It may be concluded that a good estimate of $D(H_3B-CO)$ is 23.1 ± 2 kcal./mole. This value, when combined with Burg's equilibrium data[27] gives $D(H_3B-BH_3) = 37.1 \pm 4$ kcal./mole. The value of 39 ± 9 kcal./mole obtained by electron impact measurements is in good agreement as is the value estimated recently.[22]

Although the above dissociation energies appear to be compatible to within experimental error with the best previous estimates of these energies and with independent electron impact measurements, recently

(27) A. B. Burg, J. Am. Chem. Soc., 74, 3482 (1952).

Baylis, Pressley, Sinke, and Stafford,[28] using a Knudsen-type cell coupled with a mass spectrometer, studied the dissociation of diborane and conclude that $D(BH_5BH_3) \geq 55$ kcal./mole, a surprisingly high value. The reasons for this disagreement are not clear to us and probably will have to be resolved by further work.

(28) A. B. Baylis, G. A. Pressley, E. J. Sinke, and F. E. Stafford, presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1, 1964.

Polymerization of Liquid Sulfur

J. A. Poulis,[1a] C. H. Massen,[1a] A. Eisenberg,[1b] and A. V. Tobolsky[1c]
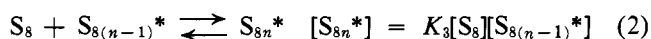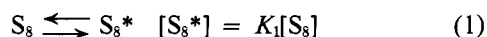
Contribution from the Physics Department, Technological University, Eindhoven, the Netherlands, the Department of Chemistry, University of California at Los Angeles, Los Angeles, California, and the Department of Chemistry, Princeton University, Princeton, New Jersey. Received July 15, 1964

The ring–chain equilibrium of liquid sulfur was previously studied by Tobolsky and Eisenberg. In this earlier theory, an assumption was made about the length of the polymer molecules. In this present paper this assumption is removed and the new theoretical results are compared with the previous ones.

Polymerization of Liquid Sulfur

The first relatively complete theory of the equilibrium polymerization of liquid sulfur was given by Gee.[2] This theory was characterized by the use of two distinct treatments: one valid below the transition temperature and one valid above the transition temperature. Tobolsky and Eisenberg[3] later presented a unitary theory valid above and below the transition temperature. It actually predicted the transition. This theory was perfectly consistent with the results of Gee; in fact it used the results of Gee as experimental data from which to evaluate numerically the pertinent equilibrium constants. The theory is also in accord with early statistical calculations of ring–chain equilibria.[4]

The Tobolsky–Eisenberg theory was based on the following chemical reactions

$$S_8 \rightleftharpoons S_8^* \quad [S_8^*] = K_1[S_8] \tag{1}$$

$$S_8 + S_{8(n-1)}^* \rightleftharpoons S_{8n}^* \quad [S_{8n}^*] = K_3[S_8][S_{8(n-1)}^*] \tag{2}$$

where the asterisk indicates chain molecules and the only nonpolymer molecule is supposed to be the eight-membered ring. With the help of these equations and a straightforward application of the theory of chemical equilibria, the weight concentration of polymers as

(1) (a) Technological University; (b) University of California; (c) Princeton University.
(2) G. Gee, Trans. Faraday Soc., 48, 515 (1952).
(3) A. V. Tobolsky and A. Eisenberg, J. Am. Chem. Soc., 81, 780 (1959).
(4) H. Jacobson and W. H. Stockmayer, J. Chem. Phys., 18, 1600 (1950).

well as the mean chain lengths was expressed in terms of K_1 and K_3.

It is obvious that eq. 2 can be replaced by eq. 2a without any change whatever in the theory or its results.

$$S_{8p}^* + S_{8q}^* \rightleftharpoons S_{8(p+q)}^* \tag{2a}$$
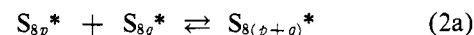
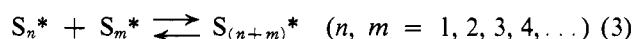$$[S_{8(p+q)}^*] = K_5[S_{8p}^*][S_{8q}^*]$$

$$(p, q = 1, 2, 3, 4, \ldots)$$
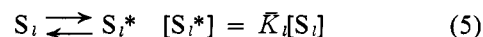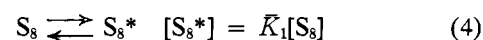
The relation between K_5, K_3, and K_1 is

$$K_3 = K_1 K_5 \tag{2b}$$

Though this theory gave an essentially correct picture of the polymerization of sulfur, its basis as given by eq. 1 and 2 or 2a contains the assumption that the number of atoms in all the molecules can only be multiples of eight.

It is possible to write alternative equations where this assumption is avoided. Consider the relations

$$S_n^* + S_m^* \rightleftharpoons S_{(n+m)}^* \quad (n, m = 1, 2, 3, 4, \ldots) \tag{3}$$

$$[S_{(n+m)}^*] = \bar{K}_5[S_n^*][S_m^*]$$

$$S_8 \rightleftharpoons S_8^* \quad [S_8^*] = \bar{K}_1[S_8] \tag{4}$$

$$S_i \rightleftharpoons S_i^* \quad [S_i^*] = \bar{K}_i[S_i] \tag{5}$$

Equation 3 is analogous to one used earlier by Gee, in that it expresses the assumption that in the polymeric molecules, units of eight do not have an exceptional position. Equation 5 accounts for the possibility of other than the eight-membered ring.

Inasmuch as eq. 3–5 represent a physical model for the equilibria, differing from the basis of eq. 1–2b, it is advisable to distinguish between the constants K_5 and $\bar{K}_5$, and K_1 and $\bar{K}_1$. The final evaluation of the equilibrium constants is achieved by comparing the theoretical equations from either model with the ex-

perimental results, and in this sense the values of the constants depend on the model used.

In order to compare the consequences of eq. 3–5 with eq. 1–2b, the following definition for $\bar{K}_3$ is introduced, in analogy with eq. 2b.

$$\bar{K}_3 = \bar{K}_1 \bar{K}_5 \qquad (5a)$$

Equation 3 still contains a simplifying assumption, namely that $\bar{K}_5$ is the same for all values of n and m. While this is true for large values of n and m, it is doubtful for values of n and $m = 1, 2$, etc.

Further development of the new theoretical model would require that $\bar{K}_5$ be allowed to vary with n and m for very small values of n and m. For the purpose of the calculations the following relations, which follow from eq. 3 and 4 are helpful as they express all the concentrations in terms of the eight-membered rings.

$$[S_n{}^*] = \bar{K}_5{}^{n-1}[S_1{}^*]^n$$

$$[S_1{}^*] = \frac{1}{\bar{K}_5}(\bar{K}_1\bar{K}_5[S_8])^{1/8} = \frac{\bar{K}_1}{\bar{K}_3}(\bar{K}_3[S_8])^{1/8} \qquad (6)$$

$$[S_n{}^*] = \frac{\bar{K}_1}{\bar{K}_3}(\bar{K}_3[S_8])^{n/8} \qquad (7)$$

$$[S_l] = \frac{\bar{K}_1}{\bar{K}_3\bar{K}_l}(\bar{K}_3[S_8])^{l/8} \qquad (8)$$

In accordance with the theory of Tobolsky and Eisenberg[3] the following definitions will be used

$$N = \sum_{n=1}^{\infty} [S_n{}^*] = \frac{\bar{K}_1}{\bar{K}_3}\frac{(\bar{K}_3[S_8])^{1/8}}{1 - (\bar{K}_3[S_8])^{1/8}} \qquad (9)$$

$$W = \frac{1}{8}\sum_{n=1}^{\infty} n[S_n{}^*] = \frac{\bar{K}_1}{8\bar{K}_3}\frac{(\bar{K}_3[S_8])^{1/8}}{\{1 - (\bar{K}_3[S_8])^{1/8}\}^2} \qquad (10)$$

$$P = \frac{W}{N} = \frac{1}{8\{1 - (\bar{K}_3[S_8])^{1/8}\}} \qquad (11)$$

where N is the total concentration of polymer molecules, W is the total concentration of ring molecules incorporated in the polymer, and P is the average chain length of the polymer expressed in units of eight-membered rings. Calling the total concentration of S_8 molecules incorporated in the whole sample $[S_8]_0$ it follows that

$$[S_8]_0 = [S_8] + W + \frac{1}{8}\sum_{l \neq 8}^{\infty} l[S_l] \qquad (12)$$

which, when combined with eq. 8 and 10, yields the equation

$$[S_8]_0 = [S_8] + \frac{\bar{K}_1}{8\bar{K}_3}\frac{(\bar{K}_3[S_8])^{1/8}}{\{1 - (\bar{K}_3[S_8])^{1/8}\}^2} +$$
$$\frac{\bar{K}_1}{8\bar{K}_3}\sum_{l \neq 8}\frac{l}{\bar{K}_l}(\bar{K}_3[S_8])^{l/8} \qquad (13)$$

With the help of eq. 11 it is possible to write eq. 13 in terms of P

$$[S_8]_0 = \frac{1}{\bar{K}_3}\left(\frac{8P-1}{8P}\right)^8 + \frac{\bar{K}_1}{8\bar{K}_3}8P(8P-1) +$$
$$\frac{\bar{K}_1}{8\bar{K}_3}\sum_{l \neq 8}\frac{l}{\bar{K}_l}\left(\frac{8P-1}{8P}\right)^l = \frac{1}{\bar{K}_3}\left(\frac{8P-1}{8P}\right)^8 + \frac{P(8P-1)}{\bar{K}_5} +$$
$$\frac{1}{8\bar{K}_5}\sum_{l \neq 8}\frac{l}{\bar{K}_l}\left(\frac{8P-1}{8P}\right)^l \qquad (14)$$

or, alternately by using eq. 9 in terms of N.

$$[S_8]_0 = \frac{1}{\bar{K}_3}\left(\frac{N}{N + \frac{\bar{K}_1}{\bar{K}_3}}\right)^8 + \frac{\bar{K}_3}{8\bar{K}_1}N\left(N + \frac{\bar{K}_1}{\bar{K}_3} + \right.$$
$$\frac{\bar{K}_1}{8\bar{K}_3}\sum_{l \neq 8}\frac{l}{\bar{K}_l}\left(\frac{N}{N + \frac{\bar{K}_1}{\bar{K}_3}}\right)^l \qquad (15)$$

For the easier solution of eq. 13, 14, and 15, we shall introduce two simplifying conditions, namely the absence of nonpolymerical molecules other than eight-membered rings and the fact that $\bar{K}_1 \ll \bar{K}_3$. In first-order approximation we find

$$[S_8] = [S_8]_0 \qquad (16)$$

$$P = \frac{1}{8(1 - [S_8]_0{}^{1/8}\bar{K}_3{}^{1/8})} \qquad (17)$$

$$N = 0 \qquad (18)$$

Substitution of $K_3 = \bar{K}_3$ shows that these results are essentially equivalent to those developed by Tobolsky and Eisenberg from eq. 1 and 2.

$$P = \frac{1}{1 - [S_8]_0 K_3} \qquad (17a)$$

Returning to the theory based on eq. 3–5, we observe that since $\bar{K}_3$ increases with temperature, we can distinguish between two temperature intervals characterized by the inequalities

$$\bar{K}_3[S_8]_0 < 1 \qquad (19)$$

$$\bar{K}_3[S_8]_0 > 1 \qquad (20)$$

Since P must be positive, the approximate results (eq. 16–18) are physically valid only in the low temperature region given by eq. 19. In the high temperature region, the second term of eq. 14 must be taken into consideration to avoid negative values of P. This term can only play a role when $8P(8P - 1)$ has a sufficiently large value to compensate for the smallness of K_1. In this case we can approximate eq. 14 as

$$[S_8]_0 = \frac{1}{\bar{K}_3} + \frac{\bar{K}_1}{8\bar{K}_3}(8P)^2 \qquad (21)$$

which leads to

$$P = \sqrt{\frac{\bar{K}_3[S_8]_0 - 1}{8\bar{K}_1}} = \sqrt{\frac{\bar{K}_3[S_8]_0 - 1}{8\bar{K}_3/\bar{K}_5}} \qquad (22)$$

This solution is physically acceptable in the high temperature region given by eq. 20.

Equation 22a too may be compared with the one resulting from the theory based upon eq. 1 and 2. This

$$P = \sqrt{\frac{K_3[S_8]_0 - 1}{\bar{K}_1}} \qquad (22a)$$

equation becomes identical with eq. 22b after substitution.

$$K_1 = 8\bar{K}_1, \qquad K_5 = \frac{1}{8}\bar{K}_5, \qquad K_3 = \bar{K}_3 \qquad (22b)$$

Returning to the theory based on eq. 3–5, it follows that in the approximation that led to eq. 22a

$$[S_8] = 1/\bar{K}_3 \qquad (23)$$

$$W = \frac{1}{\bar{K}_8}([S_8]_0\bar{K}_3 - 1) \qquad (24)$$

$$N = \frac{1}{\bar{K}_3}\sqrt{8\bar{K}_1([S_8]_0\bar{K}_3 - 1)} \qquad (25)$$

Experimental measurements of magnetic suscepti-bility[5] and electron spin resonance in liquid sulfur[5,6]

(5) J. A. Poulis, C. H. Massen, and D. V. D. Leeden, *Trans. Faraday Soc.*, **58**, 474 (1962).

(6) J. A. Poulis and W. Derbyshire, *ibid.*, **59**, 559 (1962).

confirm the estimates of polymer sulfur chain length at various temperatures made by Gee.[2] These data, as well as equilibrium monomer concentration as a function of temperature, were exceptionally well explained by the Tobolsky–Eisenberg theory both above and below the transition temperature. Exactly the same mathematical results apply to the new model presented here, with a slight reinterpretation of the numerical values of the equilibrium constants, as shown in eq. 22b.

Acknowledgment. The authors wish to acknowledge stimulating discussions with . Professor R. D. Spence of Michigan State University.

Reference Buffer Solutions for pH Measurements in 50% Methanol. Dissociation Constants of Acetic Acid and Dihydrogen Phosphate Ion from 10 to 40°

Maya Paabo, R. A. Robinson, and Roger G. Bates

Contribution from the National Bureau of Standards, Washington, D. C. Received May 23, 1964

Electromotive force measurements of cells with hydrogen and silver–silver chloride electrodes containing buffer solutions in 50 wt. % methanol–water solvents have been used to determine conventional values of pa_H* *(= $-log\ m_H \cdot {}_s\gamma_H$) for three reference solutions from 10 to 40°. The dissociation constants of acetic acid and dihydrogen phosphate ion in 50% methanol have likewise been determined over the same temperature range, and thermodynamic quantities for the dissociation processes have been derived.*

Introduction

A mixture consisting of equal parts by weight of water and methanol (referred to in this paper as 50% methanol) is a very useful solvent for many compounds whose solubility in water is too small for measurements of acidity and dissociation constants to be made. Progress in this field would be aided by a knowledge of the properties of reference buffer solutions in 50% methanol. In particular, the standardization of the conventional pH meter for use with 50% methanol solutions could then be made with confidence.

The pH values of two solutions, one of which is 0.01 *M* with respect to both oxalic acid and ammonium hydrogen oxalate and the other 0.01 *M* with respect to both succinic acid and lithium hydrogen succinate have already been determined[1] in water–methanol solutions at 25°. We now report data for solutions in three buffer series, namely acetate, phosphate, and succinate, over a range of concentration and temperature in 50% methanol as solvent. These values may be regarded as reference points for an operational scale of pH* in this useful mixed solvent.[2]

In addition, the dissociation constant of acetic acid and the second dissociation constant of phosphoric acid have been determined from 10 to 40°, the associated thermodynamic quantities have been calculated, and a comparison has been made with the behavior of these acids in aqueous solution.

Symbols

${}_s\gamma_i$ is the activity coefficient of the species i, on the molal scale, relative to the hypothetical standard state *in 50% methanol;* ${}_s\gamma_i$ approaches unity at infinite dilution in 50% methanol.

${}_sK$ is the equilibrium constant (on the molal scale) of an acid–base reaction, such as $HA \rightleftharpoons H^+ + A^-$.

$${}_sK = \frac{m_H m_A}{m_{HA}}\frac{{}_s\gamma_H \cdot {}_s\gamma_A}{{}_s\gamma_{HA}}$$

Thus $\Delta G° = -RT\ln ({}_sK)$ is the increase in Gibbs energy when a mole of HA (in its standard state *in 50% methanol*) dissociates into a mole of H^+ and a mole of A^-, each in its standard state *in 50% methanol*.

${}_s(a_H\gamma_{Cl}) \equiv m_H \cdot {}_s\gamma_H \cdot {}_s\gamma_{Cl}$ is a well-defined thermodynamic quantity; both ${}_s\gamma_H$ and ${}_s\gamma_{Cl}$ have the properties of ${}_s\gamma_i$ defined above.

pa_H* is, by definition, $p_s(a_H\gamma_{Cl}) + \log {}_s\gamma_{Cl}$, where ${}_s\gamma_{Cl}$ is assigned a conventional value (see eq. 4).

${}_sE°$ is the standard e.m.f. of the cell: H_2, HCl in 50% methanol, AgCl; Ag. Thus, $\Delta G° = -F({}_sE°)$ is the increase in Gibbs energy for the reaction $0.5H_2 + AgCl \rightarrow Ag + H^+ + Cl^-$, both H^+ and Cl^- being in their standard states *in 50% methanol*.

(1) C. L. De Ligny, P. F. M. Luykx, M. Rehbach, and A. A. Wieneke, *Rec. trav. chim.*, **79**, 713 (1960).

(2) R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, **67**, 1833 (1963).