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Viscosity and Thermodynamic Properties of Liquid Sulfur

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It has been presumed that the molten sulfur above 159°C consists of an equilibrium mixtur eof S_8 rings and S_x polymers where the number average degree of polymerization, P, is large. But it is known that admixture of halogens with liquid sulfur greatly reduce the viscosity. Constructing a new equilibrium equation, it is possible to evaluate the viscosity when halogens are added to liquid sulfur. Calculated viscosity is in good agreement with experimental values. Using the proposed model, the thermodynamic properties of liquid sulfur are also calculated over a wide range of temperature which the sulfur exists as the polymer.

Introduction

Fanelli[1] obtained the temperature variation on the viscosity when various concentration of halogens are added to liquid sulfur, which brought out the enormous modifying effect of these elements on the viscosity of liquid sulfur. He also indicates that, with each increment in the concentration of halogens, the viscosity becomes smaller. In equilibrium polymerization reaction, halogens absorb the radicals and terminate the polymerization, therefore the viscosity is reduced.

We evaluate the viscosity of liquid sulfur containing halogens by using a new equilibrium equation in which assumed that halogens, S_8 rings, and S_8 chains are in equilibrium each other.[2-5]

The partition function of liquid sulfur is obtained as the product of conventional partition function for the liquid and the configurational one for the λ-transition[6] which uses the simplified expression for Bragg–Williams approximation of order–disorder phase transition. Using this partition function, the thermodynamic properties of liquid sulfur can be calculated.

The results of the viscosity of liquid sulfur containing halogens and thermodynamic properties of liquid sulfur are in good agreement with the experimental data.

Theory

1. Viscosity of Liquid Sulfur Contatining Halogens

When halogens are added, the equilibrium polymerization of liquid sulfur can be represented as follows[5]

Initiation

$$M \xrightleftharpoons{K} M^*; \qquad K=(M^*)/(M)$$
$$(M^*)=K(M) \tag{1}$$

Propagation and termination

$$M^*\begin{cases} \xrightleftharpoons{+M,\ K_3} M_2^* \ ;\ K_3=(M_2^*)/(M)(M^*) \\ \qquad (M_2^*)=K_3(M)(M^*)=K(M)K_3(M) \qquad (2) \\ \xrightleftharpoons{+Q,K'} M^*Q \ ;\ K'=(M^*Q)/(M)(Q) \end{cases}$$
$$(M^*Q)=K'(M)(Q) \tag{3}$$

Symbolically we designate S_8 ring as M, S_8^* chain as M^*, and Q as halogen, respectively. The total concentration of polymer molecules, N', and the total concentration of S_8 unit in the polymer, W', can be represented as follows

$$\begin{aligned} N' &= M^*+M_2^*+M_3^*+\cdots\cdots+M^*Q+M_2^*Q+M_3^*Q+\cdots\cdots \\ &= K(M)/\{1-K_3(M)\}+K'(Q)K(M)/\{1-K_3(M)\} \\ &= K(M)\{1+K'(Q)\}/\{1-K_3(M)\} \end{aligned} \tag{4}$$

$$\begin{aligned} W' &= M^*+2M_2^*+3M_3^*+\cdots+M^*Q+2M_2^*Q+3M_3^*Q+\cdots \\ &= K(M)/\{1-K_3(M)\}^2+K'(Q)K(M)/\{1-K_3(M)\}^2 \\ &= K(M)\{1+K'(Q)\}/\{1-K_3(M)\}^2 \end{aligned} \tag{5}$$

When halogens are added, the number average degree of polymerization, P', can be obtained from eqs. (4) and (5).

$$P'=(W')/(N')=1/\{1-K_3(M)\} \tag{6}$$

Here, the number average degree of polymerization, P', has the relation with the viscosity such that[7]

$$P'=\left(\frac{\eta-\eta_0}{\eta_0 W}\right)^{1.1} \tag{7}$$

where η and η_0 are the viscosity of sulfur containing halogens and pure sulfur, respectively, and W means the concentration of polymers.

The quantities (M_0) and (Q_0) which are the initial concentration of S_8(ring) and halogen, respectively, are expressed by

$$\begin{aligned}(M_0) &= (M)+(W')\\ &=(M)+K(M)\{1+K'(Q)\}/\{1-K_3(M)\}^2\\ &\cong (M)+K(M)K'(Q)/\{1-K_3(M)\}^2 \qquad (8)\\ (Q_0) &= (Q)+(N')\\ &=(Q)+K(M)\{1+K'(Q)\}/\{1-K_3(M)\}\\ &\cong (Q)+K(M)K'(Q)/\{1-K_3(M)\} \qquad (9)\end{aligned}$$

In eq. (3), to calculate the equilibrium constant, K', we introduce a new equilibrium such that

$$Q\cdot+M \rightleftharpoons M^*Q \tag{10}$$

Where $Q\cdot$ represents the halogen radical.

In eq. (2), we assumed that all the equilibrium constants in the polymerization reactions are same as K_3, so it is possible to represent the equilibrium constant in eq. (10) as approximately ak_3.

Where the halogens such as chlorine, bromine, and iodine, are differ in activity to attack a sulfur ring, and the notation a means thc activity of halogens to attack a sulfur ring.

Therefore in above equation, M^*Q is represented by

$$(M^*Q)=aK_3(Q\cdot)(M) \tag{11}$$

Thus K' in eq. (3) is represented as follows

$$\begin{aligned}K' &= (M^*Q)/(M^*)(Q)\\ &=ak_3(M)(Q\cdot)/(M^*)(Q) \qquad \textit{(by eq. }\mathbf{10}\textit{)}\\ &=ak_3(M)(Q\cdot)/K(M)(Q)\\ &=a\cdot K_3/K\cdot(Q\cdot)/(Q)\\ &=a\cdot K_Q\cdot K_3/K\\ &=A\cdot K_3/K \qquad (12)\end{aligned}$$

In eq. (12), K_Q represents the equilibrium constant where the radical of halogen is produced, and we replace ak_Q by A.

2. The Significant Structure Theory of Liquids[8-10]

According to the significant structure theory of liquids, liquids have quasi-lattice structures like solids and the lattice points are occupied by molecules or fluidized vacancies of molecular size randomely distributed throughout the quasi-lattice. The fluidized vacancies provide gas-like translational degrees of freedom on the vibrational degrees of freedom of neighboring molecules because the molecules can jump into them. The fraction $(V\text{-}V_s)/V$ of the degrees of freedom are gas-like and the remaining fraction V_s/V can be thought of as being solid-like where V and V_s indicate molar volume and solid-like molar volume, respectively. Thus, one mole of liquid can be considered as if it were made of $N(V-V_s)/V$ gas-like molecules and NV_s/V solid-like molecules where N is the Avogadro number.

In view of this, the partition function, f_N, for a mole of liquid can be written as

$$f_N=f_s^{N\frac{V_s}{V}}\cdot f_g^{N\frac{V-V_s}{V}} \tag{13}$$

The solid-like partition function f_s is the usual partition function for a solid multiplied by the positional degeneracy factor $1+n_h\exp(-\varepsilon_h/RT)$, because the fluidized vacancies confer the additional site $n_h\exp(-\varepsilon_h/RT)$ to a solid-like molecule.

Here, n_h and ε_h can be written as

$$n_h=n\frac{V-V_s}{V_s} \tag{14}$$

and

$$\varepsilon_h=\frac{aE_sV_s}{(V-V_s)RT} \tag{15}$$

Where E_s is the energy of sublimation of the solid-like molecules and a and n are the proportionality constants which will be evaluated.

Once the partition function is given, thermodynamic quantities of the liquid can be obtained from the partition function

3. Partition Function of Liquid Sulfur

The partition function of liquid sulfur is written as

$$f_N=f_{\text{conv}}\cdot f_{\text{conf}} \tag{16}$$

Here f_{conv} is the conventional liquid partition function which can be obtained by applying the significant liquid structure theory to liquid sulfur. f_{conf} is the configurational partition function which is introduced to account for the thermodynamic properties accompanied by the λ-transition.

For the configurational partition function, we use the Bragg-Williams approximation which explains the nature of λ-transition.

1. *Conventional Partition Function.* According to the significant structure theory, the partition function for a mole of liquid, f_N, is given by

$$f_N=f_s^{NV_s/V}\cdot f_g^{N(V-V_s)/V} \tag{17}$$

For the solid-like partition function, we have assumed that there are two structural species in equilibrium.

$$S_8(\text{ring}) \overset{K}{\rightleftharpoons} S_8^*(\text{diradical})$$

The equilibrium constant K is written as

$$\begin{aligned}K&=x_8^*(\textit{diradical})/x_8(\textit{ring})=f_{s8}^*/f_{s8}\\ &=\exp\left\{-\left(\frac{\Delta H+T\Delta S-P\Delta V}{RT}\right)\right\} \qquad (18)\end{aligned}$$

here $\Delta V=V_{sr}-V_{sp}$, ΔH=32,800 cal/mole, and ΔS=23 cal/deg. mole[11]

Thus, the partition function, fs is

$$f_s=f_{r_8}^{x}\cdot f_{s_8^*}^{x^*}=f_{s_8}\cdot K^{\frac{K}{1+K}} \tag{19}$$

Where x and x^* are the mole fration of S_8(ring) and S_8^* (diradical), respectively, with the relation $x+x^*=1$, and the S_8(ring)-like partition function can be written as

$$f_{s_8}=\frac{\exp(E_s/RT)}{1-\exp(-\theta/T)}\cdot\left[1+n\left(\frac{V-V_s}{V}\right)\right.$$

$$\cdot \exp\left\{\frac{aE_sV_s}{(V-V_s)RT}\right\}\Big] \cdot \prod_{i=1}^{18}(1-e^{-h\nu_i/RT})^{-1} \tag{20}$$

From a mass spectrometric study,[12] the vapor of liquid sulfur is composed of many species such that S_8 ring, S_7 ring, S_6 ring, and S_2 molecules. Then the gas-like partition function, f_g is written as

$$f_g = f_{g8}^{x_8} \cdot f_{g7}^{x_7} \cdot f_{g6}^{x_6} \cdot f_{g2}^{x_2} \tag{21}$$

Where $x_8, x_7, x_6,$ and x_2 are the mole fraction of S_8 ring, S_7 ring, S_6 ring, and S_2 molecules, respectively, with the relation

$$x_8+x_7+x_6+x_2=1.$$

Thus gas-like partition function, f_g is composed of its various composition[12] as follows,

$$\begin{aligned} f_g = &(f_{g8}^{\text{trans}} \cdot f_{g8}^{\text{rot}} \cdot f_{g8}^{\text{vib}})^{x_8} \cdot (f_{g7}^{\text{trans}} \cdot f_{g7}^{\text{rot}} \cdot f_{g7}^{\text{vib}})^{x_7} \\ &\cdot (f_{g6}^{\text{trans}} \cdot f_{g6}^{\text{ro}} \cdot f_{g6}^{\text{vib}})^{x_6} \cdot (f_{g2}^{\text{trans}} \cdot f_{g2}^{\text{rot}} \cdot f_{g2}^{\text{vib}})^{x_2} \end{aligned} \tag{22}$$

Where the translational, rotational, and vibrational partition function are given as

$$f_g^{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{eV}{N} \tag{23}$$

$$f_g^{\text{rot}} = \begin{cases} \dfrac{8\pi^2(8\pi^3ABC)^{1/2} \cdot (kT)^{3/2}}{16h^3} & \text{(for three dimersional)} \\ \dfrac{8\pi IkT}{h^2} & \text{(for two dimersional)} \end{cases} \tag{24}$$

$$f_g^{\text{vib}} = \prod_{i=1}\{1-\exp(-h\nu_i/kT)\}^{-1} \tag{25}$$

Where the symbols have their usual statistical-mechanical significance. In gaseous state, molecules are in relation with each other as follows[12]

$$S_8(\text{ring}) \overset{K_2}{\rightleftharpoons} S_2(\text{ring}),\ K_2=x_2(\text{ring})/x_8(\text{ring}) \tag{26}$$

$$S_8(\text{ring}) \overset{K_6}{\rightleftharpoons} S_6(\text{ring}),\ K_6=x_6(\text{ring})/x_8(\text{ring}) \tag{27}$$

$$S_8(\text{ring}) \overset{K_7}{\rightleftharpoons} S_7(\text{ring}),\ K_7=x_7(\text{ring})/x_8(\text{ring}) \tag{28}$$

Here S_2 molecules are regarded as 2-membered ring and K_2, K_6, and K_7 can be calculated, and its method is listed in Appendix I. The values of x_8, x_7, x_6, and x_2 are temperature dependent. In the calculations, V_s and E_s are given by

$$V_s=x^*V_s^*+xV_s \tag{29}$$

$$E_s=E_{s8} \cdot x_8+E_{s7} \cdot x_7+E_{s6} \cdot x_6+E_{s2} \cdot x_2 \tag{30}$$

where V_s^* and V_s are solid-like volume of S_8(chain), and S_8(ring) respectively.

And E_{s8}, E_{s7}, E_{s6}, and E_{s2} are the sublimation energy of S_8(ring, solid)⇒S_8(ring, gas), S_8(ring, solid)⇒S_7(ring, gas), S_8(ring, solid)⇒S_6(ring, gas), and S_8(ring, solid)⇒S_2(gas) transition, respectively, and the way of obtaining a sublimation energy are introduced in Appendix II.

2. *Configurational Partition Function.* The configurational partition function is derived by the Bragg-Williams approximation.[13-15] The configurational partition function is given by the following equations:

$$f_{\text{conf}} = W(\theta) \cdot \exp\{-E(\theta)/kT\} \tag{31}$$

$$W(\theta)=NCN_+=\frac{N!}{\left\{\frac{N(1+\theta)}{2}\right\}!\left\{\frac{N(1-\theta)}{2}\right\}!} \tag{32}$$

$$\begin{aligned} E(\theta) &= N_+V_+ + N_-V_- = \frac{N}{2}\{(V_+ + V_-)+(V_+ - V_-)\theta\} \\ &= \frac{N}{2}(U_0 - V_0\theta^2) \end{aligned} \tag{33}$$

Here, θ is the long-range order parameter; N_+ and N_- are the numbers of spins in the up and down directions, respectively. $W(\theta)$ is the number of possible ways of obtaining the N_+ state of spins; $E(\theta)$ is the configurational internal energy of the system; V_+ and V_- are potential energy of the up and down directional spins; respectively; V_0 is the energy of the completely disordered state $\theta=0$; $V_- - V_+ = V_0\theta$ is assumed. The order parameter θ is obtained from

$$\theta=\tanh\left(\frac{T_\lambda}{T}\theta\right) \tag{34}$$

Resuts And Discussions

1. Viscosity of Liquid Sulfur Containing Halogens

Helogens reduce the viscosity of sulfur above 160°C through the chemical reaction with the sulfur shown in eqs. (2) and (3).

And, the following reaction can be considered as

$$\begin{aligned} &S_p^*(\text{chain})+S_q^*(\text{chain}) \overset{K_5}{\rightleftharpoons} S_{p+q}^*(\text{chain}), \\ &\quad (p, q=1, 2, 3, \cdots\cdots) \end{aligned} \tag{35}$$

Where equilibrium constant K_5 can be represented as follows

$$K_5=\frac{(S_{p+q}^*)}{(S_p^*)(S_q^*)}=\frac{K_3(S_p)(S_q^*)}{(S_p^*)(S_q^*)}=K_3\frac{(S_r)}{(S_p^*)}=\frac{K_3}{K} \tag{36}$$

Here we assumed that all the equilibrium constants in the polymerization reactions are same as K_3, and the equilibrium constant K_5 in the radical-radical reaction can be written as K_3/K without considering the effect of chain length.

Now, we consider the following reaction

$$M^*+Q \rightleftharpoons M^*Q \tag{37}$$

Although halogens are not a radical in eq. (37), halogens have very similar properties of a radical in the temperature which sulfur is existed in a liquid state.

Thus equilibrium constant K' in eq. (37) might be represented by the form which contains K_3/K term. Hence K' represented in eq. (12) is reasonable.

However, in the equation (10), when a halogen radical attacks S_8(ring), the equilibrium constant might be affected by the activity of a halogen radical toward S_8(ring).

Thus the equilibrium constant K' can be represented by a equation which contains the activity of a halogen radical such as eq. (12).

Therefore, when halogens are added, the reactions are summerized as follows

$$P=\frac{1}{1-K_3M}=\frac{M_0-M}{Q_0-Q} \tag{38}$$

$$M_0=M+\frac{KM}{(1-K_3M)^2} \cdot \frac{K_3}{K} \cdot A \cdot Q \tag{39}$$

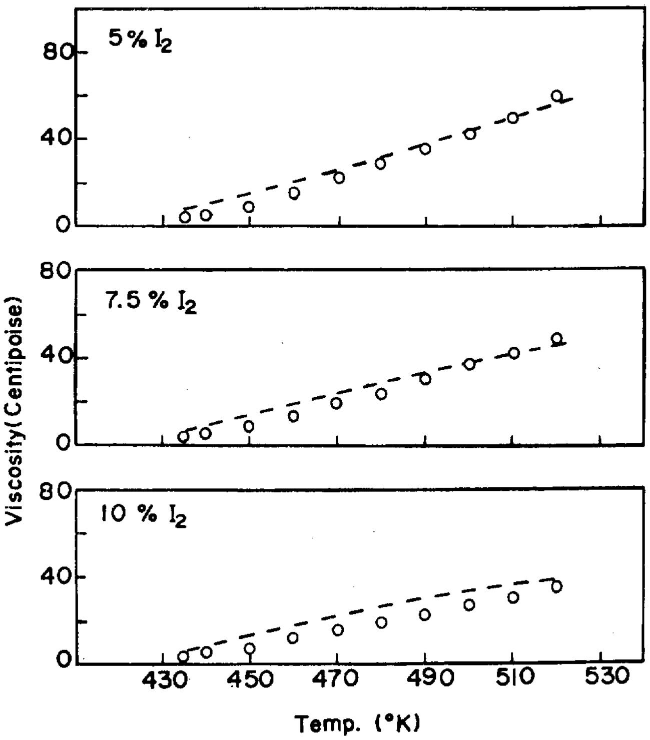


Figure 1. Viscosity of liquid sulfur containing halohens as a function of temperature (sulfur-iodine mixtures); dashed line, theoretical curve; o, experimental data, from ref. 1.

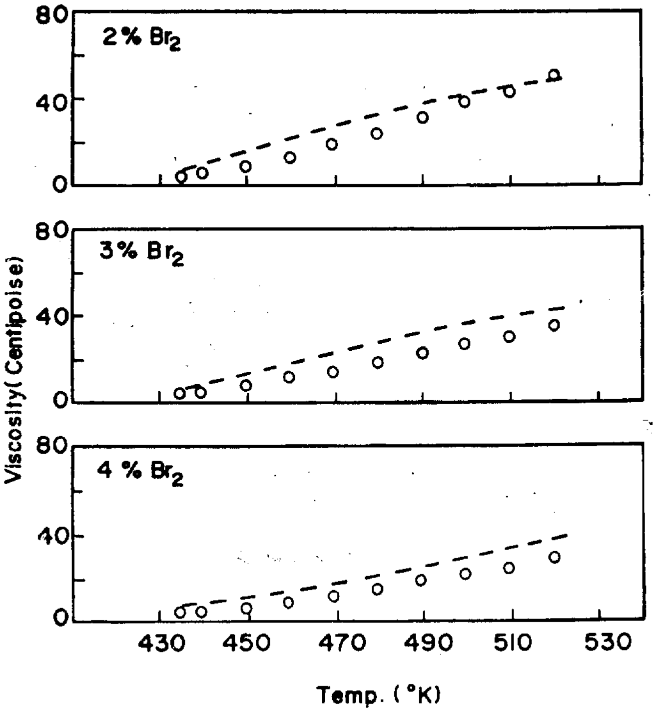


Figure 2. Viscosity of liquid sulfur containing halogens as a function of temprature (sulfur-bromine mixtures); dashed line, theoretical curve; o, experimental data, from ref. 1.

$$Q_0=Q+\frac{KM}{(1-K_3M)}\cdot\frac{K_3}{K}\cdot A\cdot Q \tag{40}$$

By introducing eqs. (39) and (40) into (38) we obtain the following equation

$$P^3-\frac{K_3Q_0+K_3M_0-1}{K_3Q_0}P^2+\frac{1-K_3M_0(1-A)-2A}{K_3QA}P=\frac{1-A}{K_3QA} \tag{41}$$

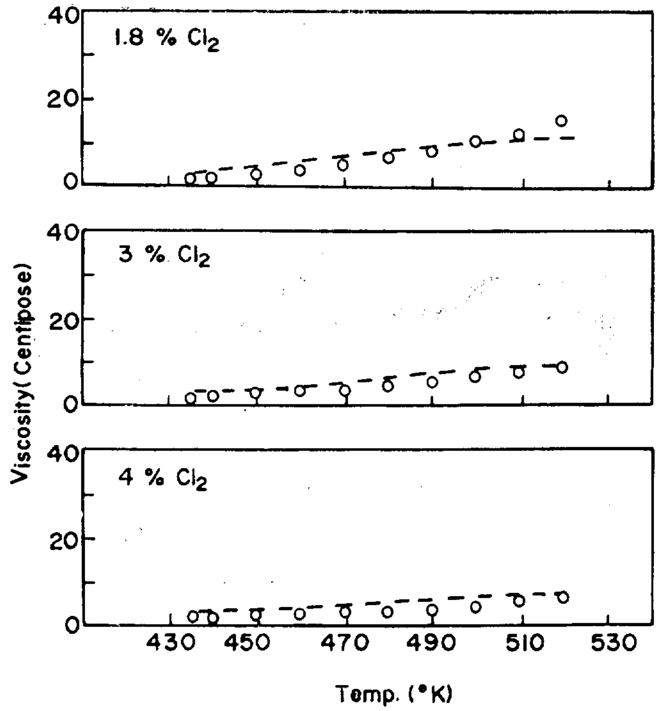
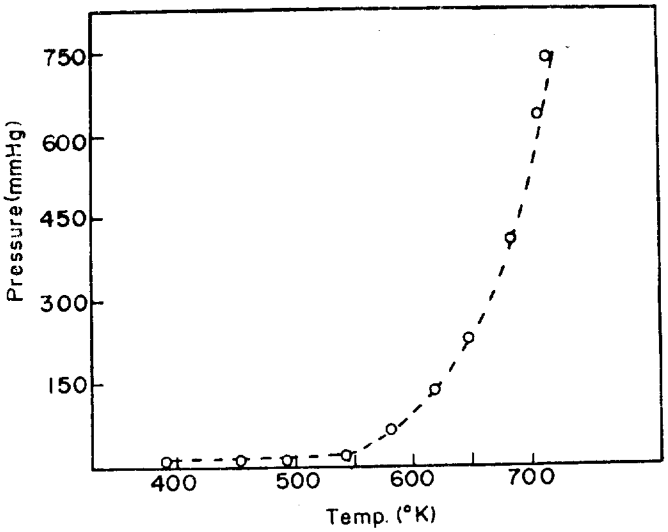


Figure 3. Viscosity of liquid sulfur containing halogens as a function of temperature (sulfur–chlorine mixtures); dashed line, theoretical curve; o, experimental data, from ref. 1.



Figuer 4. Vapor pressure of liquid sulfur as a function of temperature; dashed line, theoretical curve; o, experimental data, from ref. 17.

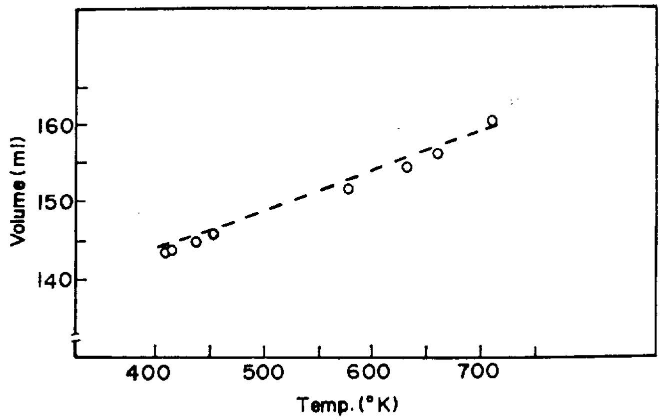


Figure 5. Liquid volume of liquid sulfur as a function of temperature; dashed line, theoretical curve; o, experimental from ref. 17.

To obtain the P in eq. (41), we introduce the simple values into A by using experimental values such that 0.1 for I_2, 10 for Br_2, and 23 for Cl_2, where A is taken as unity for a sulfur radical. Thus, above values are taken as relative values.

And the calculated values are compared with the selected values[1] in Figures 1, to 3.

The better results may be obtainable by considering the temperaturedependent activity values of halogen radical toward S_8(ring), and more accurate relations of viscosity-chainlength.

2. Molar Volume and Vapor Pressure

For the calculation of the molar volume and the vapor pressure, the relationship between the Helmholtz free energy, A, and molar volume, V, is used.

If a common tangent to the points corresponding to liquid and vapor phases is drawn, the vapor pressure is given by the slope of the common tangent, and the abscissas of two points indicate the molar volume of liquid and vapor, respectively.

To find out the common tangent at a given temeprature, the iterative Newton method is used.

Calculated results are presented in Figures 4 and 5, with the experimental values.[17] The agreement is satisfactory.

3. Entropy and Heat Capacity

The entropy is calculated by using the equation

$$S=\frac{\partial}{\partial T}(kT\ln f_N)_V$$

The calculated values are shown in Figure 6 and compared with the selected values.[18]

Heat capacity at constant volume, C_v, and those at constant pressure, C_p, are also calculated by using the following thermodynamic relations.

$$C_v=\left[\frac{\partial}{\partial T}\left\{kT^2\left(\frac{\partial\ln f_N}{\partial T}\right)_v\right\}_v\right] \tag{42}$$

$$C_p=C_v+TV\alpha^2/\beta \tag{43}$$

The calculated results are represented in Figure 7 and the results are compared with the experimental values.[11,19] The agreement between the calculated and experimental values are satisfactory except in the λ-transition region. This deviation is a natural result due to the Bragg-Williams approximation. The better results may be obtainable considering the other improved treatment of order-disorder transition such as Kirkwood method[20] or Frankel method.[16]

4. Thermal Expansion Coefficient and Compressibility

The increase of liquid volume is mainly originated from the introduction of fluidized vacancies in the significant structure theory. Thus, the solid-like volume, V_s, has been considered as a constant in the most of the publications of this theory. In the case of liquid sulfur, the solid-like volume influences severly on the liquid volume itself and related properties, and its change can not be ignored. The contribution to the compressibility and the thermal expansion coefficient by change of the solid-like volume is added to the values contributed by fluidized vacancies in the following way[21]

$$\alpha=\alpha_f+\frac{V_s}{V}\alpha_s \tag{44}$$

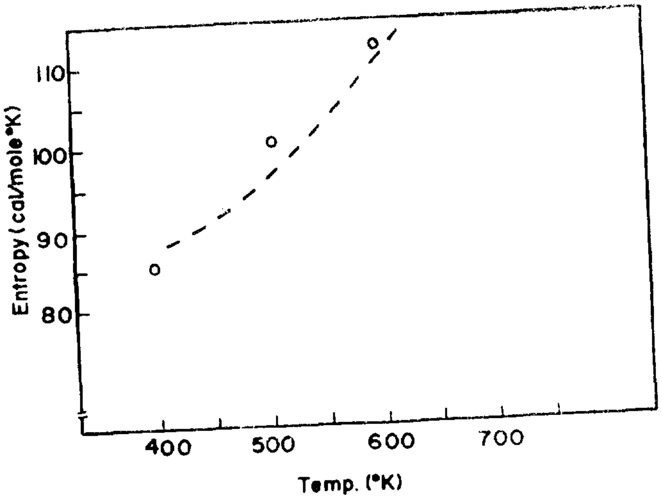


Figure 6. Entropy of liquid sulfur as a function of temperature; dashed line, theoretical curve; o, experimental data, from ref. 18.

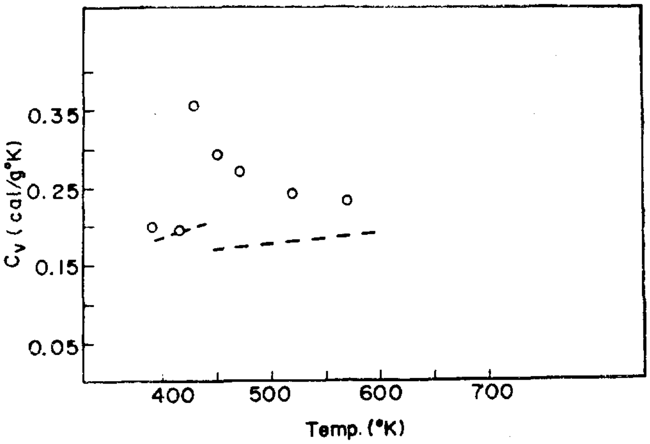


Figure 7. Heat capacity at constant volume of liquid sulfur as a function of temperature; dashed line, theoretical curve; o, experimental data, from ref. 11, 19.

$$\beta=\beta_f+\frac{V_s}{V}\beta_s \tag{45}$$

Where α_f and β_f have been commonly calculated from the partition function

$$\alpha_f=\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_r=\frac{1}{V}\left(\frac{\partial^2\ln f}{\partial V\partial T}\right)\Big/\left(\frac{\partial^2\ln f}{\partial V^2}\right)_T \tag{46}$$

$$\beta_f=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T=-1/VkT\left(\frac{\partial^2\ln f}{\partial V^2}\right)_T \tag{47}$$

The solid-like volume V_s has been expressed as a function of temperature and pressure, thus α_s and β_s are

$$\alpha_s=\frac{1}{V_s}\left(\frac{\partial V_s}{\partial T}\right)_r=\frac{1}{V_s}\left(\frac{\partial V_s}{\partial K}\right)\left(\frac{\partial K}{\partial T}\right)_r \tag{48}$$

$$\beta_s=-\frac{1}{V_s}\left(\frac{\partial V_s}{\partial p}\right)_T=-\frac{1}{V_s}\left(\frac{\partial V_s}{\partial K}\right)\left(\frac{\partial K}{\partial p}\right)_T \tag{49}$$

Thermal expansion coefficient of liquid sulfur exhibits a quite abrupt phenomena at the transition temperature range. By S_8(ring) conversion to S_8(chain), the solid-like volume is reduced and then by increasing temperatures, the solid-like volumes increase with forming the long-chained sulfur polymer. Thus at the transition temperature, thermal expansion coefficients are first reduced and then increase with increas-

TABLE 1: Parametric and Experimental Values Used in the Calculations

$a=2.54\times10^{-5}$ $n=15$

$v_{sr}=141.25(\text{cm}^3)$, $v_{sp}=140.43(\text{cm}^3)$

$E_{s_8}^a=23805(\text{cal})$, $E_{s_7}^a=29506(\text{cal})$, $E_{s_6}^a=30010(\text{cal})$

$E_{s_2}^a=47305(\text{cal})$,

$\Delta H_2^a=23500(\text{cal})$, $\Delta H_6^a=6200(\text{cal})$, $\Delta H_7^a=5700(\text{cal})$

$\Delta S_2^a=27.33(\text{cal/K})$, $\Delta S_6^a=9.75(\text{cal/K})$, $\Delta S_7^a=9.65(\text{cal/K})$

ν_i^b(cm^{-1}, for S$_8$); 2(86), 2(152), 184, 191, 218, 2(243), 2(248), 434, 435, 470, 2(475), 465, 471

ν_i^c(cm^{-1}, for S$_7$); 146, 155, 180, 193, 239, 274, 285, 360, 396, 402, 476, 482, 515, 518

ν_i^d(cm^{-1}, for S$_6$); 2(204), 2(180), 266, 312, 390, 2(451), 476, 2(62)

ν_i^e(cm^{-1}, for S$_2$); 718

ν_i^b(cm^{-1}, lattice vibration); 29, 63, 68, 44, 53,

I_{ABC}^f(kgm^2, for S_8); 3.805×10^{-132},

I_{ABC}^g(kgm^2, for S_7); 2.413×10^{-132}

I_{ABC}^h(kgm^2, for S_6); 1.024×10^{-134},

I^g(kgm^2, for S$_2$); 1.128×10^{-45}

[a] J. Berkowitz and J. R. Marguart, *J.Chem. Phys.*, **39**, 275(1963); [b] A. Anderson and Y. T. Loh, Can. *J. Chem.*, **47**, 879 (1969); [c] M. Gardner and A. Rogstad, *J.C.S. Dalton*, 1973, 599; [d] L. A. Nimon, V.D. Neff, R. E. Cantley, and R.O. Buttar, *J. Mol. Spec.* **22**, 105 (1967); [e] K.K. Yee, R. F. Barrow, and A. Rogstad, *J.C.S. Farafay* II, **68**, 1808 (1972); [f] G. B. Guthrie, D.W. Scott, and G. Waddington, *J. Amer. Chem. Soc.*, **76**, 1488 (1954); [g] J. Kao and N.L. Allinger, *Inorg. Chem.*, **16**, 35 (1977); [h] J. Donohue, A. Caron and E. Goldish, *J. Amer. Chem. Soc.*, **83**, 3748 (1961)

TABLE 2: Temperature Dependent Values

$T(°K)$	$K^i\times10^{-12}$	K_3^i	x_8^j	$V_s^k(\text{cm}^3)$
430	2.26	0.253	0.817	141.25
450	12.2	0.297	0.805	141.14
500	48.8	0.423	0.631	140.82
550	982.8	0.565	0.523	140.98
600	1.2×10^5	0.719	0.388	141.02
650	9.9×10^5	0.883	0.301	141.25

[i] from ref. 11; [j] from ref. 12; [k] from ref. 17

ing temperatures.

The calculated results are presented in Figurs 8–9, with the experimental value.[11]

5. Parametric Values

In the significant structure theory of liquids, there are five typical parameters; E_s, V_s, θ, a, and n.

In this work, six of θ and E_s have been substituted for the spectroscopic and experimental data, and the others have been determined by using Seoul Technique.[22,23]

The parametric values and experimental values used in the calculations are tabulated in Table 1.

And temperature depending values are also shown in Table 2.

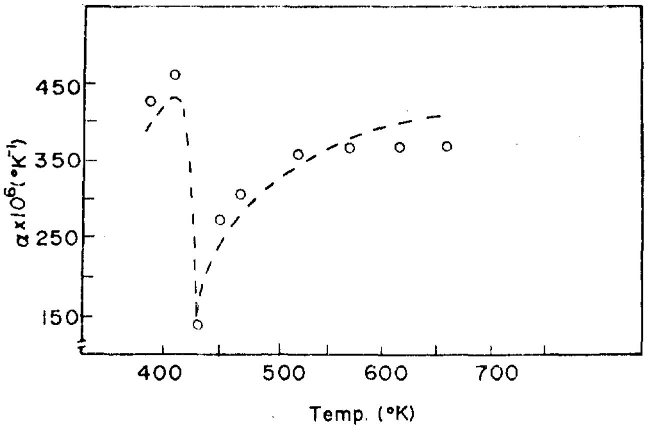


Figure 8. Thermal expansion coefficient of liquid sulfur as a function of temperature; dashed line, theoretical curve, o, experimental data, from ref. 11.

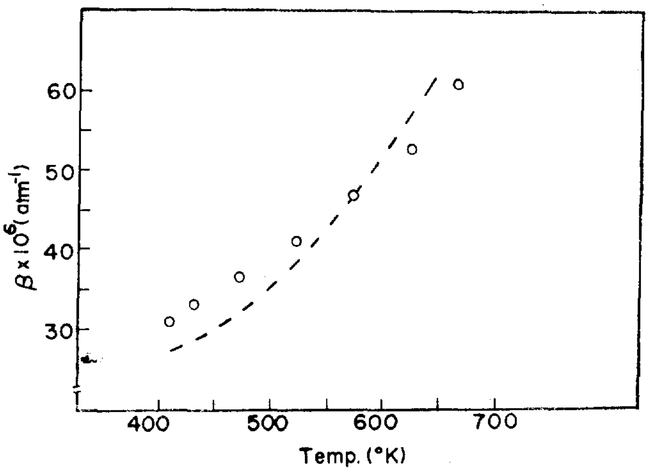


Figure 9. Isothermal compressibility of liquid sulfur as a function of temperature; dashed line, theoretical curve; o, experimental data, from ref. 11.

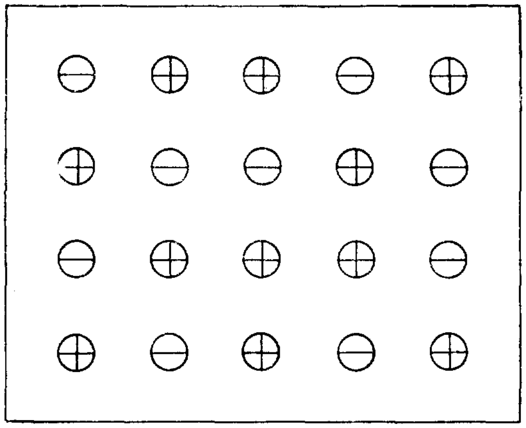


Figure 10. Arrangement of N spin-lattice sites; ⊕ and ⊖ indicate the up and down directions of spins.

Conclusions

We assumed that in sulfur-halogen system, halogens, S_8 (ring), and S_8(chain) are in equilibrium each other. Then we obtain the viscosity of liquid sulfur containing halogens by introducing a new equilibrium equation. The calculated values are in good agreement with experimental values.

And the thermodynamic properties of liquid sulfur were also obtained by applying the significant structure theory of liquids. It has been shown that the agreements between theories and experiments are satisfactory.

It is considered that liquid sulfur is consisted of molecules and the fluidized vacancies of molecular size. The fraction V_s/V of the degree of freedom is solid-like, and the remaining fraction $(V-V_s)/V$ can be thought of being gas-like.

The solid-like partition function of liquid sulfur is obtained as the product of solid-like partition function for S_8(ring) and one for S_8(chain), and the gas-like partition function is obtained as the product of partition function for each components in gaseous states.

The λ-transition of liquid sulfur is treated as a kind of order-disorder phenomena using the Bragg-Williams approximation.

Appendix 1.

$$S_8 \overset{K_2}{\rightleftharpoons} S_2,\quad K_2=x_2/x_8=\exp\left(-\frac{\Delta H_2-T\Delta S_2}{RT}\right) \qquad (A\text{-}1)$$

$$S_8 \overset{K_6}{\rightleftharpoons} S_6,\quad K_6=x_6/x_8=\exp\left(-\frac{\Delta H_6-T\Delta S_6}{RT}\right) \qquad (A\text{-}2)$$

$$S_8 \overset{K_7}{\rightleftharpoons} S_7,\quad K_7=x_7/x_8=\exp\left(-\frac{\Delta H_7-T\Delta S_7}{RT}\right) \qquad (A\text{-}3)$$

In above reactions, the enthalpy changes are taken from reference 12 and the entropy changes are obtained from reference 12 by using a graphical method.
Here

$$x_8+x_7+x_6+x_2=1 \qquad \text{(A-4)}$$

and from Eqs. (A-1) to (A-4),

$$x_8+K_7x_8+K_6x_8+K_2x_8=1 \qquad \text{(A-5)}$$

And the mole fraction of each component can be obtained as follows

$$x_8=\frac{1}{1+K_2+K_6+K_7} \qquad \text{(A-6)}$$

$$x_7=K_7x_8,\quad x_6=K_6x_8,\quad x_2=K_2x_8 \qquad \text{(A-7)}$$

Appendix 2.

Sublimation energy E_{s_7} can be obtained by using Hess Law depicted as follows

$$\begin{tikzcd}
S_8(ring,\ solid) \arrow[rr, dash, "E_{s7}"] \arrow[dr, "E_{s8}"'] & & S_7(ring,\ gas) \\
& S_8(ring,\ gas) \arrow[ur, "E^t_{s7}"'] &
\end{tikzcd}$$

Thus sublimation energy E_{s_7} can be represented by $E_{s_7}=E_{s_8}+E^t_{s7}$, therefore E_{s_6} and E_{s_2} can obtained by the same method.

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