Physico-chemical properties of sulfur: IV. Critical polymerization temperatures and polymerization equilibrium constants of sulfur

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Citation: The Review of Physical Chemistry of Japan (1965), 35(1): 18-24

Issue Date: 1965-12-20

URL: http://hdl.handle.net/2433/46858

Type: Departmental Bulletin Paper
The Review of Physical Chemistry of Japan, Vol. 35, No. 1, 1965

PHYSICO-CHEMICAL PROPERTIES OF SULFUR

IV Critical Polymerization Temperatures and Polymerization Equilibrium Constants of Sulfur

BY TSUNESUKE DOI

The critical transition temperature, at which the production of sulfur polymer starts abruptly, changes with the dilution of sulfur by inactive diluent. As to this process, some data obtained by measuring the viscosity-temperature behavior in a viscometer have already been reported by the author. By analysing these data by means of the equation of the degree of polymerization obtained by Tobolsky et al., the author succeeded to get the polymerization equilibrium constants of sulfur, independent of the data of Tobolsky et al. The equilibrium constants thus obtained are somewhat lower than those of Tobolsky et al.

The plots of the logarithm of equilibrium constant vs. the reciprocal of absolute temperature become a straight line. From the slope and the intercept of this straight line, the numerical values of $\Delta H$ and $\Delta S$ for the polymerization of sulfur were obtained as 2790 cal. mole$^{-1}$ and 2.61 cal. deg$^{-1}$ mole$^{-1}$, respectively.

Introduction

In the previous papers$^1$, the author used the numerical values obtained by Tobolsky$^3$ et al. for the equilibrium constants of sulfur polymerization. But the author wanted to obtain the constants independent of the data of Tobolsky et al., because these values were important for the previous papers and it was necessary to examine the numerical values obtained by Tobolsky et al. from another point of view.

The author has already reported the data$^2$ related to the change of temperature at which the production of sulfur polymer starts abruptly. The critical temperature changes with the dilution of sulfur by inactive reagents. One of the purposes of this paper is to obtain, independent of the data of Tobolsky et al. the equilibrium constants of sulfur polymerization, by analysing the data mentioned above, by means of the equation of polymerization degree obtained by Tobolsky et al. Another purpose is to obtain the values of $\Delta S$ and $\Delta H$ for sulfur polymerizations from the straight line obtained by the plots of the logarithm of equilibrium constants against the reciprocal of absolute temperatures. The results are compared with the data of other authors.

(Received April 6, 1965)

1) T. Doi, This Journal, 33, 41 (1963)
2) T. Doi, ibid., 35, 1 (1965)
3) A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc., 81, 780 (1959)
4) T. Doi, This Journal, 35, 11 (1965)
Physico-Chemical Properties of Sulfur

Critical Polimerization Temperatures and Calculation of Polymerization Equilibrium Constants of Sulfur

In the paper of Gee\(^5\), 159°C was selected as the critical transition temperature of polymerization, at which the polymer production of pure sulfur starts abruptly. This would be an adequate selection, because it is in accordance with the temperature of the intersecting point of the tangents of both sides of the sharp curvature of the viscosity-temperature curve of pure sulfur. The critical transition temperature of polymerization changes with the addition of the diluent to sulfur, as already mentioned.

The data related to the critical transition temperatures of polymerization were analysed by means of the equation derived by Tobolsky et al. According to the theory of polymerization equilibrium by Tobolsky et al.\(^5\), the degree of polymerization is written as

\[
P = \frac{1}{1 - KM}
\]

where \(K\) is polymerization equilibrium constant (cf. reference 4), in which \(K=K'\) and \(M\) is monomer concentration. Eq. (1) should be effective, having nothing to do with as to whether a diluent co-exists with polymer. Using the suffix 0 to denote the system without diluent, eq. (1) becomes

\[
P_0 = \frac{1}{1 - K_0 M_0}.
\]

At the corresponding points of both eqs. (1) and (2), we obtain

\[
P = P_0
\]

Especially in the immediate upper neighbourhood of the critical transition temperature of polymerization, the degrees of polymerization of sulfur in the systems both with and without diluent should be very high, and both are considered to be the same. Therefore, we obtain

\[
KM = K_0 M_0.
\]

According to the thermodynamics, we obtain

\[
\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]

\[
\ln K_0 = \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT_0}
\]

where \(\Delta S\) and \(\Delta S_0\) are the entropies of polymerization of the systems both with and without diluent, respectively, and \(\Delta H\) and \(\Delta H_0\) are the corresponding enthalpies of polymerization, respectively. In general, strictly speaking, \(\Delta S\) and \(\Delta H\) are not the same as \(\Delta S_0\) and \(\Delta H_0\), respectively. But if we substitute both \(K\) and \(K_0\) from eqs. (4) and (5), respectively, into eq. (3), regarding as \(\Delta S = \Delta S_0\) and \(\Delta H = \Delta H_0\) approximately, we obtain


Eq. (6) is identical with one of Gee°, with the exception of the unit of the concentration. In the immediate upper neighbourhood of the critical transition temperature of polymerization, we may assume $P = \infty$ and we may also assume that the monomer concentration is the same as the initial one. Therefore, from eq. (1), we obtain

$$
K = \frac{1}{M}. 
$$

The equilibrium constants could be calculated by substituting the numerical values of the paper (cf. Table 2 of reference 4) into eq. (7). The results are shown in Table 1. With each system of different dilution, the values of the equilibrium constant and the corresponding absolute temperature are obtained from Table 1. The log-log plots of the equilibrium constants against the reciprocal of absolute temperatures were found to be linear. We can obtain $\Delta S$ and $\Delta H$ from the intercept and the slope of the straight

<table>
<thead>
<tr>
<th>Naphthalene</th>
<th>Conc. of sulfur</th>
<th>$M_k$ (mole/kg)</th>
<th>$\log 1/M_k$</th>
<th>$M_0$ (mole/l)</th>
<th>$\log 1/M_0$</th>
<th>Critical trans. temp. $T$ (°K)</th>
<th>$1/T \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
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</table>

Table 1 Calculations of equilibrium constants

Physico-Chemical Properties of Sulfur

line, respectively. The concentration unit of Fig. 1 is shown in mole kg$^{-1}$. Both naphthalene and diphenyl are plotted on the same straight line whose slope is somewhat less steep compared with $p$-dichlorobenzene. On the other hand, the concentration unit of Fig. 2 is shown in mole l$^{-1}$. In this case, the three diluents mentioned above are plotted on the same straight line. The numerical values of $\Delta S$ and $\Delta H$ obtained

![Fig. 1 log $K_1$ vs. $1/T$](image1)

$K_1$ refers to a standard state of 1 mole/kg.

![Fig. 2 log $K_2$ vs. $1/T$](image2)

$K_2$ refers to a standard state of 1 mole/l.

<table>
<thead>
<tr>
<th>Standard state</th>
<th>Experimental condition</th>
<th>$\Delta H$ (cal. molec$^{-1}$)</th>
<th>$\Delta S$ (cal. deg. molec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gee et al.</td>
<td>Specific heat of pure sulfur</td>
<td>3180</td>
<td>7.4</td>
</tr>
<tr>
<td>Tobolsky et al.</td>
<td>1 mole/kg</td>
<td>3170</td>
<td>4.63</td>
</tr>
<tr>
<td>Doi</td>
<td>1 mole/l</td>
<td>2790</td>
<td>2.61</td>
</tr>
</tbody>
</table>
from this straight line are shown in Table 2. The data of Gee et al. and those of Tobolsky et al. are shown in the Table for comparison.

Gee et al. have tried to examine the effects of diluents on the sulfur polymerization. By measuring the volume-temperature behavior in a dilatometer, they obtained the result that the addition of 10% of naphthalene raised the critical transition temperature by approximately 10 degrees, as required by eq. (6). In their equation they assumed $\Delta H = 3200 \text{cal.mole}^{-1}$ and that $M$ and $M_0$ are shown in weight fractions of monomer in the liquid. This does not correspond to the author's results. According to the author's results mentioned above, the addition of 10 weight % of naphthalene raised the critical transition temperature by 28 degrees by the measurements of the viscosity-temperature behavior in a viscometer.

To the author's regret Gee et al. did not write the details of their experiments. But they wrote that naphthalene was not an ideal diluent, because it was attacked slowly by liquid sulfur as found by the smell of $\text{H}_2\text{S}$. But the author found that naphthalene added into liquid sulfur was stable against heat and that the viscosity curve was reproducible, (cf. the author's former article in this journal). Furthermore, according to the author's calculation by eq. (6), the addition of 10 weight % of naphthalene raised the critical temperature by 26 degrees, if $\Delta H$ is 2790 cal. mole$^{-1}$ and if the units of $M$ and $M_0$ are shown in the mole fraction of monomer in the liquid. (The values of $\frac{M}{M_0}$ shown in both mole fraction and mole l$^{-1}$ are almost the same in the liquid sulfur diluted with naphthalene.) Both experimental and theoretical values are shown in Table 3 and plotted in Fig. 3. The comparison shows excellent agreement.

<table>
<thead>
<tr>
<th>Table 3 Calculation of critical transition temperatures of polymerization of diluted sulfur</th>
</tr>
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<tbody>
<tr>
<td>Quantity of Naphthalene added (% to sulfur)</td>
</tr>
<tr>
<td>Sulfur conc. (mole fraction)</td>
</tr>
<tr>
<td>Cr. trans. temp. ($T_{eq} \text{ K}$)</td>
</tr>
<tr>
<td>$T_{eq} - T_{eq0}$*</td>
</tr>
<tr>
<td>Observed**</td>
</tr>
</tbody>
</table>

*; $T_{eq} = 432\text{K}$
**; See Table 2 of reference 4)

![Fig. 3 $T_{eq} - T_{eq0}$ vs. $M$](image)
Consideration

The author has succeeded to derive the equation which enables him to analyse his data, which is related to the changes of critical transition temperature depending upon the dilution of sulfur by inactive diluents, and which are obtained by measuring the viscosity-temperature behavior in a viscometer. The equation thus derived is identical with that of Gee et al. with the exception of the unit of the concentration. But the derivation is independent of their method. The comparison between the experiment and theoretical values shows excellent agreement, but the numerical values of the author and those of Gee et al. are considerably discrepant. The method of measurements and the unit of sulfur concentration for the calculation used by Gee et al. are not comprehensible to the author.

The author, furthermore, obtained the equilibrium constants of sulfur polymerization by applying eq. (1) of Tobolsky et al. for the degree of polymerization to the same data. In this case it is reasonable to use not mole kg\(^{-1}\) but mole l\(^{-1}\), because the specific gravities of diluents are considerably different from that of sulfur. Tobolsky et al.\(^{39}\) adopted mole kg\(^{-1}\) in their report. The author also adopted the same unit in his papers. In the case of pure sulfur only, it could be left out of consideration whether mole kg\(^{-1}\) or mole l\(^{-1}\) should be adopted, because, as to the specific gravities, there is hardly any difference between sulfur monomer and polymer, and because the specific gravities are slightly dependent on the temperatures. Therefore, as the authors perhaps, as the author, adopted mole kg\(^{-1}\), because it was helpful for the calculation.

The numerical values of equilibrium constant obtained by Tobolsky et al. must be divided by 1.75, the mean specific gravity in the temperature range 160 to 200°C, in order to be compared with the values of the author. The comparison is shown in Fig. 4. The author's data are plotted somewhat smaller than that of Tobolsky et al. But the differences are negligible. The values from 0.4 to 0.7, the exponent obtained previously, become 0.5 to 0.9, if the exponents of the intrinsic viscosity-degree of polymerization relationships of sulfur published previously are re-calculated with the smaller numerical values of equilibrium constants by approximately 5% with reference to Fig. 4. This does not affect the previous conclusion. The newly obtained values are on the contrary more useful in the light of the data of many other types of polymers.

As for the numerical values of $\Delta H$ of polymerization shown by the slope of straight line obtained by plotting $\log K$ vs. $T^{-1}$, the same value is obtained even if the unit of concentration and that of the

![Fig. 4 Temperature dependences of equilibrium constant](image-url)
equilibrium constant are changed, if the specific gravity of the system remains the same. On the other hand, as for the numerical value of $\Delta S$ of polymerization shown by the intercept of the straight line, the numerical values would be different, if the unit of concentration and the unit of equilibrium constant are changed. If the unit of equilibrium constant is the reciprocal of concentration, the relationship between $\Delta S_2$ shown in mole l$^{-1}$ and $\Delta S_1$ shown in mole kg$^{-1}$ is given by

$$\ln \rho = \frac{1}{R} (\Delta S_2 - \Delta S_1) \tag{8}$$

where $\rho$ is the specific gravity of the system, and $R$ is the gas constant.

Therefore, $\Delta H$ obtained by Tobolsky et al. can be compared with that of the author, because the specific gravities of the system change slightly, but $\Delta S$ obtained by Tobolsky et al. must be corrected by eq. (8) in order to be compared with that of the author. Correcting 4.63 cal. deg$^{-1}$ of Tobolsky et al. by eq. (8), we obtain 3.91 cal. deg$^{-1}$. It can be concluded, that as to the numerical values of $\Delta H$, there is no significant difference between Tobolsky et al. and the author, but that, in the case of $\Delta S$, there is some difference. The numerical value of $\Delta S$ obtained by Gee et al. is a considerably higher estimate than that of Tobolsky et al. and of the author.

Acknowledgment

The author expresses his thanks to Mr. K. Tamura, General Manager of Rayon Plant and Mr. R. Wakasa, the Manager of Development Department of Asahi Chemical Industry Co., Ltd. for their encouragement. He would like to express his gratitude to Professor Dr. J. Osugi of Kyoto University for his valuable discussions. The author is also indebted to Mr. K. Kubota for his aid to the present work.

Resident Representative (Europe)
Asahi Chemical Industry Co., Ltd.