^{-1}$  and is assumed not to vary appreciably over the temperature range of interest (120°–160°C).

$\Delta V_P$  is calculated from the experimental values of the density of sulfur<sup>8</sup> and the calculated values of the concentration of  $S_8$  (monomer) in the melt.<sup>4a,9</sup> The density of the monomer is known directly at temperatures below 160°C; since the density-temperature relationship is linear from the melting point to 160°C, the density above the temperature can be estimated by extrapolation. The difference between the experimentally determined density and the value thus obtained must be due to the presence of polymer, the density of which is different from that of the monomer; it can be calculated by use of the relation

$$\rho_{\text{polymer}} = (100 - \text{wt. \% monomer}) \left/ \left( \frac{100}{\rho_{\text{total}}} - \frac{\text{wt. \% monomer}}{\rho_{\text{monomer}}} \right) \right.$$

The  $\Delta V$  value for the polymerization reaction is obtained simply from

$$\Delta V_P = 256 [1/\rho_{\text{monomer}} - 1/\rho_{\text{polymer}}],$$

the best value being  $5.5 \pm 0.5 \text{ cm}^3/\text{mole}$  of  $S_8$ .

<sup>6</sup> O. J. Kleppa, *J. Chem. Phys.* **18**, 1303 (1950).

<sup>7</sup> M. Baccareda and E. Butta, *Ann. Chim. (Rome)* **45**, 50 (1955).

<sup>8</sup> A. M. Kellas, *J. Chem. Soc.* **113**, 909 (1918).

<sup>9</sup> G. Gee, *Trans. Faraday Soc.* **48**, 515 (1952); F. Fairbrother, G. Gee, and G. T. Merrill, *J. Polymer Sci.* **16**, 459 (1955).

The value of  $\Delta V_I$ , the volume change upon ring opening, is, of course, experimentally inaccessible; one must, therefore, resort to a comparison of this system with similar materials which are available both as rings and linear chains. The best example of such systems are the unstrained cycloparaffins ( $5 \leq n \leq 8$ ) and the corresponding linear alkenes, with the unsaturation located in any of the permissible positions, data of the physical properties of which are available in the standard reference works.<sup>10,11</sup> The results show a surprising uniformity, i.e., the molar volume of the linear 1-alkene is in all the cases greater than that of the cycloalkane by  $16.0 \pm 0.3\%$ . A change in the location of the double bond (or a change from *cis* to *trans* in cases other than the 1-alkenes) does not change that value greatly (2% in the worst case, that of *cis* pentane-2). Since the change in volume upon opening the  $S_8$  ring is experimentally indeterminable, and since no other systems are known to the author which approximate more closely the values to be expected in that reaction, 16% is taken as the approximate increase in molar volume upon opening of the  $S_8$  ring. Since the molar volume of  $S_8$  in the temperature range 120° to 160° is  $144 \text{ cm}^3$ ,  $\Delta V_I$  is taken as  $23 \text{ cm}^3$  per mole.

Calculations of the effect of pressure on the equilibrium polymerization of sulfur can now be carried out; the following being most illuminating:

- the change in the transition temperature with pressure;
- the change of the degree of polymerization with pressure at constant temperatures, preferably in the transition region;
- the change in equilibrium monomer concentration with pressure, also in the transition region;
- the initial effect of pressure on the degree of polymerization as a function of temperature.

These are now discussed in the above order.

(a) The transition temperature (floor temperature), i.e., the temperature below which polymer is unstable, occurs when the  $\Delta F$  of the polymerization reaction changes sign.<sup>5,12</sup> This is equivalent to saying that it occurs at the point at which  $K_3 M_0 = 1$ , or  $\ln K_3 = -\ln M_0$ . By use of Eqs. (4a) and (5a), it follows (after setting  $\ln[1 + \beta_M P] = \beta_M P$ ) that at that point

$$\ln K_3(0) M_0(0) = -P[(\Delta V_P/RT) + \beta_M],$$

i.e., that

$$P_{\text{tr}} = -[\ln K_3(0) M_0(0)] / [(\Delta V_P/RT) + \beta_M].$$

$K_3(0)$  and  $M_0(0)$  can, of course, be written in their temperature-dependent forms. An evaluation of the

<sup>10</sup> "Selected Values of Properties of Hydrocarbons," Natl. Bur. Std. (U. S.), Circ. C461 (1947).

<sup>11</sup> *Paradise's Encyclopedia of Hydrocarbon Compounds* (Chemindex Ltd., Manchester, England, 1946).

<sup>12</sup> A. V. Tobolsky and A. Eisenberg, *J. Colloid Sci.* **17**, 49 (1962).



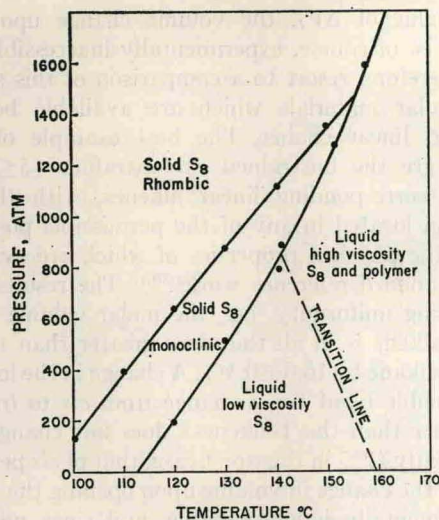


FIG. 1. Modified phase diagram for sulfur. ● Experimental points (Tamann, Ref. 13); --- this work, calculated.

transition temperature as a function of pressure shows that with increasing pressure the transition shifts to lower temperatures (Fig. 1). This is in direct contrast to the behavior expected for organic polymerizations, for which it has been shown<sup>1</sup> ( $\alpha$ -methylstyrene, for example) that the transition temperature (ceiling temperature) rises with pressure. The cause of this discrepancy can be seen if it is recalled that for sulfur the  $\Delta H (=H_{\text{products}} - H_{\text{reactants}})$  in the equation<sup>1,2</sup>

$$dT_{\text{trans}}/dP = -T(\Delta V/\Delta H)$$

is positive, while in organic polymerizations it is negative; the sign of  $\Delta V$  ( $V_{\text{reactants}} - V_{\text{products}}$ ) is positive in

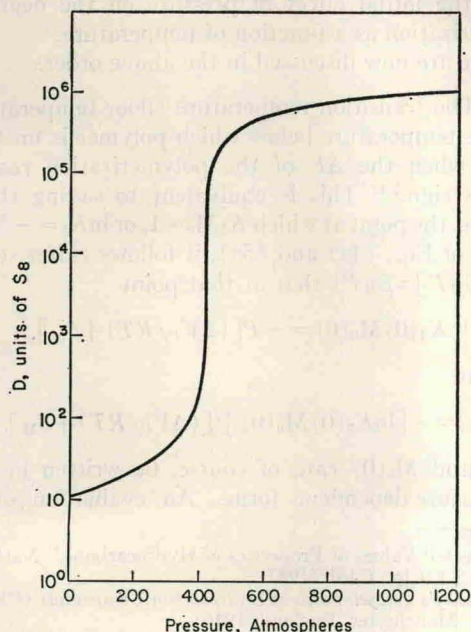


FIG. 2.  $D$  vs  $P$  for sulfur at 150°C.

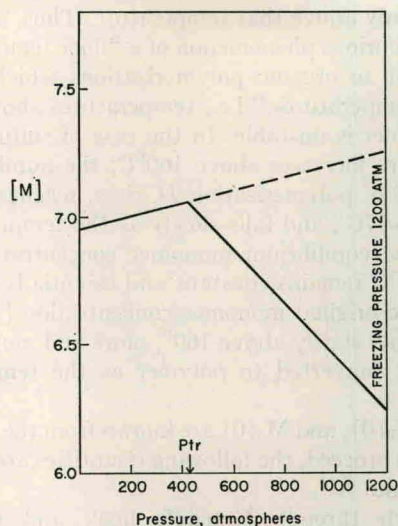


FIG. 3.  $[M]$  (in moles/liter) vs  $P$  for sulfur at 150°C.

both instances. Since the melting point of sulfur rises by about 30° per 1000 atm,<sup>13</sup> this means that at approximately 850 atm the melting line intersects the transition line and above that pressure sulfur melts to a liquid of high viscosity, just as selenium does at atmospheric pressure. The low-viscosity form of liquid sulfur is therefore merely a low-temperature and low-pressure phenomenon, the area of stability of which is shown in

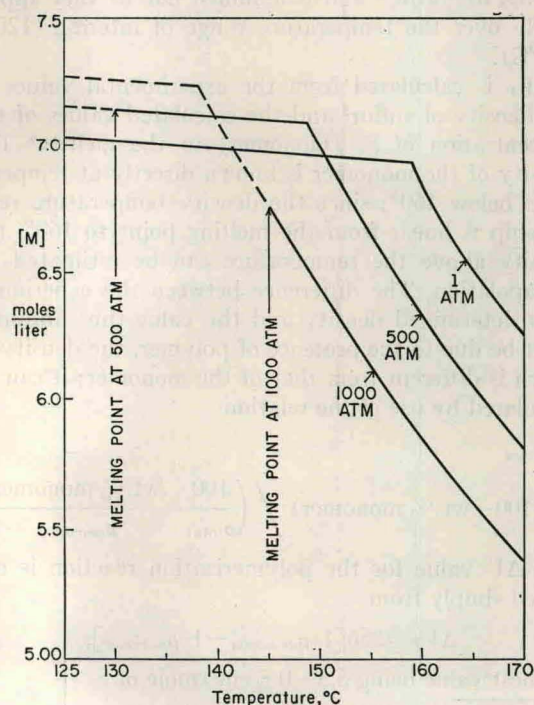


FIG. 4.  $[M]$  vs  $t$  for sulfur at various pressures.

<sup>13</sup> Gmelin, *Handbuch der Anorganischen Chemie* (Verlag Chemie, Weinheim, 1953), Vol. 9, p. 529.